Catalytic microwave pyrolysis to produce upgraded bio-oil

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Dissertation submitted in partial fulfilment of the requirements for the degree
Master of Engineering in Chemical Engineering

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October 2016

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Declaration

I, Johann André Wauts, hereby declare that this dissertation and every detail thereof is my own unassisted work. I submit this dissertation for the Degree of Master of Engineering to the University of Pretoria. I declare that this work has not been submitted to any other university or educational institution for any degree, examination or other form of qualification.

Candidate Signature

Signed at Pretoria on the 28th day of October 2016
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Abstract

To assess the performance and future possibilities of catalytic microwave pyrolysis, laboratory-scale experiments were conducted on a widely available biomass feedstock, *Eucalyptus grandis*. Non-catalysed microwave pyrolysis was conducted under varying conditions to determine important factors of the microwave pyrolysis process and to conduct a basic performance evaluation. Future possibilities of microwave pyrolysis were determined by comparison to available technologies. Calcined Mg-Al LDH clay (layered double oxide or LDO) was used as catalyst to improve the quality of the pyrolysis process and its products. The heating and reaction mechanisms for microwave pyrolysis show that it offers distinct advantages over conventional pyrolysis. The main advantages are rapid and efficient volumetric heating, as well as acceptable yields at lower temperatures (much lower than those required by conventional pyrolysis), which can possibly lead to significant energy savings.

Comparing the performance of a modified domestic microwave to an off-the-shelf microwave unit (Roto Synth) proved that cheap and comparative microwave research is possible. The yields from the domestic microwave products compared very closely to those of the Roto Synth unit, each having yields for char, oil and gas of 47.9%, 33.2%, 18.9% and of 46.8%, 32.7%, 20.55% respectively. The cost of the modified domestic setup was ~1% of that of the off-the-shelf unit. The use of a quartz reactor and slight adjustments to the stepper motor driver and thermocouple are recommended for future use.

The pyrolysis process was found to be very dependent on power and power density. Higher powers increase the liquid and gas yields and a critical power density was identified between 800W and 1000W. The effects of power density were interesting and led to conclusions regarding the penetration depth of microwaves which could possibly play a significant role in the scale-up of microwave pyrolysis technology.

Microwave pyrolysis undeniably has several advantages over conventional pyrolysis. However, for it to become competitive, microwave fast pyrolysis technologies need to be developed through the use of mixed bed reactors that can achieve fast heating rates. Possible
candidates include rotating cone and fluidised bed reactors. Hybrid technology also provides unique advantages and has huge potential. Comparison of pyrolysis technologies is difficult without good data on continuous microwave pyrolysis reactors, and therefore the development of such reactors is recommended for future research.

Catalysis of microwave pyrolysis with LDO proved effective. The catalyst promoted the formation of volatiles (gas and liquid), even when present in small ratios. It also promoted the formation of esters and even anhydrides and small fractions of hydrocarbons at high catalyst ratios. The catalyst activity led to increased water yields. This indicated that it removes oxygen from the pyrolysis products, thereby improving their quality. The catalyst was believed to be limited by the low temperatures used in this investigation and higher temperatures might increase the release of \( \text{CO}_2 \) and should be investigated. Significant reduction in the total acid number (TAN) and an improved dry-basis heating value were also achieved by the addition of the catalyst. The water content increased from 50% to 70%, the TAN reduced from 174 mg KOH/(g oil) to 72 mg KOH/(g oil), and the calorific value increased from 19.1 MJ/kg to 21.5 MJ/kg.

**Keywords:** microwave pyrolysis, biomass, Mg-Al LDH clay, LDO catalyst, conventional pyrolysis
Acknowledgements

Thanks to the Paper Manufacturers Association of South Africa (PAMSA) for funding this research project as well as Sappi Southern Africa Ltd for their support.

I would like to personally thank my family and friends for their support, without which this would have not been possible. I would also like to thank prof. Mike Heydenrych for his advice and guidance throughout this project

I would also like the extent my thanks to my colleague Ryan Merckel for his inputs and advice. I would also like to thank Dr. Yvette Naude at the Chemistry department at University of Pretoria for her assistance with product analysis. Special thanks go to the Sappi technology centre for their continued support of my project as well as use of their equipment and facilities, which was instrumental in completing this project.
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Chapter 1
Introduction

1.1 Biomass as renewable energy source

World energy demands are ever growing due to population growth and increased living standards (Domínguez et al., 2007). The exhausting reservoirs of fossil fuels and natural gas, along with their negative global warming effects, have created great interest in the generation of economical and environmentally friendly renewable energy alternatives. Renewable energy is considered to be clean energy derived from natural processes. The optimal use of these sources minimises environmental impact and produces minimum secondary waste. Renewable technologies therefore utilise sustainable resources based on the current and future economic and social needs (Panwar, Kaushik & Kothari, 2011). Biomass is a renewable energy source that is believed to have the potential to become the primary global energy source during the next century (Berndes, Hoogwijk & van den Broek, 2003).

Wood and other sources of biomass are one of the main renewable energy sources that can possibly alleviate future energy crises, reduce pollution and global warming, and contribute to sustainable development (Motasemi & Afzal, 2013). Biomass resources are renewable, carbon-neutral, have low sulphur content and are plentiful. They are therefore ideally suited as an alternative to fossil fuels.

_Eucalyptus_ genera are currently considered to be one of the most important and common tree species in tropical and subtropical plantations, being second to only _Pinus_ genera. The _Eucalyptus_ genus is said to contain some of the fastest-growing species of trees (Sappi, 2012). _Eucalyptus grandis_ is recognised as one of the most widely used eucalypts for industrial applications. Within South Africa, _Eucalyptus_ plantations obtain estimated yields of 21–25 m³/(ha·yr) (Du Toit et al., 1998; Ugalde & Pérez, 2001)

Biomass can be treated in various ways to give not only heat and power, but solid, liquid and gaseous fuels as well. Generally, biomass treatment is divided into biological and thermal processes (Bridgwater & Peacocke, 2000). Biological processes usually require long times and produce a single or specialised product. Thermal processes give complex product mixtures in short times (Wang et al., 2012). The thermal processing of wood includes: combustion to produce heat; gasification to produce a fuel gas; liquefaction to produce a
liquid product; carbonisation to produce solid products; or pyrolysis which produces solid, gas and liquid products (Bridgewater & Peacocke, 2000; Faaij, 2006). Pyrolysis has been identified as one of the most promising thermal conversion technologies.

1.2 The pyrolysis process

Pyrolysis can be described as the direct thermal decomposition of organic material in the absence of oxygen to obtain solid (charcoal), liquid (bio-oil) and gas products (Vamvuka, 2011). Each of these products can be used in various applications and add value to the pyrolysis process. The yield (product distribution) and quality of these products depend on the conditions under which they were produced, and literature results vary considerably due to different conditions. Factors known to influence the pyrolysis process include:

- Feedstock (feed composition)
- Reaction temperature
- Heating rate
- Reaction time/residence time
- Particle size
- Moisture content
- Addition of catalysts or additives or other pre-treatments
- Reaction atmosphere (inert gas type and flow rate)
- Reactor configuration (volatile cooling, char separation, etc.)

The main pyrolysis products and their applications are further discussed below.

Liquid (bio-oil)

The liquid collected from pyrolysis is called bio-oil and is a dark brown, free-flowing organic liquid consisting of a complex mixture of oxygenated organic compounds and water, and is considered as the main product of pyrolysis. Bio-oils are formed by the thermal decomposition of the main components of biomass (cellulose, hemicellulose and lignin). Rapid quenching of released volatiles leads to the collection of reaction intermediates (those that would have reacted further if the temperature had been maintained), resulting in the presence of the reactive species that give bio-oils their unusual properties. Bio-oil usually contains significant amounts of water (15–50%). The main organic compounds consist of acids, ketones and aldehydes, alcohols, phenols, guaiacols, syringols, furans, esters, sugars,
alkenes, aromatics, nitrogen compounds and miscellaneous oxygenates. Bio-oil can be considered as a micro-emulsion. The continuous phase consists of an aqueous mixture of holocellulose decomposition products and small lignin decomposition products. The continuous aqueous phase stabilises the discontinuous phase which consists mainly of pyrolytic lignin molecules. The stabilisation is achieved by hydrogen bond interaction and nanomicelle and micromicelle formation (Mohan, Pittman & Steele, 2006).

The physical properties also depend significantly on the reaction conditions and can vary greatly. Bio-oil cannot dissolve in water but is miscible with polar solvents such as acetone and methanol, and completely miscible with petroleum fuels. Bio-oils can typically not be distilled since at 100 °C the oil reacts rapidly and forms a residue that is approximately half the original weight of the liquid. Bio-oil ages and becomes unstable, causing increased viscosities, decreased volatility and phase separation, among others. This is due mainly to char and ash particles, which can be removed via filters. The viscosity of bio-oil is usually in the range of 10–100 cP at 40 °C and the average specific gravity is around 1.2. The presence of acids gives bio-oil pH values of around 2–3. Therefore upgrading is required if it is to be used as a transportation fuel. Using appropriate filters, the ash and char content of the bio-oils can be lowered to the similar standard of high-quality petroleum fuels. Bio-oil typically has a heating value of around 17 MJ/kg compared with 42 MJ/kg for petroleum fuels (Mohan et al., 2006; Vamvuka, 2011).

Bio-oil can be used for a variety of purposes, such as (Motasemi & Afzal, 2013):

- Heat and power generation
- Transportation fuels
- Wood flavouring, preservatives and liquid smoke
- The production of chemicals and resins, and for making adhesives

A detailed discussion on the uses of pyrolysis oil can be found in Czernik and Bridgwater (2004).

**Gas**

Pyrolysis gas is another valuable product from the pyrolysis process and consists of low molecular weight gases. The gas formed is often referred to as non-condensable gas and is a mixture of carbon dioxide, carbon monoxide, methane, hydrogen, ethane, ethylene, minor amounts of higher gaseous organics and water vapour. Secondary cracking of organic
vapours can lead to increased amounts of small-chain hydrocarbons in the gas phase. The gas product can sometimes be used as the primary pyrolysis product when higher temperatures or heating rates are used; these conditions favour the yield of the gas product. The gas product has a typical heating value of around 11 MJ/m$^3$, but this can vary considerably. It can in some cases contain high fractions of syngas (CO and H$_2$), which can be used for the production of synthetic natural gas or other chemicals such as methanol and ammonia. The gas can also be used for direct combustion in reboilers for heat production, or in heat turbines or engines for electricity production (Motasemi & Afzal, 2013; Vamvuka, 2011).

**Solid (char)**

Char is a carbonaceous residue which is produced in both primary and secondary reactions of pyrolysis. The char contains inorganic materials (ashed to various degrees), unconverted organic solids and carbonaceous residues produced from the thermal decomposition of the biomass components, in particular lignin, since it is thermally very stable. Depending on the reaction conditions, the composition, structure (microstructure-like pores) and condition of the char (pH, surface area, etc.) can vary considerably. It should be noted that there is a difference between bio-char and char. Bio-char is a carbon-rich solid with the primary objective of long-term carbon storage, and the requirements for bio-char are different from those of other carbonaceous residues. Bio-char needs to be highly stable to ensure long-term carbon sequestration. The formation of bio-char has been reported for slow and microwave pyrolysis processes (Mašek et al., 2013). Depending on the quality of the char, it can be used for various purposes such as: solid fuel for the production of heat or electricity; feedstock for gasification processes; and a feedstock for the production of activated carbon and carbon nanofilaments. Bio-char also has several applications such as: soil quality enhancement; carbon sequestration; soil water improvement; nutrient retention; soil erosion; and water contamination reduction, among others (Motasemi & Afzal, 2013; Vamvuka, 2011).

**Reactor conditions and pyrolysis classes**

As discussed above, there are various factors that influence both the product distribution and the quality of the products of the pyrolysis process. There are three commonly identified classes of pyrolysis: slow pyrolysis, fast pyrolysis and flash pyrolysis. These classes are identified mainly by the heating rate, but researchers agree that the definitions of “slow” and “fast” are somewhat arbitrary. Table 1 shows the different classes of pyrolysis along with their conditions, as described by Maschio, Koufopanos & Lucchesi (1992) and which has
been used by various researchers (Demirbas & Arin, 2002; Balat, Kirtay, & Balat, 2009; Babu, 2008). Table 2 shows typical yields for the different pyrolysis classes (Bridgwater, 2012). In general, it is accepted that the low heating rates (such as those for conventional slow pyrolysis) yield high fractions of solids with significant portions of gas and liquid products. Fast heating rates (such as flash and fast pyrolysis) primarily produce a liquid product when moderate temperatures are used or gas for when high temperatures are used (Demirbas & Arin, 2002; Balat et al., 2009; Babu, 2008).

Table 1: Different conventional pyrolysis classes (adapted from Maschio et al., 1992)

<table>
<thead>
<tr>
<th></th>
<th>Slow</th>
<th>Fast</th>
<th>Flash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>550–950</td>
<td>850–1250</td>
<td>1050–1300</td>
</tr>
<tr>
<td>Heating rate (K/s)</td>
<td>0.1–1.0</td>
<td>10–200</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>Particle size (mm)</td>
<td>5–50</td>
<td>&lt; 1</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Solids residence time (s)</td>
<td>450–550</td>
<td>0.5–10</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>

Table 2: Typical yields for different pyrolysis classes (adapted from Bridgwater, 2012)

<table>
<thead>
<tr>
<th></th>
<th>Liquid (%)</th>
<th>Solid (%)</th>
<th>Gas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td>500 °C short vapour residence times ~ 1 s</td>
<td>75</td>
<td>12</td>
</tr>
<tr>
<td>Intermediate</td>
<td>500 °C moderate vapour residence times ~ 10–30 s</td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>Slow</td>
<td>400 °C long solids residence time</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td>Gasification</td>
<td>800 °C–1000°C</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Torrefaction</td>
<td>290 °C solids residence time ~10–60 min</td>
<td>5%</td>
<td>80%</td>
</tr>
</tbody>
</table>

All the established pyrolysis technologies, as mentioned above, rely on conventional heat transfer mechanisms such as conduction, convection and radiation. More recently, researchers have started investigating microwave heating as a possible pyrolysis method. Microwave heating has found application in a wide variety of technological and scientific fields (Menéndez et al., 2010). Microwave processing often leads to remarkable rate
enhancements in chemical reactions. Most of these enhancements come from increased heating rates (thermal effects) due to better energy transfer compared with conventional heating methods. However, some of these enhancements cannot be reproduced by conventional heating and there are speculations that microwave heating offers additional non-thermal effects due to the interaction of the electromagnetic waves with the material. These effects are observed even though microwaves do not contain sufficient energy to break chemical bonds (Gabriel et al., 1998; Kappe, 2004). Microwave pyrolysis has gained increased interest over recent years but is still in its infancy compared with conventional pyrolysis technologies. Various challenges will need to be addressed for microwave pyrolysis to become competitive. The behaviour of microwave pyrolysis reactors, especially on a larger scale, is still not well understood. This emphasises the importance of additional research in the field.

The objective of this study is to investigate the future possibilities of microwave pyrolysis using widely available (especially in South Africa) *Eucalyptus grandis* wood. Other objectives include:

- Determine the performance of modified domestic microwave units compared with off-the-shelf microwave equipment.
- Investigate the fundamentals that govern the non-catalysed microwave pyrolysis process and determine typical microwave pyrolysis products.
- Determine future possibilities for microwave pyrolysis and determine how it compares with existing technologies within the bigger picture.
- Investigate the *in situ* catalysis of microwave pyrolysis, using Mg-Al LDH clay to determine the effect on product yield and oil quality.

These experiments were conducted on laboratory scale with the use of a Milestone Roto Synth microwave unit and a modified Defy domestic microwave. Product characterisation included GC×GC –TOFMS analysis of the liquid products, elemental analysis, proximate analysis, calorific values, total acid number (TAN), and Karl Fischer titration for moisture content, among others. Yields were determined by a simple mass balance.
Chapter 2
Microwave pyrolysis of wood: heating and reaction mechanism

2.1 Introduction

Some research was done on microwave pyrolysis in the 1970s but it faded after the oil crises subsided. Recent oil-supply concerns have sparked a renewed interest in microwave pyrolysis. This time the research is focusing on the use of biomass, rather than petrochemicals, to produce fuels and chemicals (Macquarrie, Clark & Fitzpatrick, 2012). Microwave pyrolysis addresses some of the main challenges of conventional pyrolysis and is emerging as one of the best technologies for the pyrolysis process (Yin, 2012).

Even though microwave pyrolysis differs greatly from conventional pyrolysis with regard to the heating mechanism, it can still be expected to follow very similar reaction mechanisms since microwaves do not have enough energy for bond cleavage. There may be additional non-thermal heating effects of microwaves and therefore the heating mechanism and reaction mechanism need to be discussed.

This chapter discusses the heating and reaction mechanisms of the microwave pyrolysis of wood. Specific attention is paid to the thermal decomposition of the wood components and also any additional non-thermal heating effects. Additional attention is given to important microwave heating aspects that play a crucial role in the pyrolysis process.

2.2 Heating mechanism

Microwaves are electromagnetic waves with frequencies between 0.3 GHz and 300 GHz, which correspond to wavelengths of 0.01 m – 1 m. The frequencies of 915 MHz and 2 450 MHz are reserved for industrial, scientific and medical purposes. The rest are used for radar and telecommunication. The 915 MHz frequency is typically used for large power output units (>75 kW) since 2 450 MHz results in too-high losses at these outputs. The 2 450 MHz frequency is usually used for lower-output units (<25 kW), normally for research and domestic purposes (Kappe et al., 2005).

Thostenson & Chou (1999), Clark, Folz & West (2000) and Gabriel et al. (1998) discussed the fundamentals and applications of microwave heating in great detail. The energy of a
microwave photon is 0.0016 eV, much lower than the energy needed to break chemical bonds. Microwave-assisted reactions are instead a result of efficient heating, commonly known as dielectric heating. There are various mechanisms that contribute to the response of a material under microwave irradiation. These include electronic polarisation, atomic polarisation, ionic conduction, dipole (orientation) polarisation, and Maxwell–Wagner polarisation (Thostenson & Chou, 1999). Of these interactions, only the two greatest contributors are discussed. The first is dipolar polarisation in which dipoles or ions try to align with the electric field. Since the field is oscillating, the particles continually realign, which causes molecular friction and dielectric loss and these produce heat. Dielectric solid materials undergo interfacial polarisation, which is the second contributor discussed. Charged particles (such as π –electrons in carbon materials) induce a current travelling in phase with the electromagnetic field. These particles/electrons cannot couple to the change of phase of the electric field and energy is dissipated as heat due to the Maxwell–Wagner effect (Menéndez et al., 2010).

The ability of a material to be heated in a microwave field depends on its dielectric properties. These properties are conveniently represented by the loss tangent tan δ. The loss tangent is a parameter that describes the overall efficiency with which a material utilises microwave energy and is described by Equation 1. The loss tangent consists of two constants, the dielectric constant (ε′) and dielectric loss (ε′′). These describe the ability of molecules to be polarised by an electric field and the efficiency by which microwave energy is converted to heat, respectively.

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} \tag{1}
\]

Materials can be classified according to their microwave absorption as high (\(\tan \delta < 0.1\)), medium (\(\tan \delta \) from 0.1–0.5) and low (\(\tan \delta < 0.1\)) microwave-absorbing materials (Kappe, 2004). However, materials are generally classified into three classes due to their interaction with microwaves (Clark et al., 2000).

1. **Transparent.** Microwaves pass through material with little or no attenuation (materials with a low dielectric loss).
2. **Opaque.** Microwaves reflect and do not penetrate (conductors).
3. **Absorbing.** Materials absorb microwaves according to their dielectric properties (high dielectric loss).
To enhance the heating rate of low microwave-absorbing materials in microwave fields, additives can be added that have high microwave absorption, such as silicon carbide (SiC), activated carbon or even char from the pyrolysis process. Microwave heating can lead to good rate enhancements in some chemical reactions and it is speculated that non-thermal microwave effects also play a role, but are much less important than the improved heating rate (De la Hoz, Diaz-Ortiz & Moreno, 2005; Kappe, 2004; Larhed, Moberg & Hallberg, 2002).

Microwave heating involves the direct coupling of molecules with microwave energy. This leads to efficient in-core, volumetric heating. Since microwave reactors are usually transparent or reflective to microwaves, the reactor walls have lower temperatures than the particles. This is different from conventional heating in which particles are heated from the exterior, and the reactor is usually at a higher temperature than the particles. Microwave heating involves the conversion of energy instead of the transfer of energy present in conventional heating. It offers distinct advantages over conventional heating (Yin, 2012; Menéndez et al., 2010), as follows:

1. **Non-contact heating**: This reduces the need for a heat transfer material, such as silica or other materials sometimes used in conventional heating.
2. **Energy transfer instead of heat transfer**: Energy is converted to heat by direct coupling with molecules, compared with conventional heating in which heat is transferred via conduction, convection or radiation from a heat source.
3. **Rapid, efficient heating**: Microwave heating (limited by dielectric properties) is comparatively fast and efficient compared with conventional heating (limited by material thermal conductivity and convection currents).
4. **Volumetric heating**: The whole material is heated simultaneously compared with the superficial heating of conventional methods.
5. **Selective material heating**: Heating is selective towards some materials, depending on their dielectric properties and microwave class. Conventional heating is non-selective.
6. **Heating from the interior of the body**: Microwave heating targets the interior of the particles rather than the exterior (conventional heating). This results in temperatures that are higher inside than outside. This inverse temperature profile can be advantageous in some processes.
7. **Higher level of safety, control and automation**: Energy input starts and stops immediately when the power is turned on or off. Microwave power can be increased...
or decreased immediately compared with conventional heating which is limited by the thermal lag of the heat source.

The internal heating of microwave heating is especially beneficial for reducing secondary cracking reactions which are a major problem in conventional pyrolysis. In conventional pyrolysis the particle is heated from the exterior and the outside of the particle is significantly hotter than the inside. Therefore the vapours released need to pass through a high-temperature section to be released. This results in secondary cracking. Contrary to this, under microwave heating the interior of the particle is at a higher temperature than the exterior, and thus the vapours released move through a low-temperature region which significantly reduces secondary cracking (Miura et al., 2004).

Microwave heating disadvantages include the dependency on the material dielectric properties and the formation of hotspots due to pockets of high and low energy (Thostenson & Chou, 1999). Also, accurate temperature measurements can be difficult. This is due to: (1) the presence of the electromagnetic field which interferes with thermocouples; (2) the interior heating mechanism where contact temperatures may not be representative; and (3) hotspots leading to inaccurate local temperatures (De la Hoz et al., 2005; Kappe, 2004; Larhed et al., 2002).

Clark et al. (2000) suggest that there are three key factors that are of importance in microwave processing: (1) power absorbed; (2) heating rate; and (3) penetration depth. The suggested correlations are shown in Equations 2, 3 and 4 respectively.

\[
P = 2\pi \cdot f \cdot \varepsilon_0 \cdot \varepsilon_r' \cdot \tan \delta \cdot |E|^2 \tag{2}
\]

\[
\frac{\Delta T}{\Delta t} = \frac{P}{\rho \cdot C_p} \tag{3}
\]

\[
D = \frac{3\lambda_0}{8.686\pi \cdot \tan \delta \cdot \sqrt{\varepsilon_r'}} \tag{4}
\]

where \( P \), \( \frac{\Delta T}{\Delta t} \) and \( D \) represent the power absorbed, the heating rate (assuming all energy is converted to heat) and the penetration depth (depth at which power is reduced by half) respectively. The symbols \( f, \varepsilon_0, \varepsilon_r', E, \rho, C_p \) and \( \lambda_0 \) represent the microwave frequency, permittivity of free space, relative dielectric constant, magnitude of electric field, density of
material, heat capacity of material and wavelength, respectively. \( \tan \delta \) is known as the loss tangent and represents the overall efficiency of a material for utilising microwave energy and can be calculated using Equation 1. These equations prove useful in the design of microwave reactors.

The microwave properties of wood differ between species and even region, due to the difference in composition. Wood is known to be a poor absorber of microwaves and usually the presence of water and polar extractives are the main contributors to microwave heating of wood. Robinson et al. (2010) investigated the microwave pyrolysis of wood pellets without any additives. They showed that microwave pyrolysis is possible without the use of carbon-rich dopants. They proposed a mechanism by which wood is heated during microwave irradiation. Initially, the only microwave-absorbing phase in the wood is water. This water is present in three different forms: free water, capillary water and bound water. Free water is evaporated similar to water in a cup and the particle will only reach temperatures of around 100 °C. Capillary water needs to diffuse to the surface of the wood to evaporate. If sufficiently high energy densities are used, capillary water can be superheated (up to the critical point), heating the wood particle beyond 100 °C. Bound water requires much greater energies to evaporate. The superheating of this water is said to lead to the onset of pyrolysis (Robinson et al., 2010). As the wood particles pyrolyse, they are transformed into char. This char is a good absorber of microwaves and leads to better microwave absorption, which in turn leads to increased heating rates.

Omar et al. (2011) reported the dielectric properties of an empty fruit bunch at various moisture contents, since the moisture content plays a big role in the microwave absorption and dielectric properties. Increased moisture content leads to better dielectric properties but also reduces penetration depth. They showed that for a moisture content of 18% the penetration depth was around 4 cm. Above 30% moisture the penetration depth was roughly constant at 1 cm for moisture contents up to 80%. Moisture contents below 18% see a big drop in the dielectric properties and therefore increased penetration depths. Robinson et al. (2010) confirmed this behaviour and showed that at certain temperatures where capillary and bound water start to evaporate the dielectric loss factor becomes extremely low, which will lead to very poor absorption of microwaves.

Microwave pyrolysis of wood can be explained in the following way. Initially, wet wood is a good microwave absorber. This results in low penetration depths. Upon microwave radiation
the water phase leads to an increase in temperature of the wood particles. At sufficiently high temperatures the free water is evaporated, decreasing the dielectric loss factor and increasing penetration depth. As microwave radiation continues, capillary and bound water lead to further microwave absorption and further temperature increases. This leads to the evaporation of capillary water and further reduction in the dielectric loss (giving high penetration depths). Increased penetration depths lead to the evaporation of water from neighbouring particles. Further radiation leads to thermal decomposition and the onset of pyrolysis, leading to the transition of wood into char (a good microwave absorber). This increases the dielectric loss factor significantly, increasing microwave absorption. These char particles continue to absorb microwaves and heat up the neighbouring particles, leading to further pyrolysis and char formation. This continues until the pyrolysis process is complete.

2.3 Reaction mechanism

Wood is one of the most important materials known to man and has been used for countless applications. It has been used as a fuel and structural material for thousands of years and has recently been used for the production of various chemicals and in other uses. Wood or woody biomass consists of three major components: cellulose, hemicellulose and lignin. The mass fractions of each of these components can vary significantly and depend on various parameters (species, climate, etc.). Pyrolysis of each constituent is in itself a complex process that is dependent on many factors. To emphasise this chemistry, these major components of plant biomass are introduced. The general features of the thermal decomposition of these components are then are discussed, because these processes must be considered simultaneously during biomass pyrolysis (Mohan et al., 2006). Woody biomass, together with these main components, also contains inorganic materials and extractives. Inorganic materials such as K, Na, P, Ca, Mg and Si are common in most woods. These inorganic materials report as ash during combustion and can affect the quality of the bio-oil. Extractives (polar and non-polar) are also present in wood; examples are fats, waxes, alkaloids, proteins, phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins and essential oils. These extractives serve as a defence against insects and microbes and can also serve as energy resources and intermediates for metabolism (Fengel & Wegener, 1983: 182–223). The polar compounds can affect the dielectric properties of wood and can play a significant role in microwave absorption during microwave heating.
2.3.1 Cellulose

Cellulose is the most abundant organic compound in the world and typically makes up 40-50 wt % of dry wood. It consists of β-D-glucopyranose units (between 5 000 and 10 000) connected by (1 →4) glycosidic bonds. Cellulose forms when water is removed from glucose, which is produced by photosynthesis, to form glucose anhydride, which then polymerises to form a linear cellulose chain. Cellulose is linear since the β-glycosidic bonds only allow a linear conformation due to the pyranose chair conformation and the substituents that are on the equatorial position, which leads to lowest energy. Cellulose is insoluble, with a degree of polymerisation of between 7 000 and 15 000, and is crystalline (Fengel & Wegener, 1983: 77–105). Intramolecular and intra-strand hydrogen bonds hold the network flat, allowing the hydrophobic ribbon faces to stack (Zugenmaier, 2001). Cellulose has a tendency to form crystals that utilise intramolecular and intermolecular hydrogen bonds. This makes it insoluble in normal aqueous solutions. Groups of 35–100 cellulose chains twist in space to make a microfibril. These microfibrils group together (bonded by hemicellulose and lignin) to form fibrils, which in turn form fibres; these provide the strength in cell walls (Fengel & Wegener, 1984: 66–105). The crystalline structure resists thermal decomposition better than hemicelluloses. There are amorphous regions in cellulose that contain waters of hydration, and free water is also present within the wood. This water, when rapidly heated, can disrupt the structure by a steam explosion-like process prior to chemical dehydration of the cellulose molecules (Mohan et al., 2006).

Of all the lignocellulosic materials, the thermal decomposition of cellulose has been most investigated and is best understood. The Waterloo mechanism is widely accepted to represent the reaction pathway. This mechanism is shown in Figure 1 (Van de Velden et al., 2010).
Figure 1: Schematic showing the decomposition of cellulose according to the Waterloo mechanism (Van de Velden et al., 2010)

Cellulose degradation starts at temperatures as low as 325 K; this is characterised by a decreasing degree of polymerisation. Cellulose decomposition typically occurs between 240 °C and 350 °C (Tang & Neill, 2007). The decomposition of cellulose can be seen to occur in three competitive reactions, according to the Waterloo mechanism (Van de Velden et al., 2010).

1. **Dehydration.** This type of cellulose reaction dominates at temperatures below 575 K and at low heating rates. Cellulose is converted to char, gases and water. The char consists of anhydrocellulose which is more stable than cellulose, leading to higher char yields. The gases consist mainly of water, CO₂ and CO.

2. **Depolymerisation.** Cellulose is converted to levoglucosan and other anhydrosugars. This type of reaction dominates at temperatures between 573 K and 723 K.

3. **Fragmentation.** Cellulose is fragmented into hydroxyacetaldehyde and other carbonyls, acids and alcohols. Fragmentation is most dominant at temperatures around 873 K.

This mechanism is in strong agreement with another accepted mechanism, the Broid-Shafizadeh model (Demirbaş, 2000; Balat, 2008). This model suggests that active cellulose proceeds according to two reactions. The first is gradual degradation, decomposition and charring at lower temperatures and heating rates. The second is rapid volatilisation, accompanied by levoglucosan formation at high temperatures and heating rates. The initial degradation includes reactions such as depolymerisation, hydrolysis, oxidation, dehydration and decarboxylation. Higher heating rates result in decreased formation of char, which is accompanied by increased formation of tar. The tar from pyrolysis of cellulose consists
mainly of levoglucosan, whereas the aqueous phase consists mainly of aldehydes, furan, acetone, diones (diketones) and alcohols. High char yields are obtained for slow heating rates due to the dominance of dehydration. High heating rates and high temperatures result in depolymerisation of the unstable cellulose, decreasing the time for dehydration reactions to take place; these result in lower char yields. Rapid depolymerisation can lead to the recovery of free sugars in the tar which are produced from levoglucosan and its condensation products (Demirbaş, 2000; Balat, 2008).

Budarin et al. (2010) conducted experiments on the microwave decomposition of cellulose. They concluded that microwave irradiation greatly increases the decomposition of cellulose after it has softened (this occurs at 180 °C, suggesting a glass transition). This allows the low-temperature decomposition of cellulose under microwave heating to yield products that require much higher temperatures (100 °C higher). Mašek et al. (2013) made similar observations when microwave-assisted pyrolysis at low temperatures (170–200 °C) yielded similar product yields compared with conventional pyrolysis at much higher temperatures (160 °C higher).

Budarin et al. (2009) suggested that the behaviour of cellulose is critical to the breakdown of the entire biomass sample. It triggers the formation of reactive species such as radicals, water and acids. These reactive species can assist in breaking down relatively inactive components such as lignin. Therefore lignin in the biomass matrix can decompose at conditions where lignin alone would be unlikely to break down.

### 2.3.2 Hemicellulose

Hemicellulose, also known as polyose, contributes between 15 and 35%, and 20 and 32% of dry wood for hardwoods and softwoods respectively. It is speculated that hemicellulose plays a major role in water transport and the bonding of cellulose to lignin within the cell wall. Hemicellulose differs from cellulose due to the various sugar units that make up its backbone, namely xylose, mannose, glucose, galactose, arabinose, 4-O-methyl-glucuronic acid and galacturonic acid. It also differs from cellulose in that it has short-branched chains instead having around 50–200 repeating units which result in lower molecular mass. Xylose is the dominant building unit of hemicellulose in most wood species. Hardwoods contain between 20 and 25% xylose and softwoods only 7 to 12%. Mannose, which is also very abundant in hemicellulose, is usually higher in softwoods than in hardwoods (Fengel & Wegener, 1983: 57–77).
Hemicellulose decomposes at temperatures of 200–260 °C. The decomposition of hemicellulose leads to production of more volatiles, less tars and less chars than cellulose (Goldstein, 1981: 63–95). The decomposition of hemicellulose is similar to that of cellulose with dehydration at low temperatures (< 553 K) and depolymerisation at higher temperatures. Under certain conditions fragmentation can occur as well. Dehydration produces anhydride fragments, water-soluble acids, char, gases and water. Acetic acid forms via elimination of xylan acetyl groups. Formic acid is formed by carboxylic acids or uronic acid. Depolymerisation yields volatile organics, levoglucosan and other anhydrohexoses, levoglucosenone and furans. Furfural arises from the dehydration of xylose units. Methanol originates from the methoxyl group in uronic acid (Van de Velden et al., 2010). Hemicellulose reacts more readily than cellulose, with xylan being the least thermally stable. This is because pentosans are most susceptible to hydrolysis and dehydration reactions (Balat, 2008).

2.3.3 Lignin

Lignin is the third major component of wood and typically accounts for 18–25% in hardwoods and 25–35% in softwoods. It is a complex polymer built from phenyl-propane units that occur in a variety of forms and therefore its exact composition is uncertain. Lignin is very intimately associated with cellulose in the cell walls and is responsible for some of the major properties of wood. It acts as a binder for cellulosic components, makes cell walls resistant to decay and insect attacks, and plays a vital role in the transport of water, nutrients and metabolites. Lignin is an amorphous, highly branched, three-dimensional substance and exhibits p-coumaryl, coniferyl and sinapyl structures. It is formed by a process called lignification which is the random polymerisation of phenylpropanoid compounds. Lignin precursors are derived from glucose produced during photosynthesis. The biosynthesis of lignin is complex and is not being discussed in this section. Detailed information regarding lignin and lignin biosynthesis can be found in Fengel & Wegener (1983: 132–179).

Different from cellulose and hemicellulose, ether bonds dominate lignin connections instead of acetal functions. Lignin also contains carbon-to-carbon and covalent linking to polysaccharides. This enhances the adhesive bond strength between cellulose fibres and their lignin “potting matrix” (Fengel & Wegener, 1983: 132–179).

Some studies done on lignin give different physical and chemical properties, depending on the extraction method. This is because lignin is always, in some way or another, modified or
degraded during isolation (Fengel & Wegener, 1983: 132–179). Therefore thermal degradation studies on isolated lignin will not necessarily match the pyrolysis behaviour of the component when present in its true form in the biomass. Lignin decomposes when heated at 280–500 °C. The main products of lignin pyrolysis are guaiacol and pyrogallol dimethyl ether. Lignin is more stable than both cellulose and hemicellulose and yields more char and tar fractions (Demirbaş, 2000). The liquid product from lignin pyrolysis consists of aqueous and tar components. The aqueous fraction is composed mainly of methanol, acetic acid, acetone and water. The tar component consists of phenolics and other aromatics (Mohan et al., 2006). Phenolics are formed by the cracking of phenyl-propane units in the macromolecule via the cleavage of ether and carbon-carbon linkages. Commonly, the most substituted phenols are produced selectively. It is suggested that the aromatics and phenols and their alkyl-substituted fractions are formed by recombination and cyclisation reactions via Aldol condensation. These products are formed initially and further decomposition can yield furans, ketones and aldehydes (Demirbaş, 2000). The gas product from lignin pyrolysis typically represents 10 wt % of the original lignin and consists of methane, ethane and carbon monoxide (Mohan et al., 2006). A detailed study of the mechanism of lignin pyrolysis is given by Demirbaş (2000).

Chan and Krieger (1981) proved that microwave heating of lignin had various advantages over conventional heating. They found that lignin is a poorer microwave absorber than cellulose and hemicellulose (which is expected due to the less-polar structure). They conclude that microwave pyrolysis can overcome the heat transfer limitations of conventional pyrolysis, providing rapid volumetric heating to large-sized particles.

2.3.4 Secondary reactions

Secondary reactions occur mostly in the vapour phase, or during vapour-solids contact, and produce gas. These secondary reactions reduce the yield of the desired bio-oil and therefore should be avoided (Van de Velden et al., 2010). The two main reactions are:

1. **Cracking.** High molecular weight components crack to form simpler molecules and occur above temperatures of 973 K.
2. **Water-gas shift.**
   \[ H_2O + CO \leftrightarrow H_2 + CO_2 \]
   This occurs above 1083 K.

These reactions are unfavourable and can be avoided by using fast residence times and operating below 923 K where these reactions are limited.
Microwave heating reduces secondary cracking, compared with conventional heating, due to the internal heating mechanism, as explained in Section 2.2.

2.4 Conclusions

In this chapter the reaction mechanism and heating mechanism of microwave pyrolysis were discussed. The heating rate of wood during microwave heating depends greatly on its dielectric properties. Most of the microwave absorption is due to the water phase until the wood has been converted into char with the onset of pyrolysis. This char then absorbs most of the microwave energy and results in subsequent pyrolysis. The advantages of microwave heating were discussed. One of the main advantages is rapid and efficient volumetric heating. Another fascinating and unique advantage is the low-temperature pyrolysis, whereby pyrolysis can be achieved at much lower temperatures than are typically required by conventional pyrolysis. The shortcomings of microwave pyrolysis were also briefly discussed, along with key factors of microwave processing.

A detailed discussion of the reaction mechanism of the major wood components identified dehydration, depolymerisation and fragmentation as the major reaction mechanisms, each dominating at various temperatures. The decomposition of the individual components (cellulose, hemicellulose and lignin) and the reactions associated with their decomposition were discussed, as well as their contribution to the decomposition of the wood matrix. Cellulose was found to react differently under microwave heating due to the glass transition temperature of cellulose, which is around 180 °C and leads to decomposition temperatures much lower than with conventional pyrolysis. Cellulose plays a crucial part in the breakdown of biomass samples due to the reactive chemical compounds that result from its decomposition. Possible secondary reactions were also discussed and it was found that with microwave pyrolysis wood undergoes less secondary cracking due to its inverse temperature gradient during heating.
Chapter 3
A microwave reactor for cheap and comparative research

3.1 Introduction

Microwave pyrolysis has received increased interest in the last couple of years due to the possible advantages of microwave heating over conventional heating. Even though various advances have been made, pyrolysis and, even more so, microwave pyrolysis are still not well understood (Yin, 2012). Further research is needed in the field to mature the technology to a point where it is sufficiently understood to allow for industrialisation. Yields and costs need to be optimised to make the technology more economically attractive.

There are various types of off-the-shelf microwave reactor that have recently been used for microwave pyrolysis research. These are mainly the 1 000 W Sineo MAS-II batch microwave oven (Shanghai, China) and the 1 200 W Milestone Roto Synth Rotative Solid-Phase Microwave Reactor (Milestone Srl., Italy) fitted with a VAC 2000 vacuum module in series. These off-the-self units make research very standardised and easy. The problem, however, is that these setups are expensive and therefore only limited researchers have access to such systems. This gave rise to the use of modified domestic microwaves for research purposes.

There have been various studies that used modified domestic microwaves for microwave pyrolysis (Zhao et al., 2012; Wang et al., 2012). These setups, however, utilise stationary and/or small biomass loadings (15 g). This is not necessarily representative of larger-scale processes where reactors will be limited by penetration depth and heating modes within the microwave. High energy modes will result in hotspots in stationary bed reactors and will result in regions of low microwave energy where conventional heating (conduction and convection) will dominate heat transfer. This demonstrates the importance of a mixing system in microwave pyrolysis experiments. There have also been various studies that used single-mode microwave setups (Huang et al., 2010; Huang et al. 2013; Robinson et al., 2010; Domínguez et al., 2007). Single-mode ovens tend to give lower yields (Domínguez et al., 2007) and there are concerns regarding the applicability of single-mode microwaves in large-scale reactors. Large-scale setups have also been reported (Zhao et al., 2010; Zhao et al., 2011), but mixing has also been neglected in these setups. There is therefore a need for a
cheap microwave setup, which incorporates efficient mixing and compares reasonably well with the off-the-shelf systems that are available.

The purpose of this chapter is to compare the results from a modified domestic microwave setup with those from the Roto Synth Rotative Microwave Oven to determine whether a domestic microwave can be used for comparable microwave pyrolysis research.

This chapter will investigate the results from a 1 000 W domestic Defy microwave oven and is limited to the design suggested. Because the domestic microwave is still small (21 cm × 35 cm × 35 cm) compared with large-scale reactors, it does not necessarily suggest that the findings can be extrapolated to a large scale.

### 3.2 Experimental

#### 3.2.1 Materials

*E. grandis* wood chips were supplied by Sappi Technology Centre, South Africa. Wood chips (dp< 5 mm) were used as is and had an average moisture content of 12.3% ± 2%. A large variance in the moisture content was a result of the particle size distribution within the sample, with the smaller particles having lower moisture content than the larger particles. The material of construction for the modified domestic microwave setup was mainly stainless steel and borosilicate glass.

#### 3.2.2 Apparatus

A schematic diagram of the modified domestic microwave reactor is shown in Figure 2. The design consists of five main components/systems:

1. A modified 1 000 W Defy domestic microwave which serves as the microwave generator and cavity.
2. The reactor in which the pyrolysis takes place, which consists of a Consol preserve jar made from borosilicate glass. The glass reactor is sealed via a custom-made Teflon lid and silicone rubber, as seen in Figure 3.
3. The rotation system, which consists of a stainless steel pipe assembly with a rotating union and support bearing. The rotating union is fitted with a 3D printed gear assembly that connects it to a stepper motor (bipolar stepper motor with planet gearbox with a gear ratio of 5.18). The stepper motor is controlled via an Arduino microcontroller and stepper motor driver from a computer. This allows easy manipulation of rotation direction and speed.
Rotation of the reaction vessel ensures mixing for better heating homogeneity (see Figure 5).

4. The product cooling and collection system. For rapid cooling of the volatiles, the gas goes through a cooling system which consists of an initial liquid trap and four consecutive condensers, all submerged and circulated by water at 0 °C from an ice bath and circulation pump.

![Diagram of modified domestic microwave oven with rotation, temperature and/or pressure measurement and product cooling and collection](image)

**Figure 2:** Modified domestic microwave oven with rotation, temperature and/or pressure measurement and product cooling and collection

The solid product is contained inside the vessel by a fine mesh (which serves as a solids separator), which fits into the pipe assembly (see Figure 4). The majority of the condensable volatiles are swept from the reactor via the N₂ carrier gas and are captured in the gas cooling system. The non-condensable gases then leave through an extraction fan.

5. The data acquisition system. This consists of a temperature and/or pressure transmitter that sends signals to the computer which records the measurements with time to produce pressure and temperature profiles. The current design only measures the temperature of the
emerged gas and is not in direct contact with the wood particles. Figures 3 to 5 show photos of the actual setup.

Figure 3: Teflon disks machined into a reaction vessel lid, also showing how the Consol borosilicate preserve jar is used as a reaction vessel

Figure 4: Inside of the microwave cavity, showing the pipe assembly to which the reaction vessel is attached. Also shown are the carrier gas nozzle and mesh
3.2.3 Method

Modified domestic microwave

All experiments were conducted in triplicate. The average is reported with error bars indicating the standard deviation. Before the start of an experiment all relevant glassware and pipes are weighed (OHAUS Explorer Pro balance, accuracy = 0.01 g) for mass balance purposes. The glass reactor is charged with 100 g ± 0.5 g of wood chips. For these experiments no additional microwave absorber or catalyst was added. The piping and tubes are connected as shown in Figure 2 and the reactor is screwed to the rotating pipe assembly (see Figure 4). The nitrogen supply is turned on, allowing the sample to be purged for 1 minute to remove most of the oxygen in the reaction vessel. The circulation pump is turned on, allowing the water from the ice bath to cool the condensers. The rotation speed is selected on the computer and the Arduino code uploaded to the microcontroller. The nitrogen flow is set so that it just barely provides a positive flow to carry the released volatiles to the condensers.
The microwave power is set (it was kept at maximum output power of 1000 W for all experiments) and all systems are turned on. All powers indicated represent output power value. The sample is irradiated for 6 minutes, after which the microwave is turned off. Nitrogen flow continues for 5 additional minutes which allows any remaining volatiles to be removed and the reactor to be cooled sufficiently to handle. The entire setup is then disassembled and the relevant parts are weighed. The char yield is determined from the reactor weight and the oil yield is determined from the piping and collection flasks. The gas yield (which includes the process losses) is determined by difference according to Equation 5. Wet yields are reported in this section; no corrections were made for the moisture content in the wood.

\[
\text{Gas \& Loss} = \text{Wood} - \text{Char} - \text{Oil}
\]  \hspace{1cm} (5)

**Roto Synth Rotative microwave oven**

The Roto Synth Microwave setup was treated very similarly to the domestic setup. The mass balance was achieved by weighing the relevant parts before and after each experimental run. Microwave power, nitrogen flow and treatment times were the same as described for the modified domestic microwave. A detailed description of the Roto Synth microwave setup and method can be found in Chapter 4, Section 4.3.

### 3.3 Results and discussion

Figure 6 shows the results for the microwave pyrolysis of *E. grandis* at 1000 W microwave output and a 6 minute exposure time. The wet yields for char, oil and gas for the Roto Synth and modified domestic microwaves were 46.75 ± 0.03%, 32.69 ± 0.61% and 20.55 ± 0.57%, and 47.91 ± 0.22%, 33.21 ± 0.26% and 18.88 ± 0.04%, respectively.
Taking the standard deviation into account the liquid yields for the two setups seem to be similar but the modified domestic setup produced more char (1.16% more). It is usually expected that more char means less oil would be produced. This discrepancy might be due to the improved vapour-collection system of the modified domestic setup since significant amounts of oil remained trapped in the condensers of the Vac 2000 unit, whereas these oils are collected in the custom setup. This is supported by the lower yields (1.67% lower) of gas in the custom setup. The lower amount of char for the Roto Synth apparatus suggests better conversion of energy. This might be attributed to a higher-quality magnetron and microwave cavity on the Roto Synth unit. Overall, the results are very similar and it is concluded that the results from the modified domestic microwave setup compare well with those from the Roto Synth unit.

Comparison in this chapter is limited to the maximum power output of the domestic microwave (1 000 W) and only the yields of the reactors were compared. The temperature profiles were not compared since the Roto Synth measures the surface temperature of the particles, whereas the domestic microwave setup measures the temperature of the gas (which is a mix of N\textsubscript{2} and released volatiles). The yields show that the reactors are comparable and it
will be worthwhile to compare the temperature profiles in future work. In order to compare the temperature profiles accurately, a thermocouple that is in contact with the particles will need to be used. Comparison of oil quality is expensive and was therefore neglected, but it is expected to be very similar if the heating rates are similar.

There are a few crucial design aspects of the modified domestic microwave oven that also need to be discussed. The design is very similar to that of the Roto Synth microwave, but addresses some of its limitations. It was observed that since the Roto Synth reactor is angled (approx. 45°), compaction of the chips upon rotation and mixing is not achieved. This leads to unconverted fractions at the bottom of the reaction vessel which can lead to lower yields. As the vessel in the modified domestic microwave is at a 90° angle, this, along with a slow to moderate rotation speed, allows the particles to roll over one another and leads to improved mixing. Another deficiency of the Roto Synth apparatus was the condensation of oil on the reactor walls. This was because the carrier gas was only directed above the sample and “trapped” a portion of the volatiles in the vessel. The use of a carrier gas did, however, improve the extraction of volatiles from the vessel (compared with vacuum experiments) as explained in Section 4.4.5. To further improve volatile extraction, the carrier gas was directed into the sample via a steel tube extending almost the entire length of the reactor, as illustrated in Figure 4. This allowed the carrier gas to sweep out all the released volatiles. A Consol borosilicate preserve jar was chosen as the reaction vessel since these are widely available and cheap. The borosilicate glass allows higher temperature and temperature gradients than normal glassware and makes it more suitable for this application. However, the Consol reaction vessel proved to be one of the biggest flaws of the design.

It was apparent that even though the modified domestic setup gave comparable results, it was not optimal. The main issues regarding the setup included the reaction vessel, stepper motor driver and temperature measurement. The reaction vessel gave the most significant problems, leading to misruns and repeats. This vessel, which consisted of a borosilicate Consol preserve jar, was prone to random breaking or cracking. This behaviour was inconsistent since some vessels could endure an entire 6 minute run, whereas others broke around the 2 or 3 minute mark. This random behaviour might be due to internal flaws or because borosilicate glass absorbs microwaves to some extent. The solution to this problem is easy. It is known that quartz vessels are most suitable for high-temperature and microwave application. Even though they are expensive, a quartz vessel will be crucial to improve the operation of this setup. Other problems included excessive heating of the stepper motor driver if the setup was
used continually for too long. This can be improved by using a high current driver or by cooling the driver with forced airflow. The temperature measurement as is does not provide accurate information regarding the reaction temperature. Microwave heating targets the wood particles and these are often much hotter than the released volatiles (which are also cooled by incoming nitrogen and the surroundings). Therefore measurement of the gas temperature is not sufficient for microwave pyrolysis. The solution would be to extend the thermocouple into the reactor. Usually metal objects cannot be inserted into microwave fields without severely distorting them or causing an electrical discharge (arching). However, it has been shown that it is possible to use thermocouples in a magnetic field, if they are thin, have a grounded sheath and are held directly at a 90° angle to the electric field component (Zhao, et al., 2013).

It has been established that the performance of the modified domestic microwave is comparable to that of the Roto Synth apparatus. The complete setup for the domestic microwave (excluding glassware, ice bath and computer, which are standard in most laboratories) costs around R7 000 to R10 000. The Milestone Flexiwave system which has replaced the Roto Synth typically costs around R750 000 (Magna Analytical, South Africa). This shows that this and similar modified domestic setups can be used for cheap and comparable microwave pyrolysis research.

3.4 Conclusions and recommendations

A comparison was made between the performances of a modified domestic microwave and a Roto Synth rotative microwave unit. The comparison was based on product yields only – temperature profiles and oil quality were not considered. It was concluded that the custom setup gave comparable results to the Roto Synth. The domestic setup yielded slightly higher (1.16%) char fractions with similar oil yields. This indicates that the vapour-collection system for the modified domestic setup was better compared to that of the Roto Synth unit.

It was shown that modified domestic microwave setups can provide a cheap and comparable means for microwave pyrolysis research. The custom setup is not yet optimised and it is recommended that a quartz reactor be used to improve the operation of the setup. Attention should also be given to the stepper driver and thermocouple.
Chapter 4
Microwave pyrolysis of *E. grandis*

4.1 Introduction

Microwave pyrolysis offers several advantages over conventional pyrolysis and has therefore been the recent focus of various researchers. It is not as mature as conventional pyrolysis and a lot of the key design aspects are still unknown. Efforts regarding large-scale processing, such as the absence of sufficient dielectric data, doubts about the actual costs of this technique and heat and mass transfer properties, are still needed for market penetration (Motasemi & Afzal, 2013). These uncertainties emphasise the need for additional research in the field.

Various researchers have investigated the impact of parameters such as microwave power, reaction time and temperature, but few researchers have investigated the effect of power density (apart from Robinson *et al.*, 2010). A base-case study is required to evaluate the performance of catalysts and changes they cause to the process.

The objective of this investigation was to determine the effect of power, power density, moisture content and particle size, as well as the presence of a carrier gas, on the microwave pyrolysis process. The results would serve as a basis for microwave pyrolysis to which catalysed microwave work can be compared. Specific attention was given to the applicability of the results to large-scale reactors and future possibilities for microwave pyrolysis technology.

4.2 Parameters influencing microwave pyrolysis

There are various factors that influence the microwave pyrolysis reaction and therefore the yields and compositions of the products. The effects of most of these parameters on the product yields are well known and understood. However the influence of these parameters, on product compositions, are very complex and not completely understood since they have not been a topic of many researchers. Composition effects are therefore not discussed here.

It is generally accepted that the most important parameters in microwave pyrolysis are temperature, reaction time and power. Other factors that also play a significant role are the feed material, moisture content, particle size, absorbents and catalysts. Further factors that
have a lesser effect include microwave type, reactor design, inert gas flow rate and mixing intensity.

4.2.1 Reaction temperature and time

Most researchers agree that temperature and heating rate are the most important factors for optimising any of the product yields of pyrolysis. An increase in reaction temperatures and time usually results in a decrease in the char yield. This is attributed mainly to the increase in the devolatilisation of organic material, but partial gasification can also occur to some extent (Domínguez et al., 2007). This decrease in char yield reaches a plateau at a certain temperature which is dependent on various conditions, such as the feedstock material and reactor conditions (Wang, Cao & Wang, 2009; Zhao et al., 2012). Temperature also has other influences on the char, with increases in temperature leading to increased surface areas and pore volumes and decreased pore size (Zhao et al., 2012).

As temperature and reaction time increase, the decrease in char/solid yield is accompanied by an increase in gas and liquid phase yields. The increase in gas yield with temperature increases is significantly greater than the increase in liquid yield. Syngas yields are also reported to increase under high-temperature conditions. Liquid yields have consistently been observed to increase initially with an increase in temperature up to a maximum, then to decrease with further increases in temperature (Lei, Ren & Julson, 2009; Lei et al., 2011; Ren et al., 2012; Zhao et al., 2013).

Various researchers (Lei et al., 2009; Zhao et al., 2012; Zhao et al., 2013) have conducted microwave pyrolysis at constant temperature to determine the effect of temperature on the microwave pyrolysis process. The researchers note that the heating time (up to the set temperature) should be kept as short as possible, but their results indicate that set temperatures of 500 °C were only reached within 240 s and 700 s for the Lei et al. (2009) and Zhao et al. (2012) experiments respectively. However, other researchers suggest that the pyrolysis reaction is already completed within the first 6 minutes (Budarin et al., 2009).

Even though the effect of these parameters on the product composition is not discussed in this dissertation, references for such data are given here. Ren et al. (2012) discuss the effect of temperature and retention time on the composition of microwave pyrolysis bio-oil, while Zhao et al. (2013) discuss the effect of temperature on gas product composition.
4.2.2 Power/power density and heating rate

The heating rate is of crucial importance for high oil yields. It is commonly known that for conventional pyrolysis, low heating rates promote the formation of char with low liquid and gas yields. High heating rates lead to high liquid yields and increased gas yields, with low char yields. Increased power leads to higher power densities which, according to Equations 2 and 3, should lead to increased heating rates. The effect of power and heating rate in microwave pyrolysis is similar to that of temperature and leads to a decrease in char yield, with an increase in liquid and gas yields (Robinson et al., 2010; Zhao et al., 2013). Lei et al. (2011) suggested that power had no significant effect on char and gas yield, but had a prominent effect on liquid yield. This disagrees with the results of Huang et al. (2013) who state that gas yields increase and char yields decrease with increasing power, while liquid yields remain unaffected. This gives an indication that the impact of this parameter is dependent on either the feed material or reactor conditions or a combination of these. Robinson et al. (2010) reported that power density has a much greater influence than overall energy input – increasing power densities lead to increased liquid and vapour yields. They also noted that higher power levels at the same overall energy input lead to higher liquid and gas yields. This, in essence, translates to heating rates, meaning that higher heating rates give improved oil yields. This was confirmed by the results of Lei et al. (2011). Robinson et al. (2010) suggested that a threshold power exists below which microwave pyrolysis, with only water as microwave absorber, would not occur. Salema and Ani (2011) agree with this.

Heating rates typically reported by researchers are between 10 °C/min and 100 °C/min, with Wang et al. (2012) reporting that the maximum heating rates were close to 300 °C/min.

4.2.3 Penetration depth

Clark et al. (2000) discussed the fundamentals of microwave processing as explained in Section 2.2 of this document. They explain that penetration depth plays a significant role in microwave processing. Nevertheless, the majority of researchers neglect to take penetration depth into account since their samples are usually too small. Zhao et al. (2010) showed the effect of penetration depth by placing thermocouples at different distances from the microwave source, inside the large biomass sample. They show that the outer layers absorb the majority of the microwave energy causing the inner layers to be heated partly by conduction. This shows that penetration depth may possibly limit the efficiency of large-scale reactors.
4.2.4 Feed

Fernández and Menéndez (2011) found that the feedstock material can have a significant effect on both the yield and composition of the products. The effects are mainly due to the products’ elemental analysis, volatiles, ash and fixed carbon contents. These effects are very complex and not yet fully understood. This proves that selection of the proper feed material can improve yield and oil characteristics, making the technology more economically viable. A review of pyrolysis research on different biomass sources can also be found in Macquarrie et al., (2012).

4.2.5 Microwave absorbers

Biomass is typically not a good absorber of microwaves, especially when dry, due to the weak dielectric properties of certain biomass (Robinson et al., 2010; Salema & Ani, 2011). This suggests that microwave absorbents are necessary in some microwave pyrolysis applications. Water is a very important microwave absorber and researchers (Robinson et al., 2010, Wang et al., 2012 and others) have shown that pyrolysis is possible with water as the only main microwave-absorbing phase. Other efficient microwave absorbers include char from the pyrolysis process, activated carbon and silicon carbide (SiC). The latter is an excellent inert microwave absorber that can handle extreme temperatures and could possibly play a major role in efficient heat transfer in microwave pyrolysis. Microwave absorbents have high dielectric constants and ensure efficient conversion of microwave energy into heat, thereby promoting better energy transfer. They therefore increase temperatures and in some cases initiate pyrolysis. The ratio of absorber to feed is important since too low a ratio will result in poor energy transfer, whereas ratios that are too high will lead to localised heating and hotspots (Salema & Ani, 2011). Microwave absorbers also have an effect on product compositions since they can act as catalysts as well. This is not discussed here, but related results can be found in Zuo, Tian and Ren (2011).

4.2.6 Moisture content

Robinson et al. (2010) and Omar et al. (2011) investigated the influence of moisture content on the yields of microwave pyrolysis products. An increase in moisture content leads to an increase in the bulk dielectric loss of the biomass, which improves the overall microwave energy utilisation. A moisture content of up to 45% was found to be beneficial, after which the efficiency started to decrease. However, an increase in moisture content leads to decreased bio-oil and gas yields for similar reaction temperatures and times since more water
needs to be evaporated. Most of the water reports to the liquid phase and is therefore inevitably mixed with the oil. This leads to low calorific values of oils from samples with a high moisture content. Therefore a good balance needs to be found between optimum microwave absorption and oil quality, or an efficient separation method needs to be developed.

4.2.7 Particle size

It has been widely accepted that any particle size limitation for microwave pyrolysis can be mitigated due to its characteristic rapid and volumetric heating (Zhao et al., 2010). Miura et al. (2004) suggested that large-diameter biomass particles can be pyrolysed using less electric power per unit mass than smaller particles. This was confirmed by Zhao et al. (2011) who found that an increase in mass of large-volume straw bale required less energy per unit mass. Lei et al. (2009) investigated particle sizes between 0.5 and 4 mm for microwave pyrolysis and found that the particle size had no impact on the product yields, which makes microwave pyrolysis ideal for rapid volumetric heating of large particles.

4.2.8 Catalysts and additives

Catalysts or additives can have a vast range of influences on both the product yield and composition, depending on the concentration and type of catalyst or additive. These influences are complex and material dependent. A more detailed discussion on this topic can be found in Chapter 5.

4.2.9 Other

Motasemi and Afzal (2013) suggested that other factors such as microwave type (single-mode or multi-mode), microwave reactor design, inert gas flow rate, inert gas type (nitrogen or helium) and mixing intensity also play a part in microwave pyrolysis products.

4.3 Experimental

4.3.1 Materials

Three different sizes of E. grandis wood chips were supplied by Sappi Technology Centre, South Africa. The particle sizes were small (S – 0.5 mm <dp< 1 mm), medium (M – 1 mm <dp< 6 mm) and large (L – approx. 30 mm × 15 mm × 5 mm). These can be seen in Figure 7. The moisture content (MC) was determined as 6.6 ± 0.1%, 12.1 ± 0.2 % and 25.5 ± 1.1% for the S, M and L particles respectively. The MC varied between samples,
especially for the large particle sizes, which may lead to inaccuracies. Since the small particles were most consistent in size and MC, they were used as the control experiments. The elemental analysis (dry basis) for *E. grandis* was determined by the Agricultural Research Council (ARC) and is shown in Table 3; nitrogen content was not determined. The proximate analysis, lignocellulosic composition, ash content and calorific value are also shown in Table 3, all on a mass basis.

**Table 3: Physical properties of *E. grandis* wood chips (S)**

<table>
<thead>
<tr>
<th>Lignocellulosic composition</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>Hemicellulose</td>
</tr>
<tr>
<td>45.3%</td>
<td>17.5%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>Volatile matter</td>
</tr>
<tr>
<td>6.6%</td>
<td>76.2%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate analysis</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>47.4%</td>
<td>5.4%</td>
</tr>
<tr>
<td>Calorific value (MJ/kg)</td>
<td>16.7</td>
</tr>
</tbody>
</table>

![Figure 7: Different particle sizes used and their dimensions](Image)
4.3.2 Apparatus and method

Experiments were completed in triplicate and yields shown indicate the standard deviation in the form of error bars. Process profiles represent only one set of data. The microwave treatment of *E. grandis* wood chips was carried out in a Milestone Roto Synth Rotative Solid-Phase Microwave Reactor (Milestone Srl. Italy), fitted with a VAC 2000 vacuum unit in series. A descriptive figure of the setup is given in Budarin *et al.* (2009). The Pyrex® reactor vessel was charged with 50–200 g of specific size sample and irradiated at various power levels (600–1 200 W output power). All powers indicated represent output powers. The reaction time was predominantly kept constant at 6 minutes, but longer (7–10 minute) runs were also done. Most runs were conducted under constant nitrogen flow but, for comparison, runs under vacuum only were also done. The control experiment conditions were: 100 g small-sized sample, irradiated for 6 minutes at 1 000 W under constant nitrogen flow. The pressure and temperature profiles were monitored at all times. Temperature measurement was done via an infrared pyrometer installed in the microwave cavity, measuring the surface temperature of the reaction vessel. The pyrometer is calibrated using a water sample by adjusting the emissivity level so that the infrared temperature corresponds to the temperature of the internal fibre temperature probe. The temperature probe is only rated for 180 °C and will get damaged above these temperatures and was therefore not used for these experiments. The pressure profile shows the absolute pressure. Even under nitrogen flow, pressure typically remained between 250 and 500 mBar and was still under vacuum due to the VAC 2000 vacuum unit.

The independent variables considered in these experiments are power (since power influences temperature, power density and heating rate), power density (using various powers and changing sample loadings), particle size and MC. The dependent variables are the product distribution, temperature profiles and pressure profiles. The influence of these variables on the chemical composition of the product phases (char, oil and gas) was not the purpose of the investigation and was therefore not analysed.

The temperature and pressure profiles are automatically captured via a computer interface system coupled to the Roto Synth unit. These profiles are crucial variables since from these a probable description of the reaction process can be formulated. The product distribution (the yield of the different products) is determined by use of a mass balance. The individual parts of the experimental assembly are weighed before each experiment. After the completed run,
the parts are weighed again. The increase in mass of the glass reactor is attributed to the weight of the char. The increased weight of all other tubes and fittings is attributed to condensed oil. The difference between the original sample, the collected char and the collected oil is assumed to be the gas product (similar to Equation 5). The uncondensed gas therefore includes the mass of the oil remaining in the condensers. Significant amounts of oil remained trapped in the condensers of the VAC 2000 vacuum unit. Therefore the true product distribution will yield slightly higher oil yields and lower gas yields than what are reported here.

The lignocellulosic composition was determined using the NREL/TP-510 standards (standard 42618-42622 and TAPPI T 223 cm-10 Pentosans in Wood And Pulp standard). The results varied only slightly (the main difference was in cellulose) from data in the literature which reported cellulose, hemicellulose and lignin as 51%, 19% and 23% respectively (Barneto, Hernández & Berenguer, 2011).

The MC of the samples was determined using a Precisa HA 300 infrared moisture balance. Calorific values were measured using a LECO AC-350 automatic bomb calorimeter. The method used is based on the ISO 1928:2009 standard. The calorific value for char produced at 1 000 W for 6 minutes was ~ 31 MJ/kg. The proximate analysis of the sample was done using a PerkinElmer Pyris 1 thermogravimetric analyser (TGA) and closely simulating the ATSM standard E870-82. For the TGA experiments 20 mg of fine sample was loaded into the crucible and heated to 110 °C at 10 °C/min under nitrogen flow of 50 ml/min. Temperature was maintained for 10 minutes. The sample was then heated to 900 °C at 20 °C/min and held constant for 10 minutes. Thereafter the sample was held at 900 °C for a further 15 minutes under oxygen flow at 50 ml/min. It was then held at 900 °C for a further 5 minutes, once again under nitrogen flow of 50 ml/min.

4.4 Results and discussion

It is important to provide clarity on the how the yield is defined. The majority of the yields reported in this section and shown in the figures are the yields based on dry wood. “Dry wood” yield as used in this report is defined as the mass of dry product (adjusted for the MC in the original wood sample) over the mass of dry wood. The only product that needs to be adjusted is the oil since all the free water (MC of the wood) is assumed to report to the oil product. The MC of the wood is subtracted from the oil mass to give dry oil. This dry oil will still contain fractions of reaction water and bound water, and therefore it is not the yield on a
water-free basis. The wet yield is defined as the mass of product over the mass of sample without any corrections for moisture.

4.4.1 Describing the pyrolysis process

Figure 8 shows a pressure and temperature profile gathered from a typical pyrolysis process (under nitrogen flow). There are four clear process regions that can be identified. Region 1 is an initial heating region where the pressure in the reactor increases slightly due to the effects of temperature increase and humidity. Here water is the main microwave-absorbing phase. Region 2 is the water-evaporation stage in which the wood primarily dries. This can be seen from a roughly constant temperature region and the formation of the first pressure peak. It should be mentioned that the temperature measured is a surface temperature and it is therefore expected to be lower than the actual reactor temperature which should at this stage be close to 100 °C. Region 3 is the pyrolysis stage and here brown oil starts to condense in the condensers. This stage is marked by the formation of the primary pressure peak and an increased heating rate as wood is transformed into char which now becomes the main microwave-absorbing phase. Region 4 marks the completion of the process which can be seen from the constant pressure. Here char continues to absorb microwave energy and the temperature increases steadily. These regions are similar to those reported by Zhao et al. (2010). It can be seen that at these reactor conditions the reaction temperature does not even reach 200 °C and that microwave pyrolysis occurs at much lower temperatures than are typically reported for conventional pyrolysis. These results are in good agreement with those of Budarin et al., 2009; Lei et al., 2009; and Zhao et al., 2012.

Figure 8 shows that during the water evaporation stage, most of the water is evaporated before the onset of pyrolysis. This suggests that in microwave batch processes, most of the water can be separated by switching condensers at an appropriate time, just before the onset of pyrolysis. This should remove most of the water from the liquid product, reducing moisture content restrictions and improving the liquid product quality.

It should be mentioned that the surface temperature shown as the temperature profile is not necessarily an accurate measure of the internal vessel temperature. This is because the pyrometer has not specifically been calibrated for wood samples and also due to conduction and convection effects since the wood is not in perfect contact with the surface. These temperatures/ heating rates do however correspond closely to results reported for the same setup and conditions using the in-situ fibre temperature probe (Budarin et al., 2009).
From the pressure profile in Figure 8, it is clear that, typically, the pyrolysis reaction starts at around 2 minutes and ends at the 5th or 6th minute. This questions the findings of researchers who opt to investigate the constant-temperature characteristics of the pyrolysis reaction but have heating times longer than 6 minutes, since most of the reaction will already have been completed before the reactor reaches its set temperature. This behaviour may, however, be inherent to this specific type of biomass or experimental setup or a combination of these. The typical heating rates at these microwave conditions were found to be 30 °C/min. On the other hand, this is a surface temperature and the actual particle temperatures may be much higher than this, making the true heating rate faster than that reported here. Researchers such as Wang et al. (2012) have reported heating rates much higher than these for similar microwave powers and sample loadings. Once again, this might be due to the characteristics of the biomass type or experimental apparatus. Another possible explanation is mixing and heap effects. Other researchers who have reported high heating rates used stationary setups. It is possible that localised hotspots formed close to the measuring device, promoting the transition of wood to microwave-absorbing char, which led to increased heating rates near the measuring device. Heap effects can also minimise energy losses, improving heating rates.

### 4.4.2 Power

The influence of various power levels on the pyrolysis process was investigated. These power levels ranged from 600 W to 1 200 W. Results were determined for both small and medium-
sized particles to prove consistency of the trends. Figures 9 to 11 show the pressure profiles, temperature profiles and yields for small particles respectively. Figures 12 to 14 show the same graphs obtained for medium particles.

Figure 9: Pressure profiles obtained for various power levels at constant sample loading (100 g – 6 to 8 min – S)

Figure 10: Temperature profiles obtained for various power levels at constant sample loading (100 g – 6 to 8 min – S)
Figures 9 to 11 show distinct differences between the 1000 W process compared with the 800 W and 600 W processes. The 800 W and 600 W runs are very similar in yield, heating rate and vapour evolution times. Yields for char, oil and gas are 67.2 ± 0.89%, 19.9 ± 0.78% and 12.9 ± 1.10% for the 600 W runs, and 66.8 ± 0.56%, 19.9 ± 0.69% and 13.3 ± 0.13% for the 800 W process, respectively. This shows that these power levels produce similar yields. This is unexpected since higher power level is, according to literature, supposed to result in increased gas yields with slight to negligible increases in oil yield and a corresponding decrease in char yield. The heating rate of the 800 W runs is slightly faster than for the 600 W runs, which can be expected since higher power densities result in higher heating rates. The 1000 W runs differ significantly, with yields of 52.4 ± 1.35%, 28.6 ± 1.00% and 19.0 ± 0.34% for char, oil and gas. This means there were noteworthy increases in liquid (8.7%) and gas yield (5.7%), accompanied by a decrease in char formation (14.4%).
Figure 12: Pressure profiles obtained for various power levels at constant sample loading (100 g – 6 to 8 min – M)

Figure 13: Temperature profiles obtained for various power levels at constant sample loading (100 g – 6 to 8 min – M)
Figure 14: Product yields (dry wood basis) obtained for various power levels at constant sample loading (100 g – 6 to 8 min – M)

A similar trend was observed for the medium-sized particles. The results from Figures 12 to 14 show that power levels of 1 200 W and 1 000 W result in a significant difference from 800 W. Comparing 1 000 W and 1 200 W, these results again show that these conditions produced similar yields. Char, oil and gas yields of 52.9 ± 0.31%, 27.7 ± 1.64% and 19.4 ± 1.48%, and 51.7 ± 1.00%, 27.7 ± 0.62% and 20.6 ± 1.37% were determined for 1 000 W and 1 200 W respectively. These oil and gas yields are again higher than the 800 W runs, which were 61.7 ± 1.53%, 24.3 ± 2.11% and 14.0 ± 2.96%. The heating rates and pressure profiles for the 1 200 W and 1 000 W runs were very similar, implying that there was no additional power absorbed. The significant difference in results below 800W and above 1000W suggest that a “critical” power or power density lies between 800 W and 1 000 W.

This phenomenon may be a result of a reaction or a heating mechanism shift at certain powers or power densities. A possible explanation for this shift could the transition from wood to char. If powers or power densities above the critical level are used, the transition from wood to char occurs sufficiently fast before the wood becomes transparent to microwaves. This allows additional microwave energy to be absorbed by the char. Powers below the critical level, however, do not provide enough energy for this transition to occur sufficiently fast. Instead microwave energy is rather absorbed by water in neighbouring...
particles that have not yet been dried. Only after all the water has been evaporated and enough energy has been supplied to the poor microwave-absorbing wood does the transition occur and the onset of pyrolysis starts. This leads to significantly slower reaction rates and lower yields.

Chapter 2 that cellulose decomposes at much lower temperatures under microwave heating compared with conventional heating. This suggests that the transition from wood to char can occur at much lower temperatures, around 180 °C (Budarin et al., 2009; Budarin et al., 2010). This transition is therefore affected by the effective/real power density in the specific particle. If the effective power density is high enough, the wood particle will reach the required temperature before it dries out and becomes more transparent to the microwaves, thereby forming microwave absorbing char that will promote further pyrolysis. The effective power density in the wood chips will depend to a big extent on the targeted wood volume which will be dependent on the penetration depth. This processing factor has generally been neglected by researchers, and is related to the dielectric properties and therefore to a large extent moisture content. Omar et al. (2011) showed typical penetration depths of 1–4 cm for moisture contents of 18–30 %, but increases significantly at lower moisture. Zhao et al. (2010) showed that penetration depth may possibly limit the efficiency of large-scale reactors. This suggests that penetration depth can possibly play a big role in microwave pyrolysis processes.

4.4.3 Power density

In the previous experiments power density was changed by changing the power input. To investigate power density thoroughly different sample loadings (50–200 g) of small and medium particles were treated at a constant power of 1 000 W. This resulted in various power densities. Figures 15 to 17 show the pressure profiles, temperature profiles and yields for small particles at different power densities. Figures 18 to 20 show similar graphs for runs with medium-sized particles with other power densities.
It is clear from Figures 15 and 16 that for a power of 1 000 W, the pressure profiles for all power densities follow a similar trend. Lower power densities (meaning higher sample loadings) lead to larger peaks which developed slightly later. The peaks develop later mainly
due to the increased water in the reactor that needs to be evaporated. This is evident from the longer zones of constant temperature at lower power densities, as shown in Figures 18 and 19. The pressure peaks are higher since more volatiles are released, because there is more sample in the reactor. Figures 15 and 16 show that pyrolysis at 1 000 W, even at lower power densities (5 W/g), occurs much faster than the pyrolysis in Figure 12 at 800 W (8 W/g) and 600 W (6 W/g). Figure 16 shows that at a power density of 8 W/g and a power of 1 000 W, the reaction occurs faster than at 800 W (Figure 13) with a similar power density. This suggests that the power level plays a more significant role than power density in the pyrolysis process. This can also possibly be ascribed to the penetration depth of microwaves and the argument made in Section 4.4.2. Even though the sample in the reaction vessel is more, meaning an overall lower power density, the targeted wood volume can be similar. Therefore higher powers at lower overall power densities can still have higher effective power densities, at which the wood – char transition occurs sufficiently fast, leading to faster reaction rates and better yields. This demonstrates that reactor configuration and penetration depth can be crucial for microwave pyrolysis processes.

Figure 17 shows that at lower power densities the overall heating rate is much slower than at high power densities. The overall heating rates are 31.1 °C/min, 25.1 °C/min and 19.7 °C/min for the 20 W/g, 10 W/g and 5 W/g power densities respectively. However, the pyrolysis zone (linear heating) heating rates are very similar, at 31.2 °C/min, 28.4 °C/min and 27.2 °C/min. Higher power densities give higher heating rates, as expected from Equation 3. A similar trend is followed in Figure 18 for power densities between 10 W/g and 5 W/g for medium-sized particles.
Figure 17: Temperature profiles obtained for different power densities at constant power, using different sample loadings (1000 W – 6 to 8 min – S)

Figure 18: Temperature profiles obtained for different power densities at constant power, using different sample loadings (1000 W – 6 to 8 min – M)
Figures 19 and 20 show a clear trend, namely that decreased power densities result in increased oil yields, accompanied by a decrease in char yield, with gas yield staying roughly constant. This is unexpected since higher heating rates (higher power densities) are supposed to promote oil and gas yield. This may possibly be ascribed to the following observations or a
combination thereof. With decreased loadings (increased power densities) the level in the reactor is lower. Since the carrier gas pipe does not extend into the sample, released volatiles were suppressed inside the reactor and condensed on the reactor walls. This leads to high char yields but actually a large fraction of the oil collected in the reactor, and is measured as char. Another possible reason may be that for small sample loadings, higher heat losses are expected. Therefore the energy that would have gone into the conversion of wood into char is now used to heat the surroundings. This is similar to heap effects where large heaps allow the retention of temperature better and minimise heat losses to the surroundings.

From the results above and those shown in Figures 15 to 20, it would seem like the advantages from Microwave volumetric heating become more prominent at higher sample loadings (higher volume). This is substantiated by the reduced power input for larger samples, 3 MW/kg (10 W/g for 300 s) and 28.6 % oil for 100 g sample vs 2 MW/kg (5 W/g for 400 s) and 36.7 % oil for 200 g. This suggests that the volumetric heating effects are not optimally utilised at small scale and suggest that even higher yields can be obtained with higher sample loadings. The heating rates also suggest that the linear heating regime (after the water evaporation region) is also very similar even for lower power densities and not necessarily proportional to volume in this regime. This strengthens the argument that larger scale will better utilise the effectiveness of microwave energy. Off-course there will be a limit to this effectiveness which will be controlled by the penetration depth and other factors. These results indicate that small scale experiments are not necessarily scalable for microwave pyrolysis due to the volumetric heating mechanism, making it very difficult to predict large-scale reactor behaviour. This implies that a lot of research is still required to understand the large-scale applications of microwave pyrolysis technology. Therefore it is suggested that larger-scale microwave setups (both batch and continuous) should be tested to determine the extent to which factors such as penetration depth and power density, among other, effect the performance of large-scale reactors.

4.4.4 Moisture content and particle size

The influence of MC inherent to different particle sizes was investigated. Figures 21 to 23 show the pressure profiles, temperature profiles and yields for three different particle sizes and MCs (see Section 4.3.1 for details).
Figure 21: Pressure profiles obtained for different particles sizes with inherently different moisture contents at constant power and sample loadings (1 000 W – 100 g – 6 min)

Figure 22: Temperature profiles obtained for different particles sizes with inherently different moisture contents at constant power and sample loadings (1 000 W – 100 g – 6 min)

Figure 21 shows that with an increase in particle size and therefore MC, the pyrolysis reaction takes longer to start. This is due to the vaporisation of water which takes up most of the power before the pyrolysis reaction can start. The evolution of a water evaporation peak is evident at higher MCs, corresponding to surface temperatures of ~80 °C. This peak becomes more prominent as the MC increases.
Figure 22 shows that the temperature profiles for all the particles are similar. Upon close inspection a few important results are observed. It is confirmed that the water evaporation stage continues longer with larger particle sizes (higher MC) as is evident from the larger constant temperature zones. Larger particles experience longer constant temperature zones (water evaporation), but also higher final temperatures. This leads to the conclusion that larger particles experience faster heating rates (L > M > S). This is in good agreement with the findings of previous researchers (Miura et al., 2004; Zhao et al., 2011) that larger particle sizes require less power per unit size. This effect, however, seems to be very small and can in most cases be assumed to be negligible.

Figure 23 shows the dry yields for the microwave pyrolysis of different particle sizes and MCs. It is clear from the figure that both the dry yields of these particle sizes and their corresponding MC are all the same and therefore neither MC nor particle size has a mentionable effect on the dry product yield. With regard to the wet yield, particles with a high MC result in significantly higher oil yields than do particles with a low MC. Wet oil yields for the S, M and L particles were 33.3%, 38.5% and 45.3%. This is because the large chips had a higher MC. Even though this result looks more promising, it is misleading since...
high chip moisture will result in high water content of the oil. This emphasises the importance of researchers to report their yields on a dry basis and provide the MC of their feed material.

4.4.5 Carrier gas

The influence of the carrier gas on the pyrolysis process was also investigated. The pressure profiles, temperature profiles and yields are shown in Figures 24 to 26 respectively.

![Graph showing pressure profiles for different reactor atmospheres](image)

**Figure 24:** Pressure profiles obtained for different reactor atmospheres at constant power and sample loadings and particle size (1 000 W – 100 g – 6 min – S)

Figure 24 shows that the pressure profiles are very similar, with the nitrogen flow increasing the overall pressure in the vessel as expected. The water evaporation peak is more prominent in the vacuum-only runs due to the lower pressures.

Figure 25 shows that the even though the temperature profiles look somewhat different, the heating rates are very similar. As expected, the addition of cold nitrogen gas leads to a slightly lower heating rate due to increased environmental losses. The constant temperature region is less prominent under vacuum. This can be attributed to poor thermal mixing. The carrier gas increases the mixing effects (temperature included) and provides a more accurate representation of the reactor temperature.
Figure 25: Temperature profiles obtained for different reactor atmospheres at constant power and sample loadings and particle size (1 000 W – 100 g – 6 min – S)

Figure 26: Product yields (dry wood basis) obtained for different reactor atmospheres at constant power and sample loadings and particle size (1 000 W – 100 g – 6 min -S)
In the vacuum-only runs, large portions of the oil condensed on the reactor walls. This is confirmed by the yields shown in Figure 26. The char yield for the vacuum-only atmosphere is higher than in the runs under nitrogen flow, and is accompanied by a decrease in the oil yield, with the gas yield staying very similar. This is expected since a portion of the oil is now reported as char. This emphasises the importance of a carrier gas to sweep out released volatiles and cool them rapidly to reduce gas retention times in the reactor and therefore limit secondary reactions. It is, however, suggested that hot carrier gases be used in future work. This will ensure that the effects of negative heating rates are mitigated and will further reduce the condensation of volatiles on the reactor walls.

4.4.6 The bigger picture

Ideal fast pyrolysis requires very high heating rates, carefully controlled temperatures and rapid cooling and quenching of products (short residence times) to produce the optimum amount of bio-oil (Bridgwater, Meier & Radlein, 1999). Fast pyrolysis conducted at high temperatures favours gas production, while moderate temperatures favour liquid yields. Fast pyrolysis typically yields 80% bio-oil (25–30% water), with low char and gas yields of around 10–15% each. Other pyrolysis classes include slow pyrolysis in which char is the main product. Typical slow pyrolysis yields are 30–50% for char, 20–30% for liquid with the balance being gas (Karaosmanoğlu, Tetik & Göllü, 1999; Ronsse et al., 2012; Manyà, 2012). Intermediate pyrolysis is similar to slow pyrolysis but with short residence times, and it yields more oil and less char. Oil yields of 60% have been achieved through the use of a carrier gas, with char and gas yields being 22% and 18% respectively (Wang et al., 2009). In summary, the slow pyrolysis process is simpler than the fast pyrolysis process due to less intensive feedstock pre-treatment. The reactor configurations are also typically much simpler. This leads to lower capital and running costs for slow pyrolysis processes at the expense of low liquid and gas product yields (Brown, Wright & Brown, 2010). The products from slow pyrolysis are typically less oxygenated and are of better quality (stability, heating value, etc.) compared with fast pyrolysis. Pyrolytic oil, however, has a strategic value due to its increased energy density making storage, transportation and utilisation easier since it is similar to petroleum-based fuels. It is for this reason that conventional fast pyrolysis has dominated the pyrolysis process in the last 30 years (Bridgwater, 2012).

Yoder et al. (2011) investigated the economic trade-off between bio-char and bio-oil production (fast pyrolysis vs slow pyrolysis). They concluded that the analysis is highly
dependent on the value of bio-oil and bio-char. Since no standards have been developed for pyrolysis oils and char, it is very difficult to value the products from the pyrolysis process (Bridgwater, 2012). This makes comparison of the different pyrolysis processes extremely difficult. Many researchers (Onay & Kockar, 2003; Pütün et al., 2007; among others) have used the term “fast pyrolysis” for process, which should rather be considered as slow or intermediate pyrolysis conditions. This proves that many researchers use arbitrary definitions for pyrolysis conditions, causing confusion among researchers and adding to difficulties during comparison. This stresses the importance of defining standard reaction classes and their reaction conditions.

Microwave pyrolysis (MWP) in essence differs from conventional pyrolysis (CP) in one key aspect, namely the heating mechanism. It should be stressed that microwave pyrolysis is in fact not a pyrolysis class, but instead a different pyrolysis mechanism. Heat is supplied by interaction with microwaves instead of by conventional heat transfer mechanisms. It should therefore be realised that microwave pyrolysis can also be conducted in fast, slow and intermediate classes, depending on the reactor conditions.

Ren et al. (2012) suggested that bio-oil yields of close to 60% can be achieved via microwave pyrolysis under the right conditions, which is comparable to even the best cases of conventional pyrolysis. Budarin et al. (2009) and Lei et al. (2011) reported that the oil product from microwave pyrolysis is more stable than the oils produced by conventional pyrolysis. Wang et al. (2009) and Domínguez et al. (2007) reported that microwave pyrolysis favours the increased production of syngas (CO and H₂) compared with conventional pyrolysis. Salema & Ani (2011) and Mašek et al. (2013) showed that MWP produces superior char compared with conventional pyrolysis, with the char having higher surface areas, greater pore volumes and carbon stability. Conventional pyrolysis leads to fragile char with deep cracks due to overheating of the surface. MWP produced char with pores due to internal heating resulting in colder outside particle temperatures.

To date microwave pyrolysis research has focused on small-scale batch processing, with the exception of the work done by Zhao et al. (2010) and Zhao et al. (2011). These teams conducted larger scale (~ 30 kg) batch experiments. Almost all experiments reported in the literature used fixed bed reactor setups with a sweeping gas. It should be realised that microwave pyrolysis is not limited to these reactor configurations and mixed bed microwave reactors such as rotating cone, fluidised bed reactors, etc. are also realisable. These reactors
would face some technical challenges but should in fact not be all that different from the reactors used in conventional fast pyrolysis. Robinson et al. (2009) developed a continuous microwave reactor for the treatment of oil-contaminated drill cuttings. Zhao and his colleagues have done great work to show that microwave pyrolysis is possible at larger scale. The development of such continuous and large reactors for the microwave pyrolysis process will be crucial to its competitiveness as a pyrolysis technology.

The microwave process is more comparable to slow pyrolysis than fast pyrolysis with regard to process conditions, product yields and product quality since microwave pyrolysis has, in most cases, been implemented in slow pyrolysis setups. That being said, it is undeniable that microwave heating offers some unique advantages over conventional heating. These advantages have been discussed in Chapter 2, Section 2.2. Zhao et al. (2010) conducted a large-scale comparison between the microwave and conventional heating of a large-sized corn stalk bale. They showed that for similar power inputs microwave pyrolysis gave much faster reaction times, more efficient power conversion and better temperature uniformity. They also noted that for this large-size biomass setup, higher release rates and volatile yields were realised for microwave heating over conventional heating. Aside from these advantages, many researchers have proved that under microwave heating pyrolysis can be achieved at much lower temperatures than those required for conventional pyrolysis (Shuttleworth et al., 2012). Microwave heating also offers easier control and reduced secondary reactions due to inverse heating profiles. Microwave pyrolysis therefore offers both thermal and non-thermal effects that have a positive influence on the pyrolysis process.

Many researchers (Yin, 2012; Wang et al., 2012; among others) have stated that microwave pyrolysis could possibly overcome the main shortcomings of fast pyrolysis, such as moderation of particle size and moisture content requirements. Another advantage mentioned is less agitation due to fixed bed reactor configurations, resulting in minimal contamination of vapour with char. It should be stressed that these advantages are inherent to slow pyrolysis technologies, irrespective of whether they are conventional or microwave technologies.

Researchers should not limit microwave pyrolysis to slow or intermediate pyrolysis conditions. In order for microwave pyrolysis to be competitive, fast microwave pyrolysis processes will need to be developed. The main development will need to be with regard to the reactor configurations. Mixed bed reactors used for fast pyrolysis, such as fluidised bed or rotating cone reactors, are possible candidates. These reactors can be modified to work with
microwave heating. Microwave absorbers such as SiC or activated carbon can be used and can also replace sand as a heat transfer medium. Large-scale microwave units face interesting challenges. These include the dependence of microwave pyrolysis on the dielectric properties of wood, the actual cost of implementation, the interference of microwaves with measuring equipment and scale-up factors such as penetration depth.

Another possible alternative that has huge potential is the use of hybrid pyrolysis systems. Since wood is a poor absorber of microwaves, conventional heating can be used to initialise the pyrolysis process. Once the wood has transformed to char, microwave heating can be used to sustain and accelerate the pyrolysis process. However, the purpose of this discussion is not to limit hybrid systems – creative and novel ideas need to be generated to realise the true potential of this hybrid technology. With hybrid systems it may be possible to produce an overall better and more efficient process. In future, fast microwave pyrolysis reactors or hybrid reactors will need to be developed and tested to determine whether these setups will give favourable processing characteristics.

In essence, the pyrolysis processes are not all that different. A detailed energy balance and economic analysis will be required to say for certain which pyrolysis technology is more economical. Nevertheless, comparison of pyrolysis technologies is made difficult by the lack of definite reaction classes, the lack of pyrolysis product standards and the lack of continuous microwave pyrolysis data. Before these standards, comparable fast microwave pyrolysis data and real market values for products are available, it is improbable that any type of comparative economic analysis will yield valuable results.

4.5 Conclusions and recommendations

The microwave pyrolysis reaction is seen to occur in four stages: an initial heating section, followed by a drying zone, giving rise to the pyrolysis zone, which leads to the completion of the reaction upon further heating.

A critical power was identified between 800 W and 1 000 W at which a possible heating or reaction mechanism shift occurred. A detailed explanation was given in terms of the effective power density and the targeted wood volume due to the penetration depth (Section 4.4.2). This indicates that the penetration depth can play a significant role in microwave pyrolysis. Altering the power density produced interesting results, leading to increased liquid yields with lower power densities (higher sample loadings). Moisture content and particle size were
not found to affect the pyrolysis process significantly, having no effect on the dry yield of the products. Moisture content did, however, influence pyrolysis peak formation times due to extended evaporation zones at higher moisture contents. Also, large-sized particles experienced increased heating rates, requiring less power to pyrolyse. The use of a carrier gas improved the liquid yields and emphasised the importance of using a sweeping gas to reduce secondary cracking and improve yield. It is recommended that heated carrier gases be used in future research to mitigate any negative effects on the heating rate.

It was found that since the power density results are limited by the small scale of the experiments, the results cannot be used to predict large-scale reactor performance. It is therefore recommended that future research should focus on the large-scale application of microwave pyrolysis to achieve a proper understanding of the effect of power density and penetration depth in these reactors in both batch and continuous processes.

It should be realised that microwave pyrolysis refers to the heating mechanism and is not restricted to a pyrolysis class. Research to date has focused on small-scale batch microwave experiments which are more comparable to conventional slow or intermediate pyrolysis due to similar processes. Many of the alleged advantages of microwave pyrolysis in overcoming particle size and moisture content restrictions are inherent to slow pyrolysis and not to microwave pyrolysis. However, it is undeniable that microwave pyrolysis offers unique advantages such as better power conversion, faster reaction times, better temperature uniformity, better control and less secondary cracking. Above all, the main advantage of microwave pyrolysis is that it is low-temperature pyrolysis, with pyrolysis occurring at much lower temperatures than typically required for conventional pyrolysis. As a technology, however, microwave pyrolysis is far less mature than fast pyrolysis technologies and for microwave pyrolysis to be competitive, mixed bed microwave reactors, which promote fast pyrolysis conditions, will need to be developed. Rotating cone and fluidised bed setups can be modified to accommodate fast microwave heating, but interesting challenges will need to be overcome. The use of hybrid systems also offers great opportunities for more efficient processing characteristics.
Detailed comparisons are difficult due to the absence of

1. Explicit reaction classes defining reaction conditions for slow, intermediate and fast pyrolysis
2. Standards that govern the quality of the pyrolysis products and their value
3. Microwave fast pyrolysis data that are more comparable with conventional fast pyrolysis conditions.

Developments of continuous fast microwave pyrolysis processes are vital for determining the competitiveness of microwave pyrolysis technology. These processes and the development of appropriate standards are essential for future pyrolysis research.
Chapter 5
Mg-Al LDO catalysis of microwave pyrolysis

5.1 Introduction

The importance of the pyrolysis process and the distinct advantages of microwave pyrolysis have been established in the previous chapters. The products of the pyrolysis process have various valuable applications. The liquid product (bio-oil) has generally been the focus of researchers; it can be used as a fuel source or for the production of high-value chemicals (Bu et al., 2012). The oxygen content of bio-oils is about 35–40%, which is one of the biggest differences from petroleum fuels. This high oxygen content of bio-oils requires them to be upgraded before they can be used (Wang et al., 2012). Other non-favourable properties such as complex nature, low heating values and chemical instability, among others, have led researchers to investigate the upgrading possibilities for bio-oils (Zhang et al., 2010).

The use of catalysts to overcome the challenges faced in the pyrolysis process has received increased interest, but the use of catalysts to improve the yields, selectivity and product quality of the pyrolysis process is still in its infancy (Chen et al., 2008). Many catalysts are expensive and would offer little economic advantage to the pyrolysis process. However, cheap and effective catalysts could significantly increase the viability and profitability of the pyrolysis process.

The purpose of this chapter is to determine the catalytic performance of calcined layered double hydroxides (LDH), known as layered double oxides (LDO), in the microwave pyrolysis process and their feasibility as technical catalysts in large-scale application.

5.2 Literature findings

Bio-oil can be upgraded in two main ways, physically and chemically. Physical methods include filtration, solvent addition and the making of emulsions. Some of the major chemical methods are catalysis, hydrotreating, esterification and steam reforming (Bridgwater, 2012). Chemical upgrading is more complex and costly than physical methods, but it offers significant improvements such as oil stabilisation and high-quality products (Maggi & Elliot, 1997). Catalysis is a specifically attractive upgrading method and the mechanism usually involves the removal of oxygen as either H₂O or CO₂. Research on the influences of catalysts or additives on the performances of the pyrolysis process is still in its beginning stages (Du et
al., 2010). Biomass-derived oils are generally best upgraded by HZSM-5 or ZSM-5, because zeolite catalysts promote high yields of liquid products and propylene. These catalysts, however, experience easy coking, high total acid numbers (TANs) and undesirable quantities of water (fluid catalytic cracking, sa). Various catalysts have been researched for upgrading the conventional fast pyrolysis process. Information regarding these catalysts can be found in Butler et al. (2011), Bridgwater (2012) and Bulushev and Ross (2011). The following discussion is based on the available literature for catalysts employed in microwave pyrolysis processes.

5.2.1 Zeolites as catalysts

Zeolites have been frequently used for catalytic biomass pyrolysis or bio-oil upgrading. HZSM-5 zeolites are especially common since they are known for their cracking abilities. Gayubo et al. (2004) explain that HZSM-5 provides a suitable compromise between catalyst activity, thermal stability, selectivity for hydrocarbons smaller than C₁₂ and limited deactivation by coke.

Wang et al. (2012) conducted experiments on the catalytic microwave pyrolysis of Douglas fir with ZSM-5 as catalyst. They used a Sineo MAS II microwave unit at 700 W. They report heating rates of 100 °C/min for a stationary 100 g sample. They found that the volatile and gas yields experienced with ZSM-5 were much higher than without catalyst. The bio-oil and char yields were lower with catalyst, implying that the catalyst promoted the formation of the gas product. Typical yields were around 30% bio-oil, 55% gas and 15% char. This is significantly different from the results without any catalyst at similar conditions: 45% bio-oil, 12% gas and 43% char (Bu et al., 2012). Wang et al. (2012) reported that an increase in the ratio of catalyst to sample slightly increased the bio-oil yield up to 35%.

Comparison of the oil compositions from experiments with ZSM-5 against runs without a catalyst shows that the addition of ZSM-5 led to increased aromatic hydrocarbon content (from 0.7% to 6.9%). This shows that ZSM-5 can deoxygenate oxygenated compounds in the pyrolysis process. The yields of phenols were significantly improved by the addition of ZSM-5 catalyst (from 5.5% to 58%). The addition of catalyst leads to a decrease of guaiacols (44.7% to 23.7%), furans (9% to 1.6%) and sugars (4.1% to 0%) under certain reaction conditions. Wang et al (2012) concluded that increased catalyst to biomass loadings increased the aromatic hydrocarbon content. They proved that ZSM-5 can be used to upgrade
bio-oils chemically to contain valuable chemical components such as phenols, guaiacols and aromatic hydrocarbons.

Chen et al. (2008) investigated the effect of eight inorganic additives, among which was HZSM-5. They confirm that the addition of catalyst decreased the liquid and gas product yields, increasing the amount of char formed. The addition of catalyst reduced the formation of CH₄ and CO₂, increasing the amount of H₂ produced with no significant effect on the CO concentration. HZSM-5 was shown to increase the concentration of furfural and levoglucosan in the bio-oil phase, while the concentrations of guaiacols were reduced.

5.2.2 Activated carbon as catalyst

Bu et al. (2012) investigated the catalytic microwave pyrolysis of biomass using activated carbon. The activated carbon acted as a microwave absorber as well as a catalyst. Addition of catalyst favoured gas and bio-oil production, significantly reducing char yields. Gas yields were significantly higher and bio-oil yields were lower, compared with runs without activated carbon. This behaviour was attributed to the formation of “microplasmas” that induced self-gasification (Menedez et al., 2007). Increased ratios of catalyst to biomass steadily increased the liquid yields up to a point, after which the liquid yields decreased with further addition of catalyst. Gas yields continually increased, while char yields decreased with increased catalyst loadings.

The effect of activated carbon on the oil composition was very favourable, but varied under the reactor conditions. The addition of activated carbon increased the phenolics content (2.5% to 66.9%), with a significant increase in the phenol content (0.7% to 39.0%) and a decrease in the guaiacols content (52.0% to 3.5%). These high yields of valuable phenolics could have significant economic benefits. The increase in phenol and its derivatives is said to have a close relationship to the decomposition of lignin under activated carbon-catalysed microwave pyrolysis. The concentration of esters was also increased with activated carbon as catalyst (Bu et al., 2011).

5.2.3 Ionic liquids as catalysts

Ionic liquids can function as effective microwave absorbers due to their special structure and properties. Du et al. (2010) predicted that ionic liquids would interact with biomass, causing large contact areas. Since ionic liquids are good microwave absorbers they should facilitate
the microwave pyrolysis of biomass. Ionic liquids are known to interact with woody biomass, acting as solvents for biomasses and their components (Kilpeläinen et al., 2007).

Du et al. (2010) investigated the performance of two ionic liquids (1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium tetrafluoroborate) as catalysts for microwave pyrolysis. They found that there was no bio-oil yield in the absence of the ionic liquids. The oil yield depended on the feed material as well as the type of ionic liquid used. Increased amounts of ionic liquid generally increased yield up to a certain point, after which no further yield was observed. The 1-butyl-3-methylimidazolium chloride ionic liquid yielded rapid pyrolysis, with oil forming within 2 minutes. The other ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate) had delayed initiation times. The compositions of the oils produced varied with the type of biomass and type of catalyst. The composition of the oil obtained from zeolite-catalysed conventional pyrolysis oils varied; it had high yields of ketones and phenolics. The oil from microwave pyrolysis with ionic liquids yielded large amounts of acetic acid and furfural. Du et al. (2010) claim that microwave pyrolysis was comparable to flash pyrolysis due to the rapid evolution of volatiles.

5.2.4 Metal oxides, salts, acids and other catalysts

Various studies have investigated the catalytic properties of inorganic additives in the microwave pyrolysis process. These additives include mainly metal oxides, salts and acids. A brief summary of these is given below.

Zhang et al. (2010) investigated the ex situ catalytic performance of various metal oxides and acids on two different molecular sieves (4A and 3A) and zirconium oxide supports. All catalysts were prepared by wet impregnation. It was found that molecular sieve catalysts did not affect the liquid product composition, possibly because molecular sieves are not a good support for pyrolysis vapour conversion. Zirconium oxide catalysts gave liquid yields ranging from 32%–37%. Solid acids Cl/ZrO₂ and SO₄²⁻/ZrO₂ were able to catalyse the pyrolysis vapours to different chemicals. The solid acids mainly converted the pyrolysis vapours into 1,1-dimethoxyhexane. Zhang et al. (2010) also conclude that even though Rh, Pt, Co and other metals catalyse the steam reforming and Fischer-Tropsch reaction, these metals and solid alkalines do not affect the microwave pyrolysis process.

Kuan et al. (2013) investigated the catalytic performance of various metal oxides in the microwave pyrolysis of sugarcane bagasse. The effects of the metal oxide addition include
increased heating rates and mass reduction ratios. Increased production of H\textsubscript{2} was observed for NiO and CaO. The gas yield and liquid yield were also affected, yielding higher values in the presence of CaO or MgO and NiO or CuO for these yields, respectively.

Chen et al. (2008) investigated the catalytic performance of eight inorganic additives in the microwave pyrolysis process. These catalysts were NaOH, Na\textsubscript{2}CO\textsubscript{3}, Na\textsubscript{2}SiO\textsubscript{3}, NaCl, TiO\textsubscript{2}, HZSM-5, H\textsubscript{3}PO\textsubscript{4} and Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}. SiC was added to the mixture to increase microwave absorption. All the additives increased the gas yield and decreased the char yield significantly, without the oil yield undergoing a dramatic change. The sodium catalyst had the most significant effect on the evolution of gas. Most of the catalysts decreased the CH\textsubscript{4}, CO and CO\textsubscript{2} gases, yielding higher amounts of H\textsubscript{2}. The sodium catalyst mostly promoted the formation of acetol in the liquid product. The phosphate and sulphate catalysts promoted the formation of both furfural and 4-methyl-2-methoxy-phenol.

Bu et al. (2012) investigated the effect of Zn powder on a bio-oil and formic acid-ethanol mix to assess the effect on bio-oil upgrading. The upgraded oil product contained 42% esters, of which 85% were long-chain fatty acids (\textgtr C\textsubscript{10}). They concluded that this could possibly generate fuel substitutes.

Wan et al. (2009) found that chloride salts catalysts simplified the chemical composition significantly by suppressing most of the non-catalysed reactions. MgCl\textsubscript{2} (0.08:1 g/g) produced a bio-oil that was 80% furfural. KAc and AlO\textsubscript{3} increased the liquid yield only slightly. With KAc the increase came from a decrease in the solid fraction, and AlO\textsubscript{3} suppressed the gas yield to increase the liquid yield. Na\textsubscript{2}HPO\textsubscript{4}, H\textsubscript{3}BO\textsubscript{3}, and MgCl\textsubscript{2} showed significant increases in the liquid yield, suppressing both the solid and gas fractions. Na\textsubscript{2}HPO\textsubscript{4} showed the highest (H\textsubscript{3}BO\textsubscript{3} was close) increase in liquid yield, with a greater reduction in the solid fraction than in the gas fraction. MgCl\textsubscript{2} showed promise by giving good increase in liquid yield and also promoting selectivity for producing furfural. Very little effect on the solid phase was observed, suggesting an increased release of volatiles.

5.2.5 Layered double hydroxides

Layered double hydroxides (LDH, also known as hydrotalcite) are anionic clay materials. This group of clays has attracted much attention because of their wide range of potential applications. These materials have been intensively investigated for their catalytic properties.
in many aspects such as organic synthesis, degradation of organic wastes and H₂ production by use of their specific physicochemical properties (Xu et al., 2011).

LDH clays consist of layers of MII and MIII cations that are octahedrally co-orientated by six oxygen anions as hydroxides. The layers are similar to the layered structure of brucite (natural Mg(OH)₂). Hydrocalcite (Mg₆Al₂(OH)₁₆CO₃·4H₂O) has layers (Mg₆Al₂(OH)₁₆) that exhibit charges of +2. The structure stays neutral by attracting anions (typically CO₃²⁻ or NO₃⁻) to the interlayer (the region between two metal hydroxide layers). The interlayer also contains water molecules retained by hydrogen bonding (Carlino, 1997). The calcined version of LDH, termed layered double oxide (LDO) or mixed oxide, is of particular interest as a solid base catalyst because of its unique properties for organic reactions (Xu et al., 2011). Hora et al. (2014) concluded that calcined LDH facilitated the aldol condensation of acetone and furfural (two major products of microwave pyrolysis) to produce favourable dehydrated products. Detailed literature on the catalytic properties of LDH and its derivatives can be found elsewhere (Xu et al., 2011).

Xu et al. (2011) explain that the mixed oxide obtained from moderate calcination temperatures can easily regain its layered structure (becoming similar to LDH) upon exposure to aqueous solution; this is called the memory effect. They state that for temperatures below 700 °C, the calcined LDH exhibits good cationic dispersion.

Since LDH attracts anions like CO₃²⁻ to the interlayer it is believed that it will catalyse the cleavage of these bonds releasing these anions or CO₂ / NO₂. Like mentioned above, water is also retained within the interlayer suggesting that it will also catalyse the removal of H₂O. The removal of H₂O from the interlayer would occur at lower temperatures whereas the removal of CO₃²⁻ anions among other will require higher temperatures. Due to the behaviour described above and because LDH is simple to handle, easy to separate and recycle, and low in cost, it has thought to be a good candidate for the pyrolysis process.

5.3 Experimental

5.3.1 Materials

*E. grandis* wood chips were obtained from the Sappi Technology Centre, South Africa. Wood chips with particle diameters between 0.5 mm and 1 mm were used (see Table 3 in Section 4.3.1 for details regarding the composition, moisture content, proximate analysis, ultimate analysis and calorific value. Mg-Al LDH was supplied by the Department of Chemical
Engineering, University of Pretoria. Hydranal®-Composite 5 and Hydranal®-Methanol Rapid were purchased from Sigma Aldrich for Karl Fischer titration.

5.3.2 Apparatus and procedure

A Milestone Roto Synth microwave unit (see details in Section 4.3.2) was used to investigate the performance of LDH as catalyst for the microwave pyrolysis process. Varying amounts of calcined LDH powder were mixed with 100 g of small wood chips to produce different ratios of catalyst to biomass (ratios were 0.5:1, 1:1 and 2:1). The catalyst and biomass were thoroughly mixed and charged to the Pyrex® reactor. Runs were conducted at 1 000 W power for run times between 6 and 8 minutes (making sure the reaction had completed as determined from the pressure profile). Runs were conducted under vacuum only and no carrier gas was used since carrier gas swept some of the catalyst out of the reactor, affecting product yields and contaminating the condenser systems.

5.3.3 Catalyst preparation

Calcined LDH (LDO) powder was used in the experimental runs to provide the most activity and surface area from the catalyst. LDH powder was calcined at 500 °C for 8 hours to remove all the water and carbonates from the interlayer to produce a mixed oxide/LDO. LDO was determined to be more catalytically active in the pyrolysis process. Catalyst pellets were also prepared to show that this catalyst can be easily transformed into pellets. Pellets were produced by first calcining LDH powder as described above. LDH powder is hydrophobic, whereas LDO can mix with water to form a paste. As described in Section 5.2.5, contact of the mixed oxide with water returns the catalyst to a form similar to that of LDH. The catalyst paste was extruded to form extrudates, which were dried in an oven at 110 °C for 2 hours. The extrudates were crushed through a series of sieves to produce granules of between 1 mm and 2 mm. The granules were then calcined again (for 8 hours at 500 °C) to produce LDO granules which could be used in additional experiments.

5.3.4 Methods

The experiments were conducted in duplicate and the yield indicates the standard deviation of the data. The profiles represent the averaged data points. The three product yields were determined in a similar fashion to that explained in Section 4.3.2. Pressure profiles and temperature profiles (pyrometer) were measured by the Roto Synth unit.
The liquid product composition was analysed via GC×GC – TOFMS at the Department of Chemistry, University of Pretoria. Details of the analysis conditions are shown in Table 4. Two different phases were present in oils obtained from high catalyst loadings (LDO: biomass – 2:1), namely a tar phase and an aqueous phase. These phases were analysed separately but in a similar manner. An amount of 500 uL of oil/tar was diluted in 4.5 mL of chloroform. Sodium sulphate (± 0.5 g) was added as a drying agent. Thereafter 1 μL was injected into the GC×GC – TOFMS.

The liquid moisture content was determined using Karl Fischer titration (Metrohm915 KF Ti Touch) with Hydranal®-Composite 5 as titrant and Hydranal®-Methanol Rapid as solvent. The calorific values of the oils were determined using a LECO AC-350 automatic bomb calorimeter. The method used is based on the ISO 1928:2009 standard. TAN (total acid number) was determined using titration according to the D974-14 standard test method, with modifications for bio-oils as suggested by Shao and Agblevor (2015).

Table 4: GC×GC – TOFMS conditions

<table>
<thead>
<tr>
<th>GC:</th>
<th>Agilent 7890A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector:</td>
<td>LECO Pegasus 4D Time-of-Flight mass spectrometer</td>
</tr>
<tr>
<td>Acquisition rate:</td>
<td>100 spectra/s</td>
</tr>
<tr>
<td>Mass range:</td>
<td>40 to 520 Da</td>
</tr>
<tr>
<td>Source temperature:</td>
<td>230 °C, Ionisation mode EI+</td>
</tr>
<tr>
<td>Detector voltage:</td>
<td>1 815 V</td>
</tr>
<tr>
<td>GC inlet temperature:</td>
<td>280 °C</td>
</tr>
<tr>
<td>Inlet mode:</td>
<td>Split 100:1</td>
</tr>
<tr>
<td>Carrier gas:</td>
<td>Helium 1 ml/min, constant flow</td>
</tr>
<tr>
<td>Column 1:</td>
<td>Rxi-5Sil MS, 30 m x 0.25 mm ID x 0.25 μm film thickness</td>
</tr>
<tr>
<td>Column 2:</td>
<td>Rxi-17Sil MS, 0.97 m x 0.25 mm ID x 0.25 μm film thickness</td>
</tr>
<tr>
<td>Column 1 oven:</td>
<td>40 °C for 2 min to 320 °C at 8 °C/min, hold 2 min</td>
</tr>
<tr>
<td>Column 2 oven offset:</td>
<td>5 °C (relative to primary oven)</td>
</tr>
<tr>
<td>Modulator offset:</td>
<td>15 °C (relative to 2nd oven)</td>
</tr>
<tr>
<td>Modulation period:</td>
<td>3 s (hot pulse 0.7 s)</td>
</tr>
<tr>
<td>Transfer line temperature:</td>
<td>300 °C</td>
</tr>
</tbody>
</table>
5.4 Results and discussion

5.4.1 LDO-catalysed microwave pyrolysis

The performance of LDO catalyst in the microwave pyrolysis was tested using three different catalyst-to-biomass loadings. This was compared with the results obtained for a non-catalysed run under the same conditions. Figures 27 to 29 show the pressure profiles, temperature profiles and product yields (dry wood basis).

Figure 27 shows that the addition of catalyst has a negative influence on the evolution of vapours. The vapour evolution (onset of pyrolysis) is seen to occur later with increased catalyst loading. This effect is mostly due to the increased mass in the reactor vessel. Since the catalyst material is not a good microwave absorber, the biomass now needs to heat up additional surrounding mass, and therefore some of the energy that would have gone into the pyrolysis process is now used to heat up the catalyst. This is confirmed by the reduced heating rates for increased catalyst-to-biomass ratios as shown in Figure 28.

![Graph showing pressure profiles for different LDO catalyst-to-biomass loadings](image)

*Figure 27: Pressure profiles obtained for different LDO catalyst-to-biomass loadings at constant power, sample loadings and particle size (1 000 W – 100 g – 8 min – S)*
It was observed that at a 2:1 catalyst-to-biomass ratio, an additional peak, or in some cases a plateau, appears between 200 s and 300 s. This can occur as a result of numerous factors or a combination of them. A possible explanation is the increased activity of the catalyst at higher ratios leading to the activation of additional reactions (therefore more vapours) in the reaction vessel. This is substantiated by increased oil yield (2.1 % higher) and decreased char yield (6.4 % lower) for the 2:1 run compared to no catalyst, as shown in Figure 29. This increase is present even though the heating rates for the 2:1 catalyst ratio are much lower than those without catalyst and would typically lead to decreased oil and gas yields. This suggests that the increased yield is a result of the increased activity of the catalyst. Another possibility is that due to the presence of the fine catalyst, the packing density in the reaction vessel increases. The increased packing density leads to slow evolution of particles due to mass transfer limitations, leading to a broader, but slightly lower, pressure peak.

The decreased heating rates shown in Figure 28 suggest that the catalyst in not well suited for microwave application since it is a poor absorber of microwaves. This means that heating of the catalyst takes place via conventional heating mechanisms. Catalysts such as activated carbon which can act as both catalyst and microwave absorber are more suited for microwave application.
Figure 29: Product yield (dry wood basis) obtained for different LDO catalyst-to-biomass loadings at constant power, sample loadings and particle size (1 000 W – 100 g – 8 min – S)

Figure 29 shows that for catalyst-to-biomass ratios of 0.5:1 and 1:1 the oil yields are very similar to that of no catalyst. This is true even though they experience reduced heating rates resulting from the increased mass in the reaction vessel, as shown in Figure 28. It can be observed that increased gas yields (4.4% higher) result. This suggests that even at low ratios the catalyst promotes the formation of volatiles. The increased amount of oil formation that accompanies increased catalyst ratios suggests that the catalyst does in fact actively influence the microwave pyrolysis process. It should be mentioned that significant oil fractions were lost in the condensers and therefore the real product distribution will be somewhat different.

5.4.2 Oil properties of LDO-catalysed microwave pyrolysis

Apart from the influences that a catalyst has on the pyrolysis process (product yields, product distribution, etc.), it also affects the quality of the oil product. The liquid product is the main priority and most significant changes are often observed here and in the gas phase. As described in the literature in Section 5.2, catalysts can promote the formation of high-value chemicals, change the composition (promoting the abundance of a specific compound in the oil) or increase the overall heating value of the oil. The importance of these effects depends on the application of the oil.
There are various properties that need to be considered when evaluating the quality of a bio-oil. These properties differ depending on the application. Typical properties of interest are: moisture content (MC), calorific value (CV), viscosity, total acid number (TAN), density and the solids, ash, nitrogen and sulphur contents. Table 5 shows some of the significant properties of liquid products obtained from the LDO-catalysed microwave pyrolysis of *E. grandis*.

**Table 5: Properties of bio-oils as obtained from LDO-catalysed microwave pyrolysis at different catalyst-to-biomass ratios**

<table>
<thead>
<tr>
<th></th>
<th>No catalyst</th>
<th>0.5:1</th>
<th>1:1</th>
<th>2:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC (%)</td>
<td>49.21±0.83</td>
<td>51.91±0.45</td>
<td>59.48±2.05</td>
<td>69.82±0.20</td>
</tr>
<tr>
<td>CV (MJ/kg)</td>
<td>9.7±1.0</td>
<td>9.0±1.0</td>
<td>7.9±1.0</td>
<td>6.5±1.0</td>
</tr>
<tr>
<td>CV dry basis (MJ/kg)</td>
<td>19.1±1.0</td>
<td>18.7±1.0</td>
<td>19.5±1.0</td>
<td>21.5±1.0</td>
</tr>
<tr>
<td>TAN (mg KOH/g)</td>
<td>174.1±2.8</td>
<td>129.5±3.3</td>
<td>109.0±5.9</td>
<td>72.1±1.3</td>
</tr>
</tbody>
</table>

From Table 5 it is clear that the addition of catalyst promotes the formation of water since the MC goes up from 49% without catalyst to 70% with catalyst. As described in theory section (Section 5.2.5) it was expected that the catalyst promote the formation of water. The temperature was high enough to drive water out of the interlayer, thereby continually catalysing these reactions. However due to the low temperatures it is believed that CO$_3^{2-}$ or similar anions were retained within the interlayer thereby limiting the cleavage of these bonds and the release of CO$_2$ etc. It is believed that at higher temperatures (close to calcination temperature) these reactions will be promoted and will yield more favourable catalysis. The formation of water shows that increasing portions of oxygen are removed from the products, thereby improving the product quality. Unfortunately, the water reports to the liquid phase and reduces the overall HHV (or heat of combustion) of the liquid product. Table 5 shows that the actual oil fraction in the liquid product improves in quality, as shown by the dry-basis HHV. This table also shows that the catalyst actively reduced the TAN of the respective liquid samples. The TAN achieved by a catalyst-to-biomass ratio of 2:1 was 72 mg KOH/(g oil), which compares well with good-quality bio-oils that typically have TANs of 60–100 mg KOH/(g oil) (Shao & Agblevor, 2015). It is important to mention that with higher catalyst ratios (1:1 and 2:1), the production of a tar phase was observed. The tar phase was darker and more viscous than the aqueous phase and seemed to be more non-polar.
It was very difficult to measure and collect this phase since most of the product adhered to the inside of the condensers and only small fractions were collected in the collection flasks. The low viscosity meant that the product was difficult to extract from the condensers in its pure form and therefore analysis was difficult. Figure 30 shows a photo of the oil collected from the catalysed runs; the formation of a tar fraction can be seen for catalyst ratios of 1:1 and 2:1.

The tar fractions that were collected were separated by extracting the aqueous phase from the centrifuged sample using a syringe. Perfect separation was difficult to achieve and the elemental analysis and composition results for the tar phase may include contaminations from the aqueous phase. Figure 31 shows the summarised chemical composition of the oil samples as obtained by GC×GC – TOFMS.

![Figure 30: Liquid samples obtained from LDO-catalysed microwave pyrolysis at different catalyst loadings. Note the dark phase at the bottom of the 1:1 and 2:1 samples](image)

It was observed that for all runs, especially those with higher catalyst loading, a white mist/smoke exited the second condenser into the extraction system. This suggests that a fraction of the volatiles was not condensed in the condensers. It was to be expected that hydrocarbons and other high-value chemicals would be difficult to condense due to their low boiling point, etc. These fractions that get lost, even though small, can be of significance, even more so for catalysed pyrolysis, since a true product composition is crucial in determining the effectiveness of a catalyst. It is recommended that electrostatic precipitators
or quenching systems be used for liquid collection, particularly for research experiments. This will improve liquid yields and allow proper identification of the true product compositions.

![Figure 31: Compositions of liquid samples as determined by GC×GC TOFMS for the LDO-catalysed microwave pyrolysis at different catalyst-to-biomass ratios](image)

Many of the compounds are complex and contain numerous functional groups. It is unclear how a distinction is made by other researchers, but the dominating functional group was used
here. The GC×GC – TOFMS area percentage characterisations for the different catalyst ratios are shown in Appendix A, along with the classified functional group for reference.

From Figure 31 it is clear that for non-catalysed microwave pyrolysis furans and ketones/aldehydes dominate the product composition, making up 38.3% and 37.1% of the sample respectively. Furfural is the main furan, making up 29.7% of the composition alone. Acetone and 2-hydroxypropanone are the main ketones, each close to 8%. The presence of phenolics (include phenols, guaiacols and syringols) is low, amounting to just 7.3% of the overall composition.

The tar phase collected for a catalyst ratio of 2:1 was also analysed and the 50 most abundant compounds and their respective area percentages are shown in Appendix B. The tar phase contained much higher fractions of phenolics and hydrocarbons compared with the aqueous phases reported in Figure 31. Long-chain hydrocarbons such as xylene and benzene were also observed in appreciable percentages. It is believed that the tar fraction will have much higher heating values and is a good indication that the catalyst produces favourable products.

The results indicate that the addition of catalyst seemed to promote the formation of esters. Among these esters were significant amounts of high-carbon esters which included a variety of high-carbon phthalates, with a significant amount of anhydride (due to the presence of acetic anhydride) forming at a high catalyst ratio of 2:1. It should be mentioned that the composition of the aqueous oil sample from the 2:1 catalyst-to-biomass ratio was only determined after a period of 2 months at room temperature. It should therefore be realised that the composition might be subject to changes that took place due to the stabilisation reactions that can take occur. The extent to which the composition may have changed is unknown and should be determined in future. This can be used as an indication of the stability of the oil. For all the catalysed oils it is apparent that there is still a strong presence of furans and ketone/aldehydes. The catalysts in small loadings (0.5:1 and 1:1) yielded slightly higher phenolics of around 9.3% and 9.0% respectively. At a catalyst loading of 2:1 the phenolics content decreased significantly to around 1.9%. It is possible that the presence of acetic anhydride originated from ethyl acetate (ester) and was formed via stabilisation reactions. The low presence of phenolics may also be due to this stabilisation effect.

The main components in the 0.5:1 sample were found to be glycol monoacetate (1,2-ethanediol, monoacetate) and furfural, making up 29.4% and 18.5% of the oil composition respectively. The 1:1 sample’s main components were furfural at 21.6% and
acetoxyacetone (2-propanone, 1-(acetyloxy)-) at 9.7%. The most abundant component in the 2:1 oil is acetic anhydride, dominating the composition with 25.5%. Furfural and 2-hydroxypropanone follow with 10.8% and 8.6% respectively. It is worth mentioning that at this catalyst ratio, the presence of toluene was detected (0.33%), which may indicate that higher catalyst ratios could promote the formation of other hydrocarbons.

The presence of high amounts of esters and anhydrides indicates that these catalysed oils could possibly be good candidates for upgrading to high-value chemicals or quality biofuels.

### 5.4.4 LDO as technical catalyst

Mitchell, Michels & Pérez-Ramírez (2013) explain that it is pertinent to distinguish between research catalysts and technical catalysts. Research catalysts describe catalysts in the initial stages of development, which are often tested in powder form. Technical catalysts need to reproduce laboratory results but also require the mechanical strength and chemical stability to ensure a long lifetime in industrial reactors. Technical catalysts entail large-scale manufacture, appropriate catalyst formulations and the structuring of catalysts into macroscopic forms. These authors emphasise that there is an urgent need for academic awareness to fully comprehend catalyst processes. This is because most academics fail to recognise the importance of catalyst scale-up and the preparation of a technical catalyst from research catalysts. It was therefore one of the objectives of this chapter to show that LDO powders can be easily transformed into a structured body to facilitate large-scale catalysis.

A commonly used catalyst-processing method is extrusion, as explained by Akhtar et al. (2014). The catalyst powder in paste form is extruded under pressure and dried. The dried extrudates are then usually subjected to a spheronisation process to produce sphered catalysts of a specific diameter. In the catalyst preparation section of this chapter (Section 5.3.3) it was explained that the LDO catalyst was prepared in a granular form in a process very similar to this. For this process, calcined LDH clay powder was made into a paste with water only. The processing yielded granular catalysts of between 1 mm and 2 mm. The reader may consult Section 5.3.3 for more details regarding the catalyst preparation. A photo of the processed catalyst is shown in Figure 32. Scanning electron micrographs (SEM) of the LDO powder (a and b) and LDO granules (c and d) are shown in Figure 33. The SEM images show distinct flat discs, which remained intact with extrusion and granulation. The granules seem to be porous due to the irregular packing of these discs during catalyst processing.
Figure 32: LDO catalyst granules (1–2 mm)

Figure 33: SEM images of the surface of LDO powder (a and b) and LDO granules (c and d)
Since these were only preliminary structuring experiments, additional tests (strength tests, erosion resistance, surface area, etc.) will need to be conducted to determine the applicability of this processing technique. The catalyst processing was not the main focus of this investigation and further testing is recommended for future research.

The granules were used in the microwave pyrolysis process and yielded similar product yields to those produced by the catalyst powder. Since composition analysis of the oil is expensive, this aspect was not compared. Significant amounts of volatiles seemed to condense on the pellets themselves, causing fouling. This may deactivate the catalyst to a large extent and emphasises the importance of high-temperature catalyst processing or a catalyst regeneration or circulation system in large-scale applications. Circulating beds are a good example of this. High catalyst temperatures may also increase catalyst activity and should reduce the deposition of volatiles on the catalyst.

Xu et al. (2011) explain that LDH is thermally stable at around 700 °C, a temperature at which most of the deposited volatiles will combust, which means that the catalyst can be regenerated in this manner. This was tested by heating the fouled catalyst to 650 °C and maintaining this temperature for 1 hour. The resulting catalyst appeared to be fully regenerated, being indistinguishable (by eye) from unused catalyst. More detailed tests are recommended for future studies to confirm this. Figure 34 shows the fouled and regenerated catalyst.

Figure 34: a) Catalyst after microwave pyrolysis with E. grandis. b) Catalyst regenerated at 650 °C
5.5 Conclusions and recommendations

The performance of calcined Mg-Al LDH clay (LDO) was investigated under microwave pyrolysis conditions. At higher LDO ratios, increased liquid yields were observed which were attributed to increased activity of the catalyst. Even at low catalyst ratios, the catalyst was shown to promote the formation of volatiles (gas/liquid). LDO can be considered as a poor absorber of microwaves and is therefore not specifically well suited for microwave pyrolysis since the increased mass in the reaction vessel resulted in lower heating rates, which have a negative impact on the pyrolysis process (retarded onset of pyrolysis, lower liquid and gas yields).

When the influence of the catalyst on the quality and composition of the liquid products was investigated, it was observed that the catalyst promoted the formation of water, which indicates that oxygen is being removed from the pyrolysis products – this is in fact the aim of a catalyst. Even though the formation of water is not optimal (compared with the formation of CO₂), it proves that the catalyst is active and clearly affects the pyrolysis reactions significantly. From the CV of the samples it is clear that the increased formation of water at higher catalyst ratios decreases the calorific value. On a dry basis, an increased calorific value is observed for higher catalyst ratios, which is favourable. The low temperature at which the reactions took place was suggested to limit the catalyst and it is believed that at temperatures closer to the calcination temperature the catalyst will promote the cleavage of anions like CO₃²⁻ among other and lead to the release of CO₂ etc. It is therefore recommended that the catalyst be tested at higher temperatures.

The catalyst was proved to improve the production of esters in the liquid product and gave rise to the formation of anhydrides at high catalyst ratios. The oil compositions, with and without catalyst, were dominated overall by the presence of furans and ketones/aldehydes with low amounts of phenolics. The formation of hydrocarbons, even though very low, was encountered at a high catalyst ratio of 2:1, which possibly indicates that the formation of hydrocarbons can be promoted at higher catalyst ratios. The addition of catalyst also resulted in significant reductions in the TAN of the oils, from ~170 mg KOH/(g oil) to ~70 mg KOH/(g oil).

The formation of a polar tar phase was observed at higher catalyst ratios. This tar phase contains higher fractions of phenolics and hydrocarbons than the aqueous phases and is believed to have high heating values. Overall, the quality of all the pyrolysis products was
improved due to the removal of oxygen facilitated by the catalyst. This shows that the LDO works as an active catalyst for the pyrolysis process and that the products could possibly be used for the production of quality biofuel or high-value chemicals upon upgrading.

A mist was seen to leave the second condenser in many of the catalyst experiments. This indicated that some fraction of the volatiles was not completely condensed. It is important to collect all the volatiles, especially so for catalysed experiments since many of the hydrocarbons and other high-value products might be difficult to condense. It is imperative that a true product composition be obtained when investigating a catalyst to fully understand the extent of the catalysis. It is therefore recommended that electrostatic precipitators or quenching systems be used in future work.

Work was also done to show that LDO can be used as a technical catalyst. It was proved that Mg-Al LDH clay can be structured into granules very easily and at almost no cost since water is used as binding agent. It was also shown that the catalyst can presumably be regenerated at a temperature of 650 °C.
Chapter 6
Overall conclusions and recommendations

Microwave pyrolysis is a promising new method of pyrolysis in which the heating of biomass is facilitated by its interaction with electromagnetic waves. Microwave heating has various advantages over conventional heating. The main advantages include the rapid and efficient volumetric heating of biomass. Other non-thermal effects are also prominent and provide additional benefits such as low-temperature pyrolysis which is commonly observed for microwave pyrolysis. This means that pyrolysis can occur at temperatures much lower than those typically used for conventional heating, implying significant energy savings.

Since the microwave pyrolysis process is still immature compared with conventional pyrolysis technologies, its fundamentals are still not perfectly understood. Microwave processing units can be expensive and this limits research in the field. The performances of a comparatively cheap modified domestic microwave oven and an off-the-shelf Roto Synth microwave unit were compared. The domestic microwave was shown to be very comparable and even superior in some aspects to the Roto Synth unit, yielding slightly higher oil yields even though the char yields were also higher. This indicates that the vapour collection system for the modified domestic setup was better. The domestic setup was not optimised and gave various processing difficulties. It is recommended that a quartz reactor be used for future work with attention also being given to the stepper motor and its driver, and to the thermocouple.

The microwave pyrolysis process is significantly affected by parameters such as heating rate, power, power density and temperature, among others. Initially, the majority of microwaves are absorbed via the water phase which heats the biomass to the onset of pyrolysis. This produces char which then absorbs most of the microwaves to facilitate further pyrolysis. Increased power led to increased heating rates, yielding higher liquid and gas yields. A critical power density was identified between 800W and 1000W. The effect of power density was interesting and indicated that penetration depth can play a significant role in the pyrolysis process. This could raise various challenges during the scale-up of microwave technology. Particle size had a negligible effect on the heating rate or product yields, which is a significant benefit of microwave pyrolysis. It is recommended that more large-scale microwave setups be implemented to determine the performance of large-scale microwave
pyrolysis and to achieve a better understanding of the effect of penetration depth in these larger-scale reactors.

Microwave pyrolysis is still in its infancy compared with conventional pyrolysis processes, especially fast pyrolysis, which has dominated the pyrolysis process for the last 30 years. To date microwave pyrolysis has been applied only as a slow pyrolysis technology and therefore is better compared with conventional slow pyrolysis than with fast pyrolysis. It should be kept in mind that microwave pyrolysis is a method of pyrolysis and not a class of pyrolysis. Microwave pyrolysis undoubtedly provides advantages over conventional pyrolysis and has great potential to become the future of pyrolysis. However, for microwave pyrolysis to become competitive, fast microwave pyrolysis reactors need to be designed and tested. Mixed bed reactors, such as rotating cone or fluidised beds, are possible candidates. Silicon carbide (SiC), which is an excellent microwave absorber, can be used to increase heating rates and heat transfer efficiency. Hybrid technology could possibly provide a new direction for pyrolysis, offering the advantages of both microwave and conventional heating methods. Interesting challenges will have to be faced to improve the understanding of these microwave technologies in batch and continuous large-scale processes. Comparisons of microwave pyrolysis with other pyrolysis processes are difficult due to the lack of microwave fast reactors and product quality standards. Without the development of such processes and standards it is unlikely that any comparison of pyrolysis technologies will yield valuable results. It is therefore recommended that these standards and continuous microwave fast pyrolysis processes be developed in future research.

There are various methods that aim to improve the pyrolysis process. One such method is using catalysts to upgrade the pyrolysis products. Calcined Mg-Al LDH clay (LDO) was tested as a possible catalyst for the microwave pyrolysis process. The catalyst was found to promote the formation of esters, and specifically anhydrides, at higher catalyst ratios. The presence of hydrocarbons was also detected at high catalyst ratios, which could possibly suggest that the catalyst promotes the formation of hydrocarbons at high ratios. It is recommended that higher catalyst ratios also be investigated. The catalyst increased the formation of water, which is a positive indication that oxygen is being removed from the products. The catalyst is believed to be limited by the low temperature of the reactions and it is believed that increased temperature (closer to the calcination temperature) will lead to increased cleavage of anions like CO$_3^{2-}$ leading to the formation of CO$_2$ or similar compounds. The catalyst promoted the formation of volatiles (gas and liquid), decreasing the

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char yield. This was observed even for small catalyst ratios. The catalyst facilitated an increase in the quality of the products, increasing the dry-basis heating value of the bio-oil and leading to significant reductions in the TAN (total acid number). The liquid product is thought to be a good candidate for quality fuels or high-value chemicals upon further upgrading. Since the catalyst does not readily absorb microwaves it is not ideally suited for microwave application and led to decreased heating rates due to heat losses from the biomass to the catalyst. Significant amounts of volatiles condensed on the catalyst, leading to fouling.

It was shown that LDO can be structured into granules very easily and at almost no cost with the use of water as binding agent. The catalyst could be visually regenerated at 650 °C, but it is recommended that additional tests be done on the structured catalyst to determine its applicability as a technical catalyst and its ability to be regenerated successfully. It is also recommended that future studies be done on the effect of the LDO catalyst on the other products (gas and char) to determine possible additional benefits of the catalyst. It is crucial that a true product composition be analysed when investigating the performance of catalysts for a full understanding of their activity. Condensers do not provide sufficient capture of volatiles in many experimental studies and it is recommended that electrostatic precipitators or quenching systems be used for future work.
References


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Appendices

Appendix A

Table A1: GCxGC-TOFMS identification of liquid samples at different catalyst to biomass ratios

<table>
<thead>
<tr>
<th>Name</th>
<th>Class</th>
<th>R.T. (s)</th>
<th>No Cat.</th>
<th>0.5:1</th>
<th>1:1</th>
<th>2:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>ketone</td>
<td>176 , 0.640</td>
<td>8.35</td>
<td>6.32</td>
<td>4.28</td>
<td></td>
</tr>
<tr>
<td>Formic acid</td>
<td>carboxylic acid</td>
<td>176 , 0.670</td>
<td>0.82</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>carboxylic acid</td>
<td>176 , 0.730</td>
<td>1.34</td>
<td>1.43</td>
<td>0.48</td>
<td>1.81</td>
</tr>
<tr>
<td>Propanoic acid</td>
<td>carboxylic acid</td>
<td>176 , 0.910</td>
<td></td>
<td></td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>2-Propanone, 1-hydroxy-</td>
<td>ketone</td>
<td>176 , 1.090</td>
<td>7.48</td>
<td>2.11</td>
<td>3.08</td>
<td>8.58</td>
</tr>
<tr>
<td>Vinyl butyrate</td>
<td>ester</td>
<td>179 , 1.040</td>
<td></td>
<td>0.02</td>
<td></td>
<td></td>
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<tr>
<td>Propanoic acid, anhydride</td>
<td>anhydride</td>
<td>182 , 0.780</td>
<td>0.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Butanol</td>
<td>alcohol</td>
<td>188 , 0.720</td>
<td></td>
<td></td>
<td>0.23</td>
<td></td>
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<td>(S)-(+-)1,2-Propanediol</td>
<td>alcohol</td>
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<td></td>
<td></td>
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<td></td>
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<tr>
<td>Methane, fluorotrinitro-</td>
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<td>200 , 0.660</td>
<td>0.77</td>
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<td>Ethyl Acetate</td>
<td>ester</td>
<td>206 , 1.140</td>
<td></td>
<td></td>
<td>2.54</td>
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<tr>
<td>Glycerin</td>
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<td>209 , 1.130</td>
<td>0.37</td>
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<tr>
<td>2-Propanone, 1,1-dichloro-</td>
<td>ketone</td>
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<td></td>
<td></td>
<td>7.63</td>
<td></td>
</tr>
<tr>
<td>Formamide</td>
<td>other</td>
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<td></td>
<td></td>
<td>1.01</td>
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<td>Propanoic acid, 2-hydroxy-, methyl ester, (ñ)-</td>
<td>ester</td>
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<td></td>
<td>1.42</td>
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<td>other</td>
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<td>Name</td>
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<td>No Cat.</td>
<td>0.5:1</td>
<td>1:1</td>
<td>2:1</td>
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<td>2-Methoxytetrahydrofuran</td>
<td>furan</td>
<td>224, 0.730</td>
<td></td>
<td>0.21</td>
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<td></td>
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<td>Toluene</td>
<td>other</td>
<td>239, 0.720</td>
<td></td>
<td>0.33</td>
<td></td>
<td></td>
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<tr>
<td>N-tert-Butylethylamine</td>
<td>other</td>
<td>239, 1.010</td>
<td></td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-Ethanediamine, N,N-diethyl-</td>
<td>other</td>
<td>239, 1.520</td>
<td>0.07</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>anhydride</td>
<td>242, 1.020</td>
<td>25.47</td>
<td></td>
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<td></td>
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<td>Ethanol, 2,2'-oxybis-</td>
<td>alcohol</td>
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<td>0.57</td>
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<td></td>
<td></td>
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<td>ketone</td>
<td>242, 1.520</td>
<td>0.26</td>
<td>0.33</td>
<td></td>
<td></td>
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<tr>
<td>1-Hydroxy-2-butanone</td>
<td>ketone</td>
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### Appendix B

**Table B1: Most abundant compounds and their respective area percentages**

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<th>Compound</th>
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<td>Phenol, 2-methoxy-</td>
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<td>2-Furancarboxaldehyde, 5-methyl-</td>
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<td>1H-1,2,3,4-Tetrazole-1,5-diamine, N(1)-[(2-ethoxy-3-methoxyphenyl)methyl]-</td>
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<td>Creosol</td>
<td>C8H10O2</td>
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</tr>
<tr>
<td>2,3-Dimethoxybenzyl alcohol</td>
<td>C9H12O3</td>
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<tr>
<td>Desaspidinol</td>
<td>C11H14O4</td>
<td>1.91</td>
</tr>
<tr>
<td>Phenol</td>
<td>C6H6O</td>
<td>1.89</td>
</tr>
<tr>
<td>2-Cyclopenten-1-one, 2-hydroxy-</td>
<td>C5H6O2</td>
<td>1.88</td>
</tr>
<tr>
<td>Phenol, 2,6-dimethoxy-</td>
<td>C8H10O3</td>
<td>1.81</td>
</tr>
<tr>
<td>Phenol, 2,6-dimethoxy-4-(2-propenyl)-</td>
<td>C11H14O3</td>
<td>1.80</td>
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<tr>
<td>1,2-Cyclopentanedione, 3-methyl-</td>
<td>C6H8O2</td>
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<tr>
<td>1-Hydroxy-2-butanone</td>
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<td>Phenol, 2-methoxy-4-(1-propenyl)-</td>
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<td>Furfural</td>
<td>C5H4O2</td>
<td>1.40</td>
</tr>
<tr>
<td>Ethanone, 1-(2-furanyl)-</td>
<td>C6H6O2</td>
<td>1.36</td>
</tr>
<tr>
<td>Compound</td>
<td>Formula</td>
<td>Area %</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>------------</td>
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</tr>
<tr>
<td>Benzene, 1,2,3-trimethoxy-5-methyl-</td>
<td>C10H14O3</td>
<td>1.32</td>
</tr>
<tr>
<td>(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol</td>
<td>C11H14O3</td>
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<tr>
<td>Toluene</td>
<td>C7H8</td>
<td>1.23</td>
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<tr>
<td>2(5H)-Furanone, 5-methyl-</td>
<td>C5H6O2</td>
<td>1.19</td>
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<tr>
<td>2-Cyclohexen-1-one</td>
<td>C6H8O</td>
<td>1.16</td>
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<tr>
<td>Furan-2-carbonyl chloride, tetrahydro-</td>
<td>C5H7ClO2</td>
<td>1.15</td>
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<tr>
<td>3-Furaldehyde</td>
<td>C5H4O2</td>
<td>1.15</td>
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<tr>
<td>Hydrogen azide</td>
<td>HN3</td>
<td>1.08</td>
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<td>Benzaldehyde, 4-hydroxy-3,5-dimethoxy-</td>
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<tr>
<td>(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol</td>
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<td>Eugenol</td>
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<td>Phenol, 2,6-dimethoxy-4-(2-propenyl)-</td>
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<tr>
<td>1,2-Ethanediol, monoacetate</td>
<td>C4H8O3</td>
<td>0.92</td>
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<tr>
<td>2-Cyclopenten-1-one, 2-methyl-</td>
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<td>0.91</td>
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<tr>
<td>2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-</td>
<td>C10H12O3</td>
<td>0.89</td>
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<tr>
<td>p-Cresol</td>
<td>C7H8O</td>
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<tr>
<td>3,5-Dimethoxy-4-hydroxyphenethylamine</td>
<td>C10H15NO3</td>
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<tr>
<td>Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-</td>
<td>C10H12O4</td>
<td>0.85</td>
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<tr>
<td>Phenol, 2-methyl-</td>
<td>C7H8O</td>
<td>0.82</td>
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<tr>
<td>Compound</td>
<td>Formula</td>
<td>Area %</td>
</tr>
<tr>
<td>-------------------------------------------------------</td>
<td>----------</td>
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</tr>
<tr>
<td>p-Xylene</td>
<td>C8H10</td>
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<tr>
<td>Methylene cyclopropane</td>
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<tr>
<td>Phenol, 2-methoxy-4-propyl-</td>
<td>C10H14O2</td>
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<tr>
<td>3,5-Dimethoxy-4-hydroxycinnamaldehyde</td>
<td>C11H12O4</td>
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<tr>
<td>5-Hydroxymethylfurfural</td>
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<td>Phenol, 4-ethyl-2-methoxy-</td>
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<td>Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-</td>
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<tr>
<td>2-Propanone, 1-(acetyloxy)-</td>
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<tr>
<td>Cyclopentanone</td>
<td>C5H8O</td>
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</tr>
<tr>
<td>Cyclopent-4-ene-1,3-dione</td>
<td>C5H4O2</td>
<td>0.65</td>
</tr>
<tr>
<td>3-Hexanone</td>
<td>C6H12O</td>
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<tr>
<td>Acetoin</td>
<td>C4H8O2</td>
<td>0.62</td>
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