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Fast and microwave-induced pyrolysis bio-oil from *Eucalyptus grandis*: Possibilities for upgrading

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Wood: another form of coal, just less degraded, more complicated, and misunderstood. It must be the future of energy.

DECLARATION

I, Ryan David Merckel, declare that every detail of this dissertation is my own unassisted work. It is the intention that this dissertation be submitted for the Degree of Master in Engineering at the University of Pretoria. I further declare that this dissertation has not been submitted to any other university or educational institution for any degree, examination or other forms of qualifications.

Signature of Candidate

Signed at Pretoria on this 19th day of September 2014.

ABSTRACT

RD Merckel

Fast and microwave-induced pyrolysis from *Eucalyptus grandis*: Possibilities for upgrading

The hardwood *Eucalyptus grandis* has been shown to be an important commodity for forestry-related industries as it has significantly faster specific growth rates per annum when compared with other types of tree species. It has therefore been suggested that residues from *E. grandis* may be a useful source of biomass for use in the production of biofuels for the transportation industry. Notably, *E. grandis* plantations within the Southern Hemisphere have some of the fastest growth rates worldwide. Due to the inherent nature of biomasses, such as lignocellulosic types having a significant amount of oxygen present, upgrading of biofuels produced from *E. grandis* is necessary. Several approaches were therefore evaluated to upgrade pyrolysis oils produced from *E. grandis* so as to increase their calorific values by decreasing oxygen content and subsequently increasing the hydrogen ratio. The hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios may be used successfully to evaluate the performances of catalyst-based upgrading techniques for either *in situ* or *ex situ* pyrolysis. In this regard the van Krevelen diagram, in which biofuels can be compared for their suitability as transportation fuels, along with their respective calorific values, is useful.

The pyro-gas chromatography/mass spectroscopy (GC/MS) equipment is useful for the rapid and accurate evaluation of different catalysts for fast pyrolysis applications, and it was used here to evaluate the performances of the catalysts bentonite and ZSM-5 zeolite for upgrading pyrolysis oil produced from *E. grandis* biomass. A van Krevelen diagram was used to evaluate the performance of these catalysts, in conjunction with calorific values, based on the higher heating values for the pyrolysis oils. Further studies were completed for microwave pyrolysis as it is a less harsh form of pyrolysis based on energy-transfer mechanisms. Mass balances were done and demonstrated good repeatability, with more stable pyrolysis oils being produced. This stability may be attributed to similarities between microwave pyrolysis and hydrothermal liquefaction as microwave pyrolysis induces conditions comparable to those of hydrothermal liquefaction within the wood cells, and both methods produce a stable product called bio-crude. Furthermore, it was found that these pyrolysis oils could be distilled so as to remove some of the water content and improve the higher heating value (HHV) from 13.80 to 23.30 MJ/kg. However, this was not as high as the theoretical yield of 26.70 MJ/kg, and better performance was obtained for fast pyrolysis catalysed with ZSM-5 zeolite at 300 °C, which achieved an HHV of 34.54 MJ/kg. It is recommended that ZSM-5 zeolite catalysis be used in microwave-assisted vacuum pyrolysis to determine whether a similar improvement may be realised. Microwave-assisted pyrolysis should also be investigated as a possible technology for inducing conditions similar to hydrothermal liquefaction processes within the cells that make up the biomass.

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CHAPTER 1: INTRODUCTION

1.1. Background

Energy security has been challenged through the ongoing depletion of fossil-based fuels worldwide, and there have also been many energy crises brought on by the Gulf War and the stringent government-supported regulations for global greenhouse gas reduction.[1, 2 ,3, 4] Unfortunately, not only have renewable biofuels shown poor competitiveness in the past when compared with fossil fuels,[5, 6] but also their use has been limited due to the initial abundance of fossil fuels. This situation has been somewhat improved, however, owing to ongoing research into ways of reducing biofuel prices and production costs, and increasing capacity.[7, 8, 9]. Nevertheless, the biofuel industry has been seen as the way to go to replace fossil fuels, especially in the transportation sector and the demand for such fuels is on the increase.[10, 11]

1.2 Problem statement and objectives

Issues brought on by energy security have been further complicated by food security concerns, since biomass feedstock may be derived, controversially, from agricultural industries. This has caused much debate as to whether biomass sourcing will affect food security in exchange for improved energy security.[12, 13, 14] In the background, plantations have been further developed to meet growing demands for lignocellulosic materials.[15] The most important wood species for this purpose is the hardwood *Eucalyptus grandis*, which enjoys some of the highest specific growth rates compared with all other tree species, specifically for plantations existing in the Southern Hemisphere. [16,17,18] Furthermore, plantations may be built up in regions not suitable for agriculture, which limits the impact on food security. [19] It has therefore been argued that this species may be suitable for sourcing biomass residues required for the production of biofuels, such as pyrolysis oils and their derivatives.

In this work residues from *E. grandis* were therefore investigated for their suitability for producing pyrolysis oils. Assessing the possibility of upgrading these pyrolysis oils will also be necessary for them to be considered for transportation fuel and for use in related industries. Common catalysts such as bentonite and ZSM-5 zeolite were considered here, and their performance was evaluated in terms of the final hydrogen/carbon (H/C) and oxygen/carbon (O/C) ratios realised for the pyrolysis oils produced. For further comparison, microwave-assisted vacuum pyrolysis was evaluated and similarly compared with other conventional pyrolysis technologies based on calorific values, and carbon, hydrogen and oxygen content.

1.3 Method and scope

Catalysts were tested using pyro-gas chromatography/mass spectroscopy (GC/MS) technology which is able to simulate fast pyrolysis, including *in situ* upgrading techniques of interest to fast pyrolysis. For microwave-assisted vacuum pyrolysis, a RotoSYNTH microwave system supplied by Milestone was used to conduct the microwave-based experiments. Calorific values were either predicted or measured where possible. Depictions of the H/C and O/C ratios from all the pyrolysis oils were evaluated on a van Krevelen diagram where possible for further clarification of the effectiveness of pyrolysis techniques and catalytic upgrading performance.

CHAPTER 2: LITERATURE REVIEW

2.1 Energy security: the shift towards renewable energies

The global push towards the promotion of biofuels is strongly motivated by the imminent prospect of fossil fuel depletion and energy security concerns, as well as by global warming.[1] Other socioeconomic factors that have had a marked effect on energy security have been the oil crisis of 1973 and the Gulf War in 1991, together with the gradual geographical reduction in petroleum reserves and stringent regulations on exhaust gas emissions by governments.[2, 3, 4] The competitiveness of biofuel technologies achieved through ongoing development and improvements further supports their integration with and substitution of fossil fuels. This is in contrast to the misconception that clean and renewable energies are too expensive and generally uncompetitive with conventional energy technologies.[5, 6]

Electricity generated from hydropower, for example, provides the lowest levelised cost of electricity when compared with all major fossil fuel sources.[7] Average installed costs for solar systems have decreased by as much as 60% and solar energy has already become cheaper than diesel generation.[8, 9] Biofuel production in the USA brought about a reduction in the price of gasoline by $1.09/gal in 2011 alone.[10] In the same year an additional 6 GW of biomass-based energy production was realised globally, with some biomass technologies lowering their levelised cost of electricity along with other renewable energies.[9]

In summary, both the inevitable depletion of fossil fuels and the continuing increase in cost competitiveness of renewable energy technologies are driving the shift globally towards reliance on sustainable energy sources, and specifically on biomass sources for transportation fuels in the industrialised countries.[1]

2.2 Biomass and biofuel production

The importance of developing usable biofuels lies in being able to replace the existing petroleum-based fuels. Because of this, it is expected that the demand for biofuels will continue to rise in the future along with the demand for other renewable energy technologies.[10] Moreover, biomass has a unique advantage over other renewable energy sources in that it is easy to store until needed and liquid biofuels produced from it can be applied to the existing transportation fuel systems. Biofuels are currently the only renewable resources that can address the heavy dependence on fossil fuel oils present in the transportation sector.[11]

2.2.1 Food and energy security

Procuring energy from biomass sources has the potential to offset fossil fuel usage considerably, but this is not without its drawbacks and has faced much controversy. Cultivating biomass resources may endanger conservation areas through sacrificing natural ecosystems to cultivate monocultures, pollute water resources from agricultural pollutants, and threaten food security by competing with food crops.[12] With agriculture being a necessary resource for sustaining human and domestic life in the support of human prosperity, agricultural ethics is now concerned with the proper management of these resources and what is to be done.[13]

There is much criticism against the campaign for biofuels as an energy source capable of increasing the security of supply, reducing emissions and providing a new source of income to farmers. This criticism has been levelled for notable reasons. Most of the criticism has its basis in the evaluation of first-generation fuels, but the same criticism could hold true for second-generation fuels. As they are still in the demonstration phases, it remains to be seen what impact second-generation technologies will have. Even so, it has been asserted that biofuels could cause instability to energy costs, food costs and even the life cycle of greenhouse gases.[14] According to Doornbosch & Steenblik,[14] in 2006 the global biofuels-based energy production was 0.8 EJ, which amounted to approximately 1% of the total road transport fuel consumption. From their findings they estimated that a total of 14.53 EJ of energy derived primarily from ethanol and biodiesel is theoretically possible by 2050. But in practice this might not be achievable without significant impacts on the wider global economy. Although it is likely that enough land is available to accommodate food requirements for an ever-growing world population, the underlying issue is on constraints for using the land for either fuel or food. This has led to a difficult conflict between the two crises of global food security and energy security, with land usage being the main driver of the food-or-fuel debate.[14] A further in-depth review of 17 studies, completed by Berndes, Hoogwijk & Van den Broek,[19] discusses the potential contribution of biomass to future energy supply by 2050. These authors found widely varying conclusions about the predicted contribution biomass resources would make to global energy supply, which is anywhere from 100 EJ per annum to 400 EJ per annum by 2050. The reason for such differences are is based on two parameters, namely land availability and yield levels in energy crop production. It therefore remains to be seen what the impact of land availability and utilisation will be in relation to specific yields of energy crop production.

Popp, Lakner, Harangi-Rákos et al.[20] point out three possible factors affecting the management of available land, namely (i) land purposed for urbanisation, mining, traffic and energy infrastructure, (ii) the use of agricultural products for non-food purposes, and (iii) the degradation of land. In the light of this, Berndes et al.[19] pose the question as to how an expanding bioenergy sector would interact with or affect the management of land in terms of food production, the conservation of biodiversity, of soil and of nature, and carbon sequestration.

2.2.2 Sources of biomass

The biospheric net primary production (NPP) in terms of the total annual plant growth has the ability to fix carbon on a greater scale than what is currently being consumed through the industrial energy system.[21] The ability of the biosphere to fix carbon was estimated by Behrenfeld, Randerson, McClain et al.[22] using an integrated method for both the oceans and land. They found that land NPP was nearly constant for the climate regimes investigated, and carbon fixation was found to be between 57 and 58 billion tons per annum. A similar result was found for carbon fixation in the oceans, at 57 billion tons per annum.[21, 22] In comparison, Raupach, Marland, Ciais et al.[23] found that industrial carbon emissions from fossil fuel burning and industrial processes amounted to 7.7 billion tons in 2005. From these figures it is reasonable to draw the conclusion that forest and bioenergy strategies could offer effective future management and utilisation of biospheric carbon. The effect on the net flux of carbon from such strategies is achieved through four mechanisms: (i) storage of carbon in the biosphere; (ii) storage of carbon in forest products; (iii) use of biofuels to displace fossil fuel use; and (iv) use of wood-based products as opposed to fossil-based products.[24]

Terrestrial biomass feedstocks can be sectioned into two groups, namely feedstocks that are rich in starch/cellulose or lipids (such as sugarcane, soybean, rapeseed, etc.), and feedstocks that consist of lignocellulosic biomass. The first group currently contributes to the bulk of biofuel production as the conversion technologies are mature and offer high yields and lower unit production costs. These feedstocks produce most of the first-generation biofuels. The downside of these feedstocks is that they may have negative implications regarding global food prices and production as they are typically derived from arable crops.[25] The second group has the potential to avoid these issues as they are non-starch, non-edible and non-food feedstocks, giving rise to the second-generation biofuels. These feedstocks may be sourced directly from agricultural residues, so as not to compete against food crops, or from forest residues and energy crops (woody or herbaceous crops, such as grasses).[25] Furthermore, second-generation biofuels have the upper hand over first-generation biofuels in lessening the food-or-fuel debate in that they can be produced using marginal or degraded land or land not suitable for agriculture, or using by residual biomass materials as well.[22]

Because of the limitations identified for first-generation biofuels (with the exception of sugarcane ethanol), more emphasis is now being placed on second-generation biofuels produced from lignocellulosic feedstocks.[26] Second-generation biofuels, however, still pose many technical and economic challenges, although significant progress continues to be achieved, and these biofuels will continue to experience major constraints until full commercial deployment is realised.[26]

2.2.3 Lignocellulosic material derived from *E. grandis*

The development of plantations in tropical and subtropical regions has been increasing substantially with the aim of satisfying the growing demand for forestry products. By 2024 it is expected that half of the wood fibre sourced in the world will come from these plantations, with the majority originating from the tropics and subtropics.[15] The global demand for wood products has been growing at a rate similar to that of the world population, with consumption increasing volumetrically by as much as 1.7×10^9 m^3 since 1960. This is likely to increase by a further 1.5×10^9 m^3 to 2.2×10^9 m^3 by the middle of the 21st century.[27] Currently, the most important and common tree species grown in tropical and subtropical plantations are from the *Eucalyptus* and *Pinus* genera. These two genera account for 43% of the total tropical plantation area, with pines dominating the temperate and boreal zones by 54%, based on area.[16, 28] Moreover, on a global scale, *Pinus* and *Eucalyptus* species comprise 42% and 26% of the total tree species in plantations internationally, respectively. The balance is made up of other hardwoods (10%) and softwoods (9%), acacia (6%), teak (5%), cypress (1%) and poplar (1%). Table 1 shows the total productivity (presented as the mean annual increment [MAI]) and rotation lengths for the main plantations for certain tropical countries, and Table 2 gives these same data for Northern Hemisphere-based pines. The *Eucalyptus* genus in particular is considered to contain some of the fastest-growing species of trees compared with other wood genera.[17] It is because of this that the Australian eucalypts have become the trees most widely used for commercial plantations. South African silviculture productivity assumes more typical growth rates of eucalypts, based mainly on *Eucalyptus grandis* and its hybrids. *E. grandis* is mentioned as the eucalypt most widely used for industrial applications, with plantations populating areas of 2 million ha from 1987 onwards, mostly in Brazil and South Africa.[29] Within South Africa, eucalypt plantations obtain yields (as an estimate) between 21 and 25 m^3 ha^{-1} yr^{-1}.[18, 30] In comparison with this, tree species based in the Northern Hemisphere grow at slower rates than their Southern Hemisphere counterparts, as shown by Asian teak in Table 1, and by European pines in Table 2. Based on the data presented in Tables 1 and 2, the rotation lengths for eucalypts are 78% to 94% shorter than for Northern Hemisphere pines.

Table 1: Productivity and rotation lengths for the main plantations in tropical countries[18]

Species	Country	Rotation length (years)	MAI [a] (m^3 ha^{-1} yr^{-1})
Eucalyptus	Brazil	8–10	18–20
	Burundi	8	1–2
	Congo	7	30
	Rwanda	8	8.5
	South Africa	8–10	18–20
Pinus	Brazil	16–25	15–25
	Venezuela	10–20	10
	Chile	20–30	24
	Malawi	20–25	17
	Madagascar	15–18	6–10
	Mozambique	18–25	11
Tectona	Bangladesh	60	2.6–3
	India	70	2.5
	Indonesia	50–70	1.3–2

[a] Mean annual increment

Table 2: Productivity and rotation lengths for European trees of economic importance[31]

Country	Species	Rotation length [a] (years)	MAI [b] (m^3 ha^{-1} yr^{-1})
Finland	*Pinus sylvestris*	90	6.9
	Picea abies	90	8.2
Germany	*Pinus sylvestris*	120	6.3
	Picea abies	100	9.9
United Kingdom	*Picea sitchensis*	40	14.7
Spain	*Pinus sylvestris*	100	8.6
	Pinus pinaster	80	7.3

[a] Rotation length as currently recommended
[b] Calculated as an average based on yearly annual increments

The commercial importance of eucalypts is motivated not only by their fast growing rates, short rotation lengths and productivity, but the expansion of eucalypt plantations worldwide over the last 60 years has also been driven by the superior fibre and pulping properties of these species. Because of this, eucalypts are being seen as attractive and well-motivated renewable biomass crops for energy production.[32]

Table 3 compares water usage among common agricultural commodities, and gives their harvest indices (defined as the mass of crop used divided by the total mass of above-ground biomass) and water use per harvested biomass. As can be seen from the harvest indices in Table 3, where higher harvest index values indicate a greater utilisation of the complete biomass, eucalypts offer the most utilisation, with a low water usage of 785 ℓ/$\text{kg}_{\text{biomass}}$ compared with that of other plant types, which can be as high as 3 200 ℓ/$\text{kg}_{\text{biomass}}$. The water usage per harvested biomass for eucalypts is similarly below average at 510 ℓ/kg.[33]

Table 3: Evapotranspiration of common commodities[33]

Plant type	Water usage (ℓ/$\text{kg}_{\text{biomass}}$)	Harvest Index	Water usage per harvested biomass (ℓ/kg)
Cotton/coffee/bananas	3 200	0.25	800
Sunflower	2 400	0.25	600
Soybean	1 430	0.35	500
Potato	1 000	0.60	600
Eucalyptus	785	0.65	510
Finger millet	592	0.40	225

2.2.4 Composition of *E. grandis*

Non-isothermal thermogravimetric analysis (TGA) is a well-known analytical technique for evaluating the chemical composition of biomasses and their derivatives, such as pulp and paper, under oxidising and inert atmospheres.[34] When applied to lignocellulosic materials, these two thermal degradation methods can provide valuable information in terms of quantifying the five main pseudo-components: crystalline and amorphous cellulose, hemicellulose, lignin and extractives. These naturally occurring biopolymers and organic materials can be transformed into high-value chemical products other than pulp and paper and form the basis of biorefinery research. These products include agricultural products, animal feeds, plastics, chemicals, transportation fuels and building materials, as well as power and heat generation. The types of product that can be obtained from lignocellulose depend on the specific quantities of the five pseudo-components.[35, 36] Barneto, Hernández & Berenguer[36] completed thermogravimetric characterisation on different species of eucalypts, including *E. grandis*, and compared their results for hemicellulose, cellulose, lignin and extractives with those of three other authors. Their data they presented and those from another source[37] are summarised in Table 4 on a mass basis for all components. Fengel & Wegener[38] provide a more comprehensive summary of the pseudo-components found in softwoods, hardwoods from temperate zones and important tropical woods. Based on these data, the average percentage cellulose, the percentage hemicellulose (measured as total percentage polyoses) and the percentage lignin were found to be 44.8, 29.2 and 23.4% respectively. Comparing this result with the data supplied in Table 4 shows that *E. grandis* tends to have a slightly higher average percentage cellulose content (about 49.9%), and a slightly lower average percentage hemicellulose content (17.5%). The lignin content is more or less comparable to the average presented by Fengel & Wegener[38] (at 24.6%).

Table 4: Composition of pseudo-components of *E. grandis* wood

	Hemicellulose	Lignin	Extractives	References
51	19	23	6	Barneto et al.[36]
46.3	20.68 [a]	22.9	Not measured	Garrote & Parajó[39]
50.7	14.1 [b]	25.5	3.2	Miranda & Pereira[40]
51.49	16.4	27.1	4.8	Brito et al.[41]
57.5	27.6	15.2	2.6	Joubert et al.[37]

[a] Measurements based on xylan (16.5), araban (0.54) and acetyl (3.54)

[b] Measurement only for xylan

[c] Measurements based on xylan (13.1), araban (0.47), mannose (1.54) and galactose (1.29)

CHAPTER 3: PYROLYSIS OIL PRODUCTION, UPGRADING AND CATALYSIS

Thermochemical processing dominates the biofuels sector and is used to convert biomass materials physically and/or chemically so as to increase or enhance their usability and usefulness, and to increase their calorific value.[42] Processes for manufacturing biofuels include direct combustion, heat decomposition, gasification, thermochemical liquefaction and pyrolysis. Whereas all these technologies aim to utilise energy or create high-value chemical products from biomass, further objectives of pyrolysis processes are to obtain liquid fuels of low molecular weight from biomass containing compounds of high molecular weight.[43] Pyrolysis also produces biochar, a carbonaceous material with a high specific surface area and a good heating value. Biochar is composed of up to 80% carbon with a reduced oxygen content, which gives it a much higher heating value than the biomass from which it is derived. It is useful as a carbon-neutral feedstock for power and heat generation, and as an agricultural aid in enhancing the fertility of soils.[44] Another product produced from pyrolysis is synthesis gas, obtained as non-condensable gases and also known as biogas. These non-condensable gases contain important compounds such as hydrogen, light hydrocarbons such as methane and ethane, and carbon oxides.[44]

3.1 Principles of pyrolysis: biomass to biofuels

Pyrolysis is a thermochemical process which is the precursor of gasification and combustion, and produces non-condensable gases, pyrolysis oil and biochar from crops, which can then be further processed into useful fuels or feedstock.[45, 46] The nature of the changes exhibited and the outcomes realised through pyrolysis are dependent on the material being pyrolysed, the operation temperature and heating rate, and the residence time. Changing these parameters will affect the quantity and quality of non-condensable gases, pyrolysis oil and biochar produced. This in turn has a direct effect on the heating value of the fuel and its chemical reactivity.

Feedstocks should also be kept as dry as possible as this can contribute to a lower heating value in the oil.[46] Typical feedstocks used are lignocellulosic, such as wood, straws, stalks and stover, and tend to be poor conductors of heat. Proper management of heating rates during pyrolysis for these feedstocks is based on size reduction, as well as convective and conductive energy transfer mechanisms.[46]

The operating temperature in pyrolysis is crucial and is the main process condition used to target specific products. By using temperatures below 450 °C together with slow heating rates (i.e. using larger particle sizes), the biochar yield is optimised for a process called *slow pyrolysis*.[46, 47] At temperatures greater than 800 °C the gaseous yield increases substantially and suppresses the pyrolysis oil and biochar yields. Using an intermediate temperature of between 400 and 500 °C with a sufficiently small feedstock particle size and a short residence time optimises the yield for pyrolysis oil, while still producing low yields of biochar and non-condensable gases.[46] Based on these particular parameters, a process known as *fast pyrolysis* is achieved. Figure 1 shows the generic layout of unit operations specific to the fast pyrolysis process. As pyrolysis is mildly endothermic, exogenous heating is a requirement in order to maintain the thermochemical reactions brought on by pyrolysis. This is why it is preferred to use the system of a dual fluidised bed reactor for fast pyrolysis.

Biomass is fed into the pyrolyser which operates under an inert or a reduced oxygen atmosphere and is heated using hot sand. The hot sand is kept fluidised using non-condensable gases and provides high heating rates through solid–solid contact with the biomass.[44, 47] This sand is conveyed back to the combustor where it is reheated using biochar, and in some cases an external fuel source. Vapours formed in the pyrolyser are extracted and screened to remove entrained sand, biochar and other solids. The screened vapours are then quenched to collect a liquid product and are separated from the non-condensable gases. The non-condensable gases are then sent through an electrostatic precipitator in which residual pyrolysis oil is removed. These gases may then be sent through the pyrolyser for maintaining fluidisation or bled off out of the system.[44, 47]

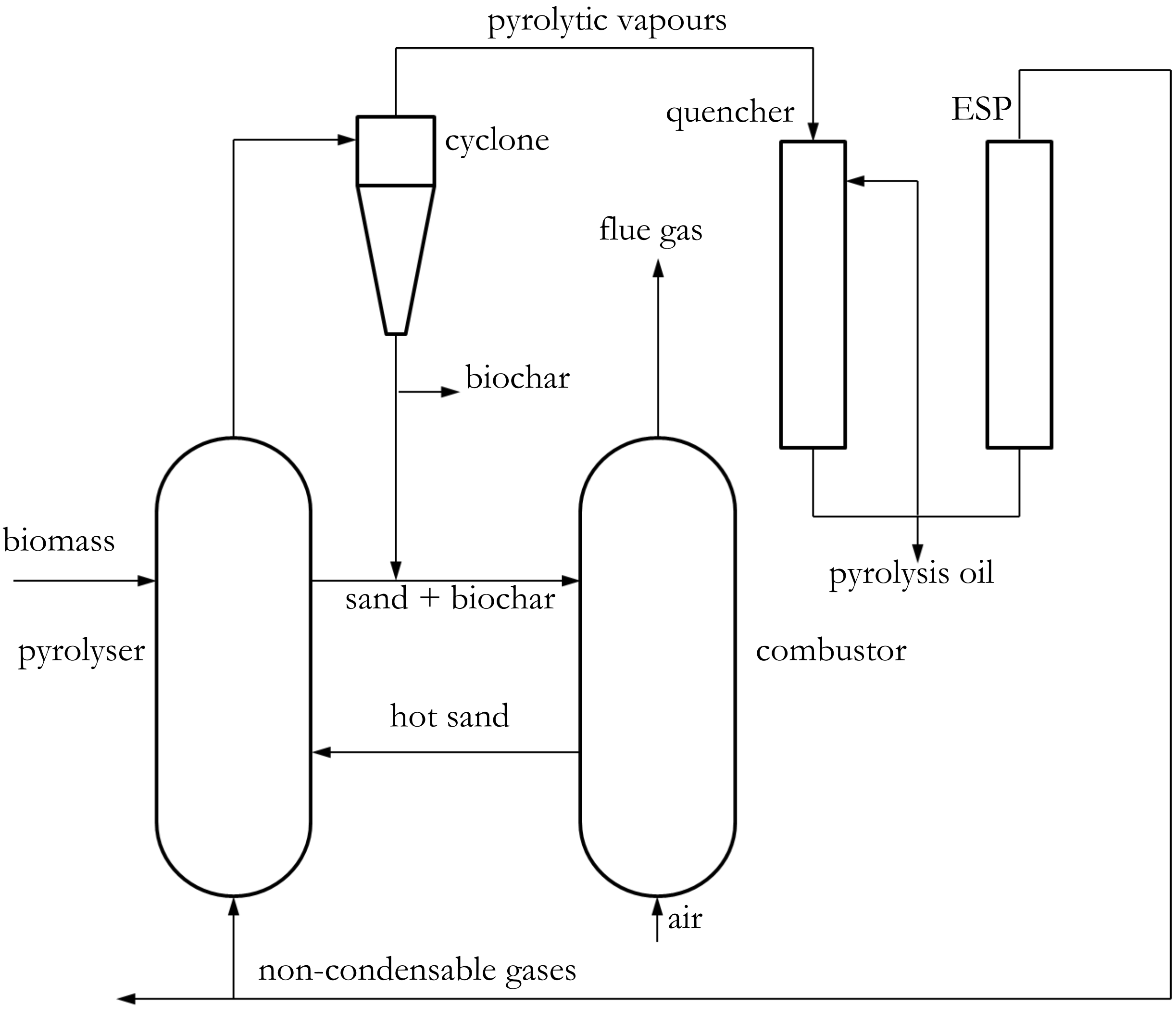


Figure 1: Generic layout of unit operations for the fast pyrolysis process[44]

3.1.1 Properties of pyrolysis oil and the objectives of catalysis

There is great variance between different pyrolysis oils in the types of major products produced from pyrolysis, the yields obtained for the product phases, and the physiochemical properties. It is not practical to compare different pyrolysis oils and other products directly with each other as these are often subject to considerable variations. However, general commonalities between the different pyrolysis products do exist, such as between the targeted operating parameters of reaction temperature, heating rate and residence time.[47, 48]

The ability to predict what compounds will be present in pyrolysis oil is very limited due to the poor selectivity for specific pyrolysis products. It is, however, expected that pyrolysis oils will still contain common groups of products due to the characteristic chemical structure of lignocellulose. Liquid products obtained via fast pyrolysis constitute a great variety of compounds which tend to be highly oxygenated, acidic and chemically unstable.[47, 48] The chemical composition of the biomass has a significant effect on the pyrolysis oil yield too, and can be related to its hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios.[48] Although it may not always be possible to select specific desired H/C and O/C ratios, selecting specific components of lignocellulose, namely cellulose, hemicellulose or lignin, as a feedstock may increase the selectivity of certain products.[49]

The rich chemical composition of pyrolysis oil is made up of an aqueous phase and a hydrophobic non-aqueous phase. The aqueous phase contains compounds such as methanol, ethanol, acetic acid, acetone, etc. The non-aqueous phase is made up of the heavier molecular weight organic compounds (namely alcohols, phenols and creosols), aromatics (such as benzene, toluene and indene), and polycyclic aromatics (such as naphthalenes and anthracenes).

The negative properties associated with native pyrolysis oil are directly linked to the high oxygen content. The oxygenated substituents give pyrolysis oils their corrosive, unstable, viscous and polar properties, which in turn make them incompatible with many fuel systems.[50] Pyrolysis oil may contain more than 300 different oxygenated compounds in the form of acids, aldehydes, ketones, alcohols, glycols, esters, ethers, phenols, phenolic derivatives, carbohydrates and lignin-derived oligomers.[51] This complex mixture of oxygenated compounds is a challenge for utilisation and, because of this, methods of upgrading pyrolysis oil focus primarily on removing as much oxygen as possible as either water or carbon oxides.[50, 51, 52] Table 5 summarises some of the important physical properties of different pyrolysis oils. The pH can range from 2.0 to 3.7, but is typically 2.5–2.8. The moisture content of pyrolysis oils is high (typically between 20 and 30%), considering that heat evolved by combusting the oils goes towards heating the water, thereby lowering the net calorific value of the oil. This forms a paradoxical challenge as the oxygenated substituents not only make refining of the oil near to impossible due to its instability, but they also cause the oil to be readily soluble with water. Furthermore, pyrolysis oil in its native form cannot be blended with conventional fuels, unlike other biofuels (such as bioethanol and biodiesel).[50, 52]

Table 5: summary of physical properties of pyrolysis oils from various feedstocks

Property	Birch [50]	Pine [50]	Poplar [50]	Various [50]	Typical [52]
% Moisture	18.9	17.0	16.8	15–30	20–30
% Solids	0.06	0.03	0.045	0.01–1	0.1–0.5
Specific gravity	1.25	1.24	1.20	1.2–1.3	1.20
Viscosity (cP)	28	28	13.5	13–80	40–100
pH	2.5	2.5	2.8	2.0–3.7	2.5
% C	44.0	45.7	48.1	32–49	55–58
% H	6.9	7.0	5.3	6.9–8.6	55–58
% O	49.0	47.0	46.1	44–60	35–40
% N	< 0.1	< 0.1	0.14	0.0–0.2	0.0–0.2

Upgrading of pyrolysis oil may be accomplished physically, chemically and/or catalytically, and much research is currently focused on improving the various upgrading methods.[52] Chemical and catalytic upgrading are more complex and costly than physical methods, but they offer significant improvements such as oil stabilisation and high-quality products.[53] Heterogeneous catalysis, such as the use of zeolites and mesoporous materials, has been widely used to decrease the oxygen content in pyrolysis oil.[52, 54] Various other methods also exist, such as catalytic hydrodeoxygenation which requires high-pressure hydrogen, aqueous-phase reforming and steam reforming over various catalysts.[52]

3.1.2 *In situ* and *ex situ* catalysis

Catalytic upgrading may be performed either in a single reactor, known as *in situ* upgrading, or in a separate unit operation following pyrolysis, also known as *ex situ* upgrading.[55] Using an *ex situ* upgrading reactor separate from the pyrolyser allows greater control over vapour-phase reactions than in the case of *in situ* catalytic upgrading in which vapours are immediately upgraded within the pyrolyser as they are formed.[56] Research and development in using the method of *ex situ* upgrading may promote a better understanding of the fundamentals of pyrolysis oil catalysis, but the benefit of using *in situ* catalysis is that both pyrolysis and upgrading can take place in the same reactor, without the need for more unit operations and process equipment.[57] Ruddy, Schaidle, Ferrell et al. briefly mention the natural progression from fast pyrolysis, to *ex situ* catalytic pyrolysis, to *in situ* catalytic pyrolysis.[57] It is therefore concluded that once enough information is available from studying the principles of *ex situ* and *in* situ catalysis, it would be possible to evaluate and compare the technoeconomics between the *ex situ* and *in situ* upgrading techniques so as to decide which is the better technology to use.

3.1.3 Evaluation of oils using the van Krevelen diagram

When dealing with carbohydrates and their derivatives (such as those generated through pyrolysis), it is important to note the atomic composition in terms of the hydrogen, carbon and oxygen content. Understanding the atomic ratios for carbon, hydrogen and oxygen helps in determining what type of heating value a fuel will have.[48] As an example, Table 6 lists the higher heating values (HHVs) from hydrogen (which has the highest heating value of -141.8 MJ/kg) through to the combustion products CO_2 and H_2O. It is clear from Table 6 that with the addition of carbon, the heating value is substantially lower since carbon has a lower HHV than hydrogen. Similarly, with the addition of more and more oxygen which has no heating value, the HHV drops even further until full oxidation has occurred and the combustion products CO_2 and H_2O are formed. By plotting the H/C atomic ratio as a function of the O/C atomic ratio for kerosene and petroleum-related substances, van Krevelen created what is now known as the van Krevelen diagram.[58]

Table 6: Higher heating values for various compounds in MJ/kg[59, 60]

H_2	CH_4	C	CH_4O	CH_2O	CO	CH_2O_2	CO_2	H_2O [a]
-141.8	-55.5	-32.8	-23.9	-19.0	-10.2	-5.5	-0.0	(44.0)

[a] Heat of evaporation for water at 25 °C [59]

Although the van Krevelen diagram is often used for differentiating and classifying various types of kerosene, coal and petroleum-based materials, it is also possible to classify different types of biomass, as well as their corresponding biofuels. Simply correlating the atomic ratios on a van Krevelen diagram to the corresponding HHV gives rise to a method of evaluating the performance of catalysts and allows them to be easily compared with each other.[48] A similar concept may be applied to a ternary diagram which has atomic hydrogen, atomic carbon and atomic oxygen plotted at the vertices, with the various components being investigated plotted within the triangle. Figure 2 shows a ternary diagram for carbon, hydrogen and oxygen, together with the main regions of fuels and combustion products (adapted from Basu[48]). An example of a van Krevelen diagram is given in Figure 3.

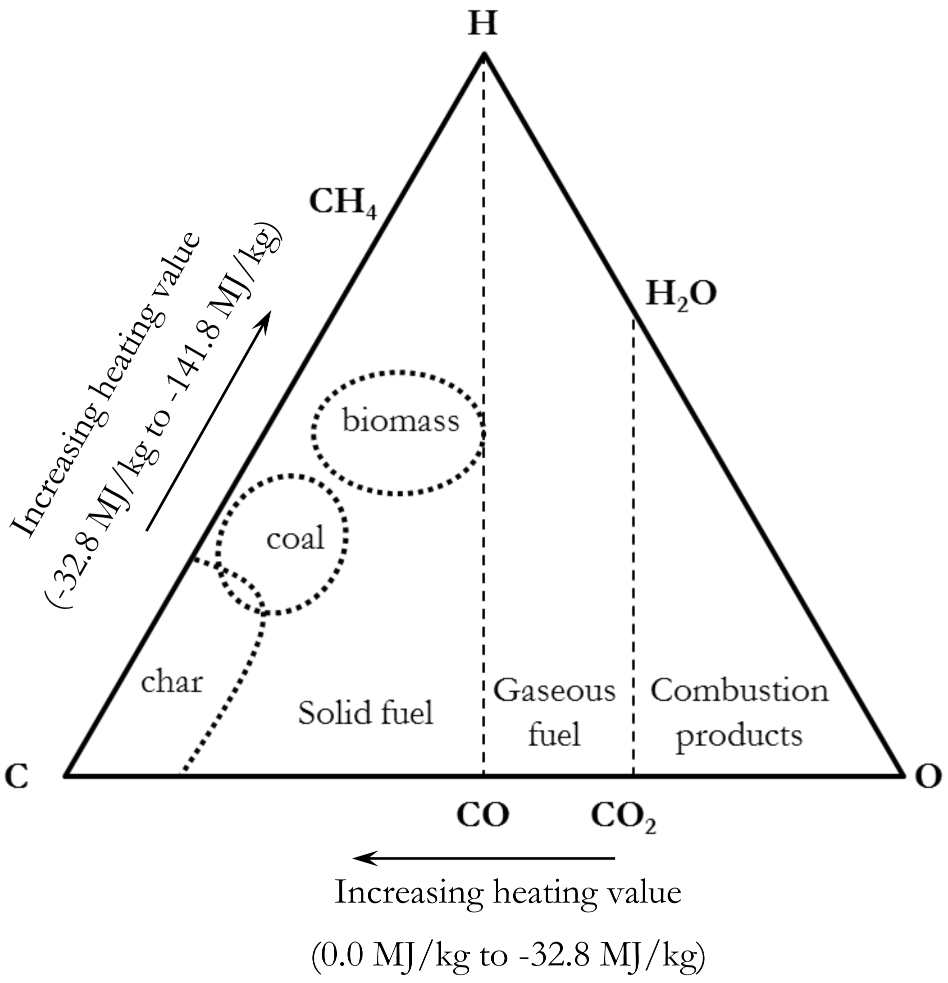


Figure 2: Ternary diagram for carbon, hydrogen and oxygen, and main regions of fuels and combustion products (adapted from Basu [48])

Referring to data on the van Krevelen diagram in Figure 3, it can be noted that petrol and diesel lie above crude oil, indicating the increase in hydrogen that takes place during refining. Increases in both the carbon and hydrogen content cause a shift towards the H/C axis and away from the O/C axis. An example of this is seen when going from lignite to subbituminous coal, and from subbituminous coal to bituminous coal in Figure 3. The heating values in each case increase with increasing carbon and hydrogen content. It can be concluded therefore that refining, whether it be that of crude oil or native pyrolysis oil, aims to achieve an increase in the hydrogen and carbon content, and at the same time decrease the oxygen content. It is not always possible to upgrade pyrolysis oil without losing hydrogen and carbon in the process to non-condensable gases and biochar; nonetheless the remaining objectives of any catalytic upgrading, whether *in situ* or *ex situ,* should be to remove oxygen, favouring the formation of carbon oxides rather than more energy-rich hydrogen.

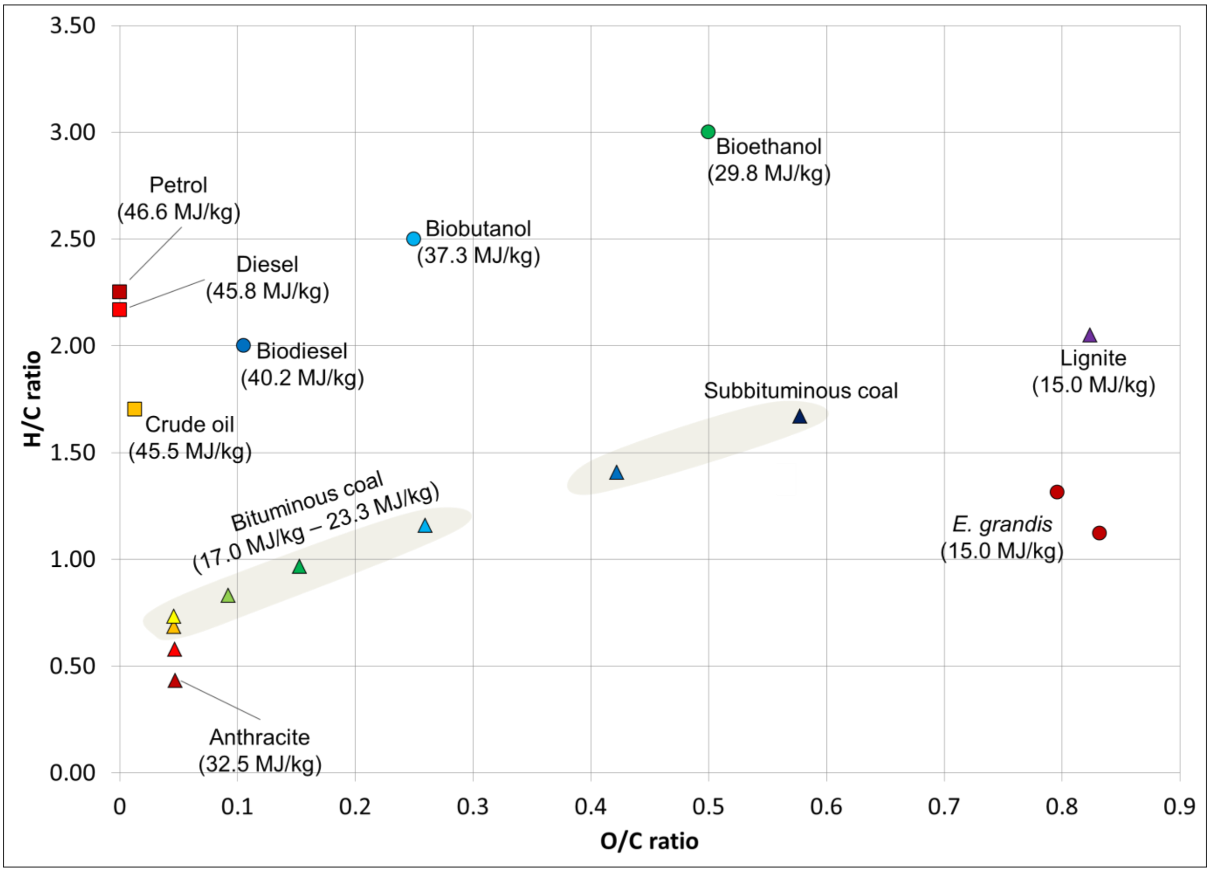


Figure 3: Plot of H/C as a function of O/C on a van Krevelen diagram

CHAPTER 4: EVALUATING CATALYSIS OF *E. GRANDIS* USING A PYRO-GC-MS

4.1 Overview

As mentioned briefly before, catalysts commonly used in the fuel industry for upgrading are based on zeolites and mesoporous materials. Along with these, salts, acids, bases, metals and naturally occurring materials and minerals have also been investigated for their abilities to upgrade pyrolysis oil[54].

Zeolites are composed of a crystalline framework consisting of silicon atoms, aluminium atoms and four oxygen atoms. The atomic arrangement forms a tetrahedron structure, which typically forms sets of rings. Frameworks constructed out of silicon and oxygen alone have neutral charges, but where silicon is replaced by an aluminium atom, a negative charge is created. This negative charge is neutralised by a metal cation or a hydroxyl proton.[54] A Lewis acid (electron acceptor) site is thereby created by the metal cation, while the hydroxyl proton creates a Brønsted acid (proton donor) site. [54]

Almost all of the naturally occurring zeolites have aluminium or silicon occupying all the tetrahedra. Synthetic zeolites are created through substitution of either aluminium or silicon by heteroatoms, such as boron, gallium, germanium, iron, titanium or phosphorus. The introduction of various other cations allows this class of catalysts to adopt various properties. A common exchange is made by substituting cation sites with H^+ ions, forming a number of strong acid sites within the catalyst.[54, 61] Čejka and Wichterlová[62] mention the main advantages of zeolite-based catalysts, as compared with conventional solid acid catalysts, as the following:

- Zeolites have well-defined inorganic crystalline structures that are usually based on metallosilicate and aluminophosphate matrices, with a variety of structures.

- They contain an inner void volume which is precisely defined and provides high surface areas of up to 1 200 m^2/g.
- They have the ability to adsorb and transform molecules within their structural voids.
- They have the ability to substitute silicate for trivalent cations which enables manipulation of the strength and concentration of acid sites present.
- They have a shape selectivity towards reagents, intermediates and products.
- They tolerate the catalytic environment well.

There are currently 201 known zeolite structures, a handful of which have subsequently been applied to catalytic pyrolysis of lignocellulosic biomass.[54] The main zeolites studied for this application are beta zeolite, ferrierite zeolite, mordenite zeolite, ZSM-5 zeolite and Y zeolite. The selection of different types of zeolites is based on their unique channel structures and their pore sizes. Small-pore zeolites are made up of 8-membered rings with a diameter of up to 0.43 nm. Medium-pore zeolites, for example ZSM-5, are made up of 10-membered rings with diameters of up to 0.55 nm. Large-pore zeolites, such as beta, Y and mordinite, have 12-membered rings with diameters of up to 0.75 nm. There are also extra-large-pore zeolites which can contain 14 or more membered rings.[61]

4.2 Zeolite and bentonite catalysis of *Eucalyptus grandis*

4.2.1 Experimental design, setup and method

Materials

E. grandis wood sawdust was sourced from the Sappi Ngodwana mill, and separated from wood chips using sieves with a particle rejection size of 6.0 mm and less. The sawdust was further processed using a Retsch cutting mill (model SM 100). The wood was also processed on the Retsch cutting mill using first a 2.0 mm screen, followed by a 0.25 mm screen. The processed wood was then screened using sieves to obtain a particle size distribution of between 250 and 150 µm. Moisture was measured as 8.88% using a Mettler Toledo Moisture Analyser LJ16.

Bentonite clay (sourced from the Boane region in Mozambique) was used as the first catalyst. The cationic exchange capacity of the clay was calculated to be 70 mmol/100 g. No further treatment was performed on the clay. ZSM-5 zeolite (sourced from Acros Organics) was used as the second catalyst in the experiments. The catalysts were placed onto alumina supports to assist with catalysis.

pyro-GC/MS equipment

A Shimadzu multi-functional pyrolyser EGA/PY-3030D from Frontier Labs was used to conduct the pyrolytic experiments and online analyses of products. Single-shot analysis (pyro-GC/MS setup) was used for all the experiments at a pyrolysis temperature of 500 °C (as well as 300 °C for *E. grandis* catalysed with ZSM-5 zeolite). A polydimethylsiloxane UA1 column with a 30 m-long – 2.0F (2 µm film) was used. Helium at a flow rate of 50 mℓ/min and a pressure of 98 kPa was used as the carrier gas. The first part of the reaction was performed at a reaction temperature of 550 °C and the second part at 500 °C. The samples enter the pyrolysis zone where they are heated rapidly to pyrolytic temperatures in less than 20 ms. Pyrolysis is instantaneous and the pyrolytic products are immediately sent through to a GC/MS for identification. The NIST (US National Institute of Standards and Technology) Standard Reference Database was used to identify all the products, based on their individual mass spectra using the pyro-GC/MS where possible. Unidentifiable products are not included in Section 4.2.2 *Results and discussion,* but their mass contributions are taken into account for all other analyses of the data.

4.2.2 Results and discussion

Tables 7 to 10 summarise the products identified from the pyrolysis of *E. grandis* without and with catalysis using bentonite and ZSM-5 zeolite, respectively. This set of tables reports on the relative masses for each of the compounds identified, given as a percentage of the total compounds produced during pyrolysis (including those not identifiable). Together with this, the relative atomic ratios of H/C and O/C for each of the compounds are given. The relative atomic ratios are represented on a mole basis to enable them to be used to compare the data using a van Krevelen diagram.

The most prominent compounds shown in Table 7 for pyrolysis oil derived from *E. grandis* are mostly the breakdown products of lignin, namely 2,6-dimethoxy-phenol, 1-(3,4-dimethoxyphenyl)-ethanone, 2-methoxy-4-benzene, 3-methoxy-1,2-benzenediol, eugenol, mequinol, 2,6-dimethoxy-4-(2-propenyl)-phenol, creosol and catechol. Other major products are derived from the hemicellulose (such as acetic acid, 2-hydroxy-2-cyclopenten-1-one) and cellulose fractions. Carbon dioxide is the most produced compound at 9.2%, although it is a non-condensable gas and does not contribute to the HHV of the oil. The next most prominent compound after carbon dioxide is 2,6-dimethoxy-phenol at 4.9%. The wide range and relatively low percentages of 9.2% or less for compounds identified in pyrolysis oil shows very little selectivity in the production of one compound over another.

Table 11 summarises the percentage C, percentage H and percentage O on a mass basis for each of the different pyrolysis oils produced, together with their respective total H/C and O/C ratios. The total H/C and O/C ratios were calculated cumulatively from the data presented in Tables 7 to 9. Without the use of a catalyst, the pyrolysis oil produced using the pyro-GC/MS system yields total H/C and O/C ratios of 0.94 and 0.27 respectively. This is an improvement from the O/C ratio determined for the feedstock (found to be 0.73 for *E. grandis*), but not for the H/C ratio (which was initially 1.27 for *E. grandis*). Furthermore, on a mass basis, a total of 63.6% carbon (39.1% on a mole basis), 6.9% hydrogen (50.6% on a mole basis) and 22.2% oxygen (10.3% on a mole basis) is obtained. Comparing these values with those of the feedstock used, the carbon content, on a mass basis, was increased by pyrolysis from an initial value of 48.1% (33.3% on a mole basis), with hydrogen increasing slightly from the initial 5.2% (42.4% on a mole basis). Oxygen was decreased substantially from 46.3% (24.3% on a mole basis).

Table 8 summarises the results for pyrolysis oil produced from *E. grandis* using bentonite as the catalyst, giving all the identifiable components together with their respective H/C and O/C ratios. Excluding carbon dioxide (produced at 20.5%), the most prominent compound is furfural (at 5.3%), which is derived from the degradation of the pentose sugars making up hemicellulose, with xylose being the most prominent of these.[38] Other major products are made up of the lower molecular weight compounds compared with uncatalysed pyrolysis oil, and include acetyldehyde, formaldehyde, acetic acid, methyl alcohol, acetone, methyl vinyl ketone, furan, cyclopentane, 5-methyl-2-furancarboxaldehyde and 2-propenal. Major compounds formed from lignin include 2,6-dimethyloxy-phenol, 3,5-dimethoxyacetophenone, phenol, 2-methoxy-phenol, 1,2,4-trimethylbenzene and 2-methoxy-4-vinylphenol.

The H/C and O/C ratios for pyrolysis oil catalysed with bentonite are given in Table 11 as 1.10 and 0.27 respectively, and exclude carbon dioxide in the summation. The H/C ratio is only slightly decreased from that of uncatalysed pyrolysis oil, with the O/C ratio remaining unchanged at 0.27. This is, however, still an improvement on the feedstock which has an O/C value of 0.73. An increase in CO_2 is also seen for this catalyst (at 20.5% on a mass basis) when compared with uncatalysed pyrolysis oil (at 9.2% on a mass basis).

Table 7: Compounds identified in pyrolysis oil produced from *E. grandis* via pyro-GC/MS

Identified compound	Relative mass (%)	Relative atomic ratios [a]	
		H/C	O/C
Methane	0.7	0.03	0.00
Carbon dioxide	9.2	0.00	0.18
Formaldehyde	2.7	0.05	0.03
Cyclopropane	1.6	0.04	0.00
Acetaldehyde	0.3	0.04	0.00
2-propenal	2.2	0.02	0.00
Acetone	1.8	0.04	0.01
Furan	0.6	0.01	0.00
Methacrolein	0.4	0.01	0.00
Acetic acid ethanyl ester	1.3	0.02	0.01
3-buten-2-ol	0.7	0.01	0.00
Acetic acid	3.3	0.06	0.03
(E)-2-butenal	1.0	0.01	0.00
1-hydroxy-2-propanone	1.8	0.04	0.01
Monoacetate 1,2-ethanediol	1.1	0.02	0.01
2-oxo-propanoic acid methyl ester	2.2	0.03	0.02
Furfural	3.4	0.03	0.01
1-(acetyloxy)-2-propanone	0.5	0.01	0.00
Propargyl alcohol	1.9	0.03	0.01
2-furanmethanol	1.0	0.01	0.00
2-hydroxy-2-cyclopenten-one	3.5	0.04	0.01
3-methyl-1,2-cyclopentanedione	1.6	0.02	0.01

Table 7 continued …

3-methyl-phenol	1.2	0.01	0.00
Mequinol	2.0	0.02	0.01
Catechol	1.9	0.02	0.01
Creosol	1.9	0.02	0.00
4-methyl-1,2-benzenediol	0.7	0.01	0.00
3-methoxy-1,2-benzenediol	3.1	0.04	0.01
4-ethyl-2-methoxy-phenol	0.9	0.01	0.00
2-methoxy-4-vinylphenol	3.1	0.03	0.01
2,6-dimethoxy-phenol	4.9	0.06	0.02
2-methoxy-4-(1-propenyl)-phenol	0.8	0.01	0.00
Vanillin lactoside	0.7	0.01	0.00
1,2,4-trimethoxybenzene	2.9	0.04	0.01
Eugenol	2.4	0.03	0.00
1-(3,4-dimethoxyphenyl)-ethanone	3.5	0.04	0.01
2,6-dimethoxy-4-(2-propenyl)-phenol	1.0	0.01	0.00
2,6-dimethoxy-4-(2-propenyl)-phenol	2.0	0.03	0.01

[a] Atomic ratios are calculated relative to the quantities of compounds identified

Table 8: Compounds identified in pyrolysis oil produced from *E. grandis* catalysed with bentonite via pyro-GC/MS

Identified compound	Relative mass (%)	Relative atomic ratios [a]	
		H/C	O/C
Carbon dioxide	20.5	0.00	0.41
Formaldehyde	3.7	0.07	0.04
Cyclopropane	2.1	0.04	0.00
Cyclopropene	0.2	0.00	0.00
Acetaldehyde	4.4	0.09	0.00
Methyl alcohol	2.9	0.12	0.03
1-propene, 2-methyl-	0.5	0.01	0.00
1-methylcyclopropene	0.4	0.01	0.00
2-propenal	2.0	0.03	0.01
Acetone	2.7	0.05	0.01
Furan	2.3	0.02	0.00
1,3-pentadiene	0.2	0.00	0.00
Acetic acid, methyl ester	1.5	0.03	0.01
1,3-cyclopentadiene	0.5	0.01	0.00
Methacrolein	0.8	0.01	0.00
Methyl vinyl ketone	2.7	0.04	0.01
Butanal	0.2	0.00	0.00
2-butanone	0.8	0.02	0.00
Acetic acid	3.1	0.06	0.03
Furan, 2-methyl-	0.3	0.01	0.00
2-butenal, (E)-	0.9	0.01	0.00
2-propanone, 1-hydroxy-	0.9	0.02	0.01

Table 8 continued …

1-cyclobutylcyclobutene	0.2	0.00	0.00
Benzene	0.2	0.00	0.00
Furan, 2,5-dimethyl-	0.3	0.00	0.00
Benzene, [(3-methyl-2-butenyl)oxy]-	0.7	0.01	0.00
3-butenoic acid	0.4	0.01	0.00
Toluene	0.6	0.01	0.00
Crotonic acid	0.2	0.00	0.00
3-furaldehyde	0.4	0.00	0.00
Furfural	5.3	0.04	0.02
2-propanone, 1-(acetyloxy)-	0.3	0.00	0.00
4-cyclopentene-1,3-dione	0.3	0.00	0.00
2(3H)-furanone, 5-methyl-	0.3	0.00	0.00
4-cyclopentene-1,3-dione	0.7	0.01	0.00
2-propenoic acid, 2-propynyl ester	0.4	0.00	0.00
2(5H)-furanone	1.4	0.01	0.01
2,4-dimethylfuran	1.0	0.01	0.00
2-cyclopenten-1-one, 2-hydroxy-	1.6	0.02	0.01
2-furancarboxaldehyde, 5-methyl-	2.1	0.02	0.01
Phenol	1.9	0.02	0.00
1,2-cyclopentanedione, 3-methyl-	0.8	0.01	0.00
Phenol, 3-methyl-	0.8	0.01	0.00
1,4-benzenediol, 2-methyl-	0.4	0.00	0.00
p-cresol	1.1	0.01	0.00
Phenol, 2-methoxy-	1.6	0.02	0.00
Phenol, 2,5-dimethyl-	0.5	0.01	0.00
Catechol	0.4	0.00	0.00
Creosol	1.5	0.02	0.00

Table 8 continued …

3,5-dimethoxytoluene	0.2	0.00	0.00
Phenol, 4-ethyl-2-methoxy-	0.6	0.01	0.00
2-methoxy-4-vinylphenol	1.5	0.02	0.00
Phenol, 2,6-dimethoxy-	2.5	0.03	0.01
Phenol, 2-methoxy-6-(2-propenyl)-	0.5	0.01	0.00
Vanillin	0.4	0.00	0.00
Phenol, 2-methoxy-5-(1-propenyl)-, (E)-	0.3	0.00	0.00
1,2,4-trimethoxybenzene	1.5	0.02	0.01
Phenol, 2-methoxy-4-(1-propenyl)-	1.3	0.02	0.00
5-tert-butylpyrogallol	0.5	0.01	0.00
3',5'-dimethoxyacetophenone	2.0	0.02	0.01
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	1.1	0.01	0.00
Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	0.5	0.01	0.00
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	1.3	0.02	0.00
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	0.2	0.00	0.00

[a] Atomic ratios are calculated relative to the quantities of compounds identified

The initial *in situ* catalysis of *E. grandis* using ZSM-5 zeolite as a catalyst for pyrolysis at 500 °C did not result in significant improvements to the H/C and O/C ratios compared with the bentonite-catalysed and uncatalysed pyrolysis oil. The pyrolytic products produced at these conditions, together with their respective H/C and O/C ratios, are summarised in Table 9. The mass percentage for the elemental composition of this pyrolysis oil was determined as 66.0% (38.9% on a mole basis) for carbon, 7.0% (49.2% on a mole basis) for hydrogen and 27.0% (11.9% on a mole basis) for oxygen. Both the carbon and hydrogen contents decreased compared with pyrolysis oil catalysed with bentonite, but were still slightly higher for uncatalysed pyrolysis oil. This reflects in the H/C ratio being slightly lower than for bentonite-catalysed pyrolysis oil, at 1.08, with the O/C ratio remaining the same at 0.27. Lastly, the CO_2 concentration was not found to be significantly higher (at 8.9%) when compared with that of uncatalysed pyrolysis oil (at 9.2%), further suggesting that ZSM-5 zeolite catalysis at 500 °C is considerably beneficial. It was therefore decided to use a different temperature to see if there would be an improvement in the carbon and hydrogen yields for ZSM-5 zeolite-catalysed pyrolysis oil. The major products for ZSM-5 zeolite-catalysed pyrolysis oil differed from those of bentonite-catalysed pyrolysis oil, with the most prominent compounds of the former being made up of degradation products of lignin, namely 2,5-dimethoxyacetophenone as the foremost compound at 5.8%.

Table 10 summarises results for the *in situ* catalysis of *E. grandis* using ZSM-5 zeolite as a catalyst for pyrolysis at 300 °C, relating to a reduction of 40% in temperature. A positive result is achieved whereby the O/C ratio is significantly reduced to 0.22 from the initial 0.73 for *E. grandis* wood, and slightly improved from the 0.27 seen in the previously discussed pyrolysis oils. This is accompanied by a significant increase in CO_2 from 9.2% for uncatalysed pyrolysis oil to 23.9%.

Table 9: Compounds identified in pyrolysis oil produced from *E. grandis* catalysed with ZSM-5 zeolite via pyro-GC/MS (at 500 °C)

Identified compound	**Relative mass (%)**	**Relative atomic ratios** [a]	
		H/C	**O/C**
Carbon dioxide	8.9	0.00	0.18
Formaldehyde	1.4	0.03	0.01
Cyclopropane	1.2	0.02	0.00
Acetaldehyde	1.9	0.04	0.00
Methyl alcohol	0.9	0.03	0.01
2-propenal	1.3	0.02	0.00
Acetone	1.5	0.03	0.00
Furan	4.1	0.04	0.00
Acetic acid, methyl ester	1.4	0.03	0.01
1,3-cyclopentadiene	0.4	0.00	0.00
Methacrolein	0.3	0.00	0.00
Methyl vinyl ketone	2.3	0.03	0.01
2-butanone	0.4	0.01	0.00
Furan, 2-methyl-	2.5	0.05	0.02
Acetic acid	1.3	0.03	0.01
2-butenal, (E)-	0.8	0.01	0.00
2-propanone, 1-hydroxy-	2.5	0.05	0.02
Benzene	0.3	0.00	0.00
Ethyl-1-propenyl ether	0.4	0.01	0.00
Furan, 2,5-dimethyl-	0.3	0.00	0.00
2-vinylfuran	0.8	0.01	0.00

Table 9 continued …

3-cyclopentene-1-acetaldehyde, 2-oxo-	2.4	0.03	0.01
2-cyclopenten-1-one, 2-methyl-	0.3	0.00	0.00
2-propanone, 1-(acetyloxy)-	0.5	0.01	0.00
4-cyclopentene-1,3-dione	1.6	0.01	0.01
Phenol	1.9	0.02	0.00
Butanoic acid, 4-hydroxy-2-methylene-	0.4	0.01	0.00
1,2-cyclopentanedione	2.3	0.03	0.01
1,2-cyclopentanedione, 3-methyl-	1.0	0.01	0.00
Phenol, 3-methyl-	0.3	0.00	0.00
p-cresol	0.4	0.00	0.00
Phenol, 2-methoxy-	1.6	0.02	0.00
Phenol, 2,3-dimethyl-	0.3	0.00	0.00
Catechol	1.4	0.01	0.00
Creosol	1.3	0.02	0.00
1,2-benzenediol, 3-methyl-	0.4	0.01	0.00
1,2-benzenediol, 3-methoxy-	1.4	0.02	0.01
Phenol, 4-ethyl-2-methoxy-	0.6	0.01	0.00
2-methoxy-4-vinylphenol	2.4	0.03	0.01
Phenol, 2,6-dimethoxy-	4.8	0.06	0.02
Eugenol	0.7	0.01	0.00
Formic acid, 2,6-dimethoxyphenyl ester	0.7	0.01	0.00
Vanillin	0.7	0.01	0.00
Phenol, 2-methoxy-4-(1-propenyl)-	0.4	0.01	0.00
1,2,4-trimethoxybenzene	3.6	0.05	0.01
3-allyl-6-methoxyphenol	2.5	0.03	0.00
Apocynin	0.6	0.01	0.00
5-tert-butylpyrogallol	1.1	0.01	0.00

Table 9 continued …

2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.4	0.00	0.00
3',5'-dimethoxyacetophenone	5.8	0.07	0.02
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	8.2	0.10	0.02
Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	2.2	0.02	0.01
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	0.8	0.01	0.00
Desaspidinol	0.7	0.01	0.00

[a] Atomic ratios are calculated relative to the quantities of compounds identified

Table 10: Compounds identified in pyrolysis oil produced from *E. grandis* catalysed with ZSM-5 zeolite via pyro-GC/MS (at 300 °C)

Identified compound	Relative mass (%)	Relative atomic ratios [a]	
		H/C	O/C
Carbon dioxide	23.9	0.00	0.48
1,3-dioxolane-4,5-dione	0.7	0.00	0.01
Cyclopropane	2.5	0.05	0.00
Acetaldehyde	5.6	0.11	0.03
Methyl alcohol	2.1	0.08	0.02
2-propenal	0.4	0.01	0.00
Propenal	0.5	0.01	0.00
Acetone	2.6	0.05	0.01
Acetic acid, methyl ester	1.0	0.20	0.07
Methacrolein	0.3	0.00	0.00
2,3-butanedione	1.6	0.02	0.01
Methyl vinyl ketone	0.3	0.00	0.00
Methyl propionate	0.2	0.00	0.00
Benzene	1.0	0.01	0.00
Acetic acid	6.0	0.12	0.06
Toluene	2.5	0.03	0.00
2-cyclopenten-1-one	1.0	0.01	0.00
Ethylbenzene	0.6	0.01	0.00
p-xylene	1.2	0.02	0.00
1,3,-cyclopentadiene, 5-(1-methylethylidene)-	0.4	0.01	0.00
2-cyclopenten-1-one, 2-methyl-	0.5	0.01	0.00

Table 10 continued …

Phenol	1.1	0.01	0.00
1,2-diphenyl-3-buten-1-ol	2.4	0.02	0.00
Benzene, 1-ethynyl-4-methyl-	1.9	0.02	0.00
Phenol, 3-methyl-	0.7	0.01	0.00
Benzene, 4-ethenyl-1,2-dimethyl-	2.7	0.03	0.00
Benzofuran, 2-methyl-	1.7	0.02	0.01
1,3,8-p-menthatriene	0.4	0.00	0.00
Phenol, 2,4-dimethyl-	0.9	0.01	0.00
Benzene, 1-methyl-4-(1-propynyl)-	4.6	0.05	0.00
2,2-dimethylindene, 2,3-dihydro-	1.1	0.01	0.00
Benzofuran, 4,7-dimethyl	1.2	0.01	0.00
1H-indene, 2,3-dimethyl-	2.5	0.03	0.00
1H-inden-1-one, 2,3-dihydro-	1.0	0.01	0.00
1H-indene, 1-ethylidene	1.7	0.02	0.00
1,2,3-trimethylindene	0.5	0.01	0.00
Naphthalene, 1,4-dimethyl-	1.5	0.02	0.00
Naphthalene, 2-(1-methylethyl)-	0.6	0.01	0.00
Naphthalene, 2,3,6-trimethyl-	0.3	0.00	0.00

[a] Atomic ratios are calculated relative to the quantities of compounds identified

This result is similar to that of bentonite and suggests that both these catalysts are able to reduce oxygen significantly via CO_2 production. The H/C ratio is still lower than that for the feedstock however. The number of compounds produced in ZSM-5 zeolite-catalysed pyrolysis oil is reduced compared with the total number of compounds identified in the other pyrolysis oils, which was first apparent when the initial chromatographs were obtained (for the graphs of the chromatographs, refer to the Appendix). This suggests a better selectivity towards certain types of compounds, with prominent lignin-derived ones such as 1-methyl-4-(1-propynyl)-benzene, 4-ethenyl-1,2-dimethyl-benzene, toluene, 2,3-dimethyl-1H-indene, 1,2-diphenyl-3-buten-ol, 1-ethylnyl-4-methyl-benzene, 1-ethylidene-1H-indene, 2-methyl-benzofuran, and several naphthalene-based compounds not produced in other characterised pyrolysis oils.

According to the summary given in Table 11, the best-performing catalyst based on increases in the percentage carbon and percentage hydrogen, and also decreases in the percentage oxygen, was found to be ZSM-5 zeolite at a temperature of 300 °C. Carbon content for this catalysis was increased from 48.3 to 76.3% (on a mass basis) and, similarly, hydrogen content increased from 5.9 to 8.0% on a mass basis. Oxygen content decreased from 45.13 to 15.7% (on a mass basis), reflecting a total reduction of 65.2%. These results are based only on the identifiable compounds that are present in each pyrolysis oil, as only 77, 93, 88 and 90% of the compounds could be identified, respectively. All pyrolysis oils, however, had improved carbon, hydrogen and oxygen compositions compared with *E. grandis* wood.

Table 11: Summary of H/C and O/C ratios for pyrolysis oils produced via pyro-GC/MS

Sample	Identifiable mass (%)	C (%) [a]	H (%) [a]	O (%) [a]	Atomic ratios H/C	Atomic ratios O/C
E. grandis	77	63.6	6.9	22.2	0.94	0.27
E. grandis + bentonite	93	66.6	7.3	26.1	1.10	0.27
E. grandis + zeolite (500 °C)	88	66.0	7.0	27.0	1.08	0.27
E. grandis + zeolite (300 °C)	90	76.3	8.0	15.7	1.03	0.22
E. grandis wood [b]	–	48.1	5.2	46.3	1.27	0.73

[a] Values are represented as a mass%

[b] Based on an average of the results given by Joubert, Carrier, Stahl *et al*.[63]; Akinrinola Darvell, Jones *et al.* [64]; and Antal, Allen, Dai *et al.* [65]

Equation 1, borrowed from Channiwala and Parikh, [66] was used to estimate the calorific values for all pyrolysis oils produced, as well as for *E. grandis* wood, based on their respective carbon, hydrogen and oxygen contents; these calorific values are summarised in Table 12. Equation 1 is given on a mass basis, in units of MJ/kg, as:[66]

$$HHV = 0.3506 \text{ x } n_C + 1.1453 \text{ x } n_H + 0.1005 \text{ x } n_S - 0.1034 \text{ x } n_O - 0.0151 \text{ x } n_N - 0.0211 \text{ x } n_a \quad (1)$$

where n_C, n_H, n_S, n_O, n_N and n_a are the mass % compositions for carbon, hydrogen, sulphur, oxygen, nitrogen and ash, respectively. Only carbon, hydrogen and oxygen content are taken into account here as none of the other components was measured in the oils. Using Equation 1, it was found that all pyrolysis oils increased in HHV when compared with the feedstock. Neat pyrolysis oil achieved an HHV of 28.26 MJ/kg, in comparison with *E. grandis* with an HHV of 18.08 MJ/kg (calculated based on the composition presented in Table 11). Both pyrolysis oils catalysed at 500 °C by either bentonite or ZSM-5 zeolite achieved further improved HHVs of 29.43 MJ/kg and 28.80 MJ/kg, respectively. The highest HHV was achieved for *E. grandis* catalysed at 300 °C using ZSM-5 zeolite with an HHV of 34.54 MJ/kg.

Table 12: Prediction of calorific values of materials/products

Sample description	Calorific values (MJ/kg)
E. grandis	18.08 [a]
Neat pyrolysis oil	28.26
E. grandis with bentonite	29.43
E. grandis with ZSM-5 zeolite (at 500 °C)	28.80
E. grandis with ZSM-5 zeolite (at 300 °C)	34.54

4.3 Conclusions

The highest heating value (based on the higher heating values [HHVs]) obtained was for pyrolysis oil catalysed using ZSM-5 zeolite at a reduced temperature of 300 °C. This suggests that pyrolysis could be performed at a much lower temperature than the conventional 500 °C if ZSM-5 zeolite is used as an *in situ* catalyst. The carbon, hydrogen and oxygen mass yields were improved from 48.3 to 76.3% for carbon, from 5.2 to 8.0% for hydrogen and from 46.3 to 15.7% for oxygen. The total reduction of oxygen and the increase in hydrogen led to an improved HHV of 34.4 MJ/kg for pyrolysis oil catalysed with ZSM-5 zeolite. This is in considerable contrast to the HHV for the feedstock at 18.08 MJ/kg, and is a significant improvement from other pyrolysis oils produced using no catalyst, or using either bentonite or ZSM-5 zeolite at 500 °C, which obtained HHVs of 28.26, 29.43 and 28.80 MJ/kg respectively. A further reduction in the number of compounds was seen for pyrolysis oil catalysed with ZSM-5 zeolite at 300 °C, suggesting that a better selectivity towards certain compounds may thereby be achieved. There was also a significant increase in CO_2 measured for catalysis using bentonite at 500 °C and ZSM-5 zeolite at 300 °C compared with the uncatalysed pyrolysis oil, suggesting that oxygen removal via CO_2 production is enhanced.

CHAPTER 5: PRODUCING PYROLYSIS OIL USING MICROWAVE-ASSISTED PYROLYSIS

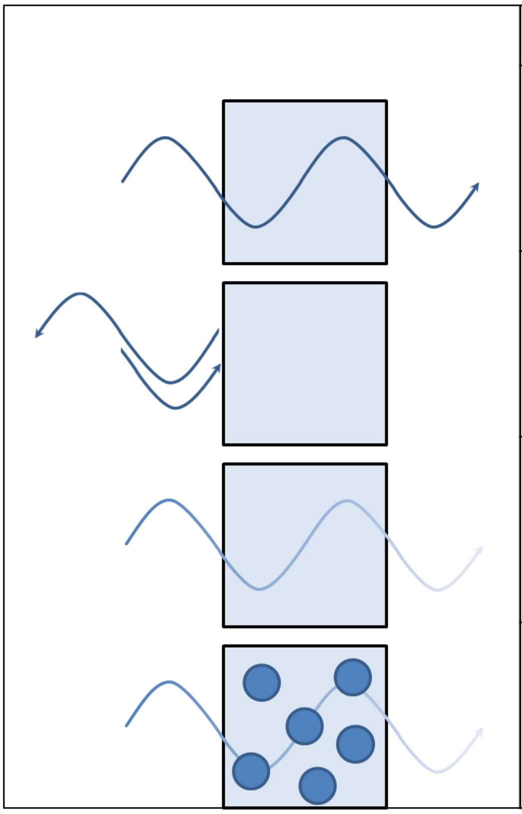
5.1 Principles and advantages of microwave pyrolysis

Numerous studies have been done to evaluate using microwave heating for pyrolysis instead of conventional heating as it has many advantages. These advantages include selective heating (which takes advantage of the different dielectric constants of materials), rapid and controlled heating (due to the permeation of energy into the material matrix), and energy efficiency.[67, 68] Microwave heating also provides products with unique properties which are not observed in conventional processes, and provides a means of synthesising new materials.[68, 69]

Materials may be classified qualitatively in terms of how they interact during microwave irradiation. There are three categories of materials, namely (i) materials transparent to microwaves, (ii) materials opaque to microwaves, and (iii) microwave-absorbing materials. Materials that are transparent to microwaves do not readily absorb energy from microwaves due to the microwaves passing through them with insignificant attenuation, whereas opaque materials do not allow microwaves to pass through at all and rather reflect them. Absorbing materials, on the other hand, are able to absorb microwaves to some degree, depending on their individual characteristic dielectric loss factor. Transparent materials have low dielectric loss factors compared with opaque materials, which have high loss factors. Microwaves transfer energy most effectively for materials that have dielectric factors in the middle of the conductivity range.[70] These principles are summarised in Figure 4.

The dielectric properties of a material determine the type of electromagnetic interaction microwaves will cause in a material. On a molecular level, these interactions result in the excitation of molecular dipoles present in the material being irradiated, relating to vibrational and rotational motions of the molecules (i.e. rotation of the dipoles).[70] The energy captured through this mechanism is dissipated as heat due to the internal resistance to the rotation.[70] With this in mind, it is possible to heat otherwise transparent materials through doping them with microwave-absorbing materials. Such mixtures of materials therefore undergo selective heating when irradiated.[68, 69]

Both carbon and water are known to be very good absorbers of microwaves, and are commonly used as dopants to assist pyrolysis of materials such as wood. [67, 71] Robinson, Kingman, Barranco *et al.*[67] cited previous studies in which pyrolysis was not achievable unless activated carbon or char was introduced as a microwave-absorbing dopant. In contrast to this, work done by Miura, Kaga, Sakurai *et al.*[72] achieved pyrolysis oil production without the use of dopants, suggesting that wood



Type of material	Penetration
Transparent material: little to no absorption	Full penetration
Opaque material: little to no absorption	No penetration
Absorbing material: Absorbs microwaves	Partial to full penetration
Matrix with dopant: Transparent matrix contains microwave-absorbing particles	Partial to full penetration

Figure 4: Classification of materials based on microwave absorptivity[69]

has sufficient intrinsic microwave-absorbing properties necessary for microwave-induced pyrolysis.

Although wood inherently contains enough water to initiate pyrolysis, once this water is lost (or not produced via pyrolysis reactions in sufficient quantities), wood becomes more transparent to microwave radiation.[67] However, Robinson *et al.*[67] demonstrated that microwave pyrolysis is achievable without the use of microwave-absorbing dopants such as carbon, which would otherwise be necessary for microwave-transparent materials. They concluded that steam trapped within the wood may be superheated in order to create temperatures high enough for pyrolysis to occur. Furthermore, it was shown that at temperatures of up to 600 °C the only microwave-absorbing phase is water, negating the need for carbon additives.

Conditions comparable to microwave pyrolysis are created when using the process of hydrothermal liquefaction, whereby water is superheated so that is may easily decompose biomass into biofuel.[68] Liquefaction has also been called "hydrothermal upgrading", since it is able to produce fuels of a better quality than those produced through conventional pyrolysis techniques.[69] Heating values of between 35 and 39 MJ/kg are created with very low oxygen content. Another advantage of both hydrothermal liquefaction and microwave pyrolysis is that they are able to accept wet biomass, as they use water as the main heating medium for decomposing biomass into biofuels. This avoids the step of first drying the biomass, as is generally required by conventional fast pyrolysis. The disadvantage of hydrothermal liquefaction is that it is capital-intensive and therefore much more expensive to implement. Microwave pyrolysis avoids this as it can operate at ambient pressures while still subjecting the biomass to superheated steam at pyrolytic temperatures.[67, 68, 69]

5.2 Microwave-assisted vacuum pyrolysis of *E. grandis*

5.2.1 Experimental design, setup and method

Materials

E. grandis wood chips were obtained from the Sappi Technology Centre, South Africa. The chips were ground up using a hammer mill, and then were further processed twice using a Retsch cutting mill (model SM 100), first using a 2.0 mm screen and then using a 0.25 mm screen. The product was screened using sieves, and a particle size distribution of between 250 and 150 μm was obtained. The moisture was measured at 39.2% using a Mettler Toledo Moisture Analyser LJ16 as the feedstock was kept moist in order for the feedstock to absorb sufficient energy from the microwave radiation.

Equipment and method

A RotoSYNTH microwave and extraction system supplied by Milestone Inc. was used to conduct the microwave-assisted vacuum pyrolysis experiments. The system is connected to two condensing units, operated at low and high pressures respectively relative to atmospheric pressure. These units aid in the collection of pyrolysis oil fractions immediately from the microwave reactor vessel. A computer interface system is used to set up and control certain parameters using different consecutive profiles, such as for microwave power, reaction temperature and pressure, as well as reaction times, etc.

Roughly 100 g of dry wood was charged to the Pyrex® reactor vessel and fitted into the microwave cavity. Reaction times were monitored in relation to the production of pyrolysis products. A power rating of 1.2 kW was used for all experiments. Runs were completed in triplicate and mass balances for the feedstock and products were measured (except for non-condensable gases and losses in products). The reaction pressure was maintained between 250 and 350 mbar, and nitrogen gas, adjusted to flow continuously throughout each experiment, was used as the inert atmosphere and also as a carrier gas to transport the volatile pyrolysis products to the condensing units. Cooling water, kept at below 10 °C, was used to condense the pyrolysis products before the non-condensable gases were fed off out of the system.

After each of the pyrolysis oils had been characterised using a GC/MS, all pyrolysis oil samples were pooled together and distilled at various levels, and their respective calorific values were measured using a LECO AC-350-Automatic Bomb Calorimeter. The method used is based on the standard ISO 1928:2009.[1] An initial determination was carried out in duplicate by combusting material of between 0.50 and 1.00 g in a bomb calorimeter. Each sample was then placed into the reaction chamber which is kept under a pressure of 30 bar in a bomb capsule. The capsule is then surrounded by 2 ℓ of water and thereafter the sample is ignited. The heat liberated into the surrounding water is used to calculate the HHV of the reaction. Benzonoic acid tablets were used as the calibration standard for this analysis.

The pyrolysis oils were characterised using a Clarus 680 GC-MS from Perkin Elmer, fitted with a 30 m-long, 0.25 mm inner diameter Elite-5ms column. Helium was used as the carrier gas with a flow rate of 1 mℓ/min. The injector temperature was 150 °C with an initial oven temperature of 35 °C. A heating rate of 15 °C per minute was used with a final oven temperature of 180 °C. Peak characterisation was completed based on forward and reverse comparisons with existing MS spectra from the NIST Database,[59] with the MS spectra for each compound being identified on the GC chromatographs.

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[1] ISO1928:2009.*Solid mineral fuels – Determination of gross calorific value by the bomb calorimetric method and calculation of net calorific value.*

5.2.2 Results and discussion

Figure 5 shows the distribution of feedstock and products produced using the RotoSYNTH microwave system, with *E. grandis* as the raw material. The values for the *E. grandis* wood are given on a wet basis, and were measured to be between 164.53 and 164.65 g ± 0.06 g. The mass balances for all components are within an acceptable range and should give good repeatability. Similar masses of pyrolysis oil and biochar were obtained. A total of 72.08, 69.33 and 28.55 g of pyrolysis oil were obtained respectively for the three feeds and the biochar yields were 63.15, 68.44 and 28.55 g respectively. The gases and losses were calculated as the difference between all other products and the initial feedstock, and values of 29.30, 26.81 and 28.55 g were obtained. The pyrolysis oil was notably different in colour from conventional pyrolysis oil, being somewhat red to brown, and with a smell similar to that of prehydrolysate liquor.

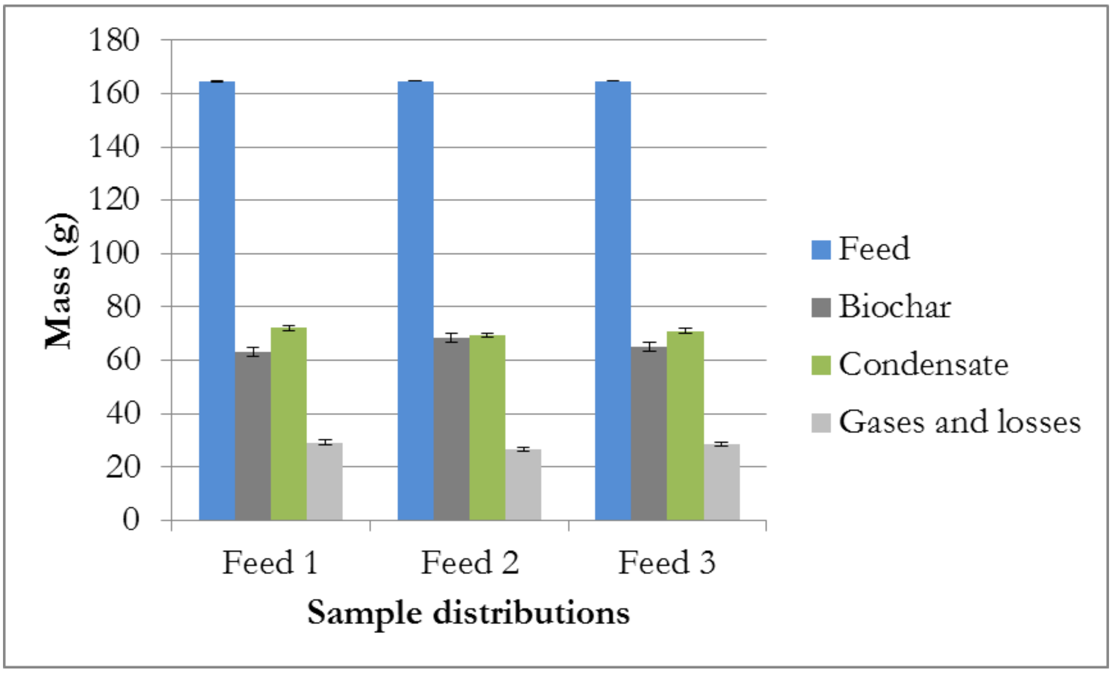

Figure 5: Distributions of feedstock and products for microwave-assisted vacuum pyrolysis

Table 13 summarises all the compounds identified in the pyrolysis oils (subsequently calculated as one set of data) produced using the RotoSYNTH microwave system. The major components are derived from lignin (2,6-dimethoxy-4-(2-propenyl)-phenol at 9.0%, 2,6-dimethoxy-phenol at 7.1% and 1,2,4-trimethoxybenzene at 5.6%) and hemicellulose (furfural at 6.4%, acetic acid at 4.5%, 1,2-cyclopentanedione at 4.2% and 5-(hydroxymethyl)-2-furaldehyde at 2.4%). The alcohols ethanol and methanol are also present in relatively significant quantities at 5.0 and 3.1% respectively, compared with pyrolysis oils produced in the pyro-GC/MS system. The distribution of pyrolytic products is once again broad, which demonstrates poor selectivity for certain compounds over others. This result is similar to what was found for uncatalysed pyrolysis oil generated using the pyro-GC/MS equipment.

Table 13: Compounds identified in pyrolysis oil produced from *E. grandis* via microwave-assisted pyrolysis

Identified compound	**Relative mass (%)** [a]	**Relative atomic ratios** [b]	
		H/C	**O/C**
2,6-dimethoxy-4-(2-propenyl)-phenol	9.0	0.11	0.02
2,6-dimethoxy-phenol	7.1	0.09	0.03
Furfural	6.4	0.05	0.03
Formic acid	5.6	0.11	0.11
1,2,4-trimethoxybenzene	5.6	0.07	0.02
Ethanol	5.0	0.15	0.02
Acetic acid	4.5	0.09	0.04
1,2-cyclopentanedione	4.2	0.05	0.02
Acetol	3.7	0.07	0.02
2(5H)-furanone	3.5	0.03	0.02
Methyl alcohol	3.1	0.12	0.03
2-cyclopenten-1-one, 2-hydroxy-3-methyl-	3.0	0.04	0.01
Ethyl citrate	2.9	0.05	0.02
Benzene, 1,2,3-trimethoxy-5-methyl-	2.7	0.04	0.01
Phenol, 2-methoxy-4-(1-propenyl)-(Z)	2.6	0.03	0.01
1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	2.6	0.02	0.01
3,5-dimethoxyacetophenone	2.5	0.03	0.01
5-(hydroxymethyl)-2-furaldehyde	2.4	0.02	0.01
Phenol, 2-methoxy-	2.4	0.03	0.01
Phenol, 2-methoxy-4-methyl-	2.3	0.03	0.01

Table 13 continued …

1,2-benzenediol, 3-methoxy-	1.5	0.02	0.01
Phenol, 2-methoxy-4-(1-propenyl)-(E)	1.2	0.01	0.00
3,5-dimethoxy-4-hydroxycinnamaldehyde	1.2	0.01	0.00
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	1.1	0.01	0.00
Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	1.0	0.01	0.00
2-methoxy-4-vinylphenol	1.0	0.01	0.00
Propanoic acid, anhydride	0.9	0.02	0.00
1,4:3,6-dianhydro-α-d-glucopyranose	0.9	0.01	0.01
Methyl formate	0.9	0.02	0.01
Phenol, 4-ethyl-2-methoxy-	0.8	0.01	0.00
Phenol, 2-methoxy-4-propyl-	0.8	0.01	0.00
2-propanone, 1-(acetyloxy)-	0.7	0.01	0.00
Acetic acid, methyl ester	0.6	0.01	0.00
b-sitosterol	0.6	0.01	0.00
2-cyclopenten-1-one, 2-hydroxy-	0.6	0.01	0.00
2-propenal, 3-(4-hydroxy-3-methoxyphenyl)-	0.6	0.01	0.00
Formaldehyde	0.5	0.01	0.01
1,2-cylcopentanedione, 3-methyl-	0.5	0.01	0.00
Propanoic acid, 2-oxo-,methyl ester	0.5	0.01	0.00
Acetaldehyde, hydroxy-	0.4	0.01	0.00
1-hydroxy-2-butanone	0.4	0.01	0.00
2-propanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.4	0.00	0.00
2,3-dihydroxybenzaldehyde	0.4	0.00	0.00
Maltol	0.3	0.00	0.00
Cholest-4-en-3-one	0.3	0.00	0.00
1,2-benzenediol	0.3	0.00	0.00
Furyl hydroxymethyl ketone	0.2	0.00	0.00
2-cyclopenten-1-one, 2,3-dimethyl-	0.1	0.00	0.00
Carbon dioxide	0.2	0.00	0.00
4-methyl-5H-furan-2-one	0.1	0.00	0.00
Furan, tetrahydro-2,5dimethoxy-	0.1	0.00	0.00
2-cyclopentene-1,4-dione	0.1	0.00	0.00
Acetaldehyde, methoxy-	0.1	0.00	0.00

[a] Based on the averages of three pyrolysis oil samples produced under the same conditions

[b] Atomic ratios are calculated based on relative mass% of compounds

The elemental composition for all the pyrolysis oils produced with regard to carbon, hydrogen and oxygen are presented in Table 14, together with their respective H/C and O/C atomic ratios. Between 85 and 91% of compounds present according to GC characterisation were identifiable, using their MS spectra and the NIST Database as a reference tool.[59] Carbon content was slightly lower on a mass basis, between 62.5 and 63.4%, compared with the results obtained for pyro-GC/MS pyrolysis oils with hydrogen content also slightly lower, at 6.7 and 6.8%. The oxygen content was higher than that for pyro-GC/MS pyrolysis oils. Nonetheless, these compositions for microwave-assisted vacuum pyrolysis oils are still improvements on the overall composition of *E. grandis*, and this is further seen in the H/C and O/C ratios obtained for these oils.

Table 14: Summary of H/C and O/C ratios for pyrolysis oils produced via microwave-assisted vacuum pyrolysis

Sample	Identifiable mass (%)	C (%) [a]	H (%) [a]	O (%) [a]	Atomic ratios	
					H/C	O/C
E. grandis pyrolysis oil #1	85	63.0	6.7	30.1	1.42	0.54
E. grandis pyrolysis oil #2	91	62.5	6.8	30.7	1.51	0.53
E. grandis pyrolysis oil #3	88	63.4	6.8	30.2	1.48	0.53
E. grandis wood [b]	–	48.1	5.2	46.3	1.27	0.73

[a] Values are represented as a mass%

[b] Based on an average of the results given by Joubert *et al*.[63], Akinrinola *et al.*[64] and Antal *et al.*[65]

The atomic ratios presented in Table 14 were used to plot data points for microwave-based pyrolysis oils in Figure 6, which shows a shift towards the vertical axis but is not as dramatic as for pyro-GC/MS type pyrolysis oils. There is, however, a slight shift away from the horizontal axis due to the increases in H/C ratios for microwave-based pyrolysis oils.

It was first noticed during the initial runs that some pyrolysis oils did not report to the condensing units, but instead found their way into exhaust tubing connected to the microwave apparatus. The oils were somewhat higher in viscosity than the pyrolysis oils collected in the condensing units. It was decided to try to distil the condensed pyrolysis oils to see whether a product similar to that found in the exhaust tubing could be obtained. Since the character of the pyrolysis oils generated is similar to that of prehydrolysate liquor, which may be distilled without issue,[73, 74, 75] there was further motivation to try distillation on microwave-assisted vacuum pyrolysis oils.

Figure 6: Van Krevelen diagram showing data points for pyrolysis oils produced, together with various types of fuels

Three concentrations of pyrolysis oil were produced at random and compared with the feed via heating values. The initial HHV for neat pyrolysis oil was measured at 13.80 MJ/kg, with a standard deviation of 1.02%. The calorific value of the bottoms product after the first distillation was measured at 14.85 MJ/kg, with a standard deviation of 1.43%. The HHV of the second bottoms product was found to increase to 21.00 MJ/kg, with a standard deviation of 1.35%, and a notable increase in viscosity was seen. The final bottoms product had an HHV of 23.30 MJ/kg, and was found to be very viscous when cooled compared with the initial feed used. The predicted HHV for this pyrolysis oil was calculated at 26.70 MJ/kg using Equation 1. The HHV of the combined condensate produced from distillation was also measured, and found to be at 4.40 MJ/kg with a standard deviation of 3.21%. Biochar was also tested for its HHV and was found to be 27.35 MJ/kg, with a standard deviation of 3.21%. These heating values (summarised in Table 15), including the predicted HHV for microwave-assisted pyrolysis oil, were found to be lower than those for pyrolysis oils produced via the pyro-GC/MS equipment, although the microwave-assisted pyrolysis oils presented more stable characteristics than what was expected for pyrolysis oil. This suggests that the method of pyrolysis in terms of the heating mechanism, the frequency of electromagnetic radiation (i.e. being based primarily on CO_2/H_2O for conventional fast pyrolysis, as opposed to being primarily microwave-based in this instance), and the intensity of degradation applied to the wood matrix determine the chemical reactivity and stability of the pyrolysis oil. This would be one reason why further distillation of pyrolysis oils generated using microwave pyrolysis has been possible compared with pyrolysis oils produced in fast pyrolysis systems using other heating mechanisms, such as heated sand or ablative technologies.

Table 15: Summary of calorific values for various pyrolysis products

Sample description	Calorific values (MJ/kg)	Standard dev. (%)
Raw pyrolysis oil	13.80	1.02
1st bottoms product of pyrolysis oil	14.85	1.43
2nd bottoms product of pyrolysis oil	21.00	1.35
3rd bottoms product of pyrolysis oil	23.30	0.00
Predicted value for pyrolysis oil [a]	26.70	–
Combined distillate product	4.40	3.21
Biochar product	27.35	0.78

[a] Calculated using Equation 1

5.2.3 Conclusions

Microwave-assisted pyrolysis produces pyrolysis oil which is able to be distilled further, which suggests good stability. The stability of the oils may be attributed to microwave-based pyrolysis being similar to liquefaction. Since water present in the wood matrix may be superheated by microwave radiation on a cellular level, its action of decomposing wood mimics the formation of biocrude produced through hydrothermal liquefaction. Distillation of the oils was accompanied by an increase in the HHV from 13.80 to 23.3 MJ/kg, although the theoretical HHV was calculated to be as high as 26.70 MJ/kg. Nonetheless, it is a significant result to be able to distil pyrolysis oil without severe chemical degradation due to instability in the oil, and this should be investigated further. The biochar gave a high heating value of 27.35 MJ/kg, and good yields of between 38.4 and 41.6% due to the slower pyrolysis obtained in comparison with fast pyrolysis. The pyrolysis oil yields were similar to those of the biochar, namely between 42.1 and 43.8%. Gas and losses were calculated to be between 16.3 and 17.8%, with good repeatability being achieved based on the mass balances performed over the system. Improved H/C ratios were observed, with only slightly better O/C ratios. In view of this, comparison of the heating values of microwave-based pyrolysis oils with those produced using the pyro-GC/MS method shows that the O/C ratio has a stronger effect on the heating value than changes in the H/C ratio. Catalysis should be tested using microwave-based pyrolysis technology, especially since good catalytic properties can be obtained for ZSM-5 zeolite at lower pyrolysis temperatures of 300 °C. In addition, conditions that simulate hydrothermal liquefaction but that use microwave energy as the heating mechanism at ambient pressures should be investigated further for upgrading possibilities.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

E. grandis wood as a feedstock for pyrolysis technologies shows much promise, with good-quality pyrolysis oils obtained using the pyro-GC/MS and RotoSYNTH microwave apparatus. The significant contribution of *E. grandis* plantations to forestry-related industries, together with the competitive specific growth rates of less than 10 years for this species (compared with others that have rotation lengths of up to 120 years), makes *E. grandis* an attractive and noteworthy species to use in biorefinery and biofuel applications. *E. grandis* also has low water usage than other cash crops, with a similarly good harvest index.

Pyrolysis of *E. grandis* was possible using two different technologies, and further demonstrated the effectiveness of commonly used catalysts such as bentonite and ZSM-5 zeolite. The performance of these catalysts and the overall performance of the pyrolysis oils produced were reviewed using the inherent carbon, hydrogen and oxygen content of the oils. It has previously been found that higher atomic ratios of hydrogen to carbon (H/C), with lower atomic ratios of oxygen to carbon (O/C), improve the higher heating values (HHVs) for these pyrolysis oils, giving them a stronger potential to compete with conventional transportation fuels. The van Krevelen diagram is a useful tool for evaluating the effectiveness of catalysts and the performance of different types of fuels, whether they are solid, liquid or gaseous in nature. Shifts in the H/C and O/C ratios may be directly correlated to HHV.

Using the carbon, hydrogen and oxygen content of the pyrolysis oils, it was possible to evaluate the effectiveness of each type of catalyst using the pyro-gas chromatography/mass spectroscopy (GC/MS) system which requires only small samples. It was found that using ZSM-5 zeolite as a catalyst at lower temperatures gave the best heating values, with an improved selectivity towards certain types of compounds. Bentonite performed just as well as zeolite catalysis under the same conditions, although there was only a negligible improvement in the heating value of the fuel.

One significant result for microwave-assisted pyrolysis oil was that the oil could be distilled conventionally in order to improve its heating value. The heating mechanism for microwave-based pyrolysis has been found to be similar to that of hydrothermal liquefaction, although at ambient pressures whereby similar conditions are created at a cellular level, which induces the decomposition of the wood matrix. An HHV of 23.30 MJ/kg was obtained from an initial 13.30 MJ/kg, although the theoretical HHV was calculated to be 26.70 MJ/kg. The biochar achieved an HHV of 27.35 MJ/kg and was produced with reasonable and consistent yields. Microwave-assisted pyrolysis oils also were able to be produced with higher H/C ratio values, at between 1.42 and 1.51, than those produced using the pyro-GC/MS system, with values of between 0.94 and 1.10.

The definitive requirements from future studies in catalysis for applications in upgrading pyrolysis oil would necessarily be to improve selectivity towards fewer compounds in order to aid further refining operations. An example supporting this notion is catalysis using the ZSM-5 zeolite catalyst at moderately lower temperatures. Another requirement should be to target certain types of compounds, such as organic acids, in order to increase the total acid number (TAN) ratings for pyrolysis fuels. Microwave-based pyrolysis, sharing similarities with hydrothermal liquefaction in principle, should also be investigated further in order to produce more stable oils which can be integrated easily with conventional fuel oils. Lastly, based on the concepts realised with regard to the effects that the H/C and O/C atomic ratios have on fuel performance, the ultimate objective for *in situ*- and *ex situ*-based catalytic fast pyrolysis should be to reduce oxygen, either by liberating oxygen with the formation of water (which is not thermally optimal) or CO_2 (which is preferred), or, if possible, by using an oxygen scavenger (which could avoid sacrificing both the hydrogen and carbon contents).

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APPENDIX

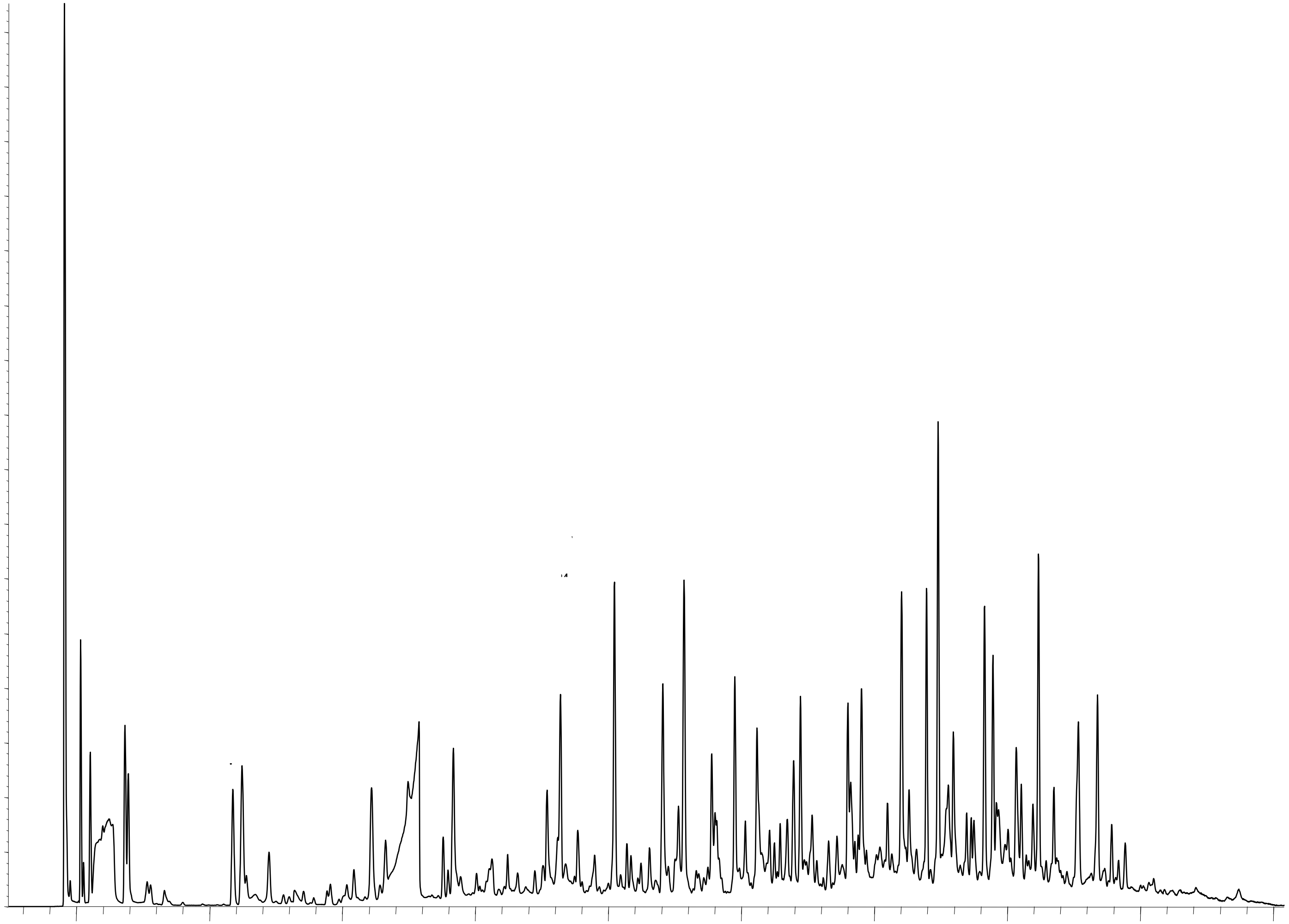

Figure 7: Chromatograph for pyrolysis oil of *E. grandis* at 500 °C

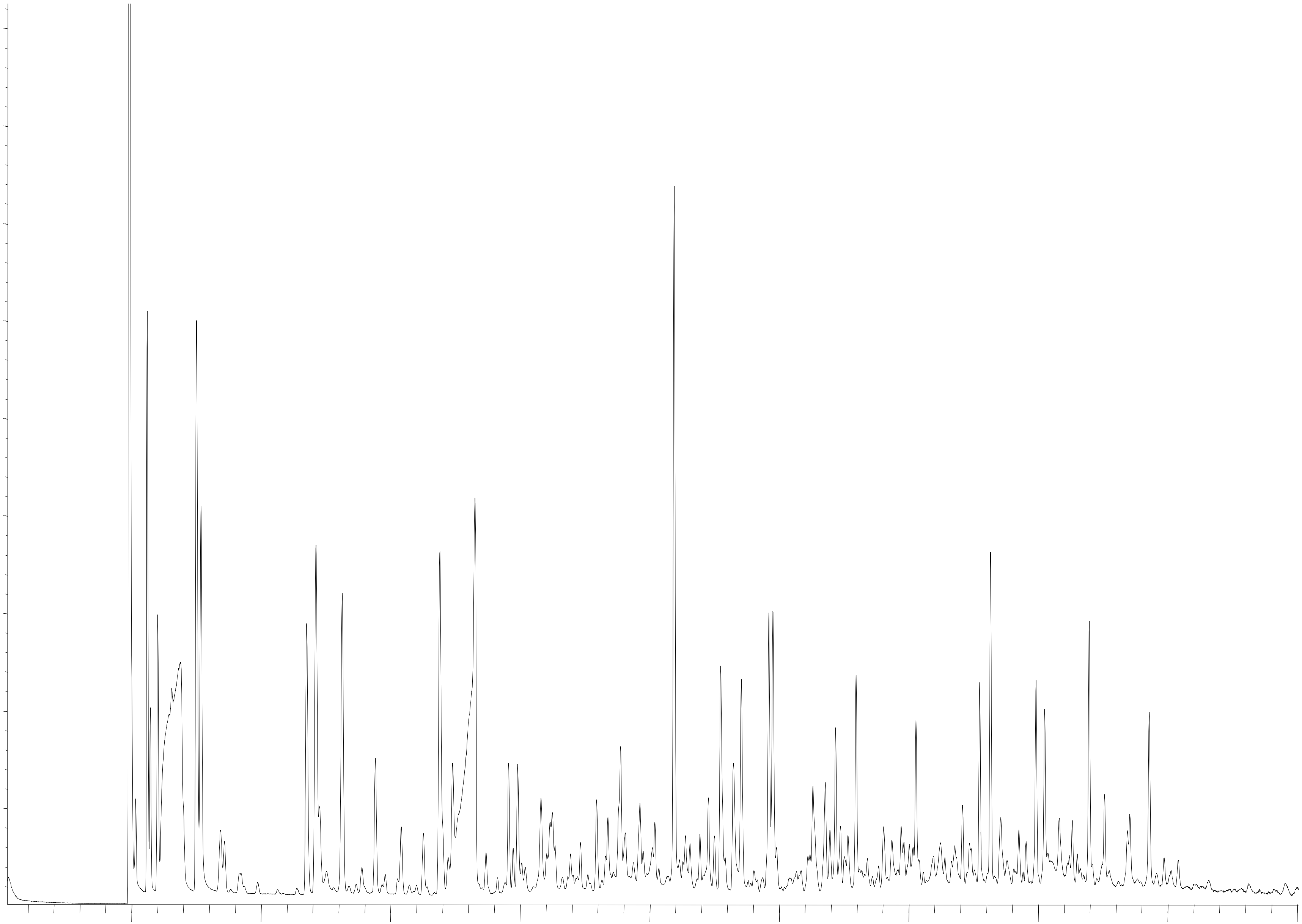

Figure 8: Chromatograph for pyrolysis oil of *E. grandis* catalysed with bentonite at 500 °C

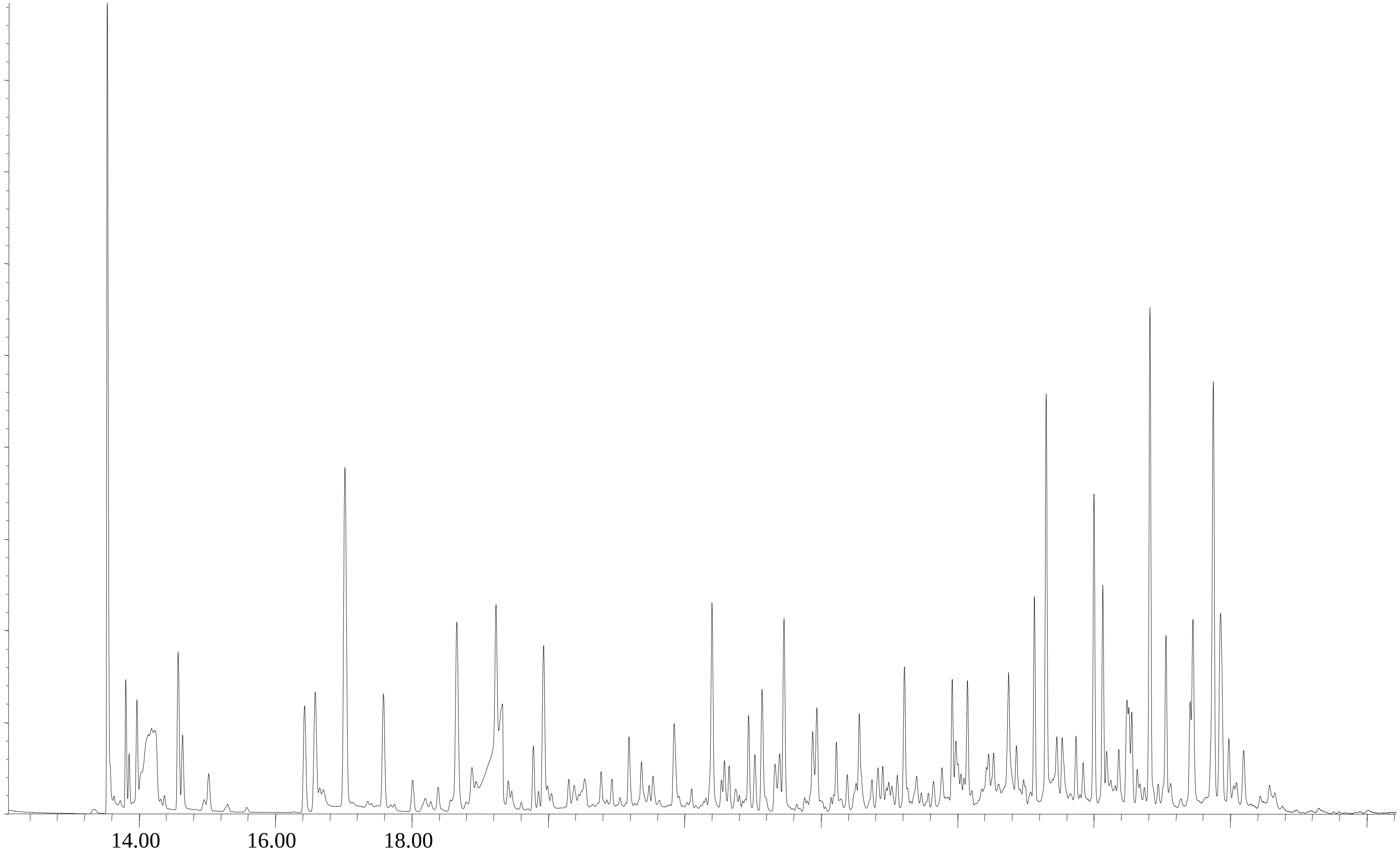

Figure 9: Chromatograph for pyrolysis oil of *E. grandis* catalysed with zeolite at 500 °C

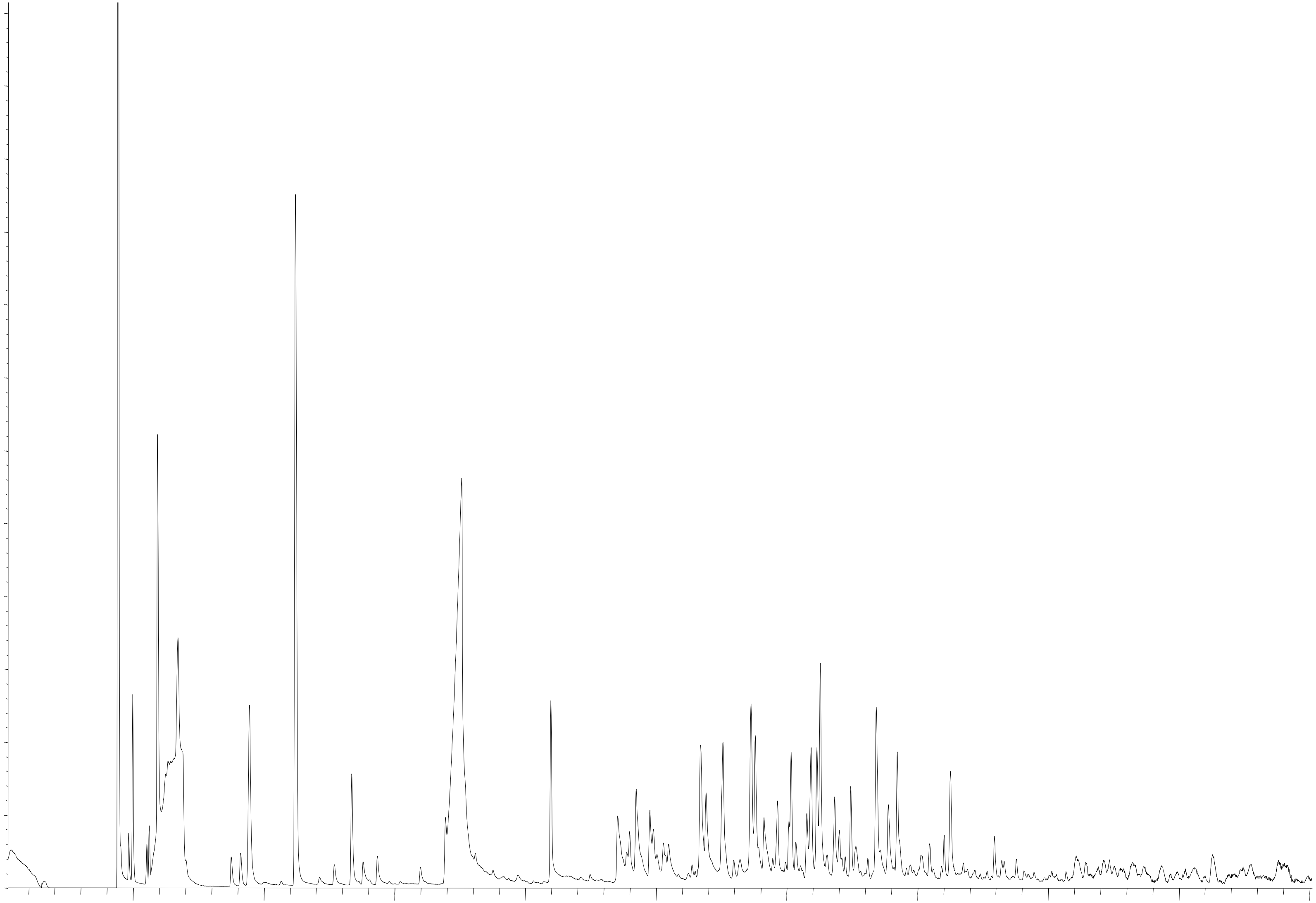

Figure 10: Chromatograph for pyrolysis oil of *E. grandis* catalysed with zeolite at 300 °C