Hydrothermal Processing of Biomass and Related Model Compounds

by

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Submitted in accordance with the requirements for the degree of PhD

The University of Leeds

Energy Research Institute

May, 2012

The candidate confirms that the work submitted is his/her own and that appropriate credit has been given where reference has been made to the work of others

Acknowledgements

I would like to offer my most sincere gratitude to Prof. Jenny. M. Jones and Dr. Andy Ross for their supervision during the research and in the writing of this thesis. Your combined guidance, help and passion for the field of renewable energy is inspiring and I am thankful that I had the opportunity to work with you both.

I would also like to thank the support staff at the ERI, particularly Simon Lloyd and Dr. Adrian Cunliffe for their help with sample preparation, operation of instrumentation, extensive analytical knowledge and providing a friendly atmosphere in which to work.

For use of the LC-MS at Aberystwyth University (IBERS) I would like to thank Barbara Huck and Dr. Gordon Allison, Also Drs. Jess Adams and Edward Hodgson for their hospitality, advice and friendship.

I wish also to thank Peter Layden for allowing the use of data obtained from my employment at Arigna Fuels Ltd for inclusion in this thesis.

The research group at Leeds was a fertile mixture of ideas, help, support, lively debate and a great place to study. Thank you Dr. Konstantinos Anastastakis, Dr. Toby Bridgman, Dr. Abby Saddawi, Dr Xiaomian Baxter, Dr. Michal Kubacki, Bijal Gudka, Paddy Biller, Brian Dillon, Dr. Elizabeth Curtis-Wright and Dr. Emma Fitzpatrick for all of the above.

Thanks also to the EPSRC for financial support during this study.

Last but by no means least, I would like to give thanks to my family; my wife and soul mate Sharon for your continuing love and encouragement, allowing me to pursue a dream and for supporting the decision to return to University; my children, Stephanie and Abigail and my parents, Bob and Margaret – I can barely begin to express my gratitude; I couldn't have wished for better. To my aunt Beryl – you have taught me much and it is to you that I dedicate this thesis.

"Science *knows* that it doesn't know everything, because if it did, it would stop." – Dara Ó Briain

Abstract

Future energy supplies, as a result of governmental policy and environmental legislation, will increasingly be borne from renewable sources. Use of biomass to provide fuels and chemicals to replace those derived from coal and oil will be crucial in providing diverse, sustainable and secure supplies for years to come. Production of the full range of solid, liquid and gaseous fuels from biomass to replace those from non-renewable sources is achievable, but not in the quantities currently consumed at present, hence demand will increase with an ever-expanding world population, coupled with competing markets for food production.

Biomass used as fuel has environmental benefits, with CO_2 emissions being reduced, however, because biomass energy density is much lower than coal or oil, more prone to microbial degradation and because many biomass sources have high water content, transportation is much more expensive, therefore energy densification techniques are required to overcome these hurdles. Various thermal technologies exist to upgrade biomass to fuels; these include gasification, pyrolysis, anaerobic digestion, hydrothermal processing and torrefaction. Hydrothermal processing (HTP) is an environmentally benign method of energy densification and can be used to produce directly liquid and solid fuels and indirectly gaseous fuels. The reactions are carried out in hot, compressed water in temperatures of 160 – 400°C for reaction times ranging from seconds to days. Benefits of HTP reactions include high energy density liquid and solid fuels, low gaseous emissions and high product yields are also claimed. For oil production, homogeneous alkali catalysts have been used with high returns with equally high temperatures.

Biological components of energy crops biomass comprise largely of cellulose, hemicellulose and lignin, with differing ratios and types between plant species. Taking each individual lignocellulosic component and reacting in isolation presents expected data from each when reacting as a whole, allowing comparisons to be drawn with 'raw' biomass, *Miscanthus* and willow in this study. Oil formation under HTL conditions with alkali catalyst was deemed to be the best fuel product, but yields were lower than expected and the catalyst concentration was brought into question. Another surprising development was the formation of oil from lignin under these conditions, though the process of lignin removal may account for this phenomenon. LC-MS analysis of HTL

derived aqueous phase lignin indicated the presence of high molecular weight polymers, heteroatomic and substituted polyaromatic compounds, with λ_{max} outside the rage of 190 – 400nm scanned and notable by their absence.

Results from the factorial study in Chapter 5 showed that of all the reaction conditions tested (temperature, reaction time and catalyst) the greatest effect on all lignocellulosic compounds was temperature. Though it was expected that cellulose and xylan would behave in a similar manner due to the likeness of their polymeric composition, this was not the case for many responses compared. At the conditions in this study, lignin was found to be the least affected by any of the variables. Overall, the use of catalyst, though beneficial for increasing the calorific content and yield of cellulose oil, had a detrimental effect on the other components. KOH catalyst reduced aqueous phase acidity through formation of buffers, but post calculation, xylan was found to have produced more acidic species.

Biomass energy crops *Miscanthus* and willow were reacted in Chapter 6. Evident from this data are similarities with individual biomass components found earlier. Hemicellulose content of *Miscanthus* was the reason for greater solubility, though with increasing reaction times, rate limiting condensation polymerisation reaction took place to increase char yields. The most energy efficient hydrothermal conversion method was HTC, with catalyst use only beneficial for oil production. Analysis of chars by AES indicated lower alkali metals concentrations than raw analysis (K, Na, Mg, Ca). Aqueous phases contained high concentrations of these leached metals. Implications are reduction of inorganic matter improves fuel quality and less likelihood of combustion boiler problems.

The final part of the study was comparison of HTC and torrefaction. Information from literature sources and pilot plant produced torrefied materials were compared and contrasted. Drying biomass is the largest processing requirement for this process. Suitability of feedstock is largely dependent therefore on water content. Similarities are evident between products and energy yields, but torrefaction is much closer to commercial realisation due to technological advancements needed for large scale HTP systems.

List of Abbreviations

HTP – Hydrothermal processing

HTL – Hydrothermal liquefaction

HTC – Hydrothermal carbonisation

DCM – Dichloromethane

GC – Gas chromatography

GC-MS Gas chromatography, Mass spectroscopy

IR – Infrared

STA – Sequential thermal analyser

TGA – Thermogravimetric analysis

KOH – Potassium hydroxide

FID – Flame ionisation detector

TCD – Thermal conductivity detector

HPLC – High performance liquid chromatography

SRC – Short rotation coppice

cP – Specific heat capacity (J/g/°K)

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Johnson R.S., Jones J.M., Ross A.B., "Hydrothermal Liquefaction of Biomass Model Compounds", paper presented at the "17th European Biomass Conference and Exhibition, from Research to Industry and Markets", 29 – 3 June/ July 2009, Hamburg, Germany.

Johnson R.S., Jones J.M., Ross A.B., "Investigation of Biochar Production from Hydrothermal Processing of Biomass Model Compounds", "Bioten" Conference 21 – 23 September 2010, Birmingham, UK.

Posters

Johnson R.S., Jones J.M., Ross A.B., "Investigation of Biochar Production from Hydrothermal Processing of Biomass Model Compounds", poster presented at "Bioten" Conference 21 – 23 September 2010, Birmingham, UK.

Introduction

Consumption of the earth's finite resources of oil, coal and natural gas for our future energy requirements is not sustainable. Coupled with the negative environmental impact from products of combustion such as CO_2, NO_x and SO_x from power stations, industry, transport and domestic use, renewable alternatives need to be sought that lessen man's footprint on earth. We have become, particularly in the west, used to seemingly unlimited supplies of energy, consuming more and more as our population increases, however, there will come a time when the last barrel of crude has been extracted and the last tonne of coal burnt.

It is energy that drives economies and industry, provides heating, increases mobilisation and allows international trade on a massive scale. The security of energy supply, especially on an island like the UK, is paramount for our continued technological expansion. With dwindling supplies of oil and gas and with many closed coal mines, renewable energy is the sensible choice of power for future generations. The development of low-carbon technologies is a growing, viable global business with huge investment and with the largest potential for future returns. While some of the more inspired methods of energy production like atomic fusion are still a number of years from being commercially realised, short to medium term CO_2 mitigating solutions are being employed.

Renewable technologies are already employed throughout the world. Solar photovoltaic cells, hydroelectric dams and wind turbines already produce increasing amounts of energy, mitigating CO_2 emissions for years to come. There are of course suitability issues at stake. Solar photovoltaic cells are more suited to sunnier climes, whereas solar thermal technology and wind turbines are a better match for the UK's unpredictable weather.

The international energy agency (IEA) has produced a 'BLUE map', outlining CO_2 emissions cuts to 50 − 80% of their current value by 2050 and the role of biomass in predicted demand areas. Biomass is expected to account for 18% of final energy consumption, the biggest share being predicted in the transport sector. Power generation from biomass and waste is also expected to account for a 6% share in 2050 with 13% of biomass sourced electricity produced using carbon capture and storage (CCS). In the

UK, the Department of Energy and Climate Change EMR White Paper produced on July 12th 2011, set out framework for energy as follows;

> At the heart of our strategy is a framework that will offer reliable contracts, administered through delivery arrangements that are trusted by investors, to achieve the diverse portfolio of generation we need to meet our goals as efficiently and cost-effectively as possible. Broadly this approach consists of four parts:
>
> - long-term contracts for both low-carbon energy and capacity;
>
> - institutional arrangements to support this contracting approach;
>
> - continued grandfathering, supporting the principle of no retrospective change to low-carbon policy incentives, within a clear and rational planning cycle; and
>
> - ensuring a liquid market that allows existing energy companies and new entrants to compete on fair terms. (DECC, 2011)

Biomass is another, potentially more valuable renewable resource, utilised fully in the developing world as a major source of heat for cooking and keeping warm and can also contribute to production of electricity, heat, biofuels and chemicals. Biomass is also co-fired with coal, producing electricity. Biofuels such as bioethanol and biodiesel already replace millions of litres of crude oil, with the EU introducing legislative controls so that a greater portion of transport fuel is from renewable sources. Speciality chemicals can be derived from biomass, replacing those from oil and coal, again providing versatile renewable solutions. The production of chemicals from biomass is nothing new; pyroliginous acid produced from wood has been used for hundreds of years and has had numerous applications. These were surpassed when chemicals were derived from crude oil and coal sources as they were cheaper and easier to obtain. The list of products that can be obtained from biomass is massive, instigating areas of research into a range of thermal conversion technologies including, but not limited to; pyrolysis, gasification, torrefaction, anaerobic digestion and hydrothermal processing.

Production of biomass and its subsequent conversion to useful products as a fossil fuel replacement is not without issue. Plant oils used in the transesterication process to make biodiesel and sugar beet to make bioethanol take foodstuffs out of the chain, prompting various "food Vs. fuel" debates. This in turn inflates the cost of food as more land is set aside globally for the production of biofuel, replacing lower value dedicated food crops.

Non-food crops are billed as the answer to replace "1st generation" biofuels. Fast growing, high yield energy crops are being championed in replacement of crops grown for food. Species such as *Miscanthus*, short rotation coppice Willow, Switchgrass and Reed Canary Grass are being researched due to their favourable growth rates and relative ease of harvesting, utilising existing machinery and farming knowledge. Of course, this change in energy production brings new challenges. Crops will need to be fertilised, therefore an increase in the global output of NPK fertilisers. There are fears that the upsurge in managed energy crop plantations will cause peak production of minerals, particularly phosphorous. An ever increasing world population will therefore require more mineral resources, increasing the speed at which the remaining reserves are used. The increase in fertilizer use, will in turn, lead to increased inorganic contents of biomass, creating issues for slagging, fouling and corrosion of boilers when combusted. Recycling minerals and nutrients such as phosphorous, potassium, sodium and silica will become crucial to prevent not only problems related to combustion, but to utilise fully the limited amount of natural resources available.

Another major challenge is volume or energy density. Wood has approximately half the energy density compared to coal, meaning twice as much has to be used to create the same amount of power, adding to greater transport and storage costs. There are other issues with storage and transportation of large volumes of biomass. One of these is off-gassing, the production of CO_2, CO and CH_4. The danger of this self, uncontrollable release of gas in confined spaces, such as the hold of a container ship, is evident. High moisture content of "wet biomass" contributes to elevated transportation costs as up to and in excess of 50% moisture is usual for unprocessed biomass products. This effectively means that 50% of the transportation cost could be for the moving of water. Processes which increase the energy density of lignocellulosic biomass by the removal of oxygen are therefore of significance and include: torrefaction; a relatively low temperature thermal conversion technique in a low oxygen environment that produces high energy yields in solid form; and pyrolysis, a higher temperature process in the absence of oxygen which produces a relatively low calorific oil and char.

Hydrothermal processing is a powerful biomass thermal conversion technique, utilising hot, compressed water to form a range of solid, liquid and gaseous products including oils, chars and water soluble hydrocarbons. There are distinct advantages of this

process; firstly, biomass can be processed "wet" negating energy and time losses from water removal. Secondly, as water is used as the reaction medium and the solvent, the process is thought to be "green". Thirdly, gaseous products produced by the reaction contain no NO_x and SO_x, harmful combustion gases, volatile compounds or fine particulate matter, when compared to torrefaction, pyrolysis or gasification conversion techniques.

Research has highlighted other potential sources of energy from biomass, apart from basic combustion. Techniques developed in the 1960's and 70's, once overlooked, are now being researched to provide not just suitable products for a power station, but a renewable source of oils, gases and chemicals. Of particular interest are conversions of biomass via thermochemical (direct combustion, gasification and pyrolysis/ liquefaction) and biochemical (anaerobic digestion, fermentation) routes to provide a range of products to include heat, electricity, fuel and chemicals.(Demirbas 2001a)

The purpose of this research thesis is to investigate hydrothermal processing of biomass and related model compounds, to further understand the reaction processes and the effect of reaction conditions on products, allowing development of a suitable environmentally benign method of increasing the energy density of lignocellulosic biomass.

Chapter 1 – Solid, Liquid and Gaseous Fuels from Biomass – Literature Review

1.1   Introduction – what is biomass?

Biomass is all biological material derived from either living or recently dead plant or animal organisms. In the context of energy production, biomass is classed as a renewable resource and usually refers to plant material as the most abundant source – world production of biomass is estimated at 146 billion tons per year mostly from wild plant growth.(D.J. Cuff and W.J.Young 1980; Demirbas 2001a) Global food production along with energy production in the developing world already accounts for a large portion of biomass consumption with the western world underutilising this valuable energy resource in favour of fossil fuels.

Biomass is composed mainly of carbon, but also usually contains hydrogen, nitrogen, oxygen and a host of other compounds including alkalis and various heavy metals. Coal, oil and natural gas, despite being originated from biomass, are not considered to be biomass as the reserves of these are the result of formation millions of years ago. The carbon contained within these reserves has been removed from the "carbon life cycle" that exists as plant life removes CO_2 from the atmosphere, replacing it with oxygen (**Figure 1.1**). (King) The combustion of these fossil fuels for industrial and domestic uses generates excess CO_2 and particulates in the atmosphere, whereas biomass releases as much carbon as is taken up – they are effectively "carbon neutral".
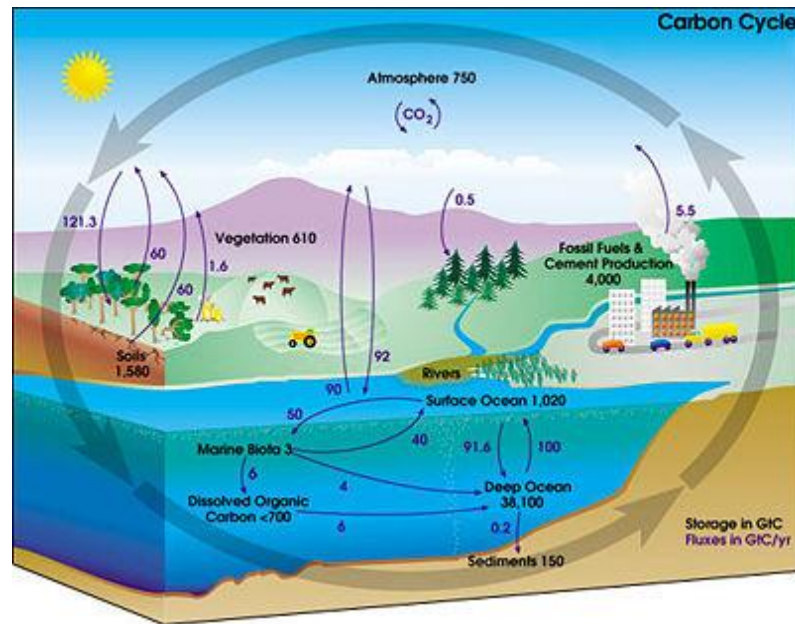
Figure 1.1: The carbon life cycle

> "Diagram of the carbon cycle. The black numbers indicate how much carbon is stored in various reservoirs, in billions of tons ("GtC" stands for GigaTons of Carbon and figures are circa 2004). The purple numbers indicate how much carbon moves between reservoirs each year. The sediments, as defined in this diagram, do not include the ~70 million GtC of carbonate rock and kerogen." (King)

There are many issues surrounding climate change following the vast amounts of CO_2 (and also related combustion products such as CH_4, NO_x and SO_x) that are released into the atmosphere when fossil fuels such as coal, natural gas and oil are burnt in power stations, internal combustion engines, and for domestic uses throughout the world. The world is now subjected to global warming as a direct result of the additional CO_2 in the atmosphere. This CO_2 cannot be removed by the usual "sinks" as part of the carbon life cycle and so remains in the atmosphere, causing a "blanket effect" resulting in the gradual heating up of the earth's surface. Changes in the concentration of CO_2 in the atmosphere have been monitored by taking ice cores from the Arctic and Antarctic, these show the steepest rise in CO_2 levels since the start of the industrial revolution, with the sharpest gradient i.e. the biggest rise noted as being from 300 to 450ppm over the last 50 years. This has been proven not to be an anomaly, as concentrations of all the greenhouse gases including methane (CH_4) and nitrous oxide (N_2O) have followed the data produced by CO_2. These gases are known by-products of combustion, and reflect

the consumption of fossil fuels for energy over the same time period (Annee and Ruytter 1986).

Since the start of the industrial revolution in the 18th century, and progression and mechanisation of industry, we in the developed world have been consuming fossil fuels at an ever-increasing rate. North Sea oil production for example, peaked at approximately 139 million tonnes a year in 1999, with the average yearly production down ~15% a year since then. (R. M. Mackaya and Probert 2001) Even now, large new discoveries of oil in the north sea of an estimated 500 million barrels will be consumed quickly considering the rate of use in the UK is ~1.8 million barrels/ day. (Parkinson 2006) Our reliance on oil and the fact that we will eventually run out, now gives a renewed urgency to find replacement sources of energy. Emerging or developing nations (China, India etc.) are now responsible for the fastest rate of consumption of fossil fuels as their economies grow at a similar rate. (Shahriar 2007)

The western or developed nations now have an obligation to the rest of the world to lead the way in new renewable technology development, reduce energy consumption and set standards in reducing greenhouse gas output, setting limits for emissions produced by nations coupled with plans to increase the proportion of energy that is sourced from renewable means and funding to develop existing and new technologies.

1.2   Sources of biomass

Biomass sources include harvestable crops such as willow or *Miscanthus* farmed on an industrial scale using current, modern techniques, waste from farming such as chaff and slurry, domestic household waste such as sewage and industrial waste. In general, these are placed into three main categories - woody, non –woody and animal waste. From these general categories, there are derived seven forms of biomass types or feedstock's. (Wereko-Bobby and Hagen 1996)

1. Forests, woodlands and plantations (woody).
2. Agro-industrial plantations (woody).
3. Trees outside forests/ woodlands (woody).
4. Agricultural crops (non-woody).
5. Crop residues (non-woody/waste).

6. Processing residues (non-woody).
7. Animal wastes (waste).

Each of these biomass feedstocks, due to the natural variation in trees, plants and waste, gives a different chemical composition and distribution and as a direct result will require processing in a specific manner. Biomass from all sources is composed mainly of lignin, hemicellulose and cellulose, the relative concentrations of which can vary enormously between plant species (Demirbas 2007a). Contained within these categories, herbaceous plants can be further subdivided into those with high or low moisture contents that lead to methods of processing that are more suited to "wet" and "dry" techniques. Higher moisture content biomass such as sugarcane lends itself to wet/ aqueous processes as does algae, whereas "dry", woody biomass is more suited to gasification, pyrolysis or combustion. "Aqueous processing is used when the moisture content of the material is such that the energy required for drying would be inordinately large compared to the energy content of the product formed" (McKendry 2002a). Farmed sources of biomass such as willow can produce up to 20 oven dry tonnes per acre per year, whereas some types of algae and grasses may produce up to 50 oven dry tonnes per acre per year with research focus globally on these high yield crops.

1.3   Characteristics of biomass

As previously explained, biomass is composed mostly of cellulose, lignin and hemicellulose, the levels of each of these components being a driving force for the subsequent processing. The natural variation of these products gives rise to ash, alkali and trace component contents, which have a negative effect on thermal conversion processes. If biomass is required for biochemical fermentation processes (first generation biofuels), the cellulose content is of great importance as it has an adverse effect on this, however, hydrolysis of cellulose can be utilised for second generation biofuels. Elemental composition of biomass again varies depending on the source, but is generally of the order (in wt %); carbon ~ 50%, hydrogen ~6% oxygen ~42% with ash, nitrogen, sulphur and other elements making up the rest. By direct comparison of biomass to coal (**Table 1.1**), it can be seen that the carbon level of coal is much higher than that of biomass at ~89% with a much lower value for oxygen ~5%.

Volatile matter or the portion lost from heating to 900°C in nitrogen is very high for biomass (>80%). In contrast, coal has a much lower volatile content

Table 1.1: Comparison of elemental and proximate analysis of willow wood and high rank coal

	Elemental analysis					Proximate analysis		
	C%	H%	N%	S%	O%	Ash%	Volatile %	Fixed carbon%
Willow wood[1]	49.9[a]	5.9[a]	0.6[a]	0.07[a]	41.8[a]	1.7[a]	82.2[a]	16.1[a]
Coal[2]	88.7[b]	4.1[b]	1.2[b]	1.6[b]	4.7[b]	15.3[a]	17.0[a]	67.7[a]

[1](Jenkins et al. 1998) [2] High rank coal >85%C(Vassilev et al. 1996) [a]dry basis [b]dry, ash free

It is this difference in carbon and oxygen levels between coal and biomass that gives rise to the lower calorific value and raised consumption of biomass if used primarily as a combustible. The greatly reduced amount of sulphur from biomass sources is linked to a large reduction in the amount of SO_x released from combustion.

Ash contents of coals can be significantly higher than biomass, as seen in **Table 1.1**

1.4 Biomass composition

In this work biomass model compounds, cellulose, xylan (for hemicellulose) and lignin, along with short rotation coppice (SRC) willow and *Miscanthus* are considered for assessment. As the natural variation in all biomass types is vast and compositional variation is also large, substrates were chosen for their uniformity and growth suitability. These biomass consists of the biopolymers listed above, but also other components (See **Figure 1.2**) such as proteins and a range of inorganic compounds, the most abundant being potassium, sodium, magnesium and calcium. The levels of inorganics found within the structure differ between species, harvest time and physical location within the plant i.e. stems leaves and roots.

Plant Biomass

- Low-molecular-weight substances
  - Organic matter
    - Extractives
  - Inorganic matter
    - Ash
- Macromolecular substances
  - Polysaccharides
    - Cellulose
    - Polyoses
  - Lignin
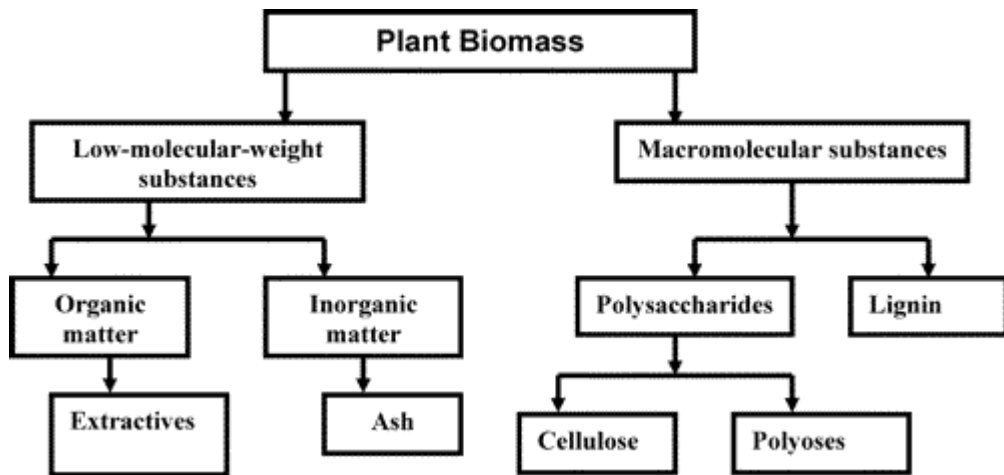
Figure 1.2: Composition of plant biomass (Mohan et al. 2006)

1.5   Cell wall composition

Plant cells are surrounded by an intricate matrix of polysaccharides making a rigid structure, reinforcing the body of the plant. The functions of this cell wall are varied and critical to the survival of the plant to include; regulating flow of water, protecting against fungal, bacterial and parasite attack, development and specialization of cells to cell types, and information exchange between cells. It is this plant cell wall that contains the main supply of cellulose, the largest, most profuse naturally occurring polymer in the world.

All lignocellulosic polymers undergo structural proportion changes as the water content varies. Cellulose, hemicellulose and lignin contained within the cell wall all contain R-OH, R-O-R and similar compounds. These groups are hydrophilic, due to hydrogen bonding. As water is drawn into the voids between each bio-polymer, this causes the cell wall to augment to a maximum level at which the cell reaches satiety - the fibre saturation point. As more water enters the formation, this is not intrinsic to the construction and cell wall expansion ceases. The route for water uptake is rescindable, contraction occurs with a lowering of water content. Lignocellulosic polymers differ in their ability to attract water. The rates of moisture uptake are; hemicellulose > cellulose > lignin, primarily attributable to R-OH groups

1.5.1   Cellulose

It is cellulose and principally the β (1-4) glycan chain that forms the main source for many hydrocarbons, it is the main component of all plants and is ubiquitous across the

planet, save in some extreme locations. From the point of organic chemistry, the construction of cellulose is uniform from any biomass type, being derived from glucose monomers covalently bonded via the β (1-4) glycan chain forming a cellobiose unit. This structure is repeated to form polymer chains with **(Figure 1.3)**. This is not to say that there aren't physical differences between cellulose, even those obtained from and within different plant sources. Indeed, the length of polymer chains, molecular morphology and molecular coordination can fluctuate within the same plant.
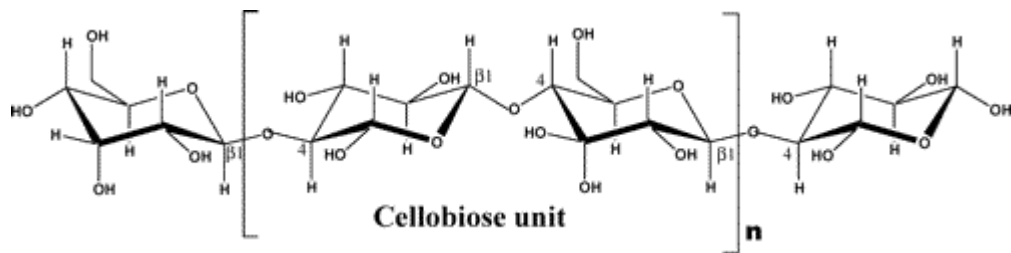
Figure 1.3: Cellulose polymer showing cellobiose unit (Mohan et al. 2006)

1.5.2 Lignin

To the analytical chemist, lignin is regarded as material which remains insoluble after treatment of a plant material with 72% sulphuric acid followed by dilution and boiling or that material which gives an ultraviolet absorbance maximum at 280 μm.

Botanists and plant physiologists have recognized for many years that a change occurs early in the development of the cell walls in the woody tissues of vascular plants whereby the cellulose is presumed to become hardened, or as it is usually described, lignified. The change comprises the addition of the cellulose of a substance or group of closely related substances which have been designated as lignin.

Early investigators in this field considered wood to be a definite chemical substance. In 1838, Anselme Payen, a French chemist, in the first of a series of studies, demonstrated that wood was a heterogeneous mixture and he attempted to separate lignified materials into their component parts. He treated wood with nitric acid, alkali, alcohol and ether to obtain a substance that was relatively resistant to the action of these reagents and solvents. Payen called this substance "cellulose". During the isolation of cellulose, Payen removed a substance or group of substances having higher carbon content than cellulose and he called this complex "true woody material". Payen later described this as "incrusting material" and hypothesised that in lignified substances; fibre forming

cellulose is embedded in and impregnated with varying amounts of this incrusting material.

With these results, a wood chemist, F. Schulze, used nitric acid and potassium chlorate to produce "pure cellulose". He named the material removed via the oxidation process "lignin", derived from the Latin lignum, meaning wood. This material is now known to consist of lignin and hemicelluloses, with the term lignin being applied only to the non-carbohydrate components of the cell wall.

The structure and morphology of lignin is complex. At the core of macro biological structures or trees lies a three dimensional polymer matrix originated from coniferyl alcohol, sinapyl alcohol, syringol or other monomers containing guaiacylpropane (See **Figure 1.4).**
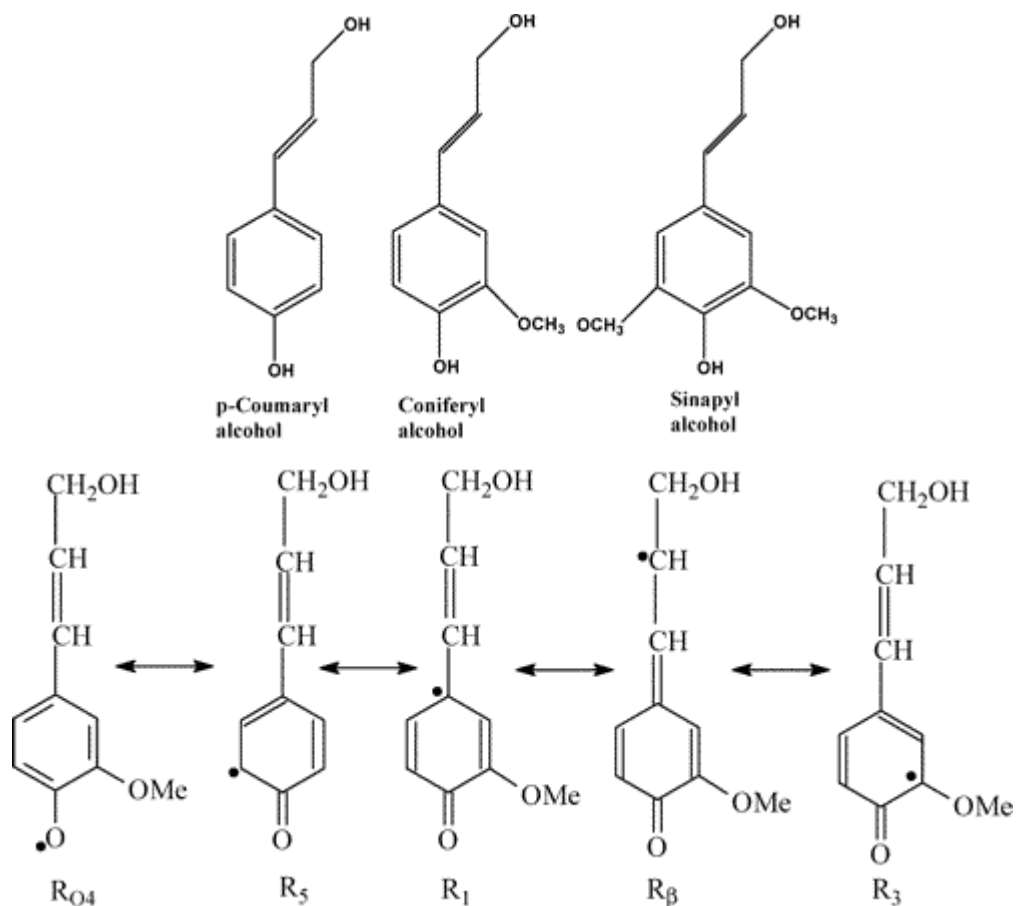
Figure 1.4: Monomers of lignin - p-Coumaryl, coniferyl, and sinapyl structures and resonance hybrid structures of phenoxy radicals produced by the oxidation of coniferyl. (Mohan et al. 2006)

Lignin is insoluble in water and, as yet, there has not been created a method that can extract lignin intact from wood and keep it identical to its natural state. The two methods for lignin isolation are either the removal of cellulose and hemicellulose by chemical treatment, leaving lignin as an insoluble material or by selectively dissolving lignin from the matrix, yielding solutions whereby the lignin can be recovered. As all the procedures produce lignin in a changed form from that of the original, subsequent analysis or experiments will never be exactly replicated when using untreated biomass. (Pearl 1967)

Types of lignin are named after their extraction techniques. Usually quoted types in reference material are − Klason; lignin that remains after treatment with dilute sulphuric acid and Organosolv: obtained by heating wood in an ethanol: water mixture at elevated temperatures. More recent developments in the field of extraction utilise ionic liquids as a 'greener' alternative to the more chemically aggressive methods of removal, allowing selective extraction of lignin whilst retaining >95% cellulose, then available for enzymatic degradation (Fu et al. 2010).

Figure 1.5 shows a portion of lignin structure from hardwood (*Fagus sylvatica).* What can clearly be seen is the random nature of the polymeric linkages, cross-linked and with hydrogen bonding to form an extremely stable structure.
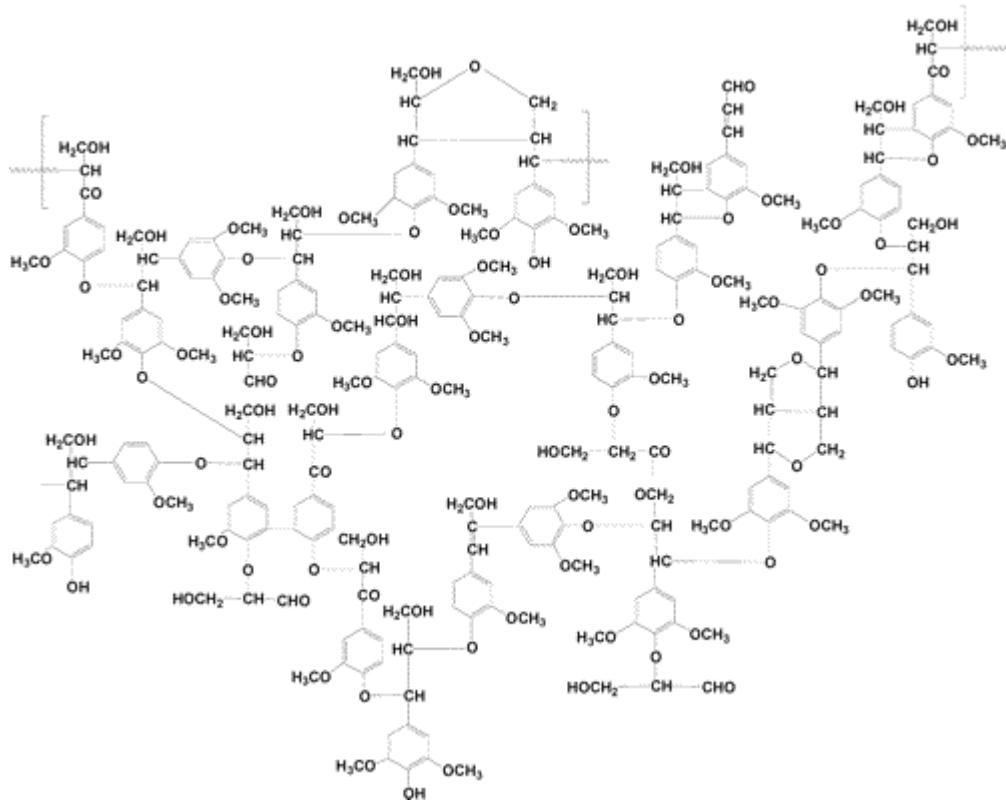
Figure 1.5: "Partial structure of a hardwood lignin molecule from European beech (Fagus sylvatica). The phenylpropanoid units that comprised lignin are not linked in a simple, repeating way. The lignin of beech contains units derived from coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol in the approximate ratio of 100:70:7 and is typical of hardwood lignin. Softwood lignin contains relatively fewer sinapyl alcohol units"(Mohan et al. 2006).

1.5.3   Hemicellulose

Hemicellulose polymers have a smaller molecular weight than cellulose, typically consisting of 100 – 200 monosaccharide monomers. There are 6 of these monosaccharides that make up the polymer chains, these being glucose, galactose, manose, xylose, arabinose and glucuronic acid (see **Figure 1.6**). As with cellulose and lignin, the actual structure differs between each tree or plant species. For woody biomass, hemicellulose contents on a dry basis are in the region of 33wt% overall. Hard and softwoods vary by approx. 7% (Mohan et al. 2006)
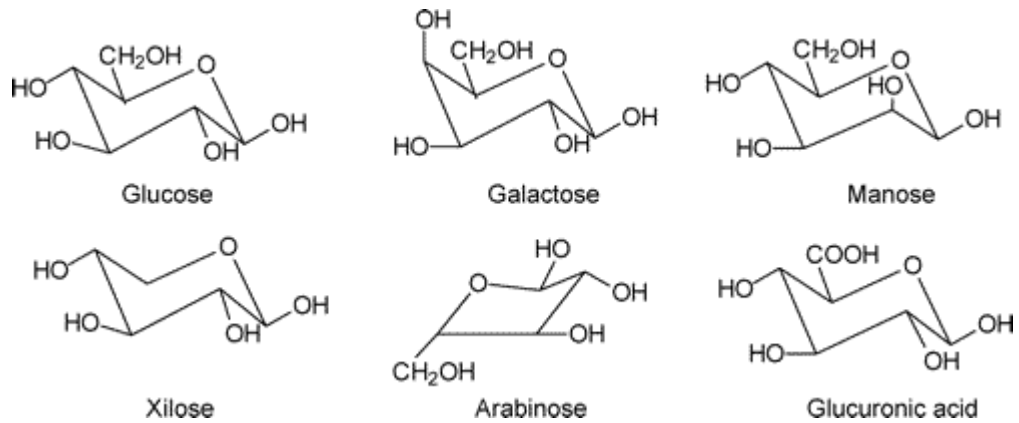
Figure 1.6: Main components of hemicellulose (Mohan et al. 2006)

As a suitable analogy, the lignocellulosic structure of wood is likened to a brick wall, with cellulose and lignin being the main constituent of the bricks, adding strength. Xylan is therefore the cement, holding the bricks together. A large degree of chemical complexity is provided by xylan, whose precise structure varies between a range of plant species, tissues and during cellular differentiation (**Figure 1.7**). Xylan is the major hemicellulosic component of the analogical wall. "*This polysaccharide includes a backbone of_-1,4-xylose residues in their pyranose configuration (Xylp), which are decorated at O2 with 4-O-methyl-D-glucuronic acid and at O2 and/or O3 with arabinofuranose (Araf) residues, whereas the polysaccharide can also be extensively acetylated. In addition, the Araf side chain decorations can also be esterified to ferulic acid that, in some species, provides a chemical link between hemicellulose and lignin*" (Correia et al. 2011)
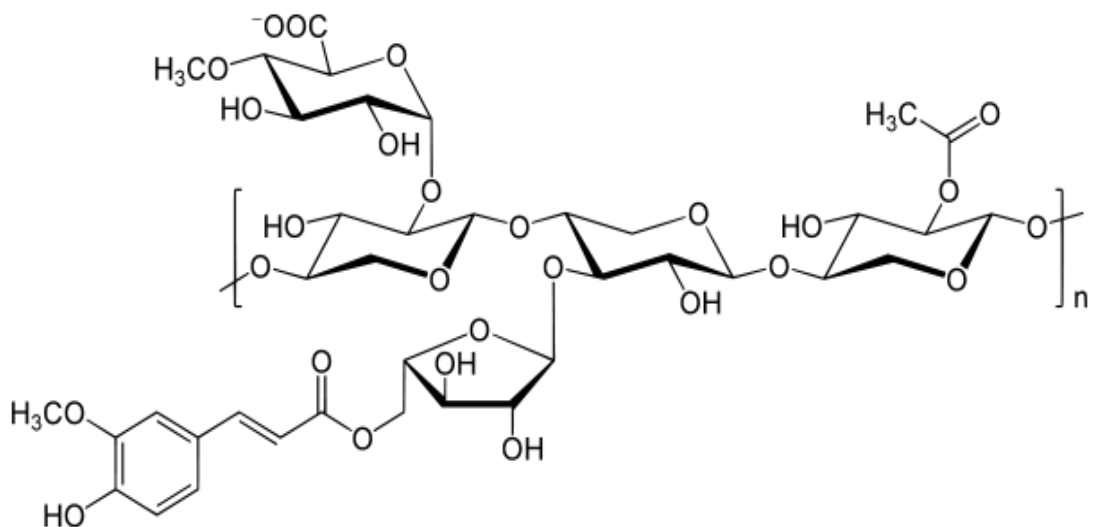
Figure 1.7: Xylan structure

1.6 Uses of biomass

The current uses of biomass are wide and varied, as the energy derived has been used by man for thousands of years. Today, biomass is used for generating electricity, heating homes, fuelling vehicles and providing process heat for industrial facilities, and also has the potential to provide various chemicals. (Demirbas 2001a) In the UK alone, there are many industries that are using and developing biomass technology. Many coal-fired power stations are now "co-firing" using biomass at levels of ~10%, there are now a handful of relatively small (<50MW) biomass power stations (compared to coal, natural gas and oil) with many more under construction. Many schools, country homes and private residences now benefit from heat and power as a result, with this approach being portrayed as the best medium term solution to the problem of climate change.

1.6.1 Food vs. Fuel

Changes to the UK and European energy policies now include targets for renewable fuel use being increased up to 15% of the total energy consumed by 2020. (IEA BLUE map) Wind farms, biomass power stations, solar and co-firing will go some way to meeting these targets, however, transport fuels are a separate issue.

Currently, renewable transport fuels account for less than 5% of the total consumed, with government policy stating increases in the amounts of biodiesel, ethanol and vegetable oil powered vehicles and respective blends with diesel and petrol. These fuels are known as 1st generation biofuels, and are either fermentable crops from which alcohols are produced (sugar cane etc.) or oil containing crops such as oil seed rape and sunflowers which have the oil removed via an extraction process and are then converted to products such as biodiesel.(Demirbas 2008) This system of biofuel production, although renewable, is not the most efficient use of the crops. There are constant food shortages throughout the world, with reports already showing that consumption is greater than production. (Ingram. et al 2008) Growing crops for fuel will undoubtedly remove even more from the food chain, causing increases in food prices and having a massive detrimental effect on the world. In the US, farmers are already switching to growing corn as the price increases.

The biggest problem with growing crops for transport fuel is the consumption required. To meet all the current transport fuel requirements for the world, vast areas of fuel crops

would have to be grown and then processed at least two times to produce fuel. The yields of oil seed crops in particular are in the region of 0-2.5 tonnes of oil/ acre depending on the crop, palm oil being one of the biggest oil producers per acre.

The rapid increase in production of bio-diesel by transesterification of various vegetable/ plant oils have produced an excess of glycerine (glycerol). These worldwide excesses have been noted by the steep drop in the price of glycerine over the last 10 years and have now become a source of interest for further processing.(Adhikaria. et al 2007; S. Adhikari. et al 2007)

2nd generation biofuels are being developed using crops which can be grown for fuel only and have much greater yields per acre (up to 50 oven dried tonnes) giving a greater return and potentially more fuel. Processing technology is similar to that developed for the coal industry. There are three methods that can be used for the production of transport fuels; gasification, pyrolysis and liquefaction. Of these methods, pyrolysis and liquefaction are suitable for producing fuel oil and distillates directly, and will be discussed in the following pages (McKendry 2002b)

1.7   Biomass conversion techniques

Biomass conversion techniques can be divided into various categories, depending on the technique and the individual products formed. They are: energy densification to produce solid fuels; direct liquefaction; indirect liquefaction; and hydrogen production. Some key, current and future technologies are described in this section.

1.7.1   Transesterification of plant oils

Transesterification of plant oils is the current technology for producing liquid fuels from biomass materials. This process is one of the so-called 1st generation biofuels. Plant oils from a variety of sources; palm oil, vegetable oils derived from sunflower seeds and oil seed rape, even olive oil contain fatty acids, which have a high calorific value and are converted into fatty acid methyl esters (FAME) through the method of transesterification. The process is simple, the natural oils are heated in the presence of a catalyst – usually sodium methoxide and stirred. After a short while, the reaction is complete and due to the formation of the major by-product glycerine, a separation step takes place. The resulting biodiesel or FAME is dewatered, filtered and ready to be

used, either as neat biodiesel as a diesel replacement, or more likely on a large scale, blended with diesel and sold through the pumps by large retailers, fulfilling obligations by fuel companies and indeed UK/EU legislation to provide renewable transport fuels. The downside to this technology is large. Biodiesel production is a woefully inefficient use of biomass due to the low yields of oil per acre and takes those very crops that are destined for food. As fuel prices increase, the price that farmers get for their oil-bearing crops also increases, which in-turn raises food prices. The ecological problems also then arise when traditionally poor countries, cultivate oil crops for fuel production over, not only food crops, but sections of forest and jungle. It is not for us to moralise, but to provide solutions to enable each country to provide sustainable fuels in the future.

1.7.2   Production of ethanol

Ethanol is also a 1st generation biofuel with the process being around for millennia, and is produced from fermentation of carbohydrates from a variety of plant sources, fruit, sugar beet/ cane, wheat, potatoes etc. The net energy gain from sugar cane in Brazil is approx. 8 times greater than that for the growth, harvest and production. This is sustainable in a large country like Brazil that has vast farms, but cannot be replicated globally. Also the sugars available for fermentation are readily available in the form of sugar cane and sugar beet and processed locally to reduce biomass transportation costs.

1.7.3   Pyrolysis

Pyrolysis is the heating of organic material in the absence of oxygen and is responsible for production of condensable moisture rich gas, containing hydrogen, tars and methane; and a char with high carbon content. The process is endothermic and flexible, having a range of tuneable reaction variables. Heating rates and final temperatures, relative proportions and source of biomass biopolymers and inorganic material contained within, contribute to a complicated reaction with many products. "Conventional pyrolysis is defined as the pyrolysis that occurs under a slow heating rate"(Maschio 1992a) and can be characterised by the changes in physical state by using techniques such as thermo gravimetric analysis (TGA). In this type of analysis, samples are heated up and losses (such as water or gasses) are measured corresponding to a particular temperature. A flow chart for biomass liquefaction via pyrolysis showing the useful products is shown in **Figure 1.8**

Biomass Liquefaction via Pyrolysis
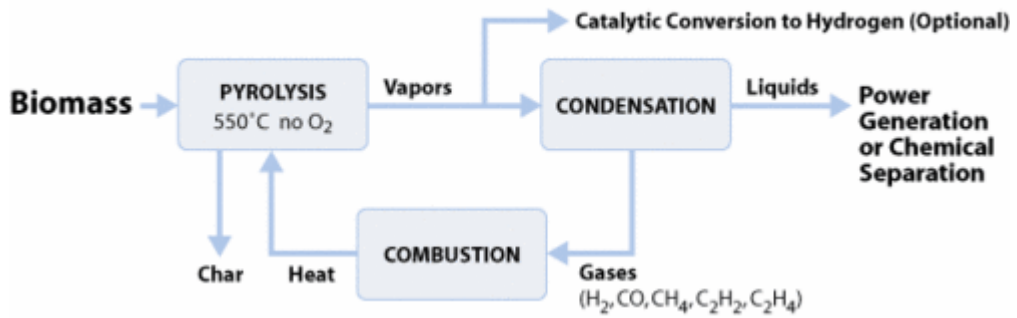
Figure 1.8: Pyrolysis flowchart (Source DOE)

Industrial pyrolysis processing can be achieved in conjunction with combustion, but yields are understandably low. Both direct and indirect heating can be used for the process, and reactor design varies, for example; screw augers, fixed and fluid bed reactors are all used. The benefits for pyrolysis are that the technology is relatively cheap; whereas the negatives are that the bio-oil produced has high oxygen content and usually high moisture content, making it both unstable and immiscible with petroleum products. Thus, pyrolysis oil requires further upgrading to provide fuel.

The temperature range of *conventional* pyrolysis in usually in the region of $300 - 700°C$ with a heating rate of $0.1 - 1°C/$ min and with a particle size of $5 - 50$mm. The dwell time of the sample in the reactor is in the region of $10 - 100$ minutes and yields higher quantities of charcoal, effective as both a fuel and active charcoal (Maschio 1992a).

1.7.4   Fast pyrolysis

Fast pyrolysis refers to the heating rate increase ($10 - 200°C/$ s) coupled with a decreased temperature of reaction (400-600 $°C$), a short residence time in the reactor (<4s) and a reduced particle size (smaller than 1mm). This method has been found to minimise the amount of charcoal produced and is the preferred route to yield liquid products, with previous analysis pointing to the theory that certain intermediate products are not formed during fast heating, causing the pyrolysis products to be directly formed and also changing the composition of the resulting products (Kothari and Antal 1985; Lede 1980; Scott and Piskorz 1984; Soltes E. et al 1981). Similar conditions of heating rate and residence time are used, when optimised for gas production, but in this case the temperature is much higher (700-1000 $°C$).

1.7.5 Flash pyrolysis

Flash pyrolysis is very similar to fast pyrolysis in terms of reaction temperature, but involves an even higher rate of heating, a brief residence time and an even smaller particle size (~1000°C/ min, <0.5s and dust respectively).

The pyrolysis and further gasification of biomass as a route for hydrogen production is also well documented. It is seen as an attractive solution to the logistical problems that arise due to the bulky nature of biomass. In this proposed solution the biomass is converted to bio-oil in the first instance at source, with the more energy dense bio-oil transported to a central point for processing (Czernik et al. 1999, 2000; Wang et al. 1998; Wang et al. 1997). Secondary to this, the bio-oil could be separated to yield products related to the lignin component (phenol substitutes in phenol-formaldehyde adhesives) (Kelley et al. 1997), or converted to components that could be blended to increase the octane content of petrol. In the latter case, the fraction derived from the carbohydrate portion of cellulose biomass could be catalytically steam reformed (Shabtai et al. 1997).

1.7.6 Torrefaction

The process of torrefaction involves the low temperature pyrolysis of woody biomass at conditions, typically 200 – 300°C, in an oxygen depleted atmosphere. At these temperatures, the hemicellulose fraction is the first to be degraded, removing oxygen by the emission of various compounds such as carbon dioxide, carbon monoxide and water, and smaller amounts of organic vapours including acetic and formic acid. This has the effect of increasing HHV of solid residue, achieved by the removal of oxygen.

Removing water and volatiles from wood/ biomass increases not only the storage capability, but also assists in the reduction in particle size required by power stations when co-firing. This increases the milling efficiency, and may also improve the combustion efficiency compared to co-firing raw biomass. Smaller, dryer particles would arise from milling torrefied biomass and these may burn-out more quickly in the boiler (Bridgeman 2008).

Torrefaction is fast becoming the preferred thermal conversion technique of choice for woody biomass. The main reason is the ease of processing, and retention of a large

portion of energy with a larger drop in mass. Depending on reaction conditions, 90% of the energy is retained with 70% mass remaining (Bergman et al. 10-14 May 2004; Uslu et al. 2008).   Bulk densities of the torrefied wood decrease to around ca. 200Kg/ m^3 from 220 – 260 Kg/ m^3 of wood chip depending on source (hard/ soft wood), but with the inclusion of on-line processing like briquetting and pelletising, this can be increased up-to 1200Kg/ m^3.

There are similarities between 'dry' torrefaction and hydrothermal carbonisation (HTC), which is sometimes called 'wet torrefaction' (Yan et al. 2010). This latter technology is relevant to this thesis and will be discussed later. Prins et al (**Figure 1.9**). reported a mass and energy balance for dry torrefaction of beech wood at 250 °C for 30 min and at 300 °C for 10 min, respectively (Prins et al. 2006b). Acetic acid and carbon dioxide are produced in significant quantities during dry torrefaction. The heat of dry torrefaction is reported to be 0.087 and 0.124 kJ g^{-1}, respectively.
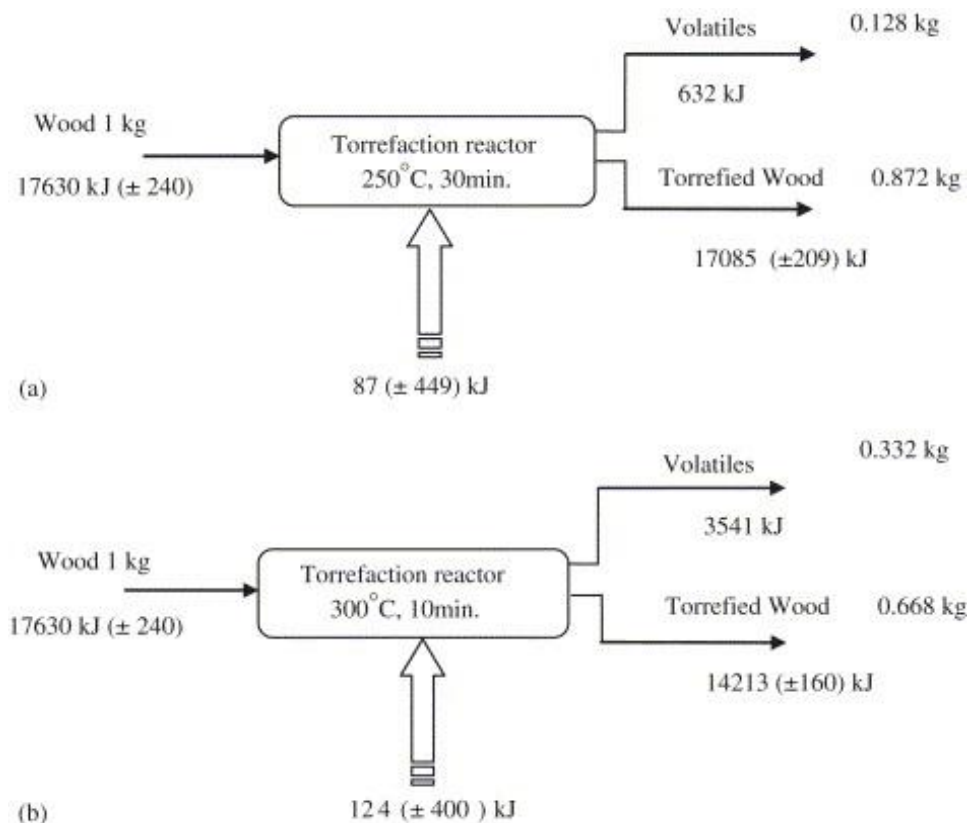
Figure 1.9: Mass and energy balance for torrefied wood reacted at 250 and 300°C (Prins et al. 2006b)

(Prins et al. 2006b) also note in their work "*Deciduous wood has been found to be much more reactive than coniferous wood under torrefaction conditions. This may be explained because the hemicellulose fraction in deciduous wood contains mainly xylan, which is much more reactive than the mannan found in coniferous wood. Important thermal decomposition reactions in torrefaction processes are dehydration, decarboxylation and deacetylation of the xylan-containing hemicellulose polymers.*" Thus, the use of xylan as a suitable model compound for hemicellulose is important, especially as it is predicted that cultivation of SRC willow and other rapid growing energy crops will be used increasingly for fuel conversion in the future.

1.7.7   Gaseous fuels from biomass

Gaseous fuels from biomass can be obtained directly and indirectly via a number of processing techniques, with the most valuable gases being hydrogen and methane. The potential value obtained from these gases, both monetary and calorific content is large, as is the shift from a carbon to hydrogen economy.
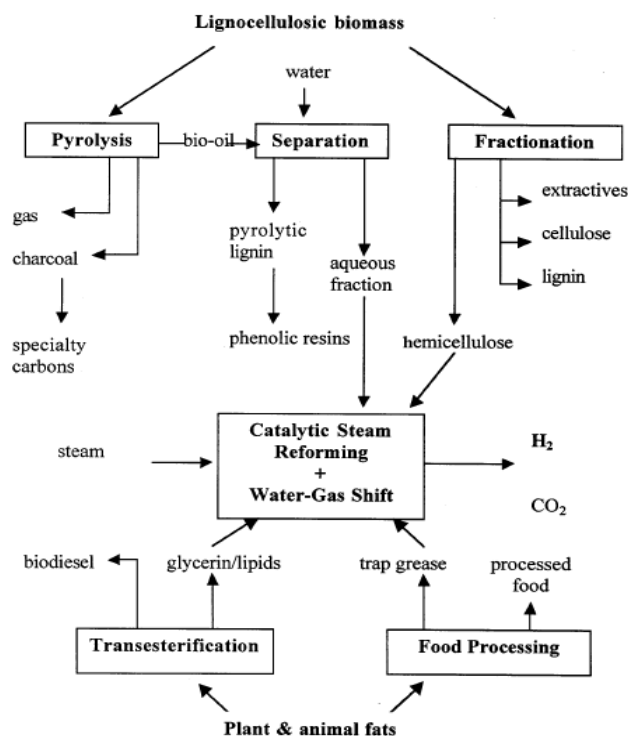
Figure 1.10: Proposed use of biomass in a bio-refinery

The production of these gases from biomass is not seen as a direct replacement for current techniques such as steam reforming of natural gas, but as a number of measures that can utilise all or many of the waste streams from the processing of biomass.

Czernik et al. quote in their paper on this topic, "*The hydrogen content of lignocellulosic biomass is only 6 – 6.5 wt %, compared to almost 25 wt % in natural gas, and on a cost basis producing hydrogen by a direct conversion process such as gasification cannot compete with the well-developed technology for steam reforming natural gas* "(Czernik et al. 2002). Therefore, the gaseous fuels obtained from this feed stock would be uneconomical in terms of recovery and processing energy requirements, with the greatest scope being the by products from a number of bio-industries. An example scenario of this type is shown in **Figure 1.10**.

1.7.8   Gasification

Gasification is the reaction of biomass or any carbon containing fuel with a fixed amount of oxygen or steam to produce synthesis gas or syngas. The benefit of this system is the production of syngas, composed of varying amounts of carbon monoxide and hydrogen. Further reactions (Fischer-Tropsch etc.) can produce synthetic fuels such as diesel or other chemicals.
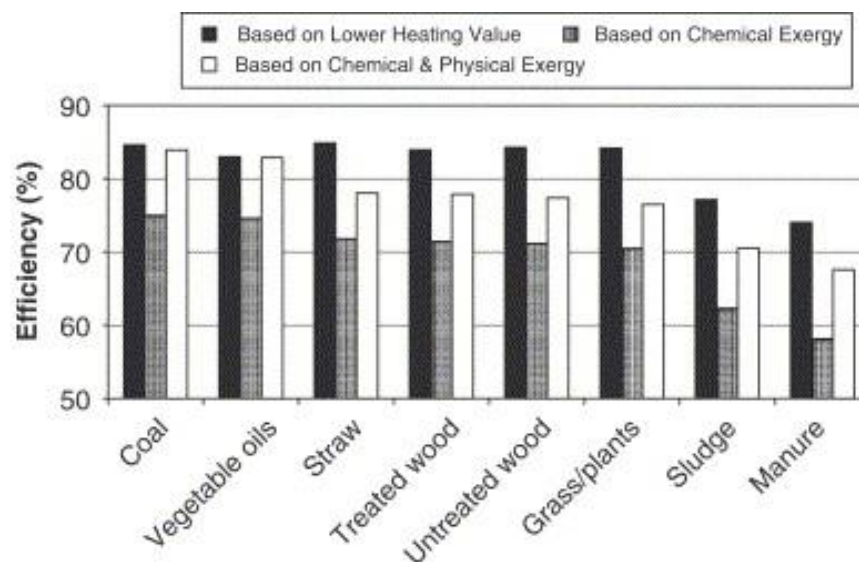
Figure 1.10: Comparison of gasification efficiency for different fuels (Ptasinski et al. 2007)

Figure 1.11 is taken from Ptasinski et. al., 2007. While efficiencies for gasification of biomass appears high, there are a number of assumptions; that equilibrium is reached between gasifier products, ashes are not considered and heat losses in the gasifier and dryer are neglected.

The following reactions take place in the gasifier;

$C + CO_2 = 2CO$, $\Delta H = 172.6kJ/mol$

$C + H_2O = CO + H_2$, $\Delta H = 131.4kJ/mol$

$C + 2H_2 = CH_4$, $\Delta H = -74.9kJ/mol$

$C + O_2 = CO_2$, $\Delta H = -393.5kJ/mol$
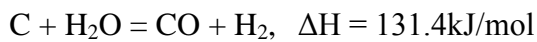
1.7.9 Steam Reforming

Steam reforming, known either as hydrogen reforming or catalytic oxidation, produces hydrogen. Currently most of the hydrogen produced worldwide is as a result of steam reforming of natural gas; however, any hydrocarbon can be used (George W. Crabtree 2004).

At high temperatures (700 – 1100 °C) and in the presence of a metal-based catalyst (nickel), steam reacts with methane to yield carbon monoxide and hydrogen:

$CH_4 + H_2O \rightarrow CO + 3\ H_2$
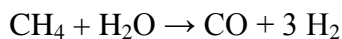
Additional hydrogen can be recovered by a lower-temperature gas-shift reaction with the carbon monoxide produced. The reaction is summarised by;

$CO + H_2O \rightarrow CO_2 + H_2$
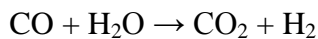
This process has potential benefits with collaboration with HTP of biomass, due to low sulphur contents and therefore less poisoning of catalysts, but mainly due to WSH produced during the reaction with the ability to add extra value to the process.

1.7.10 Hydrothermal processing of biomass

Hydrothermal liquefaction and carbonisation (HTL/ HTC) are biomass thermal conversion techniques that utilise heat, water and pressure for the production of carbon-

rich liquids (HTL) and solids (HTC), as well as water soluble hydrocarbons and CO_2 rich gaseous products. Hydrothermal conversion technology forms part of a patent attributed to Shell International Research .(Annee and Ruytter, 1986). Use of water as a solvent and as a reactant is seen as a promising path for "green chemistry" as it provides safer and less harmful alternatives to acids and toxic solvents. Energy usage is also optimised, as additional energy is not required to evaporate water from the feedstock (Hashaikeh R. et al, 2007). Hydrothermal liquefaction can produce liquid as well as solid fuels and therefore could be imperative in the production of transport fuels after upgrading. As biomass naturally contains water, the costly step of water removal is negated, reducing the processing costs when compared to co-firing.

The Shell patent (Annee and Ruytter 1986) outlines the process of biomass conversion to biocrude by the reaction involving liquid water at temperatures of 300 – 350°C and pressures of 100 – 180 bar, carried out in an autoclave. This process produces heavy oil with a much higher heating value (HHV) compared to natural biomass (15 – 20 vs. 30-35MJ/kg) (F. Goudriaan 2001) achieved by the reduction in the oxygen content of the material. The oil, when analysed by GC-MS, was found to contain a complex mix of chemicals, including phenolic compounds, oil and water soluble hydrocarbons and high molecular weight hydrocarbons. Analysis of the aqueous phase has revealed low molecular weight carbons, alcohols, water soluble hydrocarbons and related chemicals. The following sections provide a succinct summary of research to date in order to set the context for the author's research. Further details of previous work are included within each of the following Chapters, where appropriate.

1.7.10.1 Water

In the development of "green chemistry" and other "green" technologies, the use of hot, compressed water has been of major importance. Water has been found to act as both a reaction medium (and solvent) and as a reactant, negating the use of toxic and corrosive chemicals. The reaction process for biomass offers several advantages; it hydrolyses the usually-water-insoluble lignin, and breaks down the cellulose bonds, creating a range of polar and non-polar chemicals, with alkanes and aromatic products, such as phenolic compounds being produced.

The ability of water to be utilised in this way is due to the change in polarity or dielectric constant that occurs when water is heated. Water is a polar solvent, but when heated, the polarity (or dielectric constant) decreases, allowing compounds that would not usually be soluble in water to become soluble and conversely, usually soluble ionic species such as salts become much less so. The reason for this is the reduction in density of water with increasing pressure and breakage of hydrogen bonds (Shaw et al. 1991) At ~210°C, water has the same polarity as methanol at 25°C This is illustrated in **Figure 1.12**.
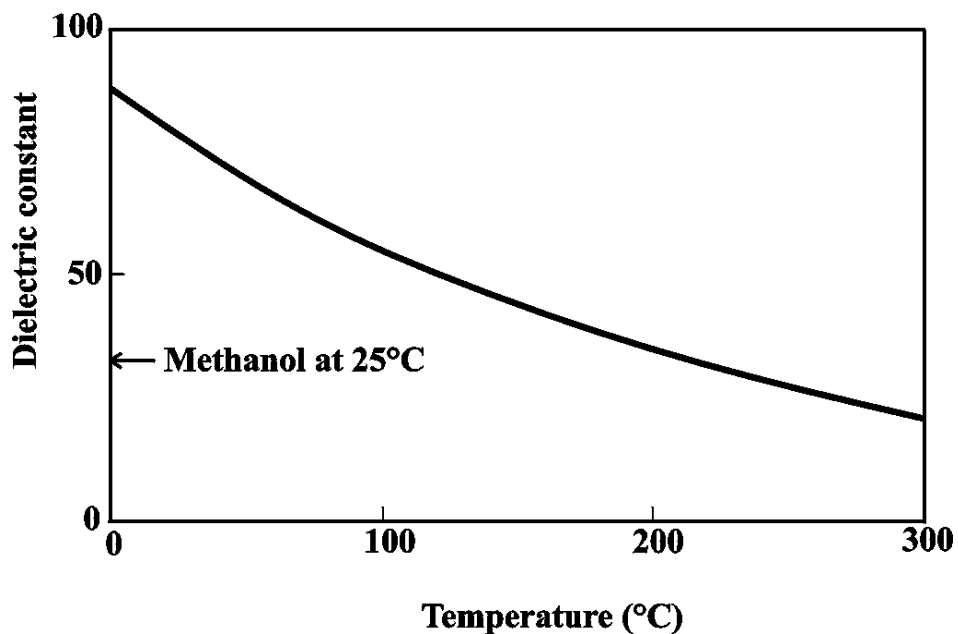
Figure 1.11: The relative permittivity (dielectric constant) of liquid water along the saturation line (Moore)

There are two defined states that occur when water is heated to temperatures greater than 100°C under pressure. From 100 – 374°C, the water is said to be superheated or at the top of the range, sub critical. This process produces a greater proportion of water molecules in the vapour phase, which increases until the supercritical temperature is reached and the water no longer forms 2 distinct phases – liquid and gas, but becomes a homogenous cross between a dense gas and a liquid. At this point the water becomes supercritical and no additional heat or pressure will have a change in the state. "*In the supercritical state, water acts like a dense gas, and organic compounds and gases become soluble, while inorganic compounds such as salt become insoluble* (Kronholm 2002; Moore ; Yesodharan 2002). *Therefore; supercritical water is a suitable medium for the degradation of hazardous compounds*" (Wahyudiono et al. 2007b).

1.7.10.2 Catalysis in hydrothermal liquefaction

The use of catalysts to increase the yields of products or to speed up reactions is of great importance in the chemical industry. It is widely accepted that catalysts are used in ~80% of all industrial chemical reactions due to the commercial benefits such as saving time, raw materials and ultimately money. These catalysts can be divided into two main groups being homogenous or heterogeneous catalysts. Homogenous catalysts take the same physical form as the reactants (or the solvent that the reaction takes place in), whereas heterogeneous catalysts have a different physical state to that of the reactants. Examples of homogeneous catalysts are mineral or organic acids and bases used in liquid reactions, and heterogeneous catalysts are usually solid materials, either powders/ granules in liquid mixtures or metallic surfaces such as those contained in a catalytic converter, where gases are converted.

For each type of catalyst there are pros and cons relating to their use. For homogeneous catalysts, the costs of using the catalyst have to be offset by the overall cost saving by using it, with a possibility of the catalyst being consumed by the reaction. There are various methods of recovery of homogenous catalysts, but again a cost constraint will also be added. Heterogeneous catalysts have generally far fewer problems in their use and are, in the main part, recoverable and reusable. Fixed catalysts such as the type seen in a catalytic converter are in high usage with little or low maintenance, and solid catalysts added to liquid reactions can be removed via sedimentation or filtration techniques.

Hydrothermal liquefaction is more suited to homogenous catalysis as the reaction is carried out in water as both a solvent and reactant, with a large portion of the end products of this reaction being also liquid or water soluble. Recently, a large amount of research has been undertaken in this area and there is information in the literature on the optimal conditions, as well as concentrations and types of catalysts that produce the greatest yields of biocrude from biomass. The most useful and relevant appear to be the hydroxides and carbonates of alkali metals and alkaline earth salts such as NaOH, KOH, Na_2CO_3 and K_2CO_3(Karagoz S. et al 2004, 2005a, b). There is plenty of evidence published for the production of oil from liquefaction, but the author notes that if yields were as high as those quoted by others then the liquefaction process would be deemed as being the most commercially favourable method for the production of biocrude. It

does seem there is insufficient data with regards the amount of energy required to process large volumes of biomass in a batch type HTL system.

Acid catalysis in hydrothermal processing of biomass using HCl, H_2SO_4 and H_3PO_4 is also documented (Li and Zhao 2007), with further studies carried out on glucose, a monosaccharide used to make cellulose, and one of the major components of biomass. This work monitored the production of 5-hydroxymethyl-2-furaldehyde and levulinic acid from glucose, with HCl found to produce the highest yields (Takeuchi Y. et.al 2007).

The following table (**Table 1.2**) contains data pertaining to previous analysis in the field of hydrothermal conversion and the related solid, liquid and gaseous products. It is evident that work on all three biomass model compounds; hemicellulose, cellulose and lignin in a single study is lacking, as is the hydrothermal processing of xylan. Work presented in this thesis in **Chapter 4** contains such a study. Research work on SRC willow and *Miscanthus* energy crops are obvious choices, because of their high yields and ease of planting, and there is little work regarding carbonisation of these. Thus, **Chapter 6** presents results from experiments under HTC and HTL conditions and with a range of catalysts.

Table 1.2 : Comparison of literature review sources

Author(s)	Year	Sample(s) used	Reaction conditions	Catalyst(s) and concentration(s)	Extraction solvent(s)	What analysed?	Analysis technique(s)
Selhan Karagoz, Thallada Bhaskar, Akinori Mutoa, Yusaku Sakata, Toshiyuki Oshiki, Tamiya Kishimoto	2005	wood biomass (sawdust) from pine wood	280°C/ 15 min 3°C/min ramp	NaOH, Na2CO3, KOH and K_2CO_3. (0.94M)	acetone, ether, ethyl acetate	All phases/ Aq by TOC and IC	GC–MS, 1H NMR, 13^C NMR, TOC and ion chromatograph.
Shou-Feng Chen et. al.	2005	Corn stover hydrolysate 100g/l	200°C/3min preheat 160°C/ 6min reaction	1%v/v H_2SO_4 (90%)	Oil not extracted	Aqueous phase	HPLC
D. Meier et.al.	1986	spruce wood, birch wood, bagasse from sugar cane, barley straw, pine bark holocellulose from spruce and birch, organosolve lignins from spruce and sugar cane bagasse and willstatter lignin from birch	to 375°C in 15 mins.	10%Pd on activated charcoal (10% of sample wt)	1-chlorobutane, chloroform, chloroform +6% ether, ether +4% EtOH, MeOH, acetic acid, water. SESC fractionation only.	All phases CHO and calorific value only	None, extraction only
R. Pecina et.al	1986	poplar wood hydrolysate	215°C, unknown ramp and residence time	Not stated	Chloroform/ P_2O_5 Derivatized with 1ml BSTFA	Aqueous phase	HPLC, GC-MS
Mitsuru Sasaki	2000	cellulose	320-400°C, 0.05 - 10s residence time	None	None	All	HPLC, 1H NMR, FAB-MS, IR
Helene. B. Klinke et al	2002	wheat straw	185 and 195°C 10-15 min residence	Na_2CO_3	None, Filtered only (SPE for GC-MS)	All	TOC, HPLC (RI/UV), IC

Author(s)	Year	Sample(s) used	Reaction conditions	Catalyst(s) and concentration(s)	Extraction solvent(s)	What analysed?	Analysis technique(s)
Tsuyoshi Sakaki et.al	1995	cellulose	250°C for 3 mins preheat then 335/ 355 and 405°C for 15s	None/ CO_2 purged.	Methanol	Solid and Aq. Phase	Solid- IR, liquid HPLC (UV/RI) 254nm, 2 columns
S Karagoz et.al	2005	wood biomass (sawdust) from pine wood	280°C/ 15 min 3°C/min ramp	RbOH and CsOH/ N_2 purged	acetone, ether, ethyl acetate	Oil fractions only	GC- MS, C-NP characterisation
Amie Sluiter et al	2007					Carbohydrate and lignin in solid biomass	HPLC (RI) UV spectrometer,
G. Bonn et.al	1988	wheat straw	200°C as per ref	water/ aq. Methanol (1:1)	None/ ultrafiltration	WS only/ organic acids	Isotachophoresis/ HPLC (cond) IC
G. Bonn et.al	1984	poplar wood and filter-paper hydrolysate	200°C	Not stated	Filtered only/ reverse osmosis concentration	WS only, sugars, gluco-oligomers	HPLC (RI)
Guanghou Shui et al	2002	fruit juices	N/A	N/A	None, filtered only	Juice	HPLC (DAD)
Tsuyoshi Sakaki et.al	1996	cellulose	250°C for 3 mins preheat then a range 337-353 for 15 - 40s	None/ CO_2 purged.	Methanol	Solid and Aq. Phase	Solid- IR, liquid HPLC (UV/RI) 254nm, 2 columns, GPC.
F. Taner et al.	2004	aqueous slurries of cotton stalk/ SEKA solid waste	300 and 350°C for 1 hour	NaOH or acetic acid (Solid 20% by mass)	Chloroform and dichloromethane	Aqueous phase	TLC, UV/Vis spectroscopy, GC, GC-MS

Author(s)	Year	Sample(s) used	Reaction conditions	Catalyst(s) and concentration(s)	Extraction solvent(s)	What analysed?	Analysis technique(s)
S Karagoz et.al	2005	wood biomass (sawdust) from pine wood, rice husk, lignin and cellulose	280°C/ 15 min 3°C/min ramp	None	acetone, ether, ethyl acetate	Oil fractions only	GC-MS, CH-P
Chongli Zhong, X Wei	2004	*Cunninghama lanceolata, Fraxinus mandshurica, Pinus massoniana Lamb* and *Populus tomentosa Carr.*	Ramp ~60 mins, residence time 10 mins. 553, 573, 593, 613 and 633K	K_2CO_3 0.8g/ 8g mass	acetone	Yields, CHNO, HHV	elemental analysis
C. Li and Z.K. Zhao	2007	cellulose various DP's	100°C, 3- 1080 mins	H_2SO_4, HCl, HNO_3, H_3PO_4	None	glucose/ TRS	ion exchange resin, glucose analyser
A. Demirbas	1997	Various woody biomass	498K, 3-9 hrs	NaOH/ Na_2CO_3/ none	None	Delignification of samples	Various lignin/ hemi/ cellulose methods
Fangming Jin et al.	2005	rice hulls	300°C 1-7 min	H_2O_2	None	Liquid phases only	GC-MS, HPLC(UV/Vis, RI) TOC,
A. Demirbas	1999	Various woody biomass	to 575K over 30 mins. To rt over 1hr.	KOH (1/5, w/w)	Acetone	Oil and residue only	Yield via calculation and weight only
A. Demirbas	1996	Various woody biomass	513/560/563 and 653K	NaOH and Na_2CO_3	Acetone, methanol, ethanol and water (reaction solvents)	Oil and residue only	Yield via calculation and weight only. SCAE fractionationof beech

Author(s)	Year	Sample(s) used	Reaction conditions	Catalyst(s) and concentration(s)	Extraction solvent(s)	What analysed?	Analysis technique(s)
Chunbao Xu	2007	Pinus banksiana (Jack pine)	200, 220, 240 and 260°C 15-60 mins	FeS, H_2 and $FeSO_4$	ethanol and acetone	Oil and residue only	GC-MS, elemental analysis, calorific value
C. Wang et al.	2008	legume straw, corn stalk, cotton stalk	10°C/ min to 350°C 2-3hrs.	None	Distillation used to separate	Oil/ gas	CHN/O, GC-TCD for gas. FTIR and GC-MS for oil
Fangming Jin et al.	2007	Various carbohydrate and lignocellulosic biomass	250 to 400°C, 10-300s	H_2O_2 10-15%	Not extracted	Liquid phases only	GC-MS, HPLC, TOC
Wahyudiono et al.	2007	Guaiacol, catechol, phenol and 0-crescol	653, 663 and 673K, 5-120 mins	None	Methanol	Aqueous phase, solid residue	GC-MS, HPLC, MALDI, FTIR
R. Hasaikeh et al.	2006	Willow	215-300°C, to 40 mins	None	None	TOC of extract over time	DAC and pictures mostly
Y. Qian et al.	2007	Silver birch	280-420°C, unknown	Sodium carbonate	Acetone	Oil	FTIR, GC-MS
A. Demirbas	2001	Various	525-600K	Sodium carbonate			
Z. Srokol et al.	2004	Carbohydrate model compounds	340°C, 25-204s	NaOH, HCl 6mM	None	Liquid phases only	HPLC (RI/ UV), 1H NMR
A. Demirbas	2007	tobacco stalk and yellow pine	625-875K, ~50s		DCM	Oil	GC - FID
J.H.Marsman et al	2007	Pyrolysis oil		Solid.			GC/ GC-MS
H.Yang et al	2007	cellulose, hemicellulose and lignin				Solids, gases	TGA, FTIR, GC-TCD

1.8 Analysis/ characterisation of hydrothermal liquefaction products

The main products of hydrothermal liquefaction (biocrude and an aqueous phase) are a multitude of chemicals. The composition of biocrude is different to crude oil composition. The nature of products derived from degradation of lignocellulosic material are largely substituted aromatic compounds including furans and cyclic hydrocarbons (Karagoz S. et al 2005a). By comparison, the composition of crude oil, depending on the source, consists of alkanes with the chemical composition C_nH_{2n+2}, naphthenes or saturated cyclic hydrocarbons, aromatic and asphaltic material. Crude oil is also characterised by very low oxygen contents (0.05% - 1.5%). In contrast, biomass oils have oxygen contents in excess of 10%, this can increase to 25% in the case of pyrolysis oils. Biocrude has a widely different composition and cannot be used in the same way as fossil crude oil due to problems such as viscosity (Sarma 2006).

To better understand the processes involved during hydrothermal liquefaction, a great deal of research has concentrated in the area of model compounds. (**Table 1.2**) This work has centred on the major components of biomass (lignin and cellulose), with little focus on hemicellulose. There is a general agreement as to the product types that are produced as each of the components are processed, be they gases, liquids (oils and aqueous phases) and chars, but there are large variations in yields with processing methods and the characterisation of products formed, along with their suitability for fuel purposes.

Each biopolymer has a different decomposition rate and decomposition temperature. Hemicellulose is the compound that breaks down with the mildest experimental conditions, followed by cellulose. Thermal decomposition of lignin proceeds over a wide temperature range. It is this difference in the rapid degradation that is most exploited by torrefaction (discussed in **Chapter 1.5.5**). Unfortunately, due to the difficulties in removal, lignin in particular, is very hard to isolate or buy in a pure form, so compounds such as guaiacol have been studied in order to relate the decomposition of guaiacol to its derived compounds (Wahyudiono. et al 2007). Compounds detected in the aqueous solution were mainly catechol, phenol and *o*-cresol, with a reaction mechanism proposed (**Figure 1.13**).
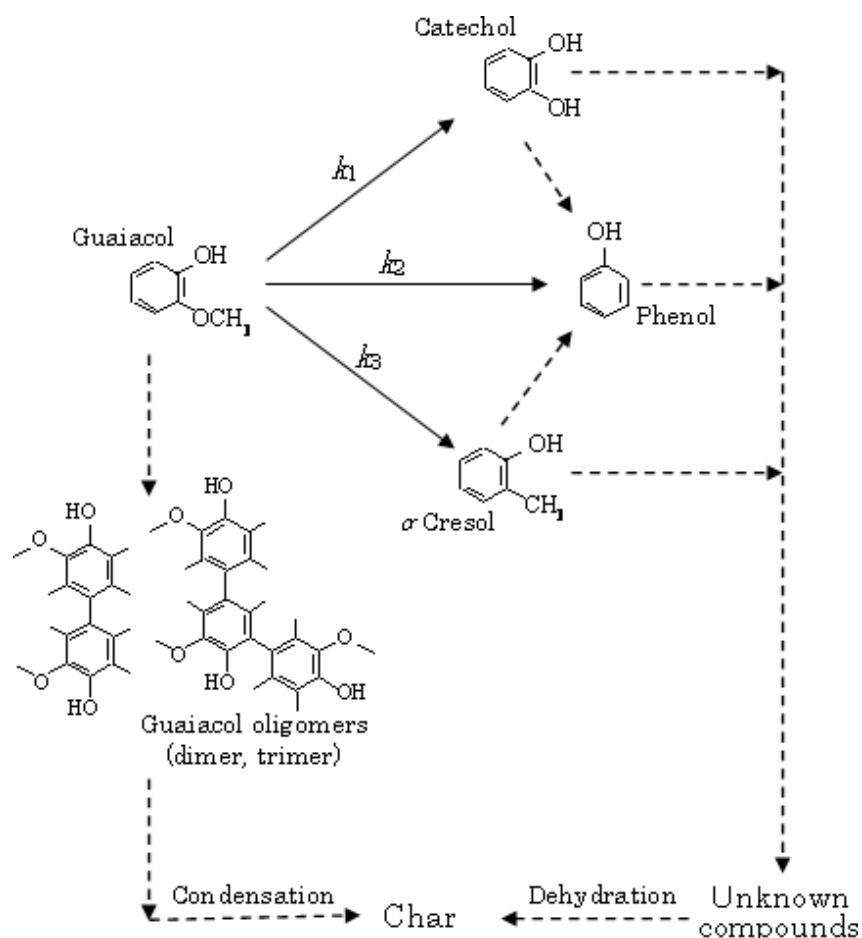
Figure 1.12: Simple reaction pathway for guaiacol in near critical and supercritical water (Wahyudiono et al. 2007a)

Analysis of the aqueous phase produced during hydrothermal liquefaction by gas chromatography and GC-MS has resulted in a number of chemicals being found contained within. All data produced in this area of analysis have confirmed the presence of oxygenated aromatic compounds, aldehydes, ketones, alcohols and water soluble hydrocarbons (WSH), but there is little analysis by high performance liquid chromatography (HPLC), this appears unusual to the author as reverse phase HPLC has the capacity to directly analyse the samples in the water phase with little or no modification of the water phase directly. By calibrating the equipment and using external or internal standards depending on the compound(s) in question, these could be quantified with a view for extraction if the amounts were significant enough.

1.8.1 The importance of oxygen

Biomass and its constituent components contain a varied amount of oxygen with the highest percentage contained in cellulose (carbohydrates) and hemicellulose (ca. 50%).

Lignin contains approximately 30% oxygen. Thus, the relative proportions of biopolymers in a biomass have an effect on the oxygen content of the resulting oil produced by liquefaction. It has been discovered that the lower the lignin content, the higher the conversion of carbohydrates into volatile and soluble products, with a low oxygen content in the solid remnant (Demirbas 2000). Crude oil contains not more than 2 wt.% oxygen (**Table 1.3**), so has little effect on the stability and the use of derived fractions as fuel, however, synthetic oils such as those produced from coal and biomass may contain >10 wt.% with biomass itself containing up to 50 wt.% oxygen. It is believed that the poor combustion characteristics of biomass derived synthetic oils are due to the polymerisation of some O-compounds in the feed leading to fuel instability, which in turn leads to poor performance during fuel combustion.

Table 1.3: Comparison of elemental analysis of oils from crude, coal, oil shale and biomass

	Conventional crude	Coal-derived naphtha	Oil shale crude	Bio-oils	
				Liquefied	Pyrolyzed
Carbon	85.2	85.2	85.9	74.8	45.3
Hydrogen	12.8	9.6	11.0	8.0	7.5
H/C	1.8	1.4	1.5	1.3	2.0
Sulphur	1.8	0.1	0.5	< 0.1	< 0.1
Nitrogen	0.1	0.5	1.4	< 0.1	< 0.1
Oxygen	0.1	4.7	1.2	16.6	46.9

Chapter 2 – Aims and Objectives and Thesis Overview

The research contained in this thesis concentrates on two main areas of thermochemical conversion, hydrothermal liquefaction and hydrothermal carbonisation. Products from these techniques are compared respectively with those typically observed from low temperature pyrolysis or torrefaction. The purpose of the research is to better understand the process whereby biomass is converted to either hydrocarbon rich oil, or a carbon-rich solid, when using water as a reaction medium. Specific aims are as follows:

1. To replicate hydrothermal liquefaction experiments from literature sources (300 - 350°C with 1M KOH as a reaction additive) so as to provide a suitable experimental starting point for direct comparison.

2. To use these baseline experimental conditions to study the hydrothermal liquefaction of cellulose, hemicellulose (xylan) and lignin and compare results to available data in the literature.

3. To extend the study on hydrothermal liquefaction of model compounds to examine the importance/role of the catalyst, the temperature, and the reaction time using a factorial experimental design matrix.

4. To study hydrothermal processing of two energy crops, *Miscanthus* and SRC willow, under a range of conditions; variables included catalyst type and temperature.

5. To compare products from hydrothermal carbonisation to those from torrefaction

For each aim, specific objectives are:

a) To obtain, where possible, a mass balance on the products from each set of reaction conditions, and to isolate products for further analysis.

b) To fully characterise the solid products for ultimate analysis, heating value ash contents, and thermal behaviour via thermogravimetric analysis.

c) To characterise the bio-crude for ultimate analysis, heating value, qualitative composition (via GC-MS), and simulated distillation by TGA.

d) To characterise qualitatively the water soluble organics by TOC, HPLC, and, after extraction, by GC-MS.

e) To characterise the main components in the gas phase by GC-TCD-FID.

f) To interpret the data sets produced in order to comment on the reaction pathways occurring during hydrothermal processing, and/or optimal processing conditions to maximise the yields of desired products.

The Thesis is split into 4 chapters as follows:

Chapter 4 contains reaction data from hydrothermal liquefaction reactions of biomass model compounds, cellulose, xylan and lignin using homogeneous KOH catalyst at 1 and 0.1M concentrations

Chapter 5 contains a factorial study on the effect of temperature, reaction time and catalyst has on individual lignocellulosic components under hydrothermal conditions, with analysis of products.

Chapter 6 contains HTP reactions of 'real world' biomass samples, willow and *Miscanthus* under HTL and HTC conditions and with a range of catalysts.

Chapter 7 contains a comparative study of hydrothermal carbonisation (known also as 'wet' torrefaction) and 'dry' torrefaction, with examples of analysis of torrefied materials produced by the author during employment at Arigna Fuels Ltd, Co. Roscommon, Ireland from Dec 2010 to Dec 2011.

Chapter 3 – Experimental Section

3.1 Introduction

The following chapter contains detailed information on equipment and analytical techniques used throughout this thesis. This also includes hypotheses, methods and assumptions derived from literature sources, providing a suitable starting point for the research to follow.

3.1.1 High Pressure Reactor

The high pressure reactor supplied by Parr (**Figure 3.1**) was used to perform the following liquefaction and carbonisation experiments. It is not equipped with a stirrer or any agitation device; hence all samples need to be homogenous prior to commencement of reactions. The reactor is rated to 515 Bar pressure and 600°C, with thermocouple and pressure transducer attached for accurate measurement. The temperature controller attached is a CAL 9500P with PID.

Heating rates are fixed at 10°C/ min, with a delay over the first 2-3 minutes due to the heat capacity of the stainless steel reactor. The thermocouple is situated in the base of the reactor meaning that the temperature measured is as close to the temperature of the reactants when compared to the heat supplied from the external heating jacket.

Figure 3.1: Parr reactor with heating jacket, pressure transducer and pressure gauge

3.1.2 Method

To the reactor are added X_1 g of the finely ground raw material (cellulose, lignin, biomass etc.) at a particle size of less than 1mm and X_2 g of liquid reaction medium/ solvent. The resulting solution is stirred until homogenous.

A program is entered into the CAL 9500P programmer and the heating rate is controlled automatically to the temperature set point (T_1) and manually via stopwatch to the final residence time (t_1). When the appropriate temperature is reached and after the required residence time has elapsed, the heating jacket is then removed and blown with compressed air, allowing the reactor to cool to <40°C where the final pressure is recorded in Bar. All reaction conditions for experiments in this study are included in **Table 3.1**.

Table 3.1: Reaction conditions for hydrothermal liquefaction and carbonisation

Reaction Variables	Liquefaction	Carbonisation
Heating rate (°C min^{-1})	10	10
Residence time (minutes) (t_1)	0 – 60	10 – 1080
Reaction temperature (°C) (T_1)	250 – 350	200 – 250
Reaction medium/ solvent and weight (g) (X_2)	Water/ KOH 1.0 and 0.1M, Acetic acid, formic acid, Na_2CO_3 1M. 20 – 25g	Water/ KOH 1.0 and 0.1M. 20 – 25g
Substrate	Lignin, hemicellulose, cellulose, Willow and *Miscanthus Giganteus*	Lignin, hemicellulose, cellulose, Willow and *Miscanthus Giganteus*
Sample weights (g) (X_1)*	2 – 10	2 – 5

*Note: Initially, 10g of raw material and 30g of 1.0M KOH solution were added, but this caused problems when releasing pressure at the end of the reaction, with product being expelled via the gas lines.

To capture evolved gasses, vent lines are first purged with nitrogen prior to the pressure release and resultant reaction gas capture is achieved via a gas sampling bag (Tedlar bag) or in the case of low pressure (1-2 Bar), via a gas syringe.

After the gas has been captured the reactor is removed to the fume cupboard for extraction of the products. The aqueous phase is decanted and weighed, then filtered via a syringe filter to remove any particulates or oil. The oil phase is then removed with 5 x 10ml aliquots of dichloromethane (DCM) solvent. The solvent is then evaporated, leaving oil. Any remaining product not soluble in DCM is classed as residue/ char.

From the residual pressure, the volume of gas produced can be calculated. The gas was also analysed for main components via GC, and from the volume of gas injected, the number of moles of each gas component can be identified.

3.2 Analytical test methods for liquefaction products

The gas phase was analysed by GC – TCD and FID for hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide and hydrocarbons.

For the aqueous phase, this was first extracted with dichloromethane (DCM) (ratio 50:50), with the DCM fraction dried using sodium sulphate and analysed by GC-MS. The extracted aqueous phase then analysed by reverse phase HPLC.

The oil fraction was obtained after DCM was dried from each extract. This was analysed by CHNO, TGA, simulated distillation and TOC

The DCM insoluble, acetone soluble and insoluble residue/ char was analysed by TGA, and via Coal/ bitumen test methods including CHNO.

Details of these tests are given in the following sections.

3.2.1 Thermogravimetric analysis (TGA)

TGA is used to determine temperature related phenomena in a range of materials. These phenomena include thermal stability, volatiles content and the ash content (residue after heating).

TGA is usually undertaken in either an inert atmosphere (helium, nitrogen) or in an oxidative atmosphere with a linear temperature ramp, but can also be used with restricted oxygen and with oxygen introduced after a fixed heating period. The system employed at Leeds has also an inert reference allowing the measurement of the temperature difference between the sample and reference pan, known as differential thermal analysis or DTA. Samples analysed by TGA can give a range of information on the thermal stability, by showing weight changes due to losses at certain temperatures.

The three main analyses carried out on biomass via TGA are (I) Proximate analysis, (II) Simulated distillation and (III) Investigation of combustion behaviour (burning profiles)

For proximate analysis, samples (< 6 mg) are heated at 25°C/ min initially in a nitrogen (oxygen depleted) environment to 105°C, to obtain the moisture content. The temperature is then increased to 900°C to determine losses that correspond to volatile components. The temperature is then lowered to 700°C where air (oxygen) is introduced and heated back up to 815°C to allow the final oxidative reaction, burning the fixed carbon until a fixed weight is achieved (10 minutes), this leaves any inorganic residues (ash). Ash content can be anything from $1 - 15\%$ depending on the source of the biomass, those from agricultural residues having the higher concentration of inorganic material as a result of fertilisers and pesticides. Proximate analysis therefore allows the simultaneous detection of moisture, volatiles, fixed carbon and ash content.

Simulated distillation (SD) via TGA involves heating a sample over a suitable heating range ($40 - 500^{\circ}$C) using a slower heating rate ($5 - 10^{\circ}$C/min) and under oxygen deficient conditions to suppress combustion at higher temperatures. Post run analysis allows the determination of component area percent that are evaporated between temperatures, allowing a comparative SD profile to be constructed. This method is comparable to other simulated distillation chromatographic techniques (Li et al. 2001)

Burning profiles involve heating samples in an oxidative atmosphere. The differential is then taken of the TG signal to produce DTG graphs. For biomass compounds, thermal degradation of hemicellulose, cellulose and lignin can be observed via these graphs, which can also include exothermic reactions, identified when volatiles and char are combusted.

Equipment used − Stanton Redcroft STA-780 series thermal analyser, DC amplifier, balance control and U.T.P. **Figure 3.2.**

Figure 3.2: Stanton Redcroft TGA analyser

3.2.2   High Performance Liquid Chromatography (HPLC)

HPLC is an analytical technique that utilises the difference in attraction between mobile and stationary phases and the sample being analysed. "It is a form of partition chromatography and is based on liquid-liquid partition where one liquid is the mobile phase (eluent) and the other is a thin film of the stationary phase over the surface of and in the pores of the support. In most cases the support is the silica used in adsorption chromatography, but covalently bonded to this is one of a number of chemical groupings which produces an appropriate reduction in polarity, e.g. C_{18}" (Ardrey 2003)

HPLC systems can be split in to two distinct groups – reverse phase and normal phase. Reverse phase is a system in which the mobile phase (eluent) is more polar than the stationary phase. These systems are likely to contain a greater proportion of water and are the most commonly used.

Normal phase is a system in which the mobile phase is less polar than the stationary phase and is likely to contain no or very little water.

The HPLC system consists of mobile phase, pump, injector, stationary phase and detector. Each item can be tuneable depending on the required use and can be employed to separate and detect thousands of different compounds.

3.2.2.1 Pump

There are two types of pump, isocratic and gradient. Isocratic pumps deliver a constant flow of mobile phase through the system at a fixed rate of flow, usually in the region of 1ml/ min. These are used in (generally) more simple analyses that involve the separation of a few compounds. Gradient pumps are more advanced and can cope with two or more eleuents, giving the user the ability to separate analytes with wildly differing polarities in the same chromatographic run.

3.2.2.2 Injector

This is the method of introduction of a liquid sample to the HPLC system. These are usually of the "loop" type and consist of a metal sample loop with a fixed volume of ~5 - 100µl. The loop injector can be filled fully or partially and is fully flushed out with mobile phase as the sample is introduced or injected into the system. The loop system is very efficient as there are negligible sample losses as all the sample makes its way to the column for separation.

3.2.2.3 Mobile and stationary phase

Separations take place in the stationary phase or column, dependent on the relative polarities of the stationary phase, mobile phase and analytes. The column is packed with tiny coated silica beads from 3-10µm in size. The coating is the stationary phase and is where the attraction to the analyte takes place. Compounds that exhibit a greater attraction to the mobile phase will stay in solution and be first out of the column to the detector. Those that are attracted to the column will be retained for a greater period of time and be detected later. A change in concentration of the mobile phase or solvent as per gradient analysis may allow those compounds that are strongly attracted to the column to be removed at a time that does not interfere with other eluting analytes and hence increase the resolution of the peaks.

3.3.2.4 Detectors

HPLC detectors can be classified in a number of ways. They can be general or selective, measure the solvent or the solute property or they can measure the concentration or be mass selective (classification can be obtained by turning the LC pump off at a peak maximum. If the device is concentration dependent, the signal intensity remains constant, if it is mass dependent; the signal will drop to zero).

A concentration sensitive detector is one for which the signal intensity is proportional to the concentration of the analyte in the mobile phase. These detectors are UV, fluorescence and refractive index (RI).

A mass selective detector is one in which the signal intensity is proportional to the mass flux, i.e. the number of analyte molecules reaching the detector per unit time; conductivity and mass spectrometer.

Solute property detectors measure properties of the analyte and may be used with gradient elution as changes in the concentration of the solvent are not measured. As a result of this, detectors can be chosen with a high degree of sensitivity and selectivity. Solvent or bulk property detectors monitor changes in a physical property of the mobile phase, caused by the elution of an analyte. These detectors are refractive index and conductivity and are not ideal for use with gradient elution. They are usually of limited sensitivity and dynamic range, but are not considered as "universal detectors".

HPLC is potentially the most effective method of analysis for the quantitative and qualitative determination of the aqueous phase produced during the liquefaction of biomass. Previous work in this particular field has met with a great deal of sample manipulation and processing prior to analysis (Karagoz S. et al 2005b) owing to the difficulty in separating the compounds contained within. The main issues appear to be the relative similarity in polarities between the compounds, (Shou-Feng Chen. et al 2006) and the subsequent identification, given that in HPLC, standards of known concentrations need to be injected first and in multiples to obtain the correct retention time, allow for quantification and ensure peak reproducibility. DAD is an important tool to aid the identification of compounds, given that each correctly resolved peak should have a distinct UV/Vis profile over a wavelength range.

The solvents acetonitrile and water are chosen due to their transparency in the lower regions of UV and can be used as low as 190nm in a 1cm cell. (Ian Fleming and Williams 1995)

3.2.3   Gas Chromatography, py-GC-MS, GC-MS and GC-TCD/FID

Gas chromatography (GC) is an analytical technique used for the separation of compounds in either the liquid or gas phase. As with all chromatographic systems, the GC contains four components, sample introduction (injector), mobile phase, stationary phase and a detector. The chromatographic process proceeds via the following: "A mixture is introduced as a narrow band on the top of a column and the components of this are separated by differential distribution between the mobile and stationary phases." (Ardrey 2003) Following this separation, the compounds migrate through the column to the detector. This then converts the response to an electrical signal via a number of potential routes (TCD, FID, etc.) or, if equipped, introduces the compounds via an interface to a mass spectroscopic detector (GC-MS) (**Figure 3.3**).

Py-GC-MS is used on solid samples and subjects them to pyrolysis conditions, separating the resulting compounds via a capillary column and analysing them with a mass spectroscopic detector. The results of which, when compared against various library data, gives information into the types of compounds that are created during pyrolysis, many of which are also formed and identified during the liquefaction process. For this thesis, GC – TCD and GC – FID are used to separate gases, enabling the qualitative and quantitative detection of hydrogen, oxygen, nitrogen, carbon dioxide, carbon monoxide and hydrocarbons.

Analysis of the extracted aqueous fraction is carried out by GC – MS, giving compounds present that are soluble in the DCM fraction.
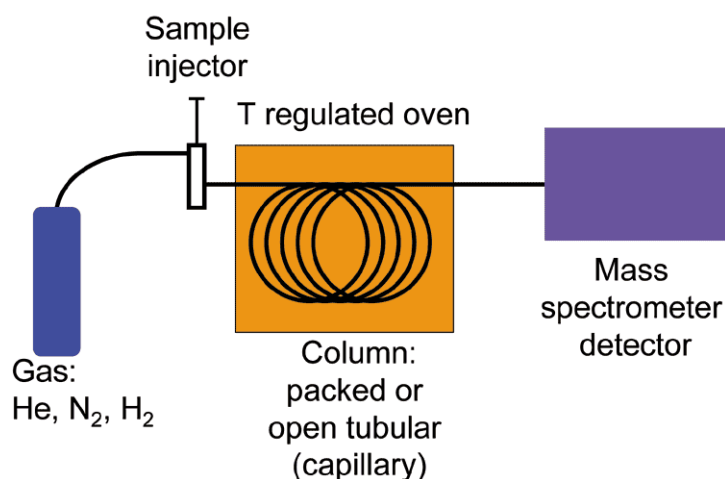
Figure 3.3: GC – MS schematic diagram (Miao et al. 2004)

GC – TCD set up for measurement of CO_2

GC – Pye Unicam series 204 chromatograph

Column – Silica gel 6' 0.25" packed column 100 – 120 mesh

Oven temp – 96°C

Injector temp – 100°C, 1ml injected

Detector temp – 100°C

Carrier gas – Argon

Gas flow rate – 23 ml/ min

GC – FID set up for measurement of permanent gases

GC – Pye Unicam series 204 chromatograph

Column – Molecular sieve 3' 0.25" packed column

Oven temp – 96°C

Injector temp – 100°C, 1ml injected

Detector temp – 100°C

Carrier gas – Argon

Gas flow rate – 23 ml/ min

GC – MS set up

GC – Agilent 6890N fitted with 5975B Mass Spec. detector

Column – DB – 1701 60m x 0.25mm x 0.25μm serial no. 723377

Oven temp/ ramp – 40°C for 2 min, then 4°C/min to 250°C, hold for 30 mins

Injector temp – 200°C, 5μl injection volume

Carrier gas – Helium

Split pressure/ ratio – 206.832 kPa, 20:1

Mass Spec range 50 – 550 mass units, 150°C Quad temp, 230°C source.

3.2.4 Analysis of gases via FID/ TCD

These analyses were carried out on a Pye Unicam series 204 chromatograph fitted with separate injection ports and respective FID and TCD detectors. This allowed quantitative analysis of the gases produced, due to the equipment being regularly calibrated with test gases. The sampling technique used initially was to have a Tedlar

bag liked up to the apparatus with an in-line trap to catch any liquids forced out under pressure. This method of collecting the gases proved not to be ideal, because the pressures involved were relatively low (<3 Bar). After the venting lines had been purged with nitrogen, the product gas was vented through the lines and the gas trap, resulting in a small volume of gas in the Tedlar bag. This gas would then be contaminated with an unknown volume of nitrogen, allowing problems with the resulting analysis. A much simplified method of extraction was to use a gas syringe with a rubber stopper, previously purged with nitrogen.

The equipment contained a molecular sieve column coupled with an FID detector and a silica gel column attached to a separate TCD detector, as described in the previous section. As a result, the GC would not allow a single injection of gas to complete both analyses.

Calculations for determination of the moles of gas present used the following ideal gas law equation (**3.1**):

$$PV = nRT \tag{3.1}$$

P = pressure (kPa)

V = volume (L)

n = moles of gas

T = temperature (K)

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ (gas constant)

The total volume of gas produced in the reaction was estimated from reading the pressure transducer at a known temperature. This was converted to total moles of gas produced using equation (**3.1**). Once the composition of the gas mixture was known (from the GC analysis), moles of each component could be determined via equation (**3.2**):

$$n_i = C_i.n \tag{3.2}$$

Where n_i = moles of component i and C_i = concentration of component i.

3.2.5   Solvent extraction

Solvent extraction of the aqueous phase by dichloromethane (DCM) is a simple technique that can be used to isolate samples suitable for GC-MS analysis, extracting

components that make up the oil. Also, water containing samples cannot usually be run through GC columns. Solvent – solvent extraction using immiscible solvents such as water and dichloromethane help to overcome this.

The separation takes place by adding equal amounts of filtered aqueous phase to DCM (5ml and 5ml respectively) in a separating funnel and shaking for 1 minute. During this time compounds are extracted into the DCM (organic) phase.

The contents are left to settle with the organic layer decanted into a clean glass container containing ~ 1g anhydrous sodium sulphate to absorb any water that may be present.

After half an hour, the organic phase is then transferred to a capped glass vial ready for injection into the GC-MS, as described in **Section 3.5**.

3.2.6   CHNS Analysis, or Ultimate Analysis

Combustion analysis is a method used in both organic chemistry and analytical chemistry to determine the elemental composition (more precisely empirical formula) of a pure organic compound by combusting the sample under conditions where the resulting combustion products can be quantitatively analysed. Once the number of moles of each combustion product has been determined the empirical formula or a partial empirical formula of the original compound can be calculated.

3.2.6.1   Method

Into a tin weighing cup is added 2.50 – 3.50 mg of sample, accurately weighed to 2 decimal places on a microbalance. The cup is then crushed into a small ball, taking care to expel all the air and not to split it. The sample is then pyrolised in a reactor, attached to a GC, where the products are analysed. In this case a CE Instruments Flash EA 1112 Series was used, as shown in **Figure 3.4**. Carbon is measured as CO_2, hydrogen as H_2O, nitrogen as NO_2 and sulphur as SO_2. The difference between total CHNS (and any moisture) is oxygen and inorganic material or a combination of the two. Further proximate analysis (**Section 3.2.7**) determines ash and moisture content and enables the oxygen content to be calculated by difference.

Figure 3.4: CHNS analyser, CE Instruments Flash EA 1112 Series

3.2.7 Proximate analysis

Proximate analysis gives information on moisture content, volatile content, free carbon and the ash (or inorganic material) in the sample. The combination of proximate and ultimate analyses can be used to estimate the high heating value (HHV) of the sample, based on the complete combustion of the sample to CO_2 and water. Both ultimate and proximate analyses are useful for the grading or rank of biomass, coal and liquefaction products.

Analyses on samples (sieved to below 1mm) are carried out con-currently. Test methods followed are as follows:

1. Preparation – European standard (prCEN/TS 14780)
2. Moisture content – CEN/TS 14774-3:2004. 1 g sample dried in a Carbolite MFS oven at $105^{o}C$ in an inert atmosphere (nitrogen) until constant weight.
3. Ash content – DD CEN/TS 14775:2004. 1 g samples undergo slow combustion in a Carbolite OAF 10/1 furnace at 800°C and the residue mass is measured.
4. Volatile content – BS 1016-104.3:1998 (From ISO 562:1998). 1 g sample heated in a lidded crucible to $900^{o}C$(+/- 5°C) for 7 min (+/- 5 sec). This was measured using a Carbolite VMF furnace (+PID/CHIM)
5. % Fixed carbon is calculated using the following equation:

Fixed carbon (%) = 100 − Ash (%) − Moisture (%) − Volatiles (%)   (**3.3**)

3.2.8   Total Organic Carbon

Total carbon content or TC is a measurement of carbon present as compounds in aqueous media. It is routinely used for wastewater analysis as a measure of purity, detecting levels of contaminants from industrial sources, decaying organic matter and from surface runoff from agricultural sources i.e. fertilisers, pesticides and herbicides. TC includes total inorganic carbon (TIC) and total organic carbon (TOC). TOC is carbon content derived solely from organic sources, be they decaying plant matter or microorganisms (bacteria/ fungi etc.).

The three stages of analysis are 1, acidification, 2, oxidation and 3, detection and quantification. The first stage removes TIC (dissolved CO_2 etc.), then oxidation of the organic carbon occurs either via combustion with an oxidising gas or chemically by using a persulphate solution and heat catalysis. Detection is carried out using thermal conductivity detector (TCD) as per GC analysis or from use of a nondispersive infrared detector (NDIR).

3.2.9   Atomic Emission Spectroscopy

Atomic emission spectroscopy (AES) is an analytical technique, which allows the quantitative measurement of emissions from excited atoms to determine analyte concentration. This is achieved by aspirating analyte atoms in solution into the excitation region where they are desolvated, vaporised, and atomised by a flame. These high-temperature atomisation sources provide sufficient energy to promote the atoms into high energy levels. The atoms decay back to lower levels by emitting light. Since the transitions are between distinct atomic energy levels, the emission lines in the spectra are narrow. The spectra of multi-elemental samples can be very congested, and spectral separation of nearby atomic transitions requires a high-resolution spectrometer. Since all atoms in a sample are excited simultaneously, they can be detected simultaneously, and is the major advantage of AES compared to atomic-absorption (AA) spectroscopy – (Johnson 2007) dissertation.

Calibration solutions were made from Na+, K+, Mg+ and Ca+ stock solutions at 1000ppm. Automatic calibration was carried out using the built in diluter to achieve linearity. The Varian AES was installed with 4 detection lamps to allow simultaneous detection of all the metal atoms from one solution.

Aqueous phases from hydrothermal processing were filtered through 0.2μm PTFE filters and diluted 1mL into 10mL volumetrically, prior to analysis.

3.3   Error study

3.3.1   Introduction

By their very nature, laboratory and research experiments are subject to errors. These are either systematic or random and are determined by the equipment used, the operator, or other external sources, such as homogeneity of reactants, impurities in chemicals or synergistic side reactions. Sometimes the largest source of error is human error and can be in a variety of guises from incorrectly trained staff to wilful negligence. Systematic errors are those which are reproducible and are linked to instrumentation defects or incorrect calibration and usually add bias one side of the true, accurate value, whereas random errors are those inherent in analytical measurements that are due to operators, limited precision of equipment or glassware and chance fluctuations. For those research and analytical laboratories that need to reduce error to a minimum, calibrated, well maintained equipment that utilise external and also internal standards are vital, but expensive, due to the precise tolerances required.

Understanding the limitations of the equipment used and the errors expected forms the basis of this study.

The following is a list of equipment used and the corresponding known error/ precision limits.

Laboratory balance – 0.1 mg accuracy last calibrated "date unknown"

Glassware – "B" graduated volumetric flasks and pipettes

Pressure transducer – Accurate to +/- 1Bar, discussed in more detail in Chapter 4

Reaction thermocouple – accurate to 1°C (checked at 100°C in boiling water)

Parr reactor – no visible leaks or loss of pressure during reaction

Nitrogen – supplied via bottle and gas line, 99.9% purity

Organosolv lignin – homogenous product sourced from Aldrich, sieved to <50μm

0.1M KOH made volumetrically by the addition of 56.11g 100% KOH up to 1000 cm^3 distilled water. This was kept as stock solution for further experiments.

pH meter − this was calibrated with pH4 and pH 7 buffer, prior to the experiments taking place.

Solvents/ chemicals − DCM and acetone were GPR grade, sourced from Aldrich. Water was distilled on site.

3.3.2   Reproducibility of Method

To the Parr reactor was added 2.00 g lignin and 20.00 g of 0.1M KOH solution. The reactor was then heated to 300°C, then cooled immediately until the temperature reached to below 40°C. The contents were then separated using the method as described in **section 3.3** the volumes of each chemical used for rinsing the reactor were 25 mL water, 50 mL DCM and 50 mL Acetone. Yields of each product, pH values and mean/ Std. deviation are presented in **Table 3.2**, with a graphical representation in **Figure 3.5**.

Table 3.2: Yields of product from error study

Reaction	Oil	Acetone	Char	pH	Oil	Acetone	Char	Conversion
	(g)	(g)	(g)		(%)	(%)	(%)	(%)
1	0.3453	1.0832	0.4332	7.28	17.27	54.16	21.66	93.09
2	0.3182	1.033	0.4844	7.28	15.91	51.65	24.22	91.78
3	0.3313	0.9835	0.4784	6.96	16.57	49.18	23.92	89.66
4	0.3303	1.0866	0.4279	6.60	16.52	54.33	21.40	92.24
				Average	16.6	52	23	92
				St Dev	0.5	2.	1	1

Standard deviation is calculated from the square root of variance from the mean. From this value is calculated the confidence limits, on a standard bell curve, 95% of all values would lie within 2σ of the mean value. Hence, for reaction yields as displayed in **Table 3.2**, the 95% confidence limits are:

Oil - +/- 1, acetone soluble char – +/-5 and char - +/- 3

The limitations of the study itself are the low number of sample sets. Had this been repeated numerous times, the standard deviation would have been more accurate.
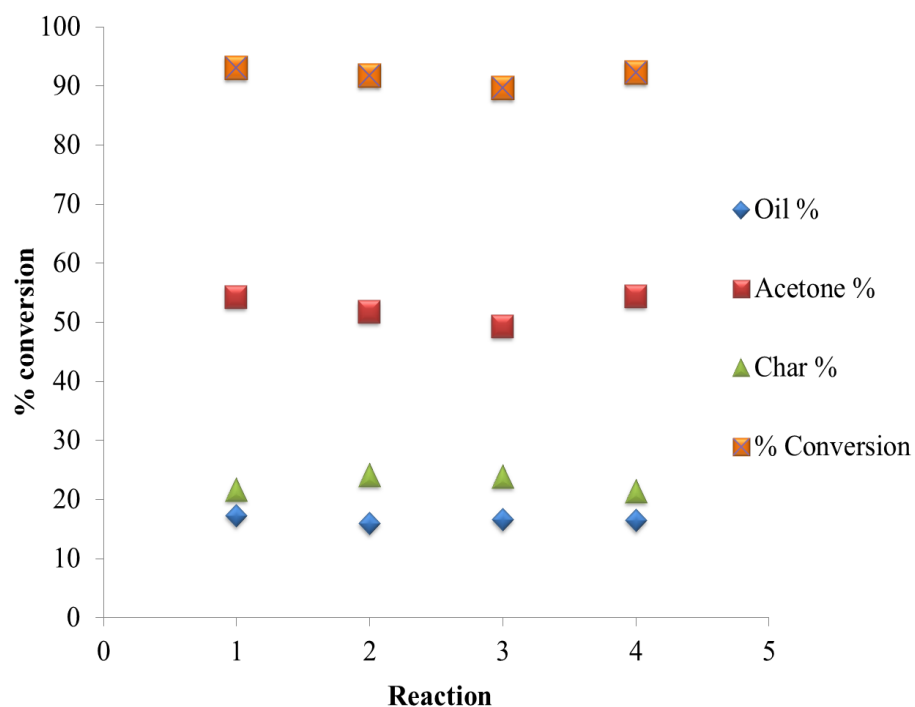
Figure 3.5: Graphical distribution of products from error study

It can be assumed from this study that, on average, the results for oil calculations are within 7% of the mean, acetone soluble char 10% and acetone insoluble char 13%.

Further observations during hydrothermal processing experiments are given in Appendix 1.

This study only covers one part of the accuracy of results obtained. For each of the analytical techniques, there are inherent errors, but these are minimised by instrument calibration where feasible. Elemental analysis via CHN/S is one technique where calibration standards are run in the expected region of what is expected. Because of the

heterogeneity of solid samples, sampling errors in CHNS analysis are usually greater than instrumentation detection errors. Previous work (Baxter, 2011 Thesis) has estimated errors in C and H to be better than 2% relative error, and the error in N to be in the range 5-10% relative error

Chapter 4 – Influence of Retention Time, Temperature and Catalyst on HTL Processing of Biomass Model Compounds

4.1 Introduction

Objectives for this introductory experimental chapter are; 1, to replicate hydrothermal experiments from literature sources, providing a suitable experimental starting point for the following chapters. 2, provide standard reaction conditions as a basis for direct comparison. The benefit of this is primarily as a starting point, to which all other reactions will be compared. Differences in experimental setup to literature sources are unavoidable, as are the method of pressure/ temperature monitoring and of course heating control. The prolific researcher Demirbas has a number of journal papers in this field, highlighting the use of alkalis for high levels of conversion of biomass and related model compounds to oil. He writes "*Alkali salts, such as sodium carbonate and potassium carbonate, can act as catalysts for hydrolysis of macromolecules, such as cellulose and hemicellulose, into smaller fragments. The micellar-like broken down fragments produced by hydrolysis are then degraded to smaller compounds, by dehydration, dehydrogenation, deoxygenation and decarboxylation. These compounds, once produced, rearrange through condensation, cyclization and polymerization, leading to new compounds.*" (Demirbas 2000)

In keeping with previous studies in the field, initial work in this chapter concentrates on detection of liquid, gaseous and solid products formed from hydrothermal liquefaction reactions of cellulose, lignin and xylan at reaction temperatures 300 - 350°C with KOH as a reaction additive at concentrations of 1M. The analysis of gaseous products was carried out by GC-FID/ TCD, solid products by CHNS/ TGA and oil via GC-MS. The second part of this chapter covers a smaller range of hydrothermal liquefaction reactions at 1M and 0.1M KOH catalyst, assessing the effect of catalyst concentration.

While the reactions of cellulose have been studied previously in some detail, (Berlin et al. 2006a; Fang et al. 2004; Minowa et al. 1997; Sakaki et al. 1996a, b; Sasaki et al. 2000; Sevilla and Fuertes 2009b)there has been less work examining lignin liquefaction (Berlin et al. 2006b; Demirbas 2000; Wahyudiono. et al 2007) and still less concerning hemicellulose models (Mok and Antal 1992; Zhang et al.)

4.2   Reaction conditions

All reactions were carried out following the experimental procedure in **Chapter 2**. For the purpose of these experiments, potassium hydroxide at 1M concentration was used as both reaction medium and solvent. Reaction conditions are presented in **Table 4.1**. Biomass model compounds used were cellulose (20μm average particle size, Aldrich chemicals), organosolv lignin (40μm average particle size, Aldrich chemicals) and xylan (100μm particle size, Sigma chemicals). Details of product work up and analysis are summarised here, while full details are given in **Chapter 3**.

Table 4.1: Experimental conditions

Experiment Abbreviation	Model Compound	Temperature (°C)	Reaction Time (minutes)
C300 10	Cellulose	300	10
C300 20	Cellulose	300	20
C300 60	Cellulose	300	60
C325 10	Cellulose	325	10
C350 10	Cellulose	350	10
L300 10	Lignin	300	10
L300 20	Lignin	300	20
L300 60	Lignin	300	60
L325 10	Lignin	325	10
L350 10	Lignin	350	10
X300 10	Xylan	300	10
X300 20	Xylan	300	20
X300 60	Xylan	300	60

4.2.1   Extraction techniques

After cooling the reactor to <40°C, gases were vented to a tedlar bag for further analysis. The contents of the reactor were then transferred into a separating funnel. To remove all traces of oils and solid residue, with the reactor washed out with DCM and acetone. The method for separation was as follows:

a. To the separating funnel was added 50cm^3 dichloromethane in 2 x 25cm^3 aliquots as well as the content of the reactor.

b. Combined organic and aqueous phases were filtered through weighed Whatman 41 grade filter papers to remove solid residue and separated.

c. Acetone, previously used to wash out the reactor was then added to the residue, mixed and filtered to retain material insoluble in water, DCM and acetone. This material was labelled as char.

d. Acetone was then evaporated at room temperature, giving acetone soluble material labelled also as char.

e. The beaker containing DCM soluble material was dried under a steady stream of nitrogen. This yielded viscous liquid material labelled oil.

Each separate phase (gaseous, aqueous, oil and char) was subjected to a number of analytical tests, establishing the various qualities and relative proportions of a number of compounds. The aqueous phase is defined as the reaction medium and solvent, in this case, potassium hydroxide solution at 1.0 and 0.1M

4.2.2 Data Analysis

Mass and elemental balances were then calculated by employing analytical techniques. Conversion of model compounds to products was calculated taking into account all elements in the closed system. Weight % of the oil and char fractions was calculated using equation (**4.1**); gas was calculated using the ideal gas equation (**4.2**) assuming 70% CO_2; and water soluble products calculated by difference. A concentration of 70% CO_2 was deemed a suitable amount for these experiments, based on the work of (Wang et al. 2008)

$$Wt\% = (\text{weight fraction (g)/ sample weight (g)}) * 100 \qquad (\mathbf{4.1})$$

$$p\text{V} = n\text{RT}, \qquad n = m/\text{ M} \qquad (\mathbf{4.2})$$

4.2.3 Analysis of gaseous products

Gas production is measured initially by the maximum pressure produced during the liquefaction reaction. After the reaction has completed and the system has cooled to ≤40°C, the residual pressure is taken from the transducer, with temperature noted for weight % gas calculations. For accurate calculation of wt% gas, the internal volume of

the reactor plus any other dead space volume was measured using water, less the volume of the sample and liquid combined. The main source of error for calculations of gas yields is the digital readout, reading +/- 1 Bar where a 1 Bar difference in pressure accounts for a yield difference of ~4.5%.

The analysis of gaseous products was performed on a PYE Unicam series 204 chromatograph, fitted with both FID and TCD detectors, silica gel packed column for CO_2 analysis and molecular sieve packed column for permanent gas analysis. Sampling of gas for GC-FID/ TCD analysis constituted another issue. Sampling using Tedlar bags, previously "rinsed" with nitrogen provided sources of contamination as volumes of gas were small ($0 - 200$ cm^3 max). To try and overcome losses and contamination, a gas syringe of much smaller volume was used with limited success. Overall, results indicated an increase in CO_2 levels to those quoted in various journal papers. Proof of contamination was found after injecting the gas samples, as the largest portion of the gas was N_2. At atmospheric pressure, N_2 constitutes ~70% of air, therefore, at a pressure of 3 Bar, only 70% of 1 Bar could contain nitrogen, equating to less than 0.7/4.0 or 17.5% of the total gas. This must be the case as the reactor did not contain nitrogen from any other source, only H, C, O and potassium. Nitrogen was not detected during elemental analysis of the model compounds.

4.2.4   Analysis of oil

Analysis via GC-MS (Agilent 6890N fitted with 5975B Mass Spec. detector). The column used was a Restek REX-1701 60m length 0.25mm diameter and 0.25µm film thickness. Temperature control was 40°C for 5 minutes, then 5°C min^{-1} to 280°C. The system solvent was DCM.

4.2.5   Analysis of char

Insoluble residue was analysed for CHNS (CHNS analyser, CE Instruments Flash EA 1112 Series) and analysed by TGA for moisture and ash content.

4.3   Results and Discussion

4.3.1   Characterisation of materials

The characteristics of cellulose, lignin and xylan are summarised in **Table 4.2**. Cellulose and xylan being of similar composition have very similar amounts of carbon,

hydrogen and oxygen, whereas lignin contains much higher carbon and much lower oxygen content. Ash was not detected in the starting materials.

Table 4.2: Analysis of model compounds by CHNS and TGA

Sample	Carbon %	Hydrogen %	Oxygen %*	Ash %
Cellulose	42.6	5.2	52.2	ND
Lignin	65.8	4.8	29.2	ND
Xylan	40.3	4.9	54.8	ND

*by difference   ND not detected

4.3.2   Analysis of products

Table 4.3 summarises the product distributions for the different reaction times and temperatures studied.

Table 4.3: Reaction pressures and product yields

	Reaction Temp (°C)	Dwell Time (mins)	Residual pressure (Bar)	@ Temp (°C)	Oil (wt %)	Char/ Solid (wt %)	Gas (wt %)	Aqueous products* (wt%)
Cellulose	300	10	2	22	5.4	8.4	9.3	76.9
Cellulose	300	20	3	37	6.0	6.8	13.2	74.0
Cellulose	300	60	3	33	4.5	12.2	13.4	69.9
Cellulose	325	10	1	23	6.2	11.0	4.6	78.2
Cellulose	350	10	3	32	6.4	9.2	13.5	71.0
Lignin	300	10	0	30	5.0	21.4	0	73.6
Lignin	300	20	0	24	30.0	6.0	0	64.0
Lignin	300	60	0	40	20.0	23.5	0	56.5
Lignin	325	10	0	25	10.0	20.1	0	65.9
Lignin	350	10	1	32	2.0	20.5	4.5	73.1
Xylan	300	10	1	30	2.1	30.5	4.5	62.9
Xylan	300	20	2	32	2.0	21.1	9.0	67.9
Xylan	300	60	2	30	3.1	30.7	9.0	57.2

*by difference

4.3.2.1 Gas production

Table 4.3 shows that for cellulose, generally speaking, both higher reaction temperatures and longer reaction times gave higher gas yields. This result is to be expected as breakdown of cellulose initiates at relatively low temperatures (180 – 200°C) forming hydrolysis products. The pattern of increasing gas yield with reaction time appears to reach a plateau around the 20 minute mark with a reaction temperature of 300°C; xylan also exhibits this phenomenon. Conclusions drawn from this are that either no further decarboxylation takes place after this time or that an equilibrium is reached in the gas phase, with the levels becoming saturated at ~13%. An increase in temperature to 350°C for cellulose does not increase gas yields particularly, indicating this could be the case.

Xylan, being very similar to cellulose in structure, but containing branched side chains gives lower gas yields under hydrothermal processing when compared to cellulose. By means of comparison and as an explanation, the process of torrefaction detailed in **Chapter 1.5.5** removes/ chemically alters mainly the hemicellulose content. This is due to its higher reactivity compared to the other components and the ease of formation of water soluble compounds (WSH) and indeed water by dehydration reactions. As these products are formed from xylan decomposition, they are seemingly more stable in solution than cellulosic compounds, resisting gas formation by degradation.

Residual pressures for lignin remained the same up to 325°C indicating there was no or little effect on gas production at these temperatures. At 350°C, gas is produced. This, when looking generally at various sources, is explained by the thermal stability of lignin, linked to the macrostructure, hindering the formation of gases. Higher temperatures can promote the rate of decarboxylation or the formation of CO_2. Other gases produced are H_2, CO, and small amounts of C_nH_m (Wang et al. 2008) What is still unknown is that when residual gas pressure increases for the same model compound, for example from 4.5 – 9%, do the relative proportions of gases produced stay the same?

4.3.2.2 Oil production

Production of oil by hydrothermal processing of cellulose and xylan using an alkali catalyst was much lower than expected for all experiments, especially when compared to literature sources, (Demirbas 1998b, 2000; Qian Y. et al 2007). The classification or

grade of oil for these sources was gleaned as 'heavy oil', being that which was extracted in acetone. It is perhaps unfair to draw correlation as acetone extracted oil was still classed as oil, even though the properties put the material in the tar category being very difficult to work with and with too high viscosity to flow.

For cellulose reacted at 300°C, an increase in reaction time from 10 to 20 minutes gave a slight (negligible) increase in oil yield, however, as the reaction time approached 60 minutes, a drop in yield of 25% was observed when compared to the previous result (4.5% Vs. 6.0%). Cellulose oil yields of 6.2% and 6.4% at 325°C and 350°C respectively, indicate a small correlation with temperature.

The explanation for the low levels of gas produced from xylan processing can also explain low oil production, since water soluble compounds are favoured and are more resistant to further degradation under this set of conditions.

Lignin produced relatively large amounts of oil, up to ~500% more than cellulose and 1500% more than xylan when comparing yields at 300°C and 20 minutes reaction time, consistent with research by Meier, et al. (Meier et al. 1986a). An obvious peak was reached around the 20 minute reaction time, with a high oil conversion (30%), and a slight reduction in char yield (6%). An increase in reaction time to 60 minutes gave rise to a 33% decrease in oil. From 300 to 325°C, oil yields increased from 5 to 10%, but as reaction temperatures increased to 350°C, oil production virtually ceased, lowering back to 2%. This is the best evidence for char formation by polymerisation.

These results are in some way consistent with research by Demirbas (Demirbas 2000), who states that "*the catalytic liquefaction suppresses the formation of char from the lignin by condensation and repolymerisation.*"(Demirbas 2000) These conclusions were drawn comparing catalytic and direct liquefaction experiments at 575K, 30 min liquefaction time and KOH (1/5, w/w).

Table 4.4 shows CHN analysis of char and **Table 4.5** CHN analysis of oil. The data contained within **Table 4.4** provides more unusual results than expected. Particularly for cellulose and lignin, which contain 42.6 and 65.8% carbon respectively. Carbon

contents of char are greater than the raw material used, but not by a great deal, particularly in the case of cellulose.

Table 4.4: CHN analysis of char

	Reaction temp (^{o}C)	Reaction time (min)	C (%)^{daf}	H (%)^{daf}	O (%)^{daf}*	HHV[1] MJ/kg
Cellulose	300	10	48.9	5.7	45.4	18.6
Cellulose	300	20	50.3	5.6	44.0	19.1
Cellulose	300	60	51.4	5.5	43.1	19.3
Cellulose	325	10	54.2	5.4	40.4	19.8
Cellulose	350	10	58.6	6.5	50.4	17.
Lignin	300	10	51.3	4.5	61.0	10.
Lignin	300	20	65.2	4.5	30.1	11.
Lignin	300	60	67.8	4.8	27.2	10.
Lignin	325	10	68.2	5.0	26.7	26.
Lignin	350	10	69.8	4.4	25.6	27.
Xylan	300	10	64.5	6.7	28.8	24.2
Xylan	300	20	64.8	6.7	28.5	24.3
Xylan	300	60	65.3	6.8	27.9	24.6

[1] (Channiwala and Parikh 2002)^{daf} dry, ash free * by difference

Table 4.5: CHN analysis of oil

	Reaction temp (°C)	Reaction time (mins)	C (%)[daf]	H (%)[daf]	O (%)*	HHV[1] MJ/kg
Cellulose	300	10	72.3	8.3	19.3	33.5
Cellulose	300	20	73.0	7.3	19.3	33.0
Cellulose	300	60	70.1	8.3	17.7	33.7
Cellulose	325	10	74.6	8.3	16.9	34.1
Cellulose	350	10	76.0	8.3	15.7	34.4
Lignin	300	10	68.4	7.3	24.1	30.0
Lignin	300	20	69.3	8.4	22.1	28.9
Lignin	300	60	67.8	4.8	27.2	29.7
Lignin	325	10	64.5	6.4	28.6	27.1
Lignin	350	10	69.8	7.5	22.2	30.3
Xylan	300	10	73.3	7.9	18.7	32.9
Xylan	300	20	74.8	8.1	17.0	33.9
Xylan	300	60	74.3	8.2	17.4	33.8

[1] (Channiwala and Parikh 2002) [daf] dry, ash free * by difference

The low carbon content of the chars (**Table 4.4**), prompted further analysis for ash content using thermogravimetric analysis (TGA). Compared to other work in the field, ash contents are much higher on these materials, some found to be exceeding 50% of the total weight of char. Analysis of these ash contents by atomic absorption spectroscopy (AAS) found very high levels of potassium metal, obviously coming from the potassium hydroxide catalyst as there were no other likely sources. Bound potassium to the chars posed an obvious problem when using relatively high concentrations of catalyst to sample. The fact that a proportion of catalyst was indeed reacting with the char material forming a complex matrix, has an inevitable consequence on fuel quality. Alkali metals are the major source of boiler issues, namely slagging and fouling when biomass is combusted for electricity generation purposes. High potassium containing char would then have to be processed prior to combustion, adding a further step to an already expensive reaction process.

Production of char (or charcoal) should be synonymous with an increase in the calorific value i.e. a greater percentage of carbon. It would be reasonable to suggest that an increase in reaction temperature, or a longer residence time would produce more carbon rich char, owing to dehydration and decarboxylation, measured by an increase (especially for cellulose and xylan) in the residual pressure post reaction and an increase in the amount of CO_2 produced, but as displayed, this is not always the case. The carbon to hydrogen ratio when calculated from moles to an empirical formula shows a different pattern for cellulose and lignin. Higher Heating Values (HHV) calculated using the unified correlation equation (Channiwala and Parikh 2002) show a similar pattern when comparing cellulose, lignin and xylan.

Analysis of the oil, given in **Table 4.5** indicate an empirical formula for the oils from cellulose and xylan of $CH_{1.3}O_{0.18}$, while the oil from lignin contains a higher oxygen content and an average empirical formula of $CH_{1.3}O_{0.27}$. As a result of the higher oxygen contents of the oils from hydro-processing lignin, heating values are lower than oils produced from cellulose and hemicellulose, (27.1-30.0 MJ/kg as compared to 32.9-34.4 MJ/kg). Comparing with literature sources, there is not an obvious reason why this would be so. Indeed, Karagoz et.al, when analysing oil from hydrothermal treatment of sawdust, rice hulls, cellulose and lignin in their 2005 paper identify the greatest amount of compound detected in ether extracted oil (comparable to DCM extracted oil) from lignin to be 2-methoxy-phenol. (46.92 area%). Most compounds detected have 1-3 oxygen atoms, present at a similar atomic ratio to cellulose. It is possible that higher oil oxygen contents are the product of hydrolysis and the formation of hydroxyl groups as the macromolecular structure is broken down.

For this initial set of experimental conditions it is apparent that the one stage reaction system is not ideal for maximising yields of oil, gas or char. The difference in these results compared to previous studies in the literature together with the amount of oxygen/ inorganic material present provided scope for further analysis. High levels of ash were detected in the char, showing that catalyst was present. At 20 mls 1.0M KOH, the amount of solid potassium hydroxide is approx. 1g, this in a ratio of ~1:2 with sample is obviously too high, acting more as a bulk additive than a catalyst. This is an interesting point, since many previous published studies have utilised this quantity of KOH. Adapting this process to a commercial scale will have little value, owing to the

vast quantities of KOH that would have to be supplied. To provide any possibility of scale up processing and development of a commercial hydrothermal liquefaction technology, the costs need to be taken into account. Later work in the thesis will examine whether lower concentrations of KOH can be used (**Chapter 5**).

4.3.3 Van Krevelen diagrams and fuel quality

As an indication to fuel quality, van Krevelen diagrams can be used. The relationship between relative atomic amounts of hydrogen, oxygen and carbon contained in a fuel, obtained by elemental analysis, is graphically presented on an X,Y axis, with atomic O:C ratio (X) plotted against atomic H:C ratio (Y). Of interest is the location of various hydrothermal char (or oil) compared to anthracite, bituminous, sub-bituminous and petroleum coals, lignite, peat and raw biomass. The diagram bears relation to the calorific value of such fuel, with obvious increases in energy related to low oxygen and high carbon containing fuels, i.e. crude oil.

Studies on "chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides" (Sevilla and Fuertes 2009a) reveal, via means of a van Krevelen diagram, "*that the elemental reactions that occur during carbonisation can be described by straight lines that describe the dehydration, decarboxylation and demethanation processes*". This figure is reproduced here (**Figure 4.1**) and clearly shows the path of dehydration being the dominant method for conversion of different saccharides to char (hydrochar). It also touches on the idea that production of oil and coal from their respective sources also undergoes a degree of decarboxylation, prior to formation.
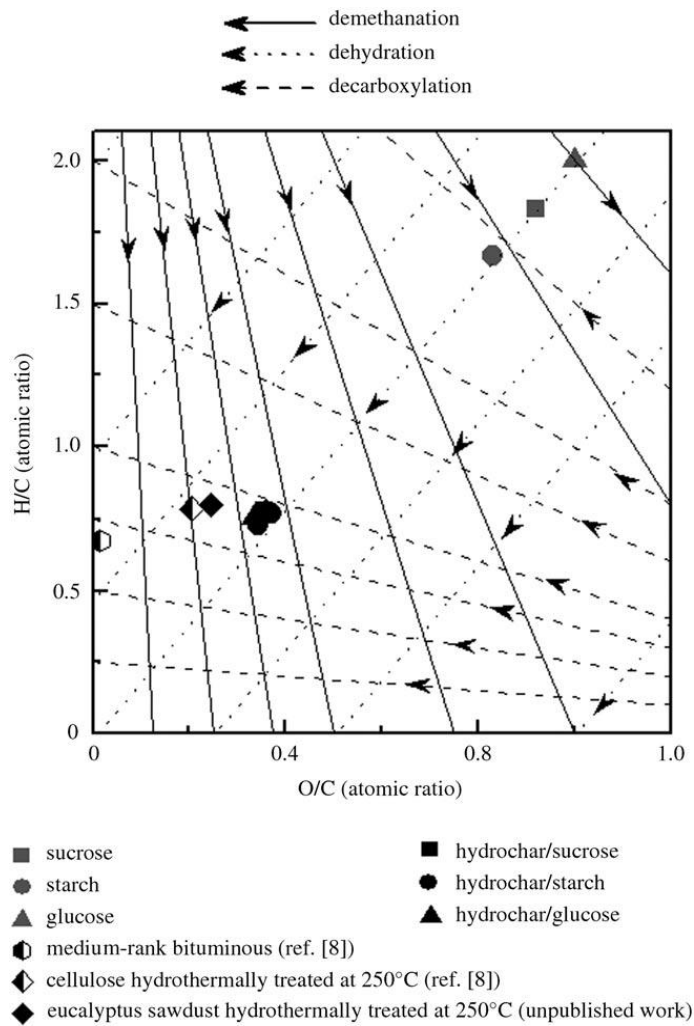
Figure 4.1: H/C versus O/C van Krevelen diagram of different saccharides and the hydrochar products resulting from hydrothermal carbonization. For comparison purposes, other carbonaceous materials are also represented (Sevilla and Fuertes 2009a)

Van Krevelen diagrams of hydrothermally produced oils (**Figure 4.2**) and chars (**Figure 4.3**) show interesting patterns. It would appear that reaction conditions have little effect on the quality of oil produced from all experiments in this chapter, the obvious major difference being yield. It is also prudent to note the evident "wall" that is reached during the formation of oils, with ratios of atomic O: C not less than 0.17. The path for oil formation also lies on the decarboxylation route, as opposed to the dehydration route, favoured by char formation (**Figure 4.3**).
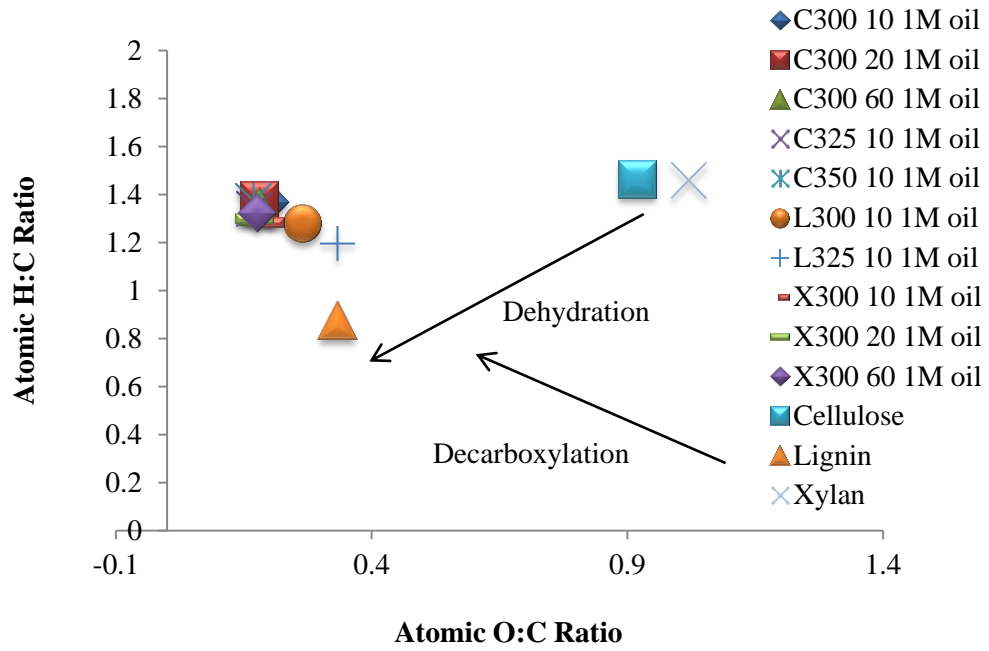
Figure 4.2: Van Krevelen diagram of oils produced via hydrothermal processing of biomass model compounds using 1m KOH solution.
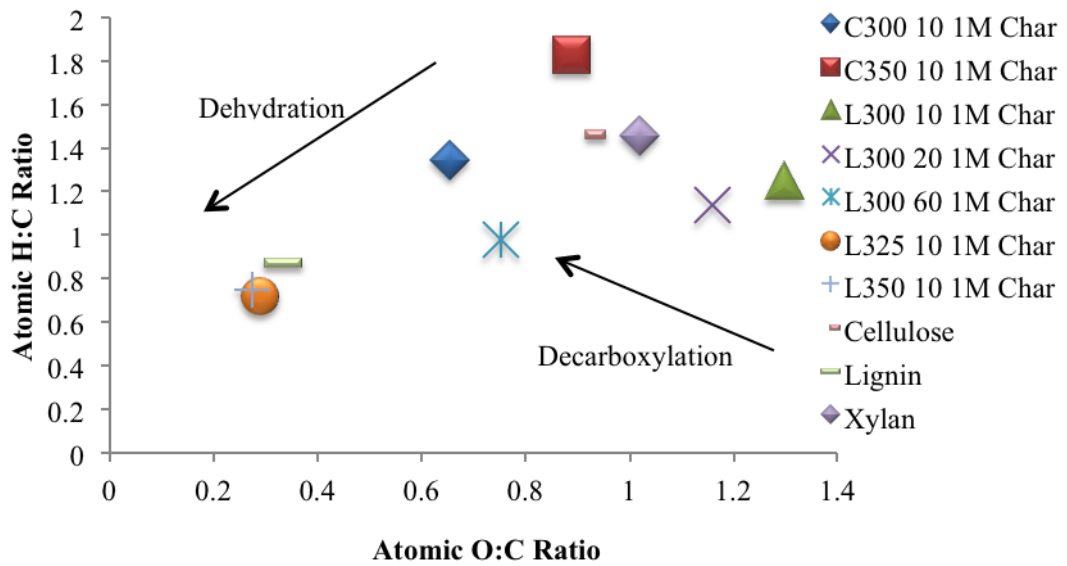
Figure 4.3: Van Krevelen diagram of chars produced via hydrothermal processing of biomass model compounds using 1M KOH solution.

For char production, lignin follows the expected pathway of dehydration, with a small amount of decarboxylation. The results suggest an increase in heating value with increases in both reaction temperature and time.

4.4　GC-MS analysis of oils

GC-MS chromatograms of oil for cellulose (**Figure 4.4**) lignin (**Figure 4.5**) and xylan (**Figure 4.6**) show differences in the distribution and amount of products detected. Cellulose and xylan gave a greater number of oxygenated hydrocarbon compounds detected, with these present at lower concentrations than lignin (when compared by relative abundance). The method described in section 3.4 was used to produce the chromatograms and results seen in this section. MS data was run using library searches and then checked manually against the compounds to find the more likely products as on occasion very unlikely compounds were chosen by the software with low correlation. MS data does not give a definitive answer, but by checking against the MS data library, gives a % correlation depending on the major peaks found and how many times they have been analysed. Common compounds are more likely to yield positive identification, whereas rare compounds are much less likely. GC-MS analysis of the DCM extracted aqueous phases provided valuable data to allow direct comparisons to the literature.
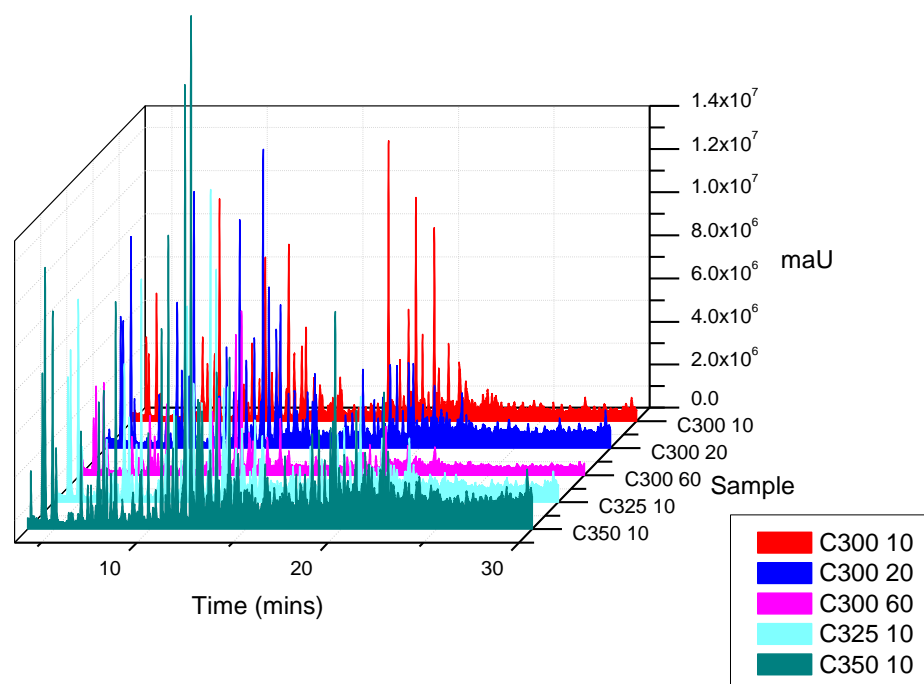
Figure 4.4: GC-MS chromatograms of oil for cellulose reacted at 10, 20 and 60 minutes using 1.0 M KOH as catalyst at 300°C, and 10 minutes reaction time for 325 and 350°C. Main peaks are assigned as follows: A: cyclopentanone; B: 2-cyclopenten-1-one; C: 2-methyl-2-cyclopenten-1-one; D: 2,3-dimethyl-2-cyclopenten-1-one; E: 2-hydroxy-3,4-dimethyl-2-cyclopenten-1-one.
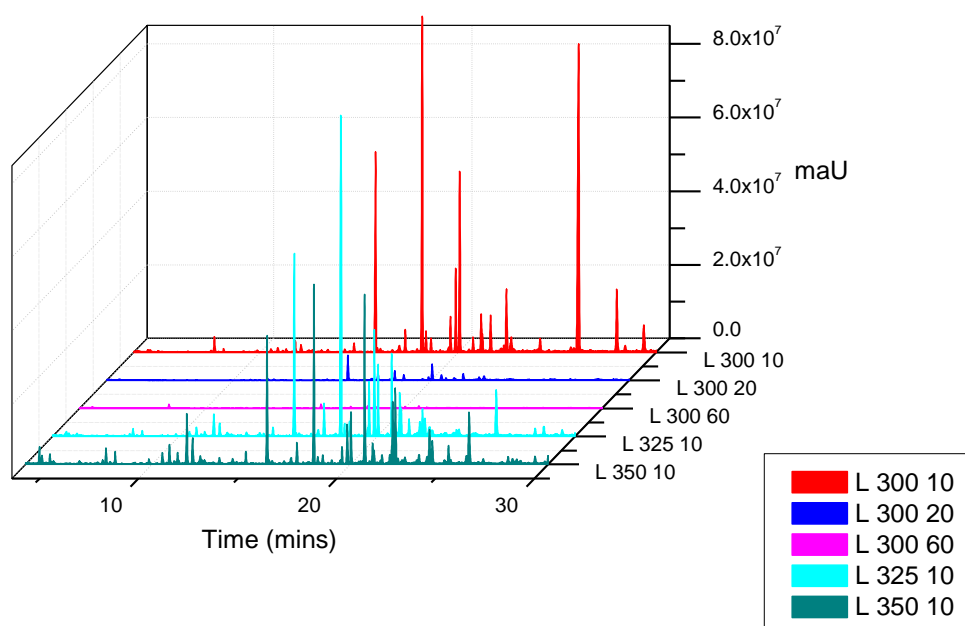
Figure 4.5: GC-MS chromatograms of oil for lignin reacted at 10, 20, and 60 minutes using 1.0 M KOH as catalyst at 300°C, and 10 minutes reaction time for 325 and 350°C. Main peaks are assigned as follows: A: 2-methoxy-phenol; B: 1,2-dimethoxy-benzene; C: 2,6-dimethoxy-phenol; D: 1,2,3-trimethoxy-benzene.
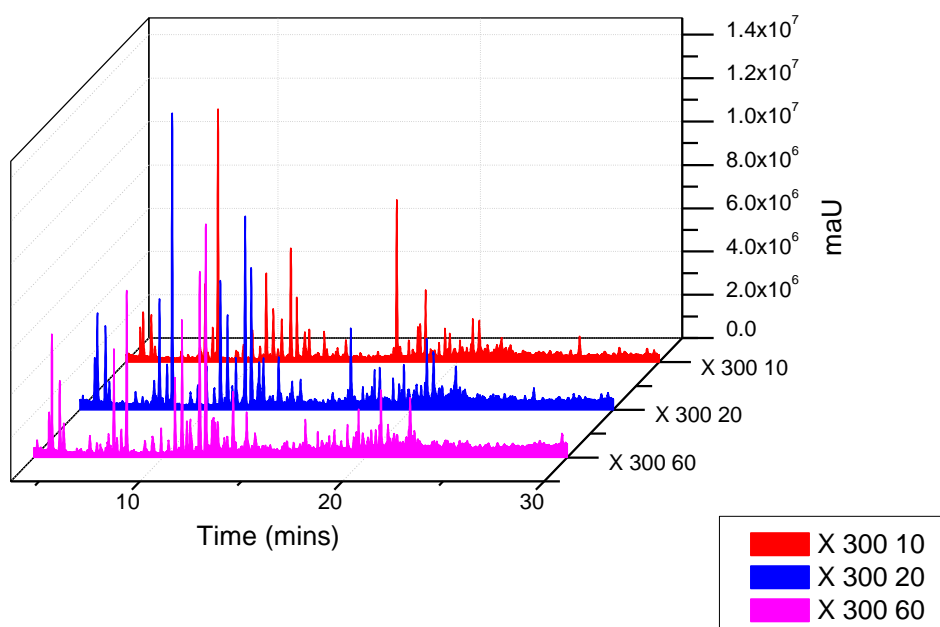
Figure 4.6: GC-MS chromatograms of DCM extracted aqueous phase for xylan reacted at 10, 20 and 60 minutes using 1.0M KOH as catalyst at 300°C. Main peaks are assigned as follows: A: 2-methyl-2-cyclopenten-1-one, B: 3,4-dimethyl-2-cyclopenten-1-one, C: 2,3-dimethyl-2-cyclopenten-1-one, D: 2,3,4-trimethyl-2-cyclopenten-1-one.

Comparing area % of the detected compounds via GC-MS alone, and not the relative abundance, shows evidence for breakdown of components and reaction pathways in the aqueous phase. **Table 4.9** shows the distribution of products relative to the total area of all peaks detected. Only the peaks with largest area % are shown for simplicity, as there are many to choose from. **Figure 4.4** shows the distribution of compounds detected in oil for all cellulose reactions. What can be clearly seen is a change in product distribution as reaction times are increased from 10 to 60 minutes. At a 10 minute reaction time, a large proportion of organic material is seen to exit the column from 15 minutes; these compounds have higher boiling points than compounds that exit the column sooner, as the oven ramp is in effect. Chromatograms produced from cellulose reacted for 20 minutes; however, show an increase in relative concentrations of compounds exiting prior to 15 minutes and a large reduction in overall relative concentration from 20 to 60 minutes. It can also be seen that the distribution of the compounds changes over time.

Lignin (**Figure 4.5**) gives a predominant product of 2-methoxy phenol for all residence times. As the reaction proceeds from 10 to 20 minutes, a much smaller proportion is present, with other di and tri-substituted phenolic and benzene compounds being reduced. Again, as with cellulose, at 60 minutes, the relative total concentration of products is greatly reduced, with 2-methoxy phenol being by far the most abundant compound detected, albeit in a much lower concentration. As the gas pressure remains the same for all residence times and reaction temperatures, it can be assumed that rearrangement reactions are taking place within the aqueous phase and not the evolution of gases such as CO_2 and CH_4. It is formation of water via dehydration reactions that increase yield and energy density for all model compounds following hydrothermal liquefaction, with oxygen forming more water molecules than WSH, or gaseous products, resulting in a larger proportion of carbon in both oil and char.

Xylan chromatograms give a similar spread of cyclic oxygenated hydrocarbons to those found in cellulose. From 10 to 20 minutes residence and as with cellulose and lignin, the relative abundance of all compounds detected increases.

Studies on glucose by Williams and Onwudili (2005) (Williams and Onwudili 2005) give a reaction pathway for the formation of furfural and cyclopenten-1-one. Reaction

temperatures were 330, 350, 374 and 380° for 0, 30, 60 and 120 mins. Results obtained from the GC-MS analysis of bio-oil produced from the gasification of glucose indicate a reduction in the amount of compounds formed (47 – 36 – 29 – 20) and an increase in the concentrations of these compounds, with the largest amount (µg/g) being phenol, after a reaction times increased from 0 – 120 minutes. It is therefore interesting to note the disappearance of furfural in both cellulose and xylan reactions at the higher catalyst concentrations and the increases of aromatic products, namely 2-methyl-phenol.

Xylan particularly shows the best indication of the degradation of furfural with a loss of the furfural peak at 18.1 area% and the increase in others, some not detected at the lower catalyst amount. Cellulose also shows a similar pattern with the loss of furfural and an increase in structurally similar chemicals (2,3-dimethyl-2-cyclopenten-1-one and their derivatives). It is unclear if the furfural peak would be greater for cellulose at either an even lower catalyst concentration or at a lower reaction time or temperature. 5-hydroxymethylfurfural, detected by others (Antal et al. 1990; Kabyemela et al. 1997; Kruse et al. 2007; Sasaki et al. 2002) and produced by the breakdown of monomeric sugars in both the aqueous and oil phases, is notable by its absence. This is likely due to the reaction having proceeded passed the point of formation and subsequent reaction to compounds detected.

4.5   LC-MS analysis of aqueous phase

Samples of aqueous phase, collected from cellulose and lignin codes C 300 10 and L 300 10 respectively were analysed at IGER at the University of Aberystwyth, Wales on 22 and 23/07/2008 via LC-MS. Sample preparation for LC-MS analysis consisted of a simple volumetric dilution with deionised water in the range of 50:1 water: sample to 5:1, followed by centrifugation to remove any particulates. The aqueous phase samples had been filtered, but this was just a precaution. Half of the cellulose sample had also been extracted in DCM to see what effect this would have on the products detected, if, as expected, the total organic content had dropped and which compounds were removed during this step.

The equipment used was made by Thermo Electron Corporation and consisted of a Finnigan surveyor PDA plus detector, auto sampler plus, LC pump plus and LQT Mass spectral analyser. The chromatographic column was a Waters C18 Nova-Pak, 4µm

particle size, 3.9mm x 100mm. Due to time constraints, and due to the MS requiring a proton donor within the mobile phase, formic acid at a concentration of 0.1% was used in place of phosphoric acid. The solvent gradient and runtime was also changed to maximise elution of the compounds without losing resolution of the peaks. The method parameters can be seen later.

Initially the mobile phase was monitored using the PDA detector, prior to entering the mass spec. detector, scanning from 190-400nm to pick up aliphatic and aromatic compounds. 210nm and 254nm are the respective wavelengths, with the scan allowing detection of any other peaks present outside those expected.

After passing through the PDA detector, the mobile phase then passed through an interface, whereby the flow was split, with the greater proportion being removed to waste and what remained was introduced to the mass spec. detector via high vacuum and electrospray.

Both cellulose samples (neat aqueous phase and DCM extracted) produced poor chromatograms with only traces of peaks found. Peaks detected were only just above the noise threshold of the instrument and in all the peaks detected by UV, a contaminant was also seen in the mass spec data, with m/z of 99 (positive ion mode), making it impossible to get the true m/z data for each peak. A common impurity peak is noted by Dudley H Williams and Ian Fleming in their book, as being a plasticizer (tributyl phosphate).

Lignin aqueous phase fared better with good separation of a 10:1 dilution of the sample. The following chromatograms are from this run and include a total content PDA chromatogram with subsequent UV cross sections of the individual peaks, showing maximum absorbencies contained within the 190 – 400nm cross section. This does not necessarily conclude that pure compounds are being detected, as indicated with a number of peaks showing maximum absorbencies in 2 or more areas. This could be evidence of products co-eluting. In addition to these are the mass spec. chromatograms, run in positive and negative ion mode and with a similar total ion spectrum to the PDA as expected – this shows a much greater degree of correlation than with the cellulose samples.

The next runs were at higher fragmentation energy and at specific windows to enable the detection of fragment ions and calculate losses from the parent ion, allowing a more in-depth look at the products and distinguish which were more likely to be pure compounds. It must be noted at this point that the m/z range was fixed from 50 to 500. Obviously simple aliphatic acid - formic and other simple aliphatic compounds with atomic weights of less than 50 would not be detected, as would any compound with a m/z greater than 500.

Sample Name:	L 300 10 (produced on 160708)
Tune file:	chlorogenic0608
HPLC column:	Waters C18Nova-Pak4um 3.9x100mm
Gradient:	2% ACN isocratic for 5min, up to 50% over 25min
Instrument Method:	C:\Xcalibur\methods\barbara\instrument methods\RobertJLeeds0708\grad3.meth
Injection Vol. (µl);	25.00
Dilution	1:10
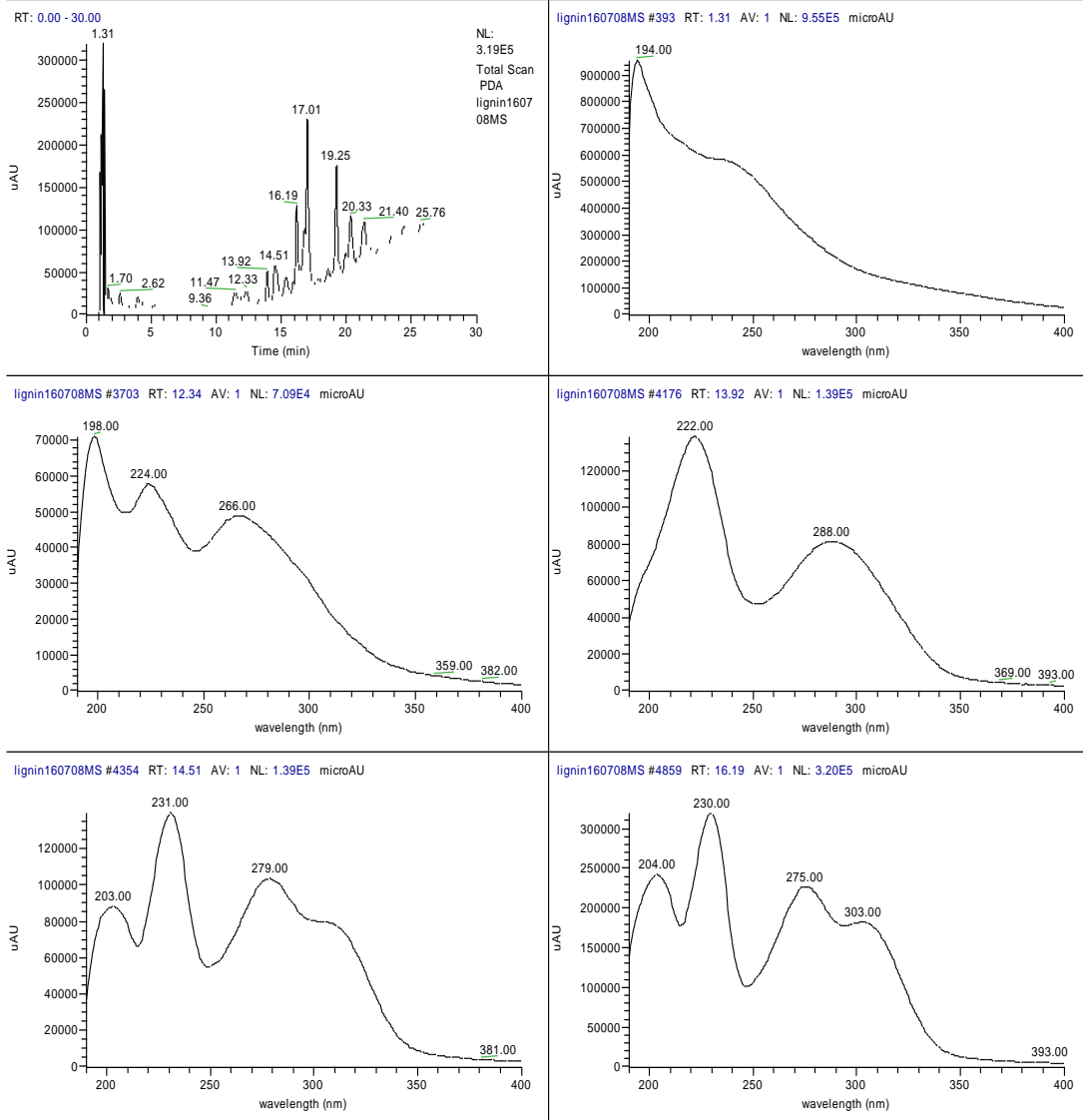
Figure 4.7: LC-MS analysis PDA spectra of individual peaks detected at 1.31 to 16.19 minutes run at 190 to 400nm

The above spectra (**Figure 4.7** and **4.8**) show the total scan content detected by the PDA from 190 – 400nm and the subsequent individual peak scans at various retention times throughout the run. The PDA total scan shows an increase in baseline as the gradient shifts from 2% to 50% acetonitrile over 25 minutes and then drops off at the end as the concentration returns back to 2% acetonitrile and 98% 0.1% formic acid soln. The peak at RT 1.31 is discounted as the solvent front.
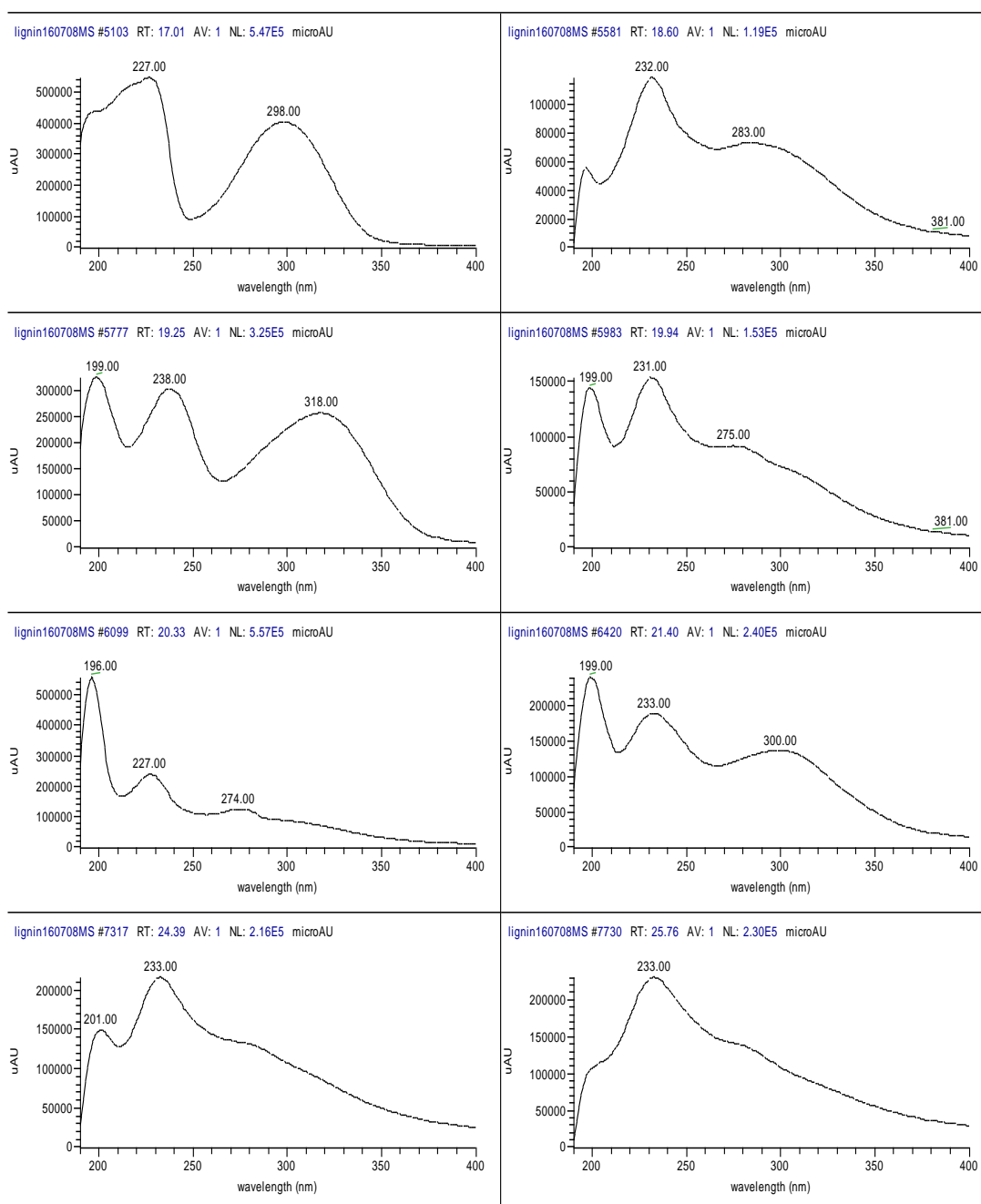
Figure 4.8: PDA spectra of individual peaks detected at 17.01 to 25.76 minutes run at 190 to 400nm

Contained within the individual PDA cross sections are a number of λ_{max} values that are similar that could indicate a number of possible compounds, with the most likely being heteroaromatic compounds, ketones and polyaromatic compounds containing oxygen.

Benzene for instance absorbs at ~184, but electron withdrawing substituents such as carboxylic acid groups (R-CO$_2$H) cause a massively different absorption maxima when compared to the un-substituted aromatic compound. Disubstituted benzene rings of the

formula R- C_6H_4 – R' can also have largely different absorption maxima depending on the stereochemistry and the orientation of the substituents.
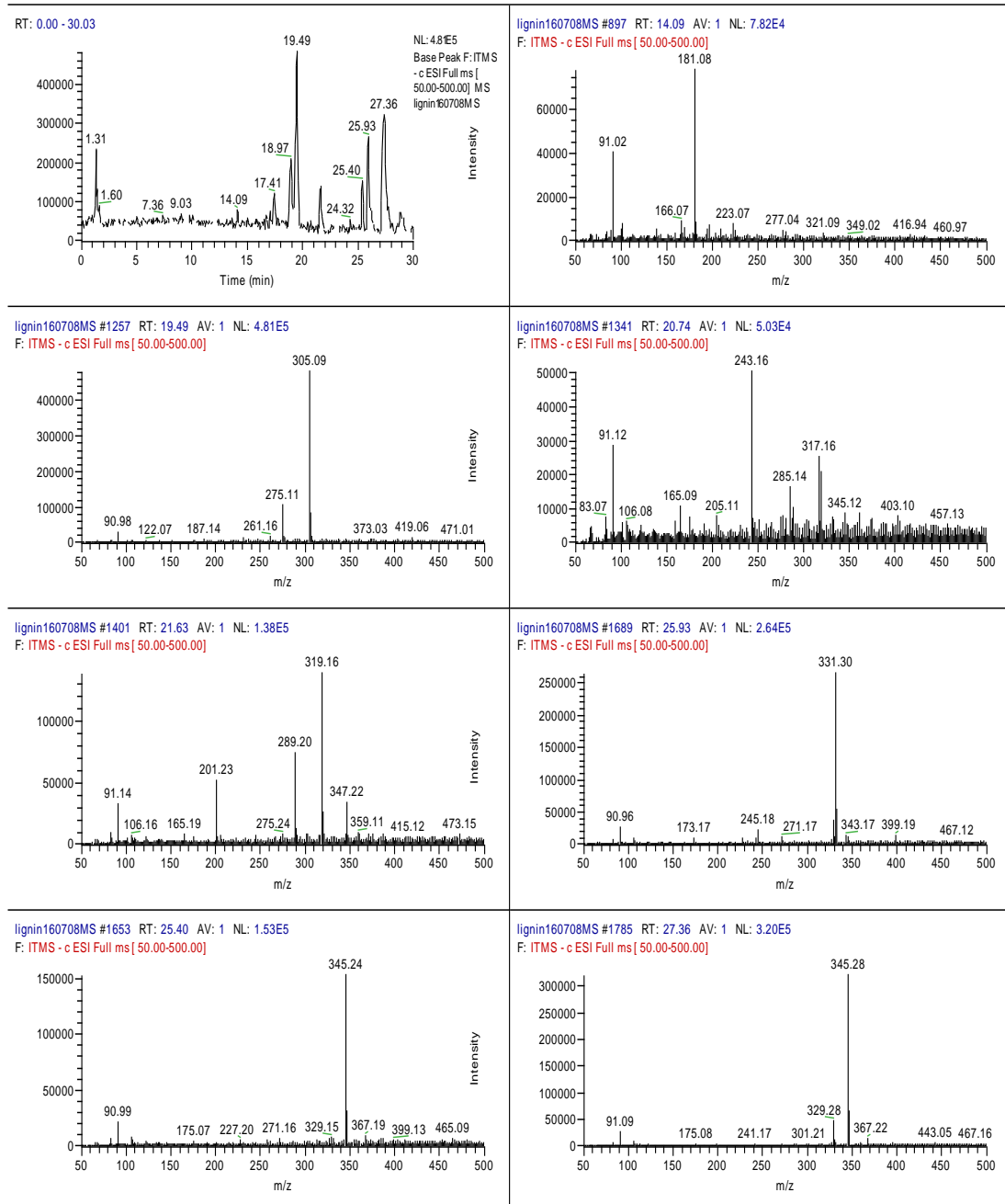
Figure 4.9: MS negative mode full MS sample L 300 10 run on peaks from refractive index chromatogram (top left)

The spectrum (**Figure 4.9**) viewed in the top right is full mass spectrum in negative mode, this shows the relative abundance of what was detected in the mass spectrum run in refractive index (RI) mode. When compared to the total PDA spectrum in **Figure 4.7**,

there are a number of additional peaks, indicating the presence of compounds not monitored via UV/ Vis or at least not in the range of 190 – 400nm. The MS spectrum of these individual peaks shows high molecular weight compounds with m/z parent ions in excess of 300. This is consistent with retention time and with the relative polarity of the mobile phase increasing towards the end of the run, allowing the compounds to be eluted, again showing the reduced polarity and more hydrocarbon like qualities. As the mass of the parent ions is high, it would be expected that the compounds detected would not be straight chain hydrocarbons, these would be obvious with losses of fragments m/z 15, 29 and 43 as methyl, ethyl and propyl groups are removed. More likely are the heteroaromatic and substituted polyaromatic compounds, with more complex structures than mere disubstituted benzenes. The author feels this is a good explanation as the λ_{max} values for these compounds are in the region >400nm and therefore would not be detected via the PDA.
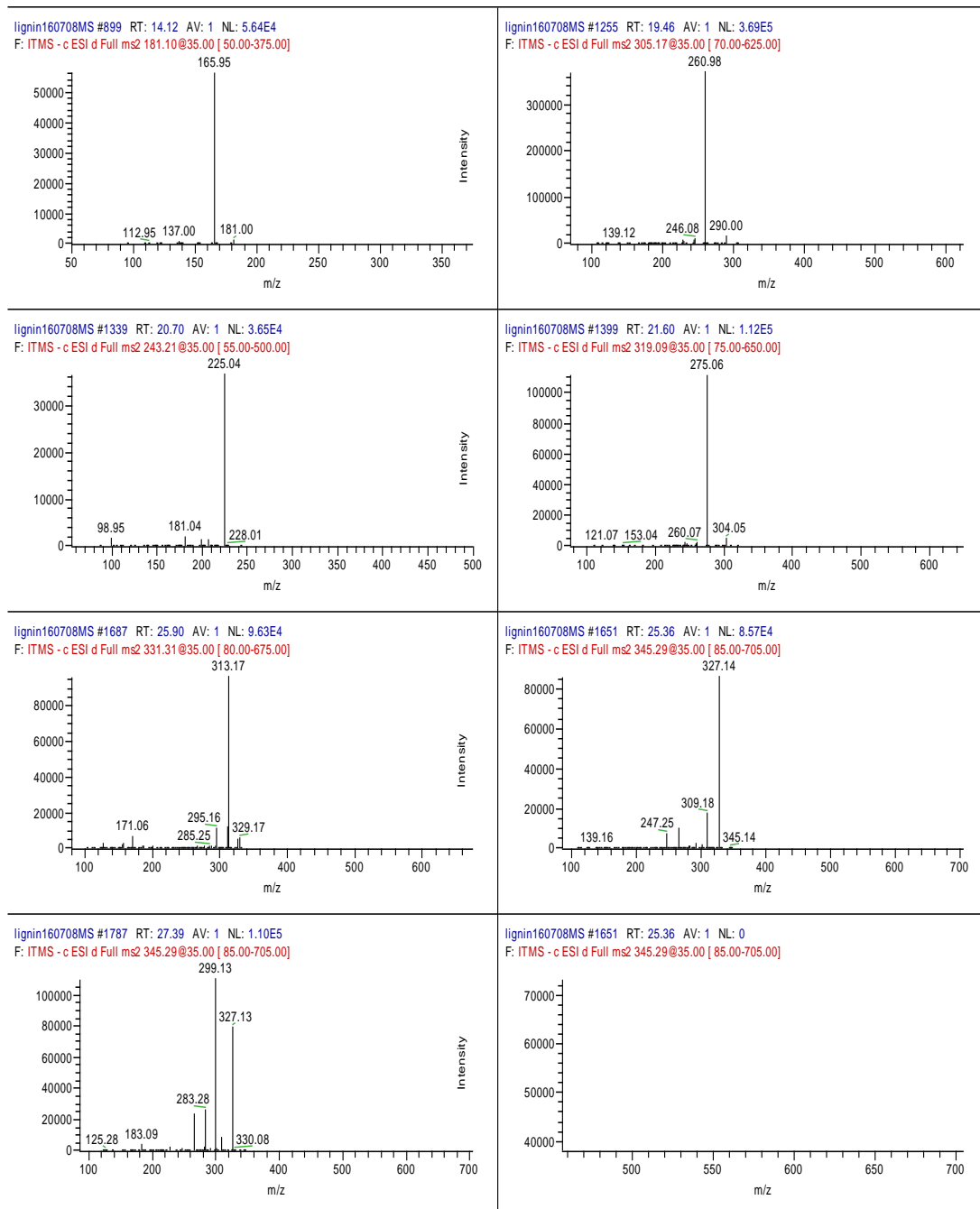
Figure 4.10: MS2 Negative mode sample L300 10

After completing the full MS using negative mode, secondary information was obtained by looking at the parent ion and seeing what initial losses were seen after increasing the fragmentation energy. Losses are calculated from the parent ion which seem most likely, and the most obvious i.e. losses of m/z 15 generally relate to CH_3, 18 relate to H_2O and 28 CO.
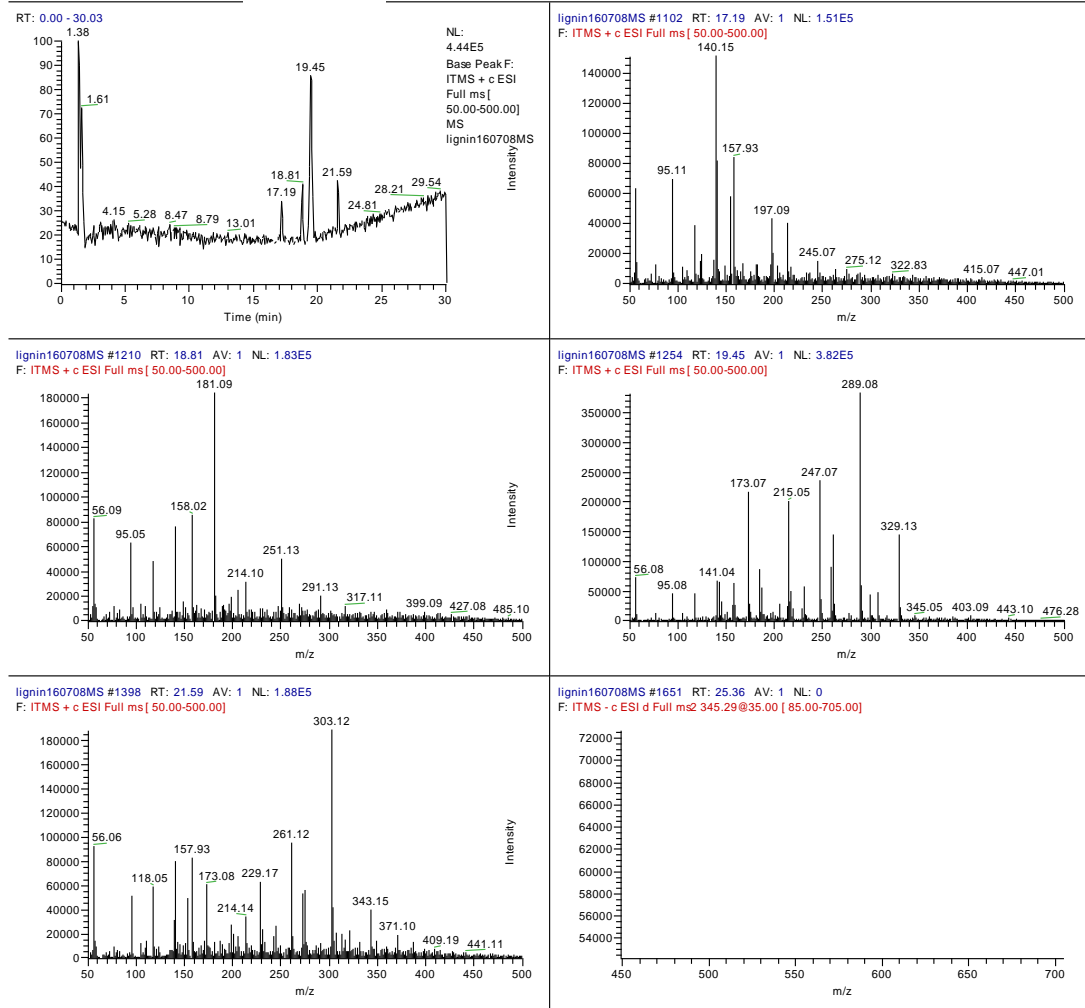
Figure 4.11: Full MS positive mode sample L 300 10

With only 4 peaks noticeable when analysing during positive mode (**Figure 4.11**) showing 4 main positive ions with by far the most abundant ion being that located at RT19.45, discounting the solvent front. The MS chromatogram shows a sample with a high molecular weight parent ion (m/z 329.13). This in itself proves that there are relatively large water soluble compounds with aromaticity contained in the aqueous phase.
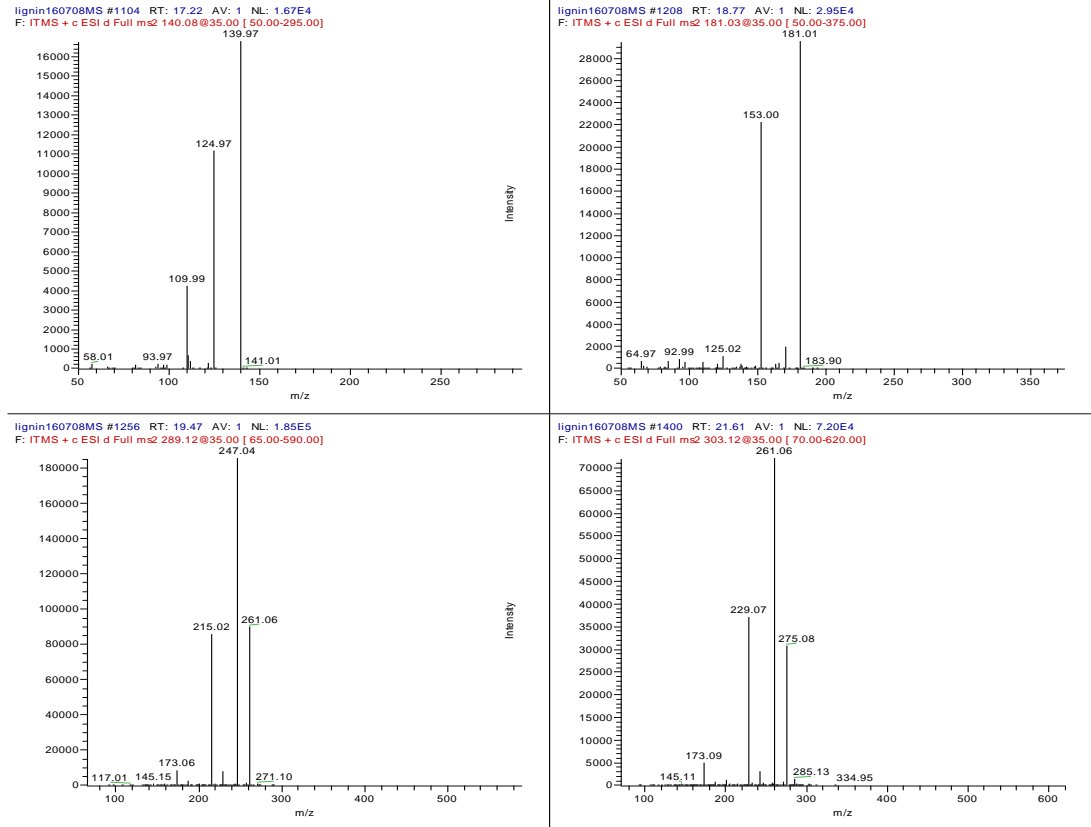
Figure 4.12: MS2 Positive mode sample L 300 10

Fragmentation energy was increased to further break the parent ions. In the case of RT 17.22, losses of 15 and 15 can be seen in **Figure 4.12**. As CH_3 is the easiest neutral compound to remove, this would indicate 2 separate losses of CH_3. The spectrum for RT 18.77 shows the loss to be 18, indicative of a loss of water. Losses of water are seen when alcohols, aldehydes and ketones are present.
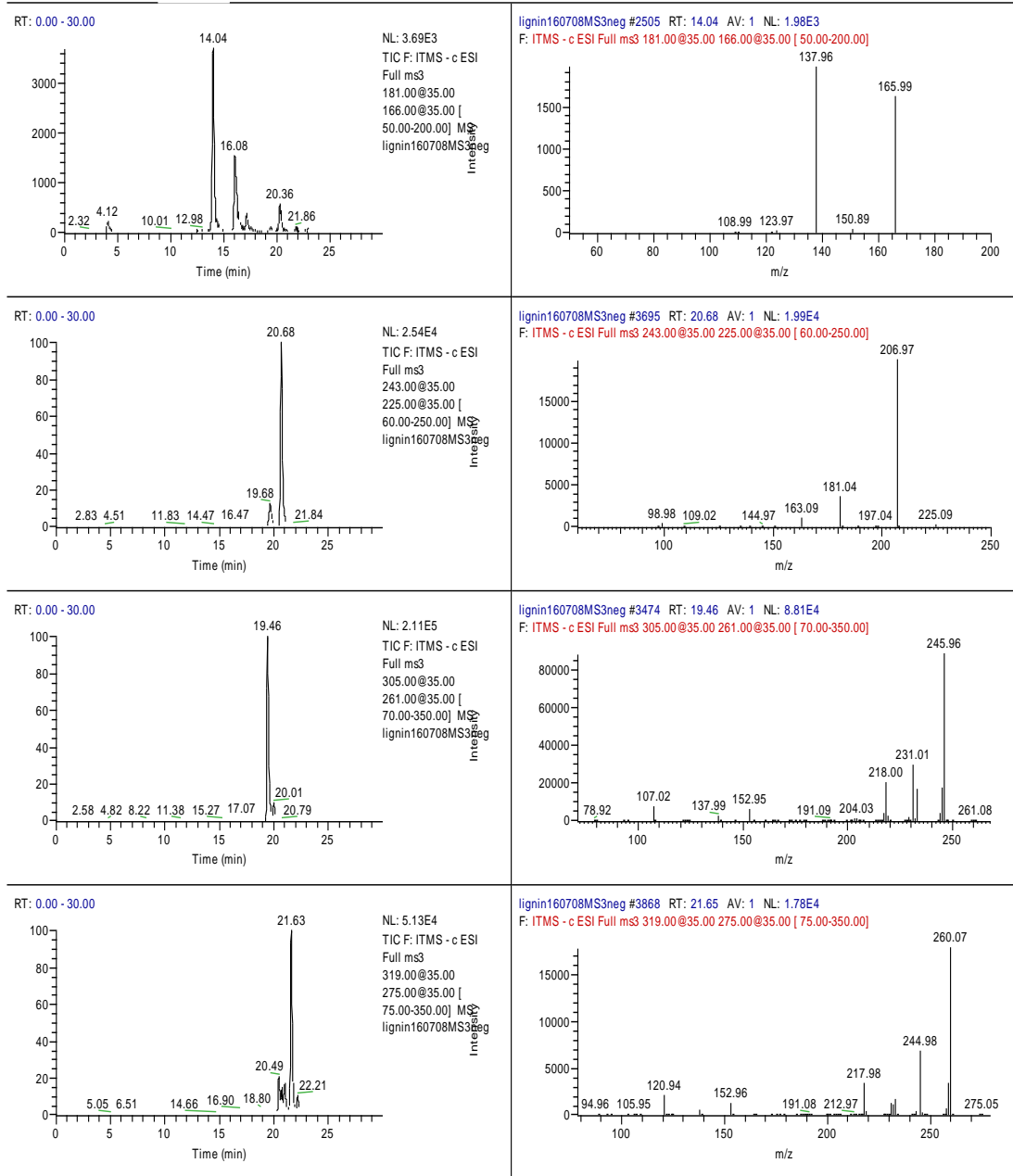
Figure 4.13: MS3 Negative mode sample L 300 10

C:\Xcalibur\...\lignin1607(23 Jul 08 13:00:17
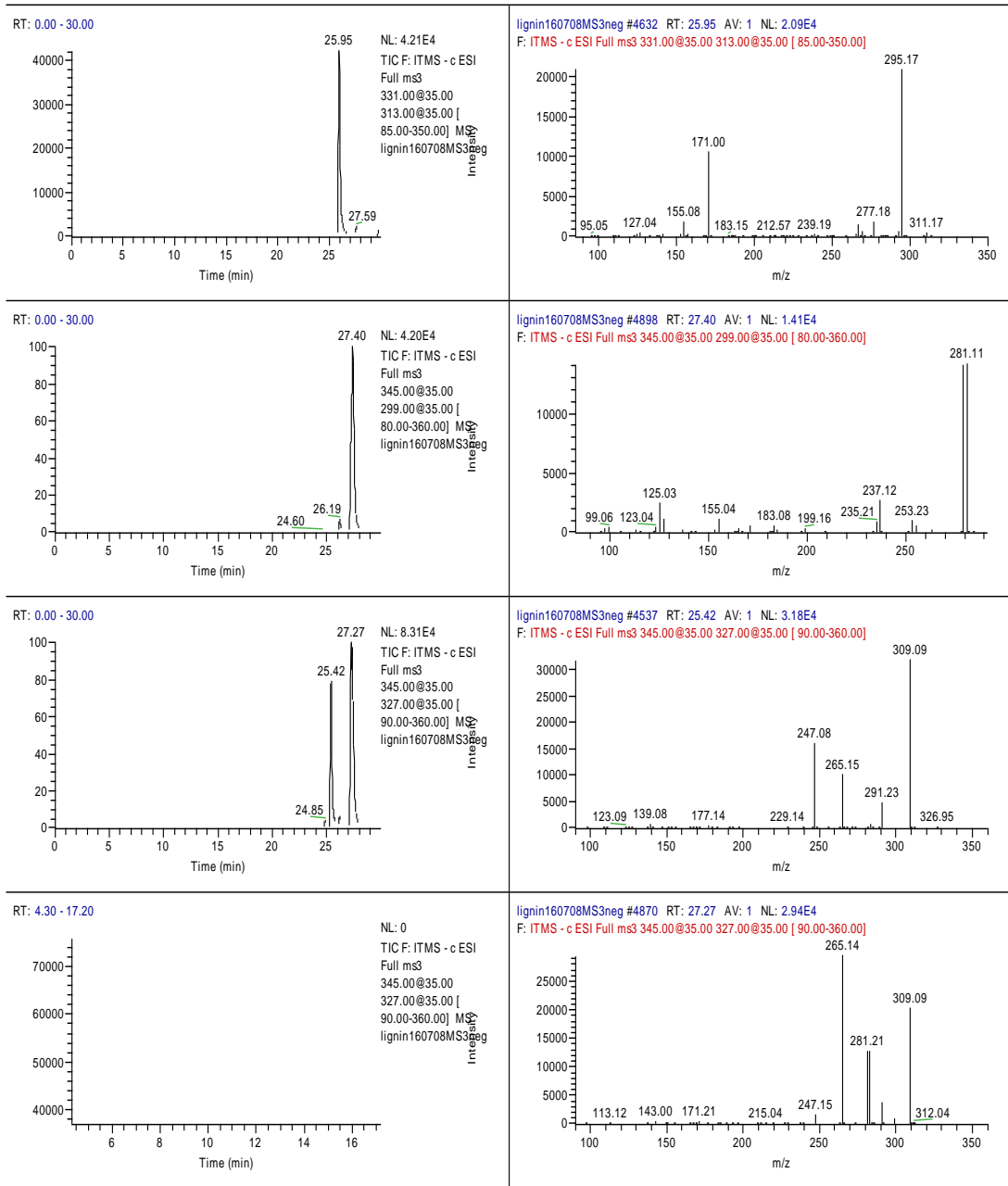
Figure 4.14: MS3 Negative mode sample L 300 10
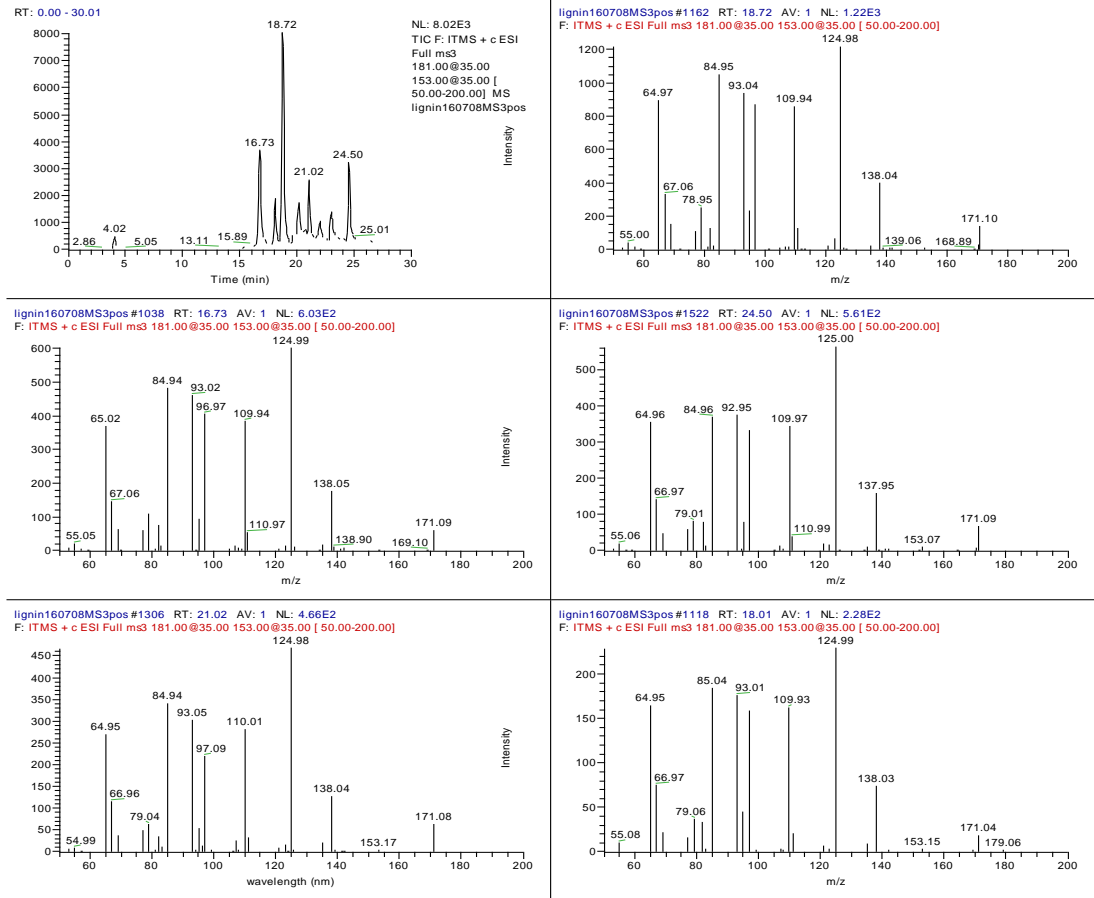
Figure 4.15: M S3 Positive mode sample L 300 10
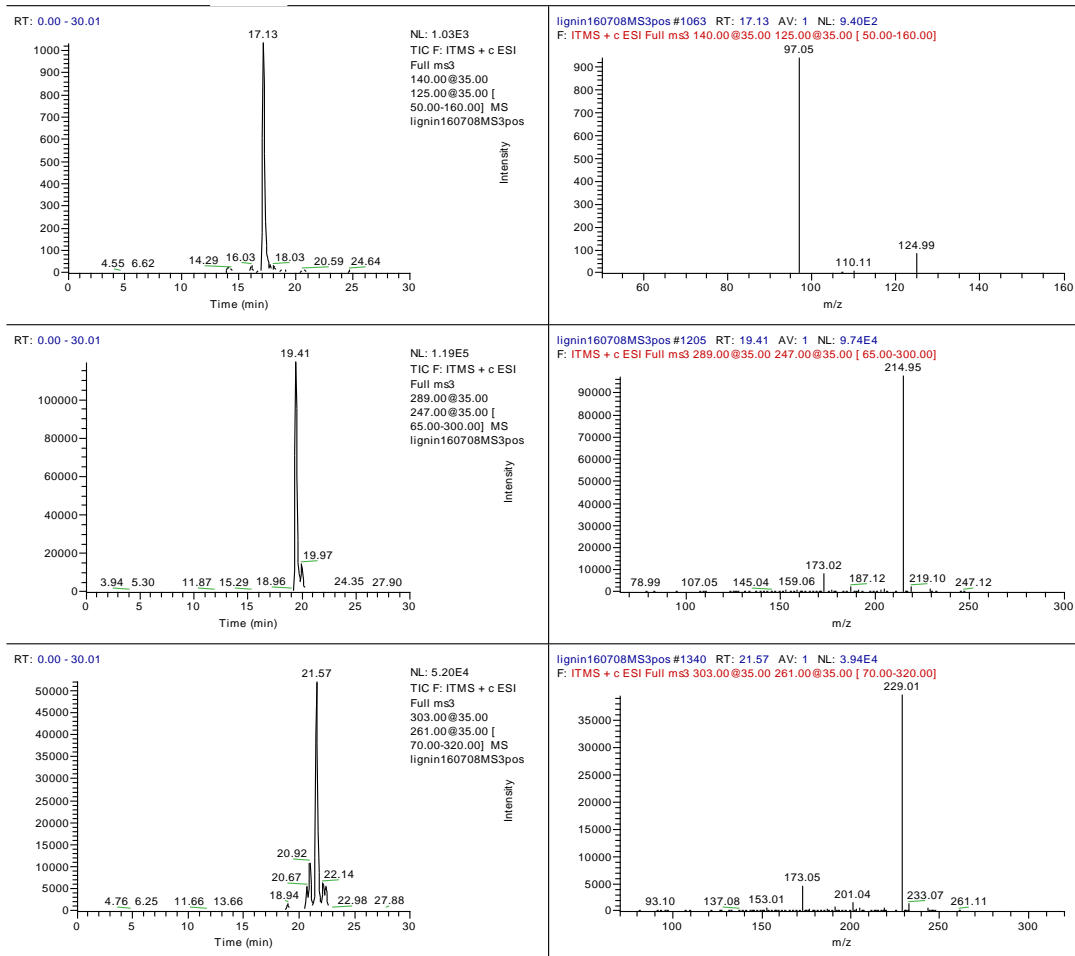
Figure 4.16: M S3 Positive mode sample L 300 10

Due to time constraints and because the results for LC-MS analysis of cellulose aqueous phase were difficult to obtain, lignin aqueous phase samples were studied in much more detail. It became apparent early on, that due to co-elution of compounds, it would be difficult to isolate and analyse HTL aqueous phases and say with any certainty what products were contained within. When it comes to identifying products via LC-MS, there is no NIST database or comparison software currently available. This is because of the vastly more flexible setup of LC, with a plethora of columns and mobile phases available. There is a shortage of information in this field, which would warrant future study.

4.6   Catalyst concentration reactions

The earlier part of the chapter discusses hydrothermal liquefaction of biomass model compounds using potassium hydroxide catalyst at 1M concentrations. In a typical

liquefaction run, 20g of 1.0M KOH solution would contain ~1g of solid material. This is a very high ratio of catalyst to sample (1:2) and as seen, is more a bulk additive.

This part of the chapter investigates how catalyst concentration affects liquefaction products – gases, WSH, oils and char by comparing high and low concentration KOH catalyst (1.0 and 0.1M respectively).

4.6.1 Results and discussion

4.6.1.1 Analysis of products

Results from the influence of KOH concentration on the bulk product yields are given in **Table 4.6**.

Table 4.6: Reaction pressures and product yields

Experiment		Gas Production		Mass Balance				Water Phase
	Catalyst	Residual pressure (Bar)	@ Temp (°C)	Oil (wt %)	Char/ Solid (wt %)	Gas (wt %)	Water soluble products (wt %)*	pH (10% solution)
Cellulose	1.0M KOH	2	11	13.2	22.7	8.5	55.6	6.7
	0.1M KOH	3	39	18.6	21.1	11.7	49.9	3.8
Lignin	1.0M KOH	1	18	4.6	13.2	4.4	76	8.8
	0.1M KOH	1	16	13.0	64.7	4.2	18.1	6.2
Xylan	1.0M KOH	3	20	8.2	12.2	12.3	67.6	6.9
	0.1M KOH	4	40	12.6	16.6	15.4	55.4	4.7

*by difference

4.6.1.2 pH measurement

Dilutions of the aqueous phase were measured for pH (**Table 4.6**). The majority of readings were under pH 8, indicating the presence of organic acids. Identification of these acids has been reported by various researchers, (Bhaskar et al. 2008; Bonn et al. 1988; Chen et al. 2006; Karagoz et al. 2005b; Meier et al. 1986b; Williams and Onwudili 2005) notably the production of acetic and formic acid detected in both aqueous and oil phases. In addition to organic acid formation are other acidic species;

phenols, furans and related compounds, all of which have been detected in the aqueous phase by a range of researchers (Bonn et al. 1988; Sinag et al. ; Taner et al. 2005).

The ACID + BASE = SALT + WATER equation explains how the reaction proceeds and also explains why organic acids have not been detected by analysis of the aqueous phase detailed later, or by inclusion in oil analysis via GC-MS. Hydrothermal processing reactions with strong base produce potassium acetate and potassium formate. It is clear that there is an excess of acid produced relative to the 20g 1.0 M or 0.1 M KOH in the reaction mixture (**Table 4.6**). Using the following equation and equimolar amounts, the amount of acid that needs to be produced to lower the pH to the value displayed is as follows:

$$H^+ Cl^- + K^+ OH^- \rightarrow KCl + H_2O \qquad pH \sim 7$$

However, when considering weaker organic acids such as formic and acetic acid, the resulting equimolar equation is this:

$$H^+ CH_3COO^- + K^+OH^- \rightarrow H_3COOK + H_2O \qquad pH \sim 9.7 \text{ (0.1M Solution)}$$
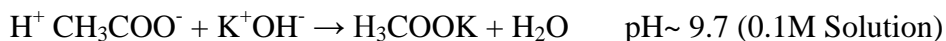
As acetic (and formic) acids are weak and KOH is a strong base, the resulting salt is alkaline when enough acid is produced to neutralise the KOH in solution. To explain the low pH values reported in **Table 4.6** further acid over the equimolar amount must have been produced. Any phenolic compound formed is unlikely to be reacted further by KOH with obvious evidence for this being the detection of phenolic compounds via GC-MS (**Figure 4.7** and **Table 4.9**). KOH is used in niche chemical reactions at 300°C to form phenols from *p*-toluene sulphonates or from other substituted halides/ leaving groups. (Morrison Boyd, 1992)

Comparing results for 1M to 0.1M KOH, the values for pH are of a similar magnitude, and in fact are lower for each of the lower concentration experiments., However, the process is particularly prevalent in the case of cellulose, producing more acidic compounds at 0.1M KOH concentration. Amounts of acid produced, relative to the lignocellulosic component, is in the order cellulose > xylan > lignin for each catalyst strength.

4.6.1.3   Gas production

Earlier in the chapter, gas production was discussed, and it was noted that the main gas component produced for all hydrothermal reactions being CO_2. In this set of experiments, for cellulose and xylan, a lower catalyst concentration gave a higher production of gas (**Table 4.7**). Implications for this are the increased production of CO_2, and the removal of carbon from the resulting liquid and solid products.

As discussed previously, Van Krevelen diagrams indicate that the reaction pathway resulting in loss of CO_2 is the same pathway that increases the product heating value; however, this is at the expense of yield, as 1 mole of carbon is lost for every 2 moles of oxygen removed. Given that the loss of oxygen is the most important factor for fuel development, this is a contributing factor in the natural formation of crude oil and its place as a high energy density fuel.

The reason why use of 1M KOH catalyst does not produce as much gas as 0.1M KOH is not completely clear at present. However, the answer may lie in the formation of organic acids with CH_3COO^- functional groups. Degradation of these compounds is known to form CO_2, but the potassium salts of acetic and formic acids are more stable thermally and therefore less likely to do so. In these experiments with specific reaction conditions, use of 1M KOH seemingly saturates the solution with salts made from the respective acids, (the concentration being 10 times higher than 0.1M). This prompts an interesting question. As the concentration of KOH is a factor of 10 higher, does that mean 10 times more acid is produced to neutralise it or are there other reactions taking place within the system?

Residual pressures for lignin remained the same at both catalyst strengths, with little effect on gas production at any given temperature. Gas production under these conditions for this particular compound is therefore not likely to be pH dependent.

4.6.1.4   Oil and solid residue production

For identical reaction conditions, production of oil by the hydrothermal liquefaction of cellulose and xylan was also found to be inversely affected with the amount of catalyst (**Table 4.7**). Lignin produced little oil under liquefaction conditions at high potassium hydroxide concentrations, consistent with research by Demirbas (Demirbas 2000).

Interesting high oil yield was observed from lignin when lower catalyst concentration is used. Oil and chars produced at the higher concentration, 1.0M KOH, were also found to have lower carbon content and higher oxygen/ inorganic content. Thus, it appears that lower catalyst concentration is beneficial for both oil production, and for better quality char. This is explored further in the next Chapter.

Char formation from cellulose under hydrothermal conditions is discussed by Seville and Fuertes (Sevilla and Fuertes 2009b) with their reaction pathway reproduced in **Figure 4.7**. Their proposed mechanism starts initially by hydrolysis at temperatures >220°C, forming smaller polymers and glucose. Glucose forms fructose via isomerisation, which decomposes to organic acids, (catalysing further degradation reactions) or dehydrates and fragments forming furans and other aromatic structures. It is at this stage that polymerisation reactions then take place, with subsequent intermolecular and intramolecular dehydration reactions. The resulting effect is the formation of a carbon rich char, low in oxygen (**Figure 4.17**)

Use of KOH as a catalyst changes this process, by the production of greater amounts of CO_2, oil and water soluble products, thereby reducing potential char yields. The mechanism for this happening is likely due to the initial degradation of cellulose, producing greater amounts of glucose and therefore fructose. As high levels of organic acids are formed, they are neutralised by acid – base reactions and formation of stable potassium salts.

The phenomenon is observed by monitoring of pH levels, as described in the section **4.5.3**. The use of 0.1M KOH appears to be sufficient to initiate cellulose breakdown to glucose and therefore organic acids. As the reaction proceeds, more acid is produced and neutralisation of KOH occurs, but as pH is still high at this point, cellulose continues to be broken down to glucose, again producing an acid species. As the reaction proceeds further, one can speculate that a point is reached where there is insufficient KOH available to catalyse further degradation reactions from aromatic species (furans, phenols, benzene species). The result of this would effectively mean that the reaction stops and a greater oil yield is observed. As will be discussed further in **Chapter 5**, water soluble organics (WSH) produced at low catalyst concentration have a greater proportion with boiling points in excess of 250°C, i.e. high molecular weight

components. By inference, we can assume that the oil fraction also has higher molecular weight oils.

From the results discussed so far it is clear that not only is control of reaction time and temperature important but also KOH concentration is critical if the desired products are liquid fuels. Control reactions (not shown here), in the absence of catalyst, resulted in a lower conversion of model compound to oil, showing a requirement for catalyst, with the system optimised at lower concentrations.

Char production exhibits a large variation according to model compound and KOH amount. The most surprising result being much higher char for lignin at 0.1M conc. (64.7% Vs. 13.2% at 1M).
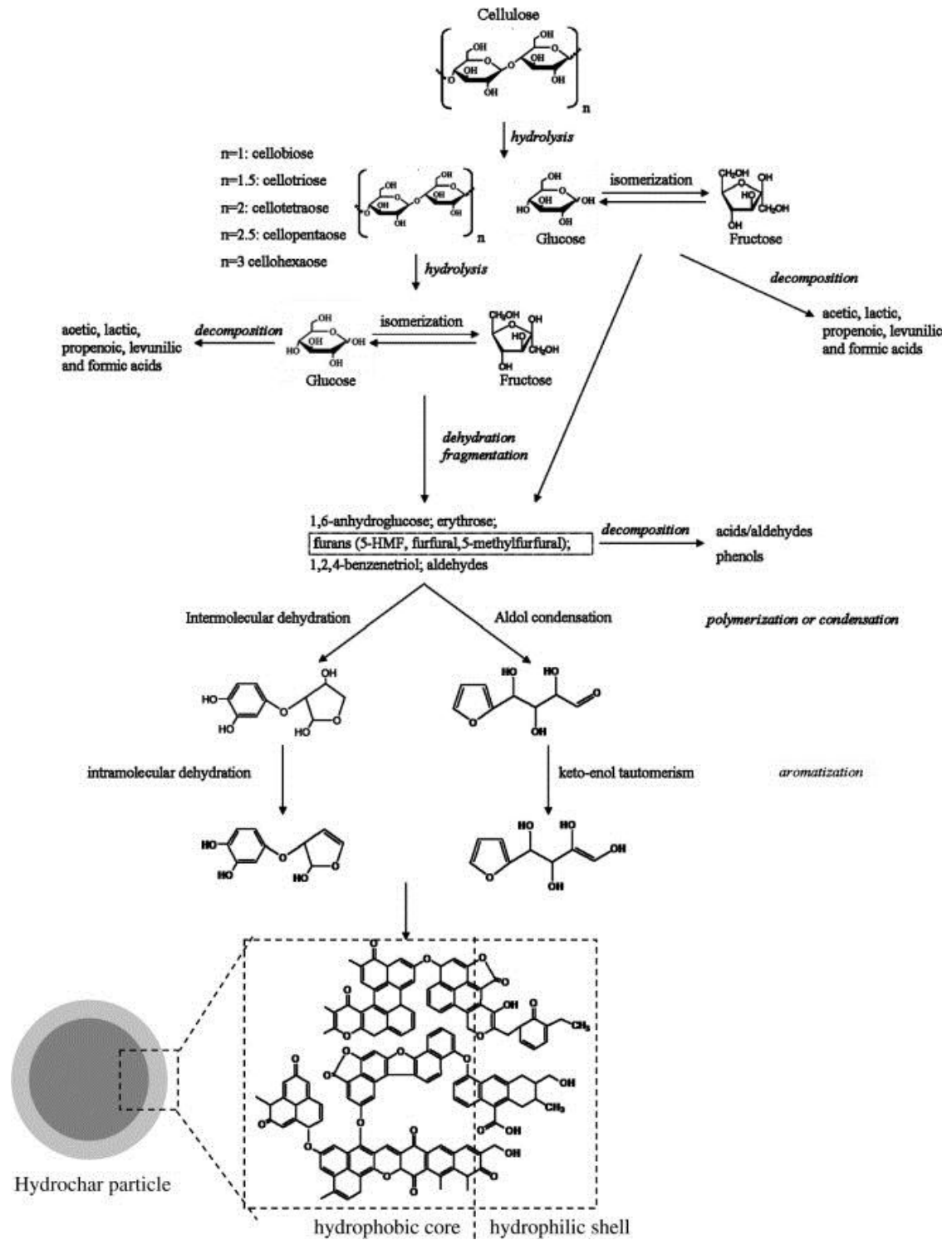
Figure 4.17: Mechanism of formation of hydrochar particles from cellulose by hydrothermal carbonisation

4.6.1.5 Aqueous products formation

The aqueous phase generated from hydrothermal processing contains a high number of water soluble hydrocarbons formed after thermal degradation of biomass model compounds and real world biomass samples. The aqueous phases from the experiments

summarised in **Table 4.6** were extracted in dichloromethane and the extracts analysed by GC-MS. The resulting chromatograms are compared in **Figure 4.18** and the products identified are listed in **Table 4.7**. The reaction of the model compounds results in a large mix of oxygenated hydrocarbons contained in the aqueous fraction as shown in **Figure 4.18**. Cellulose and xylan produce more cyclic aldehydes and ketones, with lignin producing more phenolic compounds, di-substituted phenols in particular. Cellulose and xylan (**Figure 4.18a** and **c**) give a greater number of products detected compared to lignin (**Figure 4.18b**). Relative concentrations of compounds found in the solvent-extracted aqueous phase for lignin, measured by relative abundance, were observed to increase with higher catalyst concentration.

Of particular note in **Table 4.6** is the large increase in the amount of water soluble material produced by lignin when 1M KOH was used (76% vs. 18.1%). This anomalous result is intriguing and does not correspond with an increase in oil, giving evidence of high levels of water soluble organics produced from lignin degradation.

Comparing area % of the detected compounds, and not the relative abundance, shows evidence for breakdown of components in the aqueous phase following predicted reaction pathways.(Srokol et al. 2004; Wahyudiono. et al 2007) **Table 4.7** shows the distribution of products relative to the total area of all peaks detected. Only the peaks with largest area % are shown for simplicity. Each lignocellulose component shows marked differences when compared to the other. For lignin, it can be seen clearly that using the catalyst at lower concentration gives a predominant product of 2,6-dimethoxy phenol (equates to ~60 area%), with only 5 other compounds of a similar structure of any notable abundance. At the higher end of catalyst concentration, greater amounts of other di and tri-substituted phenolic and benzene compounds are produced, coupled with a disappearance of furfural, indicating, as described by others, (Sevilla and Fuertes 2009b) formation of furan derived intermediate products and confirmation of reaction pathways. As the gas pressure remains the same for both catalyst concentrations, it can be assumed that rearrangement reactions are taking place within the aqueous phase, rather than the evolution of gases such as CO_2 and CH_4; however, the relative proportions of each gas produced are at this stage unknown, prompting further research.
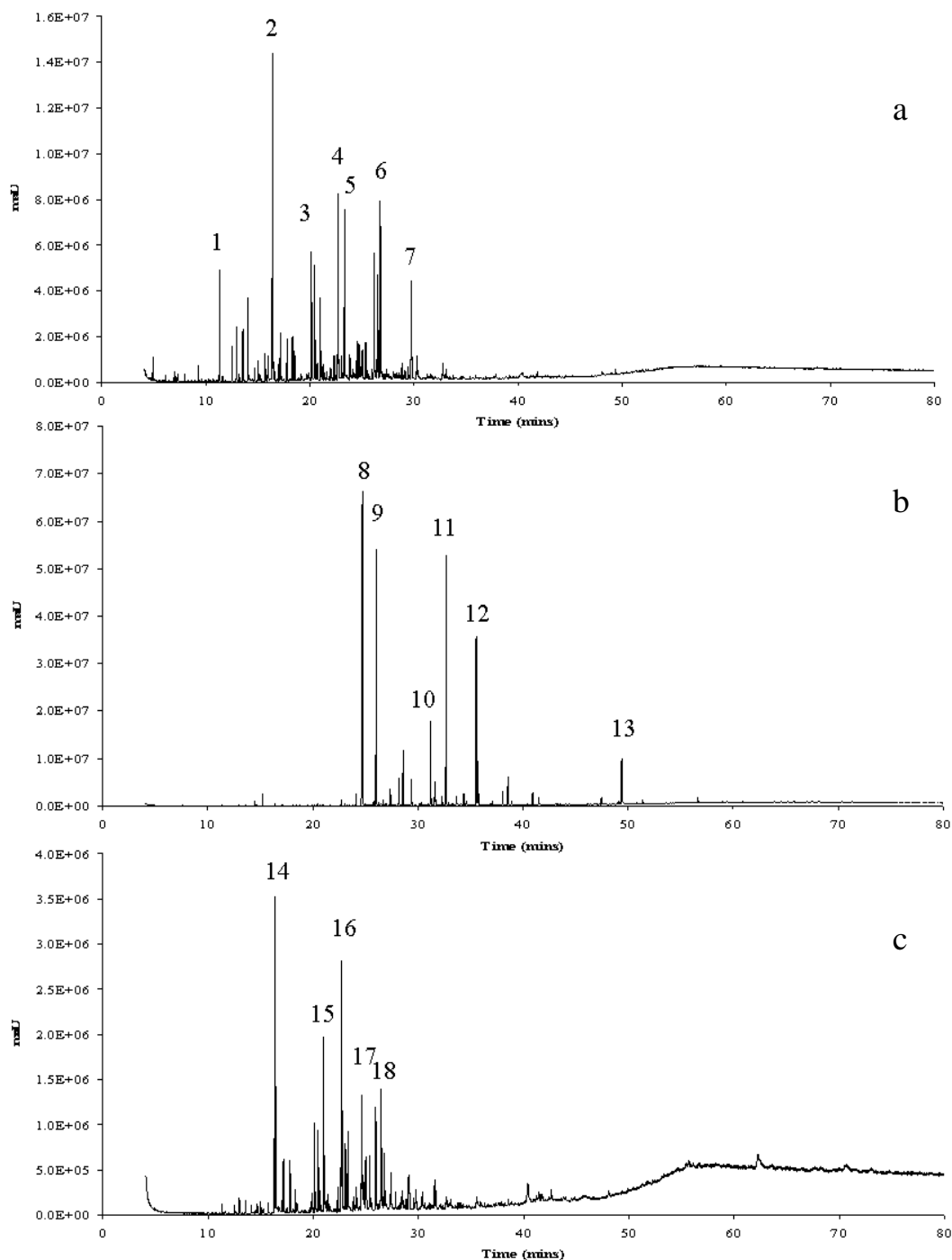
Figure 4.18: G GC-MS chromatograms of DCM extracted aqueous phase for (a) cellulose, (b) lignin and (c) xylan using 1.0M KOH as catalyst at 300°C. Main peaks are assigned as follows: 1: cyclopentanone; 2: 2-methyl-2-cyclopenten-1-one; 3: 2,3-dimethyl-2-cyclopenten-1-one; 4: 2,3-dimethyl-2-cyclopenten-1-one; 5: 2-hydroxy-3,4-dimethyl-2-cyclopenten-1-one; 6: 3-ethyl-2-hydroxy-2-cyclopenten-1-one; 7: 2-ethyl-2-methyl-1,3-cyclopentanedione; 8: 2-methoxy-phenol; 9: 1,2-dimethoxy-benzene; 10: 2,6-dimethoxy-phenol; 11: 1,2,3-trimethoxy-benzene; 12: 2,6-dimethoxy-phenol; 13: 1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone; 14: 2-methyl-2-cyclopentanone; 15: 3,4-dimethyl-2-cyclopenten-1one; 16: 2,3-dimethyl-2-cyclopenten-1-one; 17: 3-ethyl-2-cyclopenten-1-one; 18: 2-methyl-phenol.

Table 4.7: Comparison of major detected products analysed via GC-MS (area %) in oils from hydrothermal liquefaction reactions of cellulose, lignin and xylan using 1.0 and 0.1M KOH as catalyst at 300°C.

Compound	Lignin		Cellulose		Xylan	
	0.1M KOH	1.0M KOH	0.1M KOH	1.0M KOH	0.1M KOH	1.0M KOH
2-methoxy-phenol	12.6	28.6	-	-	-	-
1,2-dimethoxy-benzene	-	17.2	-	-	-	-
2,6-dimethoxy-phenol*	57.6	5.0	1.9	-	-	-
1,2,3-trimethoxybenzene	-	15.8	-	-	-	-
2,6-dimethoxy-phenol*	-	11.7	-	-	-	-
1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone	5.6	3.5	-	-	-	-
furfural	1.7	-	2.9	-	18.1	-
2-cyclopenten-1-one	-	-	6.4	3.6	4.3	-
2-methyl-2-cyclopenten-1-one	-	-	11.7	15.2	11.7	15.8
2-hydroxy-3-methyl-2-cyclopenten-1-one	-	-	7.3	-	-	-
1-(2,5dihydroxy-phenyl)-ethanone	-	-	3.6	-	-	-
2,3-dimethyl-2-cyclopenten-1-one	-	-	1.7	6.4	3.5	4.2
2,3-dimethyl-2-cyclopenten-1-one	-	-	2.4	10.2	7.6	13.0
2-hydroxy-3,4-dimethyl-2-cyclopenten-1-one	-	-	1.8	9.3	2.5	3.9
3-ethyl-2-hydroxy-2-cyclopenten-1-one	-	-	1.8	6.8	-	-
3-methyl-2-cyclopenten-1-one	-	-	3.4	5.9	4.1	4.8
2,3,4-trimethyl-2-cyclopenten-1-one	-	-	-	2.0	-	7.2
2-methyl-phenol	-	-	-	1.4	-	5.7
4-methylbenzoylacetone	-	-	-	-	5.9	-
Totals (area %)	77.5	71.8	44.9	60.8	57.7	54.6

*For lignin, the compound 2,6-dimethoxy-phenol is displayed twice. This is because of 2 distinct peaks, both identified as the compound at different retention times (R_t) when 1.0M KOH catalyst was used. This was verified by manually checking the NIST library against the search parameters.

If we compare the results in **Table 4.7** for 1M to 0.1M KOH for the same reaction conditions, we observe a marked difference in the amounts and types of products. Generally, with higher amounts of catalyst, the concentration of water soluble hydrocarbons increases and the number of products formed decreases, showing various degradation pathways.

The most significant difference between 0.1M and 1.0M KOH reactions with lignin is the presence of 1,2-dimethoxy-benzene and 1,2,3-trimethoxy-benzene, missing from the reaction with the lower concentration catalyst. In their 2008 paper, Bhaskar *et. al.* also quote a reduction in 2,6-dimethoxy-phenol in oil produced from cherry wood when using K_2CO_3 catalyst at $0 - 1.0M$ concentrations, but there is an absence of methoxy-benzene derivatives. For cypress wood, there is evidence of very low levels of methoxy-benzene (under 10 area%).

Studies on glucose by Williams and Onwudili (2005) (Williams and Onwudili 2005) give a reaction pathway for the formation of furfural and cyclopenten-1-one. Results obtained from the GC-MS analysis of bio-oil produced from the gasification of glucose indicate, reduction in the amount of compounds formed, and an increase in the concentrations of these compounds, with the largest amount (µg/g) being phenol, after a reaction time of 120 minutes. It is therefore interesting to note the disappearance of furfural in both cellulose and xylan reactions at the higher catalyst concentrations and the increases of aromatic products, namely 2-methyl-phenol.

Xylan particularly shows the best indication of the degradation of furfural with a loss of the furfural peak at 18.1 area% and the increase in others, some not detected at the lower catalyst amount. Cellulose also shows a similar pattern with the loss of furfural and an increase in structurally similar chemicals (2,3-dimethyl-2-cyclop-enten-1-one and their derivatives). It is unclear if the furfural peak would be greater for cellulose prior at either an even lower catalyst concentration or at a lower reaction time or temperature.

5-hydroxymethylfurfural, detected by others (Antal et al. 1990; Kabyemela et al. 1997; Kruse et al. 2007; Sasaki et al. 2002) and produced by the breakdown of monomeric sugars in both the aqueous and oil phases is notable by its absence. This is likely due to

the reaction having proceeded passed the point of formation and subsequent reaction to compounds detected.

Srokol et al., 2004 reported a loss of reactivity from D-sorbitol when subject to HTL conditions (50mM solution, 240s at 340°C). The reason given for this is the hemi-acetal function of sugars being essential for their conversion. Formation of enediol intermediates (+/- anion) were hypothesised to be important for basic catalysed reaction pathways and cyclic structures for acid reactions. (Srokol et al. 2004)

GC-MS analysis provides a great deal of data, particularly relative abundance of each compound, allowing searches against NIST databases to accurately detect individual separated compounds, however, the viscous DCM extract was in some cases much more representative of tar or pitch than crude oil. Amounts of oil collected were too small to conduct accurate viscosity measurements, but were visibly thicker than other samples of high viscosity materials such as molasses. This high viscosity oil points to not only high molecular weight, undetectable by the existing GC-MS system (scan range of $m/z = 50 - 550$), but also higher boiling points of the compounds. Evidence for this was gathered from the injection port of the GC-MS liner, which contained a black residue following injection of a number of DCM extracted aqueous phase/ oil. The injector inlet temperature is set at 250°C, meaning any material volatilised greater than this temperature would condense on the liner and not pass through the column. In order to check what fraction of DCM extracts contained species with boiling points in excess of 250°C, simulated distillation experiments were run on the TGA (as described in **Chapter 3.2.1**) in air at 10°C/ min ramp to 250°C, isothermal at 250°C for 10 minutes. The results of this confirmed higher molecular weight species. The % DCM extract boiling at >250°C is shown in **Table 4.8** for the hydrothermal reactions of the model compounds in 1M KOH.

Table 4.8: TGA data for DCM extracted oil fraction >250°C for hydrothermal reactions in 1.0M KOH.

	10 minutes	20 minutes	60 minutes
Cellulose 300°C	60.1%	58.1%	58.0%
Cellulose 325°C	50.3%	N/A	N/A
Cellulose 350°C	44.4%	N/A	N/A
Lignin 300°C	44.0%	N/A	N/A
Lignin 325°C	45.3%	N/A	N/A
Lignin 350°C	57.7%	N/A	N/A
Xylan 300°C	64.5%	49.4%	47.6%

Data contained within **Table 4.8** gives a distinct pattern for both cellulose and xylan, how reaction time and temperature affects the boiling point distribution. For cellulose, an increase of time at 300°C from 10 to 60 minutes gives a 3.5% decrease in the amount of oil that has a boiling point in excess of 250°C, whereas the amount of high boiling point oil from xylan reduces from 64.5 to 47.6 over the same time period.

4.7   Conclusions

Biomass model compounds cellulose, xylan and lignin were reacted via hydrothermal liquefaction in the presence of potassium hydroxide catalyst at 1.0M concentration. The outlined process of phase separation via solvent – solvent extraction and subsequent GC-MS, TGA and CHNS analysis showed changing amounts and types of thermal degradation products as the experimental conditions were altered. The product yields of solids and liquids were low, and it is believed that the cause of this was the KOH concentration, which actually had a detrimental effect. High concentrations of inorganic material were present in chars leading to artificially high char yields (and artificially low oil yields). Reaction temperatures at 300°C and residence time of 20 minutes gave the greatest relative concentrations of chemicals detected by GC-MS for cellulose and xylan. As all the reaction runs were completed for each compound, it appears that temperature has the largest effect on the lignin compound; cellulose and xylan appear to exhibit similar degradation products, based on this set of results.

There was a significant change in char quality, with van Krevelen diagrams proving increases in energy density were caused mainly by dehydration reactions. Oil production and quality was found to follow dehydration and decarboxylation reactions, reaching a limit of oxygen removal with an atomic ratio of O:C being 0.17:1.

Biomass model compounds were then reacted via hydrothermal liquefaction in the presence of potassium hydroxide catalyst at concentrations of 1.0M and 0.1M. A reduction in the catalyst concentration had a beneficial effect on the conversion process for cellulose and xylan, allowing a tenfold cost reduction and minimisation of inorganic material present. Use of potassium hydroxide as catalyst for hydrothermal liquefaction reactions appears to catalyse the initial step of conversion of cellulose and (to a lesser degree) xylan to water soluble products, specifically a high proportion of organic acids. Amounts of these acids produced using 1.0 and 0.1M KOH, retard production of char; the proposed mechanism for this is formation of potassium salts from acid/ base calculation, thus removing acid catalysts required for subsequent aromatic char polymerisation and dehydration reactions. A direct result of this is increased oil production, albeit high molecular weight oil. As intermediate aromatic products are formed they in turn react, producing higher molecular weight polymers, but crucially not char.

Organic content of cellulose and lignin aqueous phases produced using 1M KOH catalyst were analysed by LC-MS at IBERS in Aberystwyth. Detection of compounds from cellulose was too difficult under the short timescale allowed for this work. Lignin was more successful, with the aqueous phase found to contain high molecular weight material, detectable outside the UV scanning wavelength of 190-400nm. Discovery of these obviously polar compounds, likely to be polyaromatic hydrocarbons as the greatest response from RI was not mirrored within the detectable UV wavelength. This indicates that either large fragments of the lignin macromolecular structure are severed and held within the aqueous phase or that polymerisation reactions are taking place between lignin monomers.

This initial study now provides the basis to compare analysis using a change of catalyst concentration. The following chapter will concentrate on lower catalyst concentrations to try and improve on yields, with reactions carried out in water as a basis of control.

Chapter 5 – Biochar, Oil and Gas Production from Hydrothermal Processing of Biomass Model Compounds

Chapter overview

In **Chapter 4** the influence of KOH catalyst at 1.0 and 0.1M concentrations on liquefaction products was investigated. One of the conclusions drawn from this chapter was that it was unnecessary to use the higher concentration catalyst (1.0M KOH). The reasons for this are that high catalyst concentration actually produced lower yields of useful products. Also, high levels of potassium were detected in chars, and, of course, there is a prohibitive cost of using high catalyst concentrations. The work in **Chapter 5** extends the study in **Chapter 4** but explores the influence of reaction time (t), reaction temperature (T) and additives (cat) on yield and fuel quantity and characteristics, from the three main biochemical components of biomass, cellulose, xylan (a main constituent in hemicellulose) and lignin. The main focus of the chapter concerns char (biochar) and gas production. A three stage factorial study was initiated (Box et al. Wiley 1979). This is discussed in more detail in section **5.2**.

5.1   Introduction

The increasing global release of CO_2 caused by burning fossil fuels and deforestation is producing atmospheric CO_2 excesses which cannot be removed by existing carbon sinks. The development and production of stable carbonaceous material by processes other than pyrolysis may provide additional carbon sinks sourced from managed energy crops and agricultural or household waste. The process of hydrothermal conversion is particularly suitable for wet biomass and negates energy losses encountered by the removal of water. Changes in reaction conditions can yield varying amounts of products (Bhaskar et al. 2008; Demirbas 2001b; Fang and Fang 2008; Hashaikeh R. et al 2007; Jin et al. 2006; Kumar and Gupta 2009; McKendry 2002c; Meier et al. 1986a; Qian et al. 2007; Srokol et al. 2004; Yip et al. 2009), importantly oils with a high energy density and chars referred to as biochar or hydrochar. Hydrothermal carbonization, a low temperature biomass conversion method, is receiving interest due to potential carbon sequestration and soil remediation qualities, (Beesley et al. ; Dehkhoda et al. ; Hartley et al. 2009; Lee et al. ; Sohi et al. ; Steinbeiss et al. 2009; Van Zwieten et al.) both environmentally sound applications. Hydrothermally produced hydrochar, when compared to other thermal methods e.g. torrefaction and pyrolysis, may also possess

improvements in combustion properties, having a higher heating value (HHV), in the region of sub-bituminous coal (Ozcimen and Ersoy-Mericboyu).

Environmental benefits of hydrochar are 1, removal of CO_2 from the atmosphere via photosynthesis and 2, soil remediation. (Glaser et al. 2001; Sohi et al. ; Steinbeiss et al. 2009). Areas of land with hydrochar dug into the soil have reported greater yields of crops, resistance to chemical leaching, stabilisation of pH and other benefits (Lal 2008).

Usually formed by slow pyrolysis, (Ozcimen and Ersoy-Mericboyu) hydrochar can be made by the process of hydrothermal carbonization (HTC). This is a thermal conversion method carried out in an excess of water at relatively low temperatures (180 – 200°C), for a number of hours. Exothermic chemical conversion of the biomass feedstock via dehydration and decarboxylation occurs, (Funke and Ziegler) lowering feedstock oxygen and hydrogen content. This is measurable by elemental analysis, and the important reactions can be inferred from a plot of atomic ratios of oxygen: carbon vs. hydrogen: carbon on a van Krevelen diagram. Yields of char can be high, but at the expense of long reactor residence times. Reactions carried out in higher temperature, sub-critical water, produce greater amounts of bio-oils and gases. Measured levels of CO_2 in gas produced by hydrothermal liquefaction (HTL) processes indicate a greater degree of decarboxylation compared to HTC, favouring high molecular weight bio-oil production over hydrochar and removal of oxygen from the feed.

As discussed in **Chapter 4**, thermal decomposition routes of biomass model compounds in aqueous media include decarboxylation, dehydration, hydrolysis and polymerisation (Sevilla and Fuertes 2009a) to greater and lesser degrees, forming a carbon dioxide rich gas, water soluble hydrocarbons, oxygenated polycyclic compounds and carbon rich fuels, both solid and liquid. (Bhaskar et al. 2008; Bonn et al. 1988; Bonn et al. 1984; Demirbas 1998b, 2007b; Fang and Fang 2008; Fang et al. 2008; Hashaikeh et al. 2007; Jin et al. 2006; Karagoz et al. 2005a; Kumar and Gupta 2009; McKendry 2002c; Meier et al. 1986a, b; Srokol et al. 2004; Zhang et al. 2008). Reactions in alkaline media increase aromaticity and form the building blocks to coal type structures. (Funke and Ziegler)

Natural variation of biomass species, harvest times, rainfall, use of fertilisers and many other factors influence inorganic biomass contents, particularly sodium and potassium. Use of these metals in alkaline solutions for catalysing hydrothermal processes is well documented, but these are generally used at temperatures >250°C. (Demirbas 1998b; Karagoz et al. 2005b; Klinke H. et al 2004; Zhong and Wei 2004). It is perhaps no surprise then that the inorganic contents of biomass, especially the alkali metals contents (Na, K) have a major effect on liquefaction reaction products. This phenomenon is particularly observed when hydrothermally processing seaweeds. (Anastasakis and Ross 2011)

Differences observed in the atomic ratios of hydrogen: carbon and oxygen: carbon measured in char and oil; identify changes in composition following hydrothermal treatment. For fuel use, it is desirable that products of thermochemical processes have lower atomic O: C and higher H: C ratios than their corresponding biomass based feedstock. Residual pressures, measured at the end of the reaction give a good indication to the efficacy or conversion via decarboxylation (CO_2 production). These two approaches have proved useful in analysing results from the current study.

5.2   Experimental method

Details of experimental methodology are given in **Chapter 2.2.1**. In addition, the residual pressure and temperature was recorded to calculate moles of gas using the ideal gas equation (equation **5.1**) and an average molecular weight of 28 for the gas (Biller and Ross) (*note;* for safety and pressure reduction, gases were vented at under 40°C). Product yields were calculated using equation **5.2**; higher heating values (HHV) using equation **5.3**. (Channiwala and Parikh 2002)

$$pV = nRT \quad n = \frac{m}{M}$$

$$(5.1)$$

$$wt\% \, char = \frac{char\,weight(g)}{sample\,weight(g)} * 100$$

$$(5.2a)$$

$$wt\% \, oil = \frac{oil\,weight(g)}{sample\,weight(g)} * 100$$

$$(5.2b)$$

$$wt\% \, gas = \frac{gas\,weight(g)}{sample\,weight(g)} * 100$$

$$(5.2c)$$

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034*O - 0.015N - 0.211A$$

$$(5.3)$$

A three stage factorial study was undertaken and an example of experimental factorial design with variables of temperature, time and catalyst is given in **Table 5.1**. This experimental pattern is repeated for all model compounds, giving 12 experiments in total. Individual responses are calculated using equation 4.4 which determines which system variable has the greatest effect. Experiments E1 – E4 are carried out using cellulose, E5 – E8 using xylan and E9 – E12 lignin (**Table 5.1**).

Table 5.1: Experimental factorial design

Design number & Substrate			Factor A (cat)	Factor B (t)	Factor C (T)	Response
Cellulose	Xylan	Lignin				
E1	E5	E9	KOH 0.1M	10 minutes	200°C	*a*
E2	E6	E10	Water	5hrs	200°C	*b*
E3	E7	E11	Water	10 minutes	250°C	*c*
E4	E8	E12	KOH 0.1M	5hrs	250°C	*d*

Response values (*a, b, c* and *d*) calculated were; char yield (**Figure 5.2**), oil yield (**Figure 5.7**), pH of aqueous phase (**Table 5.3**) and HHV of both oil & char (**Figure 5.4** and **5.6**).

The following equations, (**5.4a-f**) and (**5.5a-c**), are taken from ("Statistics for experiments", Box, Hunter and Hunter, Wiley 1978). Average results of the three factor design are calculated for each model compound (cellulose is shown) as:

High catalyst average, $\left(\overline{0.1M\ KOH}\right)_{Cellulose} = 0.5(a+d)$ 　　　　　　(**5.4a**)

Low catalyst average, $\left(\overline{Water}\right)_{Cellulose} = 0.5(c+b)$ 　　　　　　(**5.4b**)

High temperature average, $\left(\overline{250°C}\right)_{Cellulose} = 0.5(c+d)$ 　　　　　　(**5.4c**)

Low temperature average, $\left(\overline{200°C}\right)_{Cellulose} = 0.5(a+b)$ 　　　　　　(**5.4d**)

Long residence time average, $\left(\overline{5\,hours}\right)_{Cellulose} = 0.5(b+d)$ 　　　　　　(**5.4e**)

Short residence time average, $\left(\overline{10\,min}\right)_{Cellulose} = 0.5(a+c)$ 　　　　　　(**5.4f**)

These are then used to calculate the influence of catalyst, temperature and residence time as follows:

For the effect of catalyst;

$$\Delta_{Cat} = \left(\overline{0.1M\ KOH}\right)_{Cellulose} - \left(\overline{Water}\right)_{Cellulose} \qquad \textbf{(5.5a)}$$

For the effect of Time (t)

$$\Delta_t = \left(\overline{5\ hours}\right)_{Cellulose} - \left(\overline{10\min}\right)_{Cellulose} \qquad \textbf{(5.5b)}$$

For the effect of Temperature (T)

$$\Delta_T = \left(\overline{250°C}\right)_{Cellulose} - \left(\overline{200°C}\right)_{Cellulose} \qquad \textbf{(5.5c)}$$

If, for example, the high catalyst average is very different from the low catalyst average, then it follows that the catalyst factor has produced this difference. This method enables the study of the role of three factors at two levels in only four tests (four for each model compound). It also determines the interdependence of the variables. A positive Δ_{cat}, Δ_t or Δ_T indicates that the higher level (0.1 M KOH, 5 h, or 250°C) is having a larger impact on the response (e.g. char yield).

5.3   Results and discussion

Reactions carried out in this study provided observable visual differences between products and are worthy of mention. At the lower temperature and residence times, experiments E1, E5 and E9 (200°C, 10 minutes 0.1M KOH) solid residues were similar in appearance to the respective starting materials, light coloured fine powders. As the conditions changed to 250°C and 5 hour residence times, these residues became black in appearance and formed much larger particles or agglomerates, similar to coal fragments, some matt and others with a glossy appearance. This development in itself indicates polymerisation reactions occurring at higher temperatures and residence times, producing black, apparently carbon rich macrostructures.

Post reaction, when the reactor had cooled to below 40°C and gases had been vented; there was evidence of dissolved gases in the aqueous phases, with visible release of gases like those present in carbonated drinks. Aqueous phases were generally light brown and transparent, but within 6 hours of exposure to air, became black solutions, indicating further oxidation reactions had taken place.

Gas, char, oil and water soluble hydrocarbon (WSH) yields (measured by difference) are displayed in **Figure 5.1** with elemental analysis and other characteristics given in **Table 5.2** These results are discussed in the following sections.

Table 5.2: Analysis of oil, char and aqueous phase

Experiment Number	Oil^{daf}				Char^{daf}				Aqueous phase	
	C %	H %	O %*	HHV MJ/Kg	C %	H %	O %*	HHV MJ/Kg	TOC g/L	pH
E1 (cellulose)	65.3	7.3	27.1	28.6	43.2	6.5	50.2	17.6	6.6	5.02
E2 (cellulose)	59.0	5.6	35.4	23.5	47.0	6.2	46.6	18.9	11.3	2.70
E3 (cellulose)	51.1	4.7	44.1	18.8	61.5	4.6	33.9	23.4	27.9	2.51
E4 (cellulose)	68.3	7.0	23.7	29.7	74.3	5.8	19.8	30.7	10.2	4.25
E5 (xylan)	63.4	6.4	30.1	26.5	49.2	5.2	45.5	18.6	29.2	4.72
E6 (xylan)	63.7	7.0	29.2	27.5	63.6	5.1	31.1	25.0	12.2	4.01
E7 (xylan)	63.9	7.2	28.9	27.8	64.6	5.5	29.8	26.0	7.6	3.85
E8 (xylan)	66.7	6.7	26.6	28.4	72.8	5.5	21.5	29.7	3.7	4.75
E9 (lignin)	59.0	6.9	34.0	25.3	65.1	5.8	28.9	26.5	3.3	7.29
E10 (lignin)	58.0	6.4	35.5	24.1	67.9	5.7	26.1	27.8	5.1	3.27
E11(lignin)	55.3	5.8	38.9	22.1	67.4	5.4	26.9	27.2	2.6	2.97
E12 (lignin)	56.8	5.4	37.7	22.3	69.6	5.5	24.6	28.3	5.6	6.93

* by difference

^{daf} dry, ash free

	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11	E12
% WSH	16.9	35.1	57.8	55.1	65.1	64.9	69.4	70.3	15.3	11.8	12.0	30.0
% Gas	0.0	2.0	2.1	12.2	4.2	8.0	6.2	10.5	0.0	2.0	2.0	4.0
% Oil	0.8	2.0	3.5	9.0	4.7	5.2	7.9	6.0	5.8	9.6	19.1	9.1
% Char	82.3	60.9	36.6	23.7	26.0	21.9	16.5	13.1	78.9	76.6	66.9	56.9
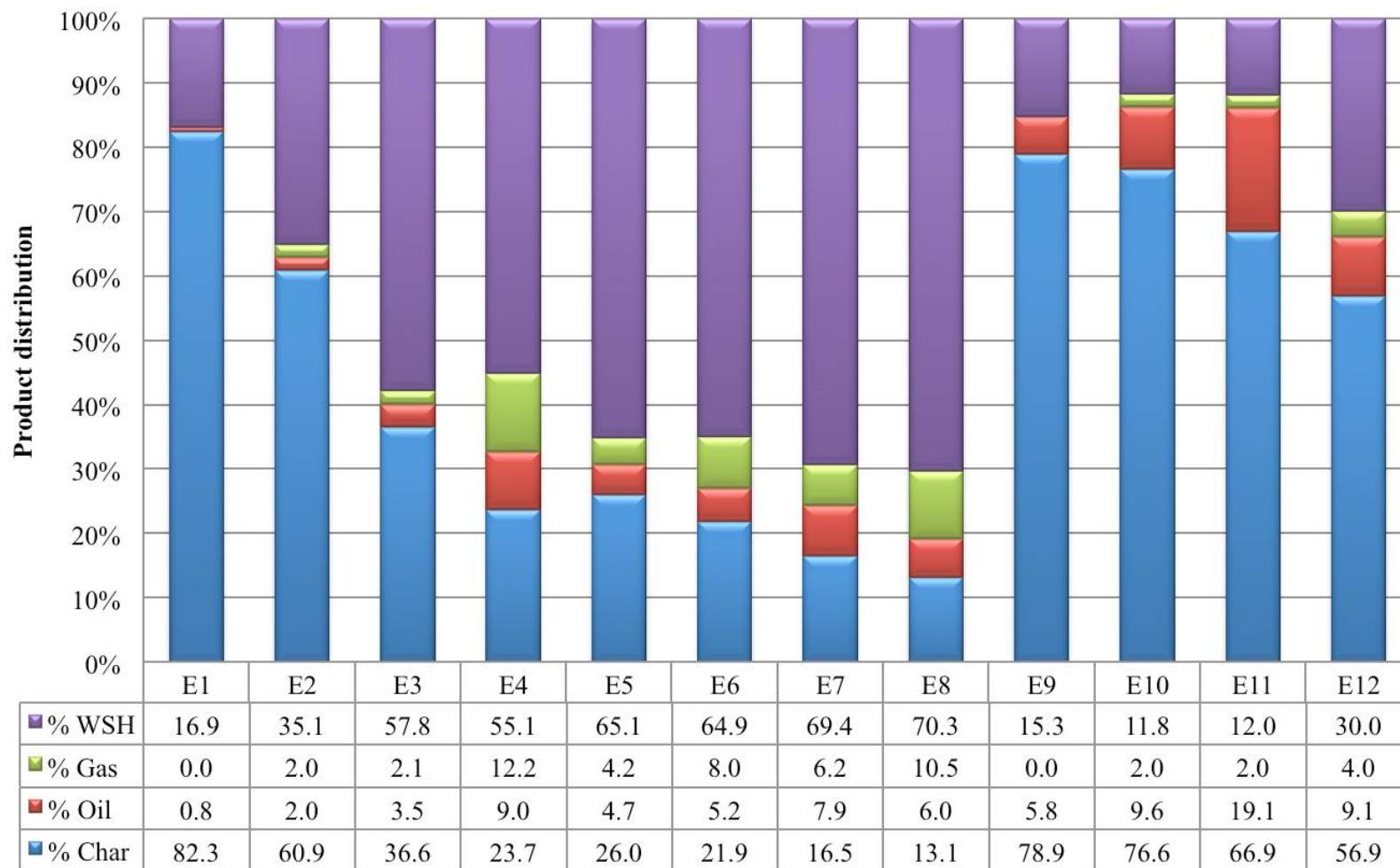
Figure 5.1: Product distribution from hydrothermal processing of cellulose (E1 – E4), xylan (E5 – E8) and lignin (E9 – E12).

5.3.1 Char yields and compositions

It is clear from **Figure 5.1** that cellulose and lignin give higher char yields than xylan under nearly all reaction conditions. Char yield is particularly favoured by low temperatures. This is shown more clearly in **Figure 5.2**. For each model compound, temperature has the most significant influence on char yield, then residence time, and finally catalyst. Use of KOH has a minor positive increase for cellulose, but as previously explained in **Chapter 4.4**; this could be due to inorganic material from the catalyst being contained within the char. There are significant differences also between reactivities of each model compound. For char production, cellulose is the most sensitive compound to changes in reaction time and temperature; lignin is less sensitive by a factor of 2-3 and xylan exhibits even smaller changes in char yield, particularly with increased reaction time.

	Cellulose char	Lignin char	Xylan char
delta temp	-41.47	-15.85	-9.11
delta time	-17.14	-6.21	-2.06
delta KOH	4.28	-3.84	0.36
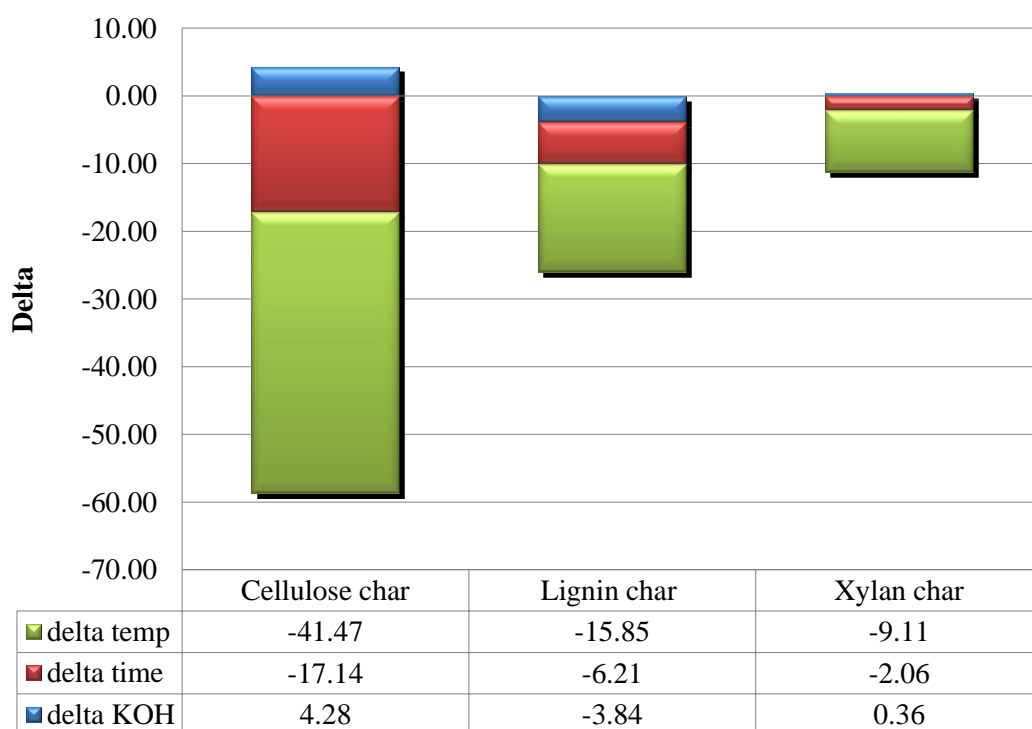
Figure 5.2: Change in char yield relating to each reaction variable

	Cellulose carbon in char	Lignin carbon in char	Xylan carbon in char
delta temp	22.79	1.98	12.27
delta time	8.36	2.51	7.23
delta KOH	4.49	-0.30	-3.11
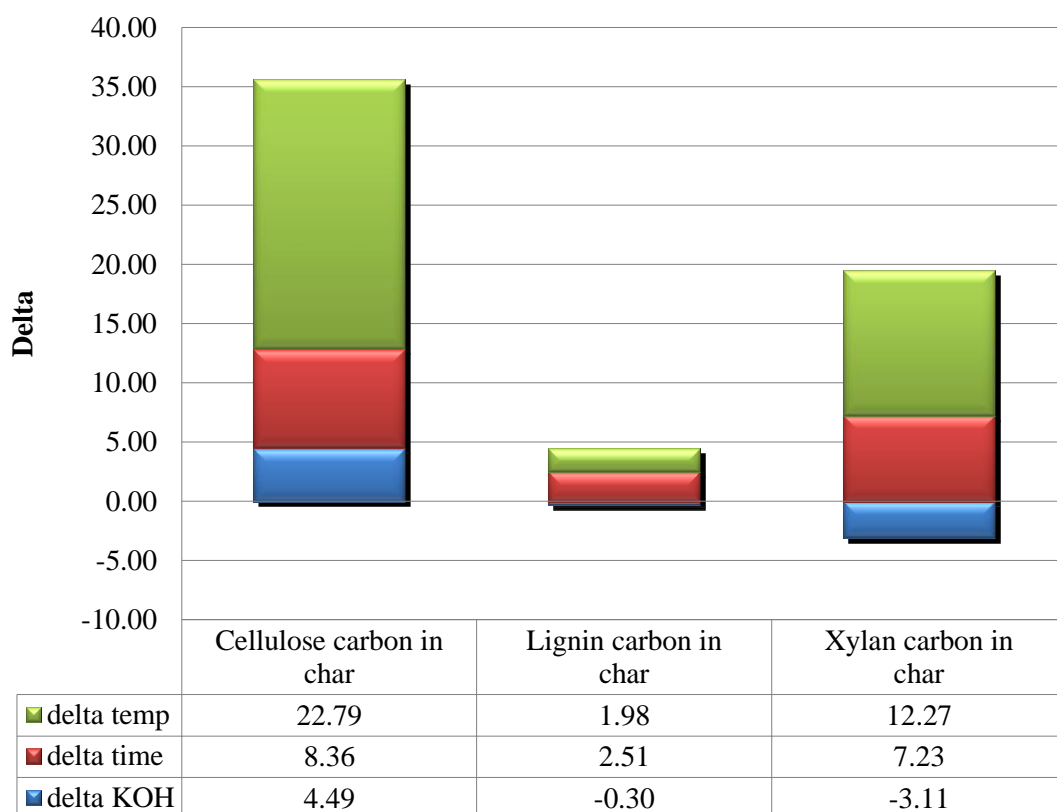
Figure 5.3: Change in carbon content of char relating to each reaction variable

Carbon contents of produced chars and the change in response with reaction variables are given in **Figure 5.3**. Here it is shown that Δ_T produced the biggest increase in char carbon contents for both cellulose and xylan, with cellulose again being the compound most affected. Thus, for cellulose and xylan, high temperature favours lower char yield, but the char produced has higher carbon content. Residence time has the next most significant impact on carbon content of the char, and the presence of catalyst the least influence on this response. Interestingly, for lignin, the char carbon contents have very little dependency on temperature, time or catalyst.

	HHV cellulose char	HHV lignin char	HHV xylan char
▨ delta temp	8.8	0.6	6.05
▨ delta time	4.3	1.2	3.2
▨ delta KOH	3	-0.1	-1.35
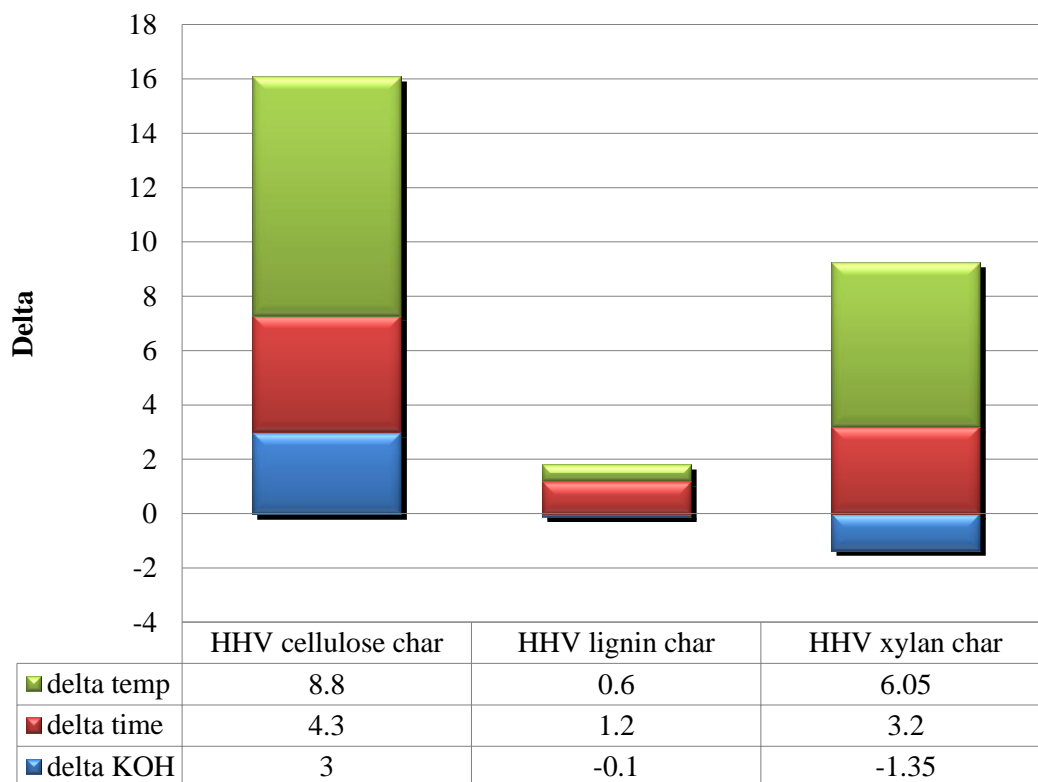
Figure 5.4: Change in HHV of chars produced by hydrothermal processing of biomass model compounds with respect to reaction variables

HHV of biomass derived chars (**Figure 5.4**) followed an expected pattern, with increases in reaction time and reaction temperature having the greatest effect on all three model compounds. Lignin HHV was least affected by the change in conditions, with the smallest response overall. It is clear though, that lignin char HHV is more affected by reaction time than temperature, whereas for cellulose and xylan the reverse is true. Addition of catalyst had a positive effect on char HHV for cellulose, negative for xylan and neutral for lignin.

5.3.2 Oil yields and compositions

When comparing the effect of reaction variables on oil yields (**Figure 5.5**), it is clear that Δ_T has the largest positive effect on oil production. Of these, it is lignin that has the most significant change, even though there are various literature sources that dispute degradation of lignin below 280°C. It is clear from the data that addition of catalyst and a prolonged reaction time impedes the production of oil from lignin. This is yet more evidence that KOH has greatly differing effects on reaction products.

	Cellulose oil	Lignin oil	Xylan oil
delta temp	4.90	6.39	2.01
delta time	3.34	-3.11	0.23
delta KOH	2.13	-6.90	-1.16
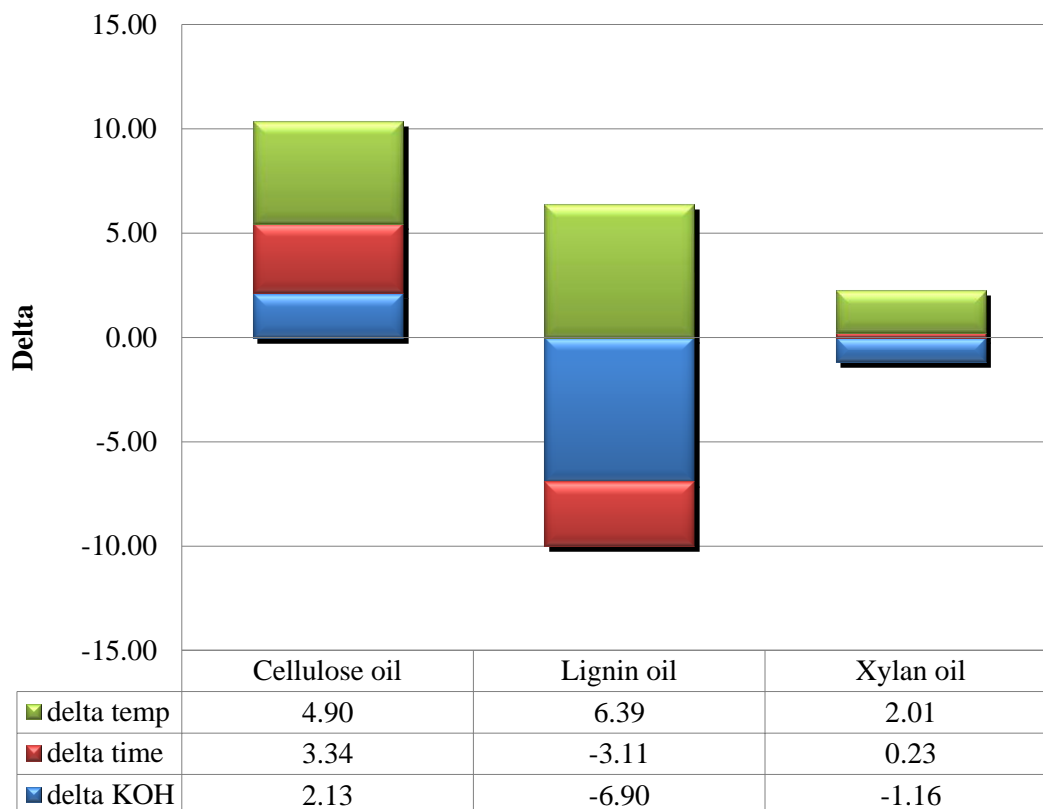
Figure 5.5: Change in oil yield for each reaction variable

For the effect of Δ_t (reaction time), there is a corresponding increase in oil yield for cellulose at longer reaction time, a similar decrease for lignin and a negligible increase for xylan. Again, as with char production, the least reactive compound is xylan. The relationship between individual model compounds and oil yields becomes more complex with the following:

Δ_T Lignin > Cellulose > Xylan

Δ_t Cellulose > Xylan > Lignin

Δ_{cat} Cellulose > Xylan >> Lignin

A change in reaction conditions affects yields; this also usually corresponds to a change in higher heating value of the oil (HHV). Data in **Figure 5.6** shows this is not always the case. Interestingly, for cellulose, it is the addition of catalyst that produces the greatest increase in oil HHV. There is also a small increase for lignin and a negligible decrease for xylan.

A temperature increase has the effect of reducing the HHV of oil from cellulose and lignin by comparable levels. Xylan, however, displays increased oil HHV with increasing temperatures, a surprising outcome.

	HHV cellulose oil	HHV lignin oil	HHV xylan oil
delta temp	-1.8	-2.5	1.1
delta time	2.9	-0.5	0.5
delta KOH	8	0.7	-0.2
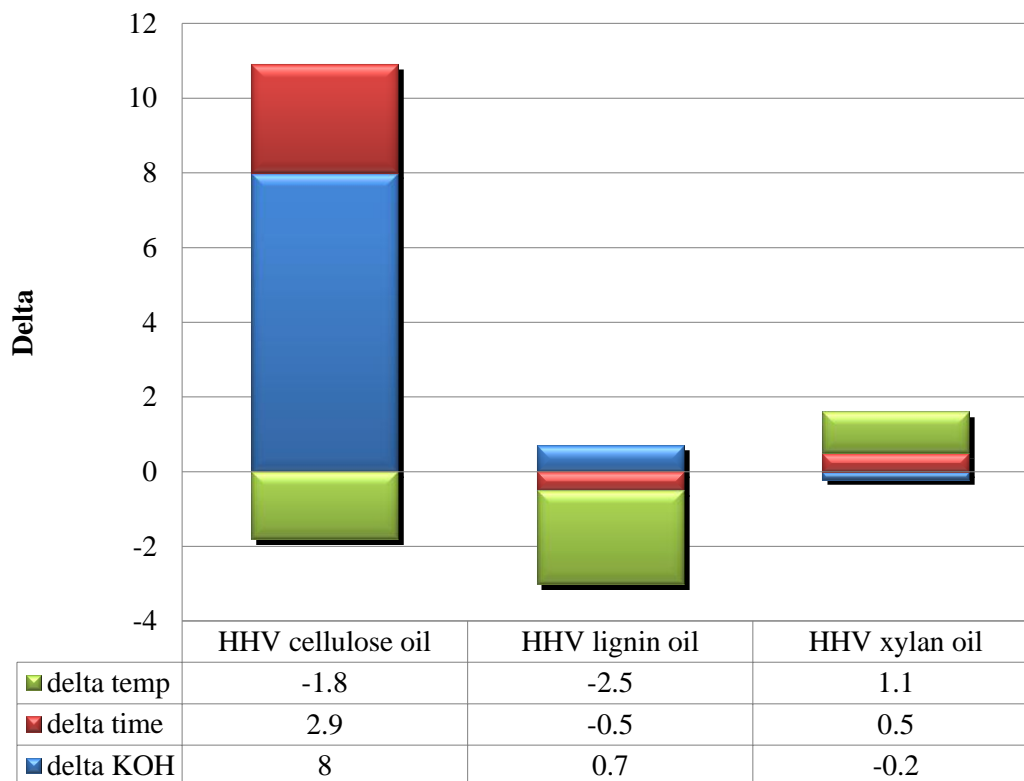
Figure 5.6: Change in HHV of oils produced by hydrothermal processing of biomass model compounds with respect to reaction variables

For the change in HHV of oils pertaining to differing reaction conditions, the following were noted.

Δ_T Xylan $>$ $>$ Cellulose $\geq$ Lignin

Δ_t Cellulose $>>$ Xylan $>$ Lignin

Δ_{cat} Cellulose $>>$ Lignin $>$ Xylan

5.3.3 Aqueous yields and compositions

The aqueous phase, after solvent extraction to remove oil, was analysed to determine total organic carbon (TOC) levels. Differing reaction conditions, relating to a change in measured TOC can be viewed in **Figure 5.7**. Results for lignin are as expected, with little change in the solubility of lignin-related degradation compounds. A minor increase is observed as the reaction time is extended to 5 hours, hinting to a slow rate

determining step, allowing the production of water soluble compounds. This also corresponds to the smallest changes in pH for lignin (**Table 5.3**), with noticeably reduced levels of water soluble acidic compounds being produced.

	Cellulose TOC	Lignin TOC	Xylan TOC
delta temp	10.11	-0.07	-15.05
delta time	-6.55	2.37	-8.53
delta KOH	-11.19	0.62	6.57
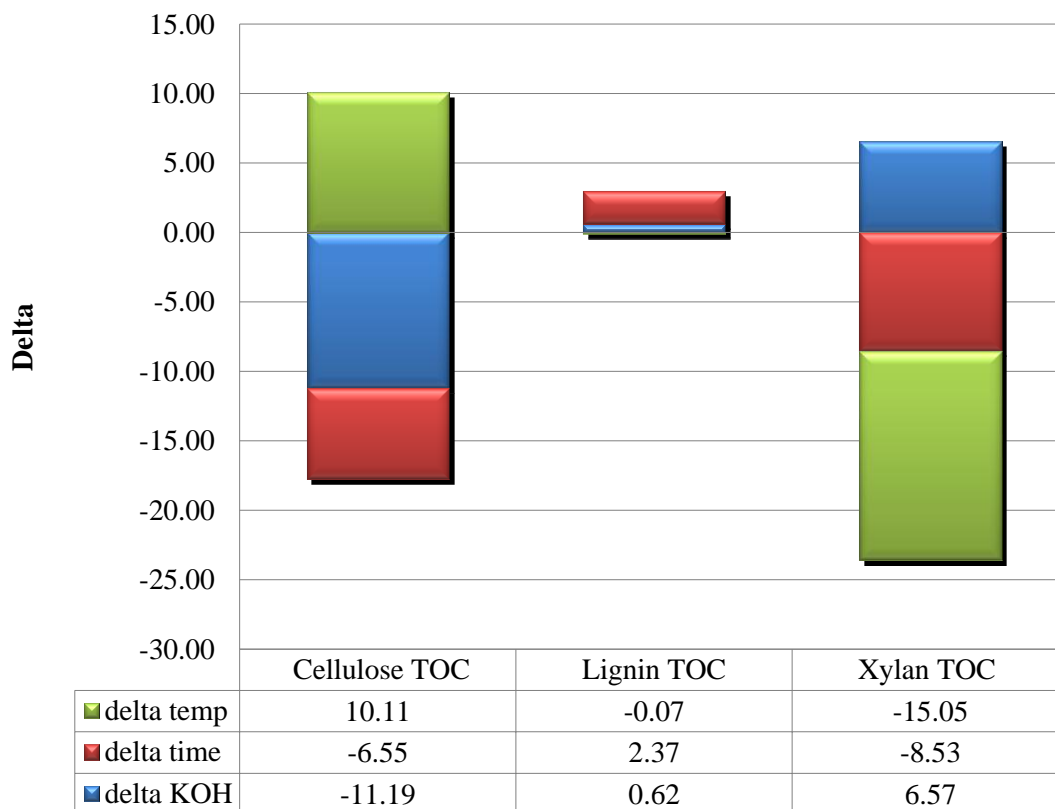
Figure 5.7: Change in TOC yield relating to each reaction variable

For cellulose alone, Δ_T increases TOC of the water phase by the highest amount. Conversely, xylan TOC is reduced. A similar, inverse, relationship is observed with Δ_{cat} – increased TOC for the water phase from xylan and a drop for cellulose.

Both cellulose and xylan exhibit a reduction in the TOC of their aqueous phases as the reaction time increases. This information tallies nicely with expected carbonization reaction routes for the formation of hydrochar.

Aqueous phase TOC levels relating to reaction conditions and model compounds exhibit the following trends:

Δ_T Cellulose $> >$ Lignin $>>$ Xylan

Δ_t Lignin $>>$ Cellulose $\geq$ Xylan

Δ_{cat} Xylan $>$ Lignin $>>$ Cellulose

For experiments carried out in water, temperature has the biggest effect in acid production for cellulose and lignin, lowering the pH by an average of 0.5 for cellulose and 0.3 for lignin (**Table 5.3**). Xylan, however, shows the smallest change in response for temperature, indicating acid production is barely affected by temperature in the range 200 – 250°C. This is discussed in more detail at the end of this chapter.

Table 5.3: Average response values and change in response for aqueous phase pH

	pH cellulose	pH lignin	pH xylan		cellulose	lignin	xylan
$\overline{Water}$	2.6	3.1	3.9	Δ_{cat}	2.0	4.0	0.8
$\overline{10\ min}$	3.8	5.1	4.3	Δ_{t}	-0.3	0.0	-0.4
$\overline{200°C}$	3.9	5.3	4.4	Δ_{T}	-0.5	-0.3	-0.1
$\overline{0.1M\ KOH}$	4.6	7.1	4.7				
$\overline{5hrs}$	3.5	5.1	3.9				
$\overline{250°C}$	3.4	5.0	4.3				

5.3.4   Gas yield and composition

	Cellulose gas	Lignin gas	Xylan gas
delta temp	6.13	2.00	2.26
delta time	6.05	2.02	1.93
delta KOH	4.03	-0.01	0.23
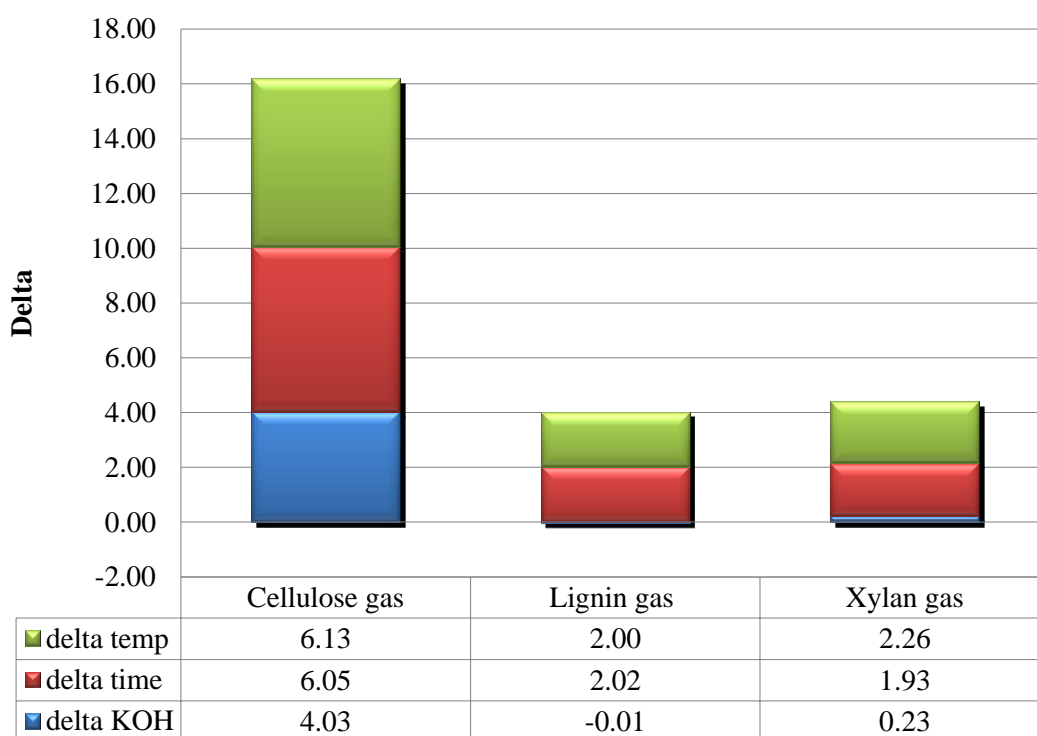
Figure 5.8: Change in gas yield relating to each reaction variable

At temperatures of 200°C, gas evolution from each model compound is low (**Figure 5.1**). It is evident from the graphs in **Figure 5.8** that both Δ_T and Δ_t contribute to gas production for all model compounds, with cellulose being the compound most affected by changes in reaction conditions. Xylan and lignin exhibit similar proportional increases for Δ_T and Δ_t. For cellulose, it is the addition of catalyst that again has the greatest effect on gas production; little change is witnessed with xylan or lignin in the presence of KOH.

5.4   Discussion

There has been much research surrounding hydrothermal liquefaction and carbonisation of biomass model compounds at both super and sub-critical temperatures, with and without reaction additives or catalysts. The general consensus, confirmed by experiments carried out in **Chapter 4**, is that temperatures in the super and sub–critical region (300°C +) produce more oil and gas, whereas lower temperatures (<250°C) and reaction times in excess of 2 hours favour the production of char and water soluble organic compounds, particularly for cellulose and hemicellulose (xylan). Catalyst effect has also been measured, with reactions taking place in both alkali and acidic media, with supported metals on alumina and zeolites. With regard to the effect on the reaction products, it is clear that liquefaction reactions for biomass are influenced by potassium hydroxide as a catalyst, specifically hydrolysis reactions and the formation of acids. It is evident from aqueous phase pH values (**Table 5.2**) that OH^- is not regenerated, and reacts further with H^+ producing water. The form of potassium post reaction is neutral to acidic, compared to alkaline at the start.

In terms of char yield, the factorial analysis conducted here found that for all three model compounds, this has sensitivity to the three process variables of temperature, time and catalyst concentration in the order temperature > time > catalyst concentration. A similar trend is observed for both carbon content and heating value of the char. **Figures 5.9** and **5.10** show the linear correlation between HHV and % carbon for hydrothermally produced chars and oils respectively from this study. R^2 values >0.95 for each graph denote a linear correlation. These formulae are able to provide a quick approximation of the HHV if carbon contents are empirically measured via elemental analysis (CHN/S).
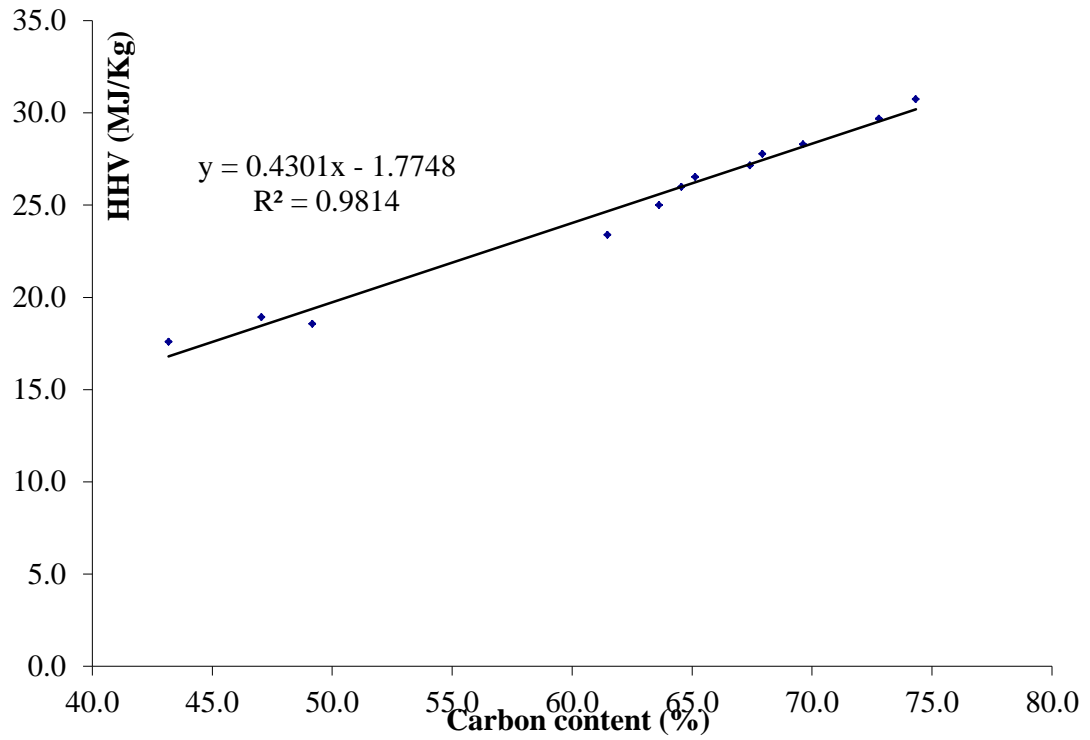
Figure 5.9: Correlation between HHV of hydrothermally produced chars from biomass model compounds with respect to carbon content
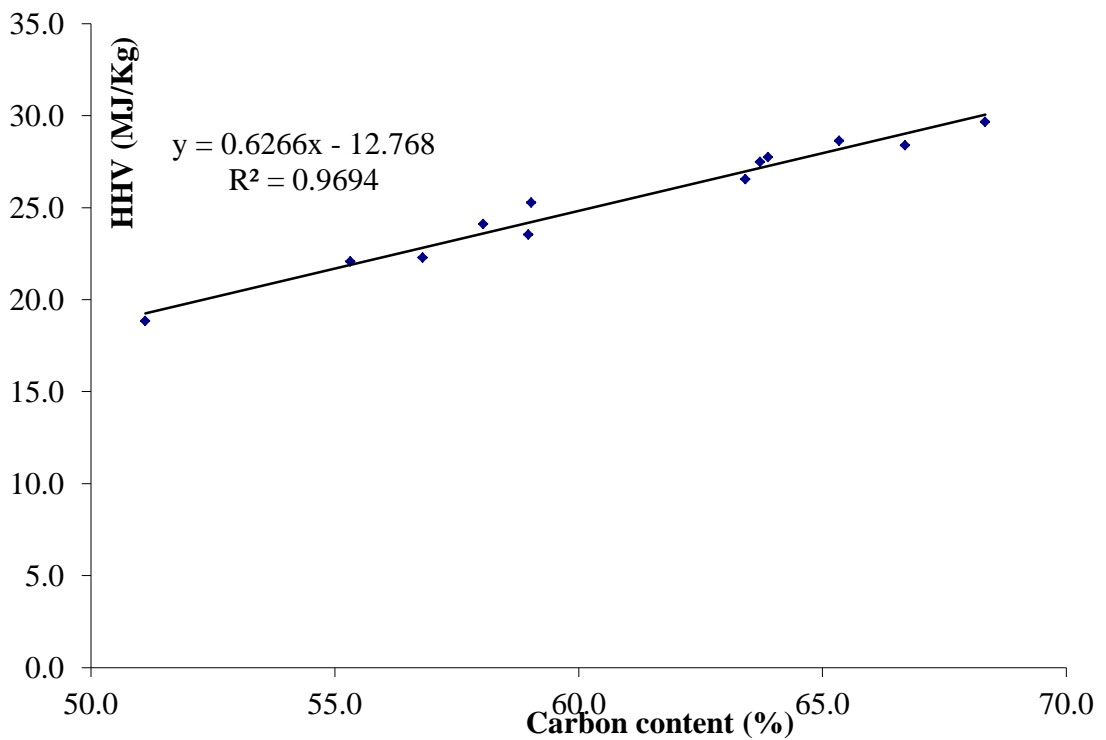
Figure 5.10: Correlation between HHV of hydrothermally produced oils from biomass model compounds with respect to carbon content

Previous chapters have discussed dehydration and decarboxylation reactions that take place when processing biomass model compounds under hydrothermal conditions and how these reactions can be monitored and observed by plotting van Krevelen diagrams of the resulting oils and chars. **Figure 5.11** contains atomic H: C data plotted against atomic O: C for all the oil and char products from this survey. Clear patterns emerge, concurrent with **Chapter 4.** Cellulose and xylan chars follow the path of dehydration with an increase in severity of reaction conditions, whereas lignin chars are largely unchanged in their atomic ratio, which is not to say that the chars are physically similar to the raw material, because they are not.
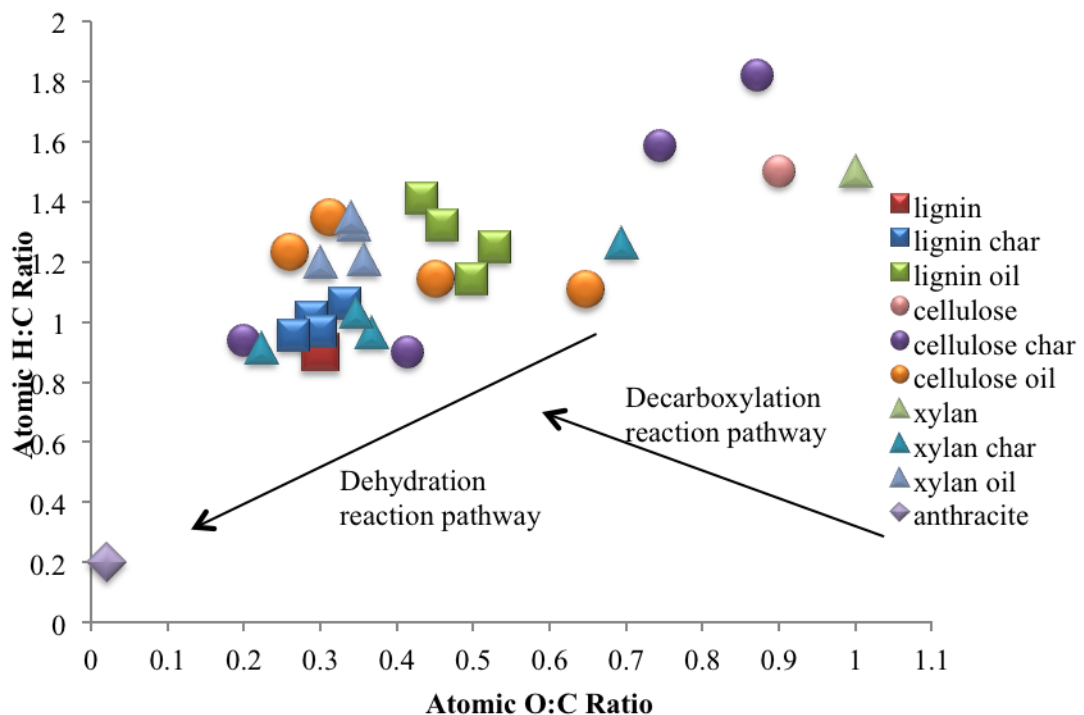
Figure 5.11: Van Kreveln diagram of biomass raw materials and hydrothermally produced oils and chars with anthracite coal as a reference

It is also evident that oils from cellulose and xylan are subject to both dehydration and decarboxylation reactions, with xylan oils appearing to be resistant to further degradation, denoted by the bunching on the graph (**Figure 5.11**). Cellulose oils are subject to a greater degree of decarboxylation with increasing reaction severity, achieving higher HHV's. The statement could therefore be made that cellulose oils produced via hydrothermal processing conditions in this experiment are less stable or more prone to degradation/ microbial attack similar to those experienced by pyrolysis oils,(Maschio 1992b) due to having increased oxygen content compared to lignin and

xylan oils; both groups of oils bunch at a particular area on the graph. The reasons why this may be the case could be due to the components in cellulose oils being more polar or indeed more reactive. Lignin remains relatively insoluble after partial degradation, forming oils rich in phenolic compounds and higher molecular weight hydrocarbons (**Chapter 4**), thereby resistant to further degradation under the conditions used. Xylan is the opposite in terms of solubility, forming WSH with ease due to the polar side chains and forming higher levels of furan based compounds, containing, importantly a stable aromatic ring. Cellulose produces low levels of aromatic compounds at the temperatures employed, preferring the formation of 5-membered carbon ring structures containing (in some cases) unsaturated double bonds, with reactive ketone, aldehyde and alcohol functional groups. It is likely that these products, including greater levels of organic acid production from cellulose are the intermediates from which CO_2 and H_2O are produced.

Increases in HHV for both oils and chars produced also coincided with a drop in yield and an increased gas production; removing more precious carbon in the form of CO_2 thereby decreasing the overall energy yield.

The findings, which quantify the effect that a change in reaction variables has on the energy content of biomass model compounds, are significant, but contrary. Increased temperature from 200 to 250°C has a negative effect on oil HHV for cellulose and a greater negative effect for lignin. Xylan, on the other hand, was calculated to produce an increase in oil HHV with increased reaction temperature with little or no effect from time or catalyst. This also ties in with the cluster of data points observed in the van Krevelen diagram (**Figure 5.11**) for xylan and a similar level for lignin oils.

The inference from this data is the availability of cellulose oil for further degradation via decarboxylation, a likely source being organic acids; lactic, formic and acetic acids are well known to degrade in this manner (Jin et al. 2005). Lower concentrations of acids produced, along with more stable aromatic compounds in lignin and xylan oils account for the resistance of these oils to degrade further, also indicating that the oil conversion reaction is much quicker.

Catalyst concentration had the greatest influence on oil HHV for cellulose, and indeed, was the most significant reaction variable for this response. The cellulose degradation in the presence of KOH is likely to follow the reaction pathway of:

Cellulose → cellobiose → hexose (glucose, fructose) →5HMF →Carboxylic acids →CO_2 (Jin and Enomoto 2008), detected by the decarboxylation pathway in **Figure 5.11** for cellulose oils. This proposed degradation is discussed further on in the chapter with respect to acid formation and corresponding pH values of the aqueous phase.

The impact of variables on oil yield is given in **Figure 5.5** The most surprising result is oil formation from experiment E11 (lignin, water 10 minutes, 250°C), but also as a whole for lignin overall. Breakdown of lignin, particularly at temperatures around 250°C is not well reported, with many researchers using reaction conditions ≥300°C. (Bonn et al. 1988), however, distinguish "soluble lignin" as a product following hydrothermal and organosolv processes to break down lignin, occurring at 200°C alongside hemicellulose degradation. In the journal paper "Direct liquefaction of different lignocellulosics and their constituents" (Meier et al. 1986a), the highest oil yielding products based on dry feedstock weight were lignin obtained from spruce and bagasse using organosolv as the production method, however, these reactions took place at 375°C.

Significance of oil formation at temperatures of 250°C and lower is potentially threefold. 1) It is wholly possible that the extraction method for production of organosolv lignin (explained in detail in **Chapter 1**) has not only altered the physical structure of lignin, compared to the natural form, but also its chemical reactivity. Thus, hydrothermal processing leads to oil and gas production not usually observed at the reaction conditions given. 2) Another explanation is that indeed, lignin degradation in hot, compressed water occurs at a much lower temperature than previously expected, exacerbated by the reality that 3), exothermic reactions occur in hot, compressed water, triggered by achieving temperatures in excess of 180°. This technology is currently employed on a commercial scale by a German – Swiss enterprise, AVA-CO2 in the production of bio-char and is the basis of their operation. However, the company's website highlights only the dehydration of 'carbohydrates' via the mechanism contained in **Figure 5.12**, with the greatest carbon efficiency or CE of 100% when compared to fermentation or anaerobic digestion.
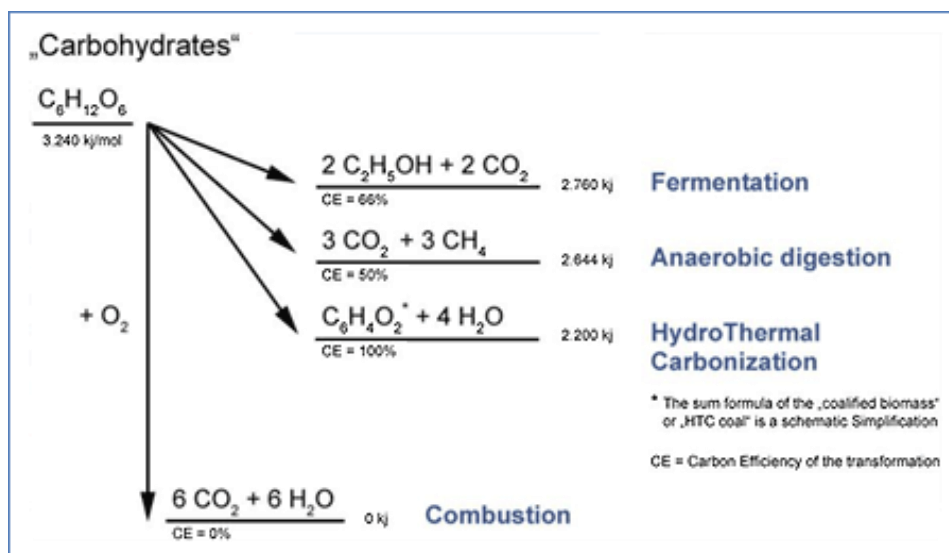
Figure 5.12: Reaction pathways of carbohydrates to products utilising fermentation, anaerobic digestion, hydrothermal carbonization and combustion

It is likely that an exothermic reaction occurred during heating of samples. For a number of reasons, this was impossible to detect. With only 3g biomass being used, heat for the process delivered via an external PID controller and with a thick, stainless steel reactor filled with water; any heat produced would have soon dissipated.

Cellulose gas yields increase with all high variable levels, with both temperature and time having a similar effect. Use of catalyst also gives raised gas production when compared to water alone (no catalyst). Gas yields of xylan exhibit a similar pattern to cellulose with regard to the influence of temperature and time, but the effect of catalyst is much less pronounced, if indeed, at such a low level, the effect can be detected. It is clear that thermal degradation of xylan is less influenced by the presence of KOH, but the reason for this is not established. Branched side chains from the main xylose polymer chain, particularly those containing carbonyl groups are more readily reduced to alcohols especially in basic media, producing water soluble compounds and liberating CO_2 (Shafizadeh et al. 1972). This corresponds with the high levels of WSH and gas measured. It may be that the uncatalysed hydrothermal processing of xylan is so rapid at the conditions studied, that the catalysed route cannot be probed easily.

From higher heating values (HHV) of oil and char produced (**Table 5.2**), energy recovery in terms of yields was calculated (Table IV) using the formula:

$$\% \ Energy \ re\mathrm{cov}\,ery = \frac{\left[HHV \ char \times char \ yield\left(g\right)\right] + \left[HHV \ oil \times oil \ yield\left(g\right)\right]}{\left[HHV \ sample \times sample \ yield\left(g\right)\right]} \times 100$$

This calculation, though simplistic, gives a good approximation as to the conversion of each compound to fuels, with xylan forming the least amount of useable fuel in the form of oils or chars for all conditions due to formation of WSH in significantly large amounts. This suggests corresponding "real world" biomass with high hemicellulose levels processed via hydrothermal means will produce lower yields of oils and chars and higher levels of WSH, relative to the original composition, indeed, as will be discussed in later chapters, the breakdown of wood hemicellulose under mild pyrolysis or torrefaction conditions, is responsible for initial changes in the structure and physical properties, such as a decrease in the fibrous nature and ease of grinding.

	1	2	3	4	5	6	7	8	9	10	11	12
% Energy Recovery	94.3	76.7	59.1	63.8	42.9	48.6	45.7	39.6	87.4	92.2	87.6	70.8
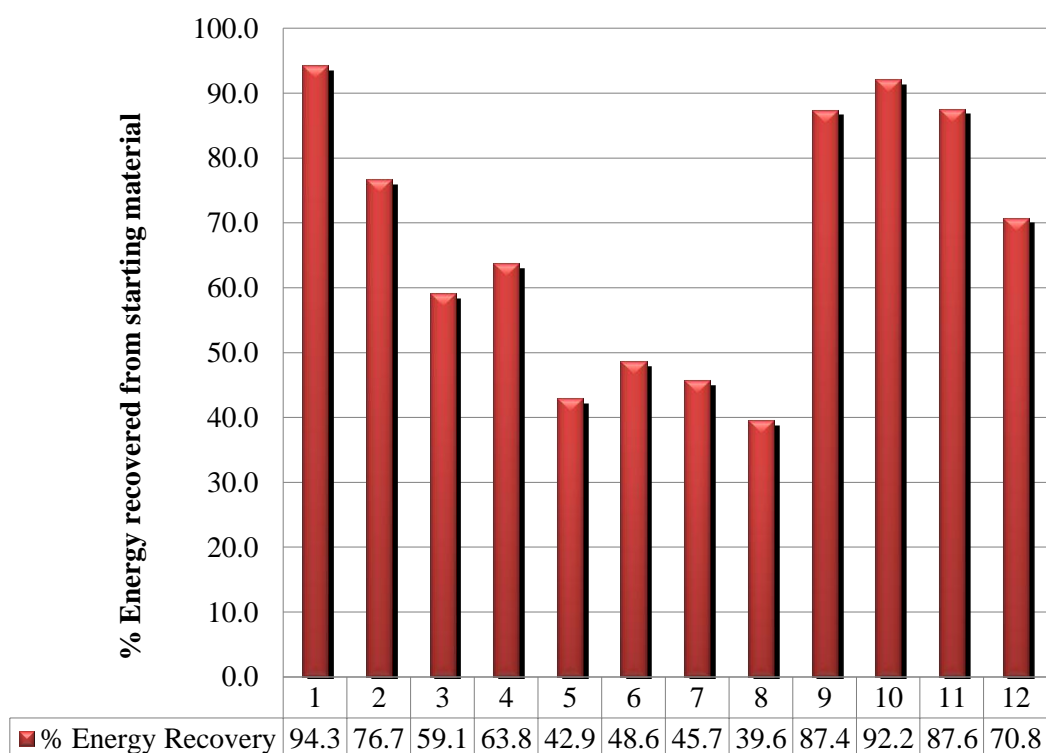
Figure 5.13: % Energy recovery calculated from CHNS analysis of hydrothermally produced oils and chars. Gas and WSH analysis omitted

Energy recovery, plotted in **Figure 5.13**, highlights a similar trend for energy recovery between xylan (E5 – E8) and lignin (E9 – E12). Values for cellulose show a slightly different trend. They are highest for conditions of KOH, 200°C, 10 min residence time (E1) and lowest for conditions of no catalyst, long residence time (5h) and 200°C, (E3).

Even so, energy recovery from cellulose is better than that from xylan under all conditions. The apparent low energy recovery from xylan is presumably in part because of the high water solubility of the organics, and in part from the high gas yields in these experiments. For liquefaction or carbonisation of biomass at low temperature, and long residence time (E2, E6 and E10), energy yields are greater than under conditions of high temperature, short residence times (E3, E7 and E11). Yields of chars are also higher and oil yields, much lower at the less severe conditions.

Data was also analysed for any relationship between TOC in the aqueous phase and carbon content of the char, under the premise that decreasing TOC would relate to an increase in percentage carbon in char. While a correlation can be found for xylan, correlations between cellulose TOC at high temperature and char carbon content is less clear, where both TOC and char carbon content are seen to increase. This is viewed in **Figure 5.3** and shows the greatest increase in cellulose and xylan carbon content with ΔT. This phenomenon is not mirrored in **Figure 5.7**, xylan displays an expected corresponding drop in TOC with ΔT, whereas cellulose TOC increases. This occurrence is worthy of further study and highlights significant differences in reactivity between cellulose and hemicellulose.

Comparing lignin TOC and carbon content in chars **Figure 5.3** and **5.7,** results of these calculations for lignin and the negligible response to changes in temperature, and reaction time reinforce the theory that chars formed are much more resistant to changes in reaction conditions not only between 200 – 250°C, but from 10mins – 5hrs.

HHV of lignin for char production exhibit the smallest change in values over all the experimental sets, with values increasing mildly as temperatures increase, slightly more as the reaction time is increased and with no change as catalyst is used (**Figure 5.4**). HHV's calculated for lignin oil (**Figure 5.6**) display different characteristics than for char, with 250°C resulting in a HHV drop of 2.5 MJ/kg, 5 hr reaction time a drop of 0.5MJ/kg and catalyst showing an increase in the calorific value of 0.7MJ/kg. These values are practically the inverse of the char HHV's and are evidence to support the formation of lignin char from oils via condensation polymerisation.

For this set of experiments and under these reactions conditions, volumes of gas production when reacting lignin, are the lowest of all the model compounds tested. The fact that lignin has been broken down to form gaseous products, again adds weight to the theory that the breakdown of lignin occurs at a lower temperature than previously expected. From the calculations, use of catalyst has no measured effect on the yield of gas created when using lignin, with temperature having only a minor effect. Calculated values for the influence of 0.1M KOH on gas production is in the order cellulose>>> xylan ≥ lignin (**Figure 5.8**). Both raised temperatures and longer reaction times for all biomass model compounds at a similar magnitude. Components of gas produced by liquefaction reactions contain CO_2, C_nH_m, CO, H_2 and O_2. Relative proportions of these compounds measured by GC analysis show that CO_2 is by far the most abundant gas species present in hydrothermally processed material. (Karagoz et al. 2005a; Wang et al. 2008)

The most surprising results observed by aq. phase TOC levels is for xylan (**Table 5.2**), especially when comparing calculated WSH levels (**Figure 5.1**). WSH calculated by difference range from 64.9% (E6) to 70.3% (E8), however, empirically determined TOC levels, decrease drastically over the same range from 29.2g/L carbon (E5) to 3.7g/L carbon (E8). It is unknown at this time the reason for this, although oils and chars produced from xylan were the lowest yielding, but contained relatively high carbon contents, particularly when compared with cellulose, given that they have a similar elemental composition (**Table 5.2**) (**Chapter 3**). It is feasible that gases produced from xylan could have been a source of larger amounts of carbon, either by an increased proportion of CO_2 or C_nH_n. Van Krevelen diagrams however, (**Figure 5.10**) do not fully support this hypothesis.

Cellulose has a more predictable response to aq. phase TOC levels. A rise in temperature relates to a corresponding rise in TOC, large and expected as cellulose is hydrolysed, forming water soluble compounds. The reduction in TOC with extended reaction time is also expected, substantiating the theoretical method of biochar formation from water soluble material (Sevilla and Fuertes 2009a, b). This is a slow reaction, frequently taking in excess of 24hrs to convert biomass to biochar. The more unexpected effect on TOC is from the use of KOH. With cellulose, TOC is reduced, whereas for xylan, levels increase with the addition of catalyst. This would indicate that

KOH either aids hydrolysis of cellulose, increasing the aqueous phase concentration thereby allowing a larger proportion of compounds to be available for dehydration to biochar, or it reduces the activation energy of the rate determining step of biochar conversion from WSH as described earlier.

With the focus on xylan, this compound presented the smallest change in pH of the reacted process water with addition of catalyst (pH 3.9 with water vs. pH 4.7 with 0.1M KOH). This small change in pH, even with the initial addition of alkali, indicates that the catalyst had the effect of increasing the yield of acidic compounds. Previous work (**Chapter 4**) highlighted greater production of furans from xylan liquefaction, measurable in oil by gas-chromatography/ mass spectroscopy (GC-MS), extracted from the aqueous phase using solvent – solvent extraction. The major degradation products of furans include formic acid (Jin et al. 2005) and explain the more acidic aqueous phase when alkali was added. Again, the reactivity of carbonyl containing, branched side chains help to explain this.

Addition of alkali to cellulose reactions, like xylan, has the effect of increasing the acid yield, with production of acetic and propanoic acids, but at a lower level (Karagoz et al. 2005a). Assumed oxidation pathways of carbohydrates to acetic acid are proposed by Jin (Jin et al. 2005). By utilizing a two-step process Jin obtained a yield of 16.3% at 68.5% purity when compared to conventional wet oxidation (WO) 9.0% yield at 26.6% purity.

The biomass model compound that exhibits greatest change in pH with KOH addition when compared to reactions in water is lignin. This is due to thermal degradation products being mostly phenolic compounds (e.g. 2-methoxy-phenol) with only small amounts of acetic and formic acid produced. (Karagoz et al. 2005a) Weakly acidic species such as phenols neutralize strong bases at a much reduced rate. GC-MS analyses of oils produced from hydrothermal processing of lignin in the previous experimental chapter reinforce this theory.

Approximate calculations can be made for the amount of acid generated by each reaction, it must be stressed however, that accurate calculations are made more difficult due to the formation of buffer solutions that exist past the equivalence point, resisting

changes in pH with small amounts of H^+ created. The following calculations have a number of reasonable assumptions:

- pH of process water is 7
- Acetic acid is the main acidic product
- Ka acetic acid = 1.74 x 10^{-5} at 25°C
- 30mL 0.1M KOH contains 3 x 10^{-3} mol or 0.1683g solid KOH
- At the end point of the reaction, 3 x 10^{-3} mol is equal to the amount of potassium ethanoate produced or $[CH_3COO^-]$
- The pH measured of the aqueous phase is a buffer solution

pH of the resulting salt formed by the reaction of KOH with acetic acid at the end point is derived from $pH = \frac{1}{2}pK_a + \frac{1}{2}pK_w + \frac{1}{2}\log S$. Substituting 4.75 for pK_a, 13.5 for pK_w and 0.1 mol kg^{-1} for S gives an endpoint of pH 8.63. This will be the same for all reactions. With further production of acetic acid, $(CH_3COO^-\ H^+)$ and potassium acetate, $(CH_3COO^-\ K^+)$ an equilibrium is reached between acetic acid, acetate and hydronium ions.

The calculation is as follows using the pH from the aqueous phase in cellulose experiment E1 (pH 5.02)

pH = $-\log_{10}[H^+]$
5.02 = $-\log_{10}[9.55 \times 10^{-6}]$
H^+ = 9.55 x 10^{-6} mol dm^{-3} or 2.86 x 10^{-7} mol in 30 cm^3

$Ka_{[CH3COOH]} = \frac{[H^+]\ [CH_3COO^-]}{[CH_3COOH]}$

$1.74 \times 10^{-5} = \frac{[9.55 \times 10^{-6}\ ] \times [3 \times 10^{-3}]}{[CH_3COOH]}$

Hence there is an excess of CH_3COOH of 1.65 x 10^{-3} mol dm^{-3} produced. This would be sufficient to produce a pH of 2.78. Data for experiments E1-E12 are contained in **Table 5.4**.

Table 5.4: Comparison of measured pH and calculated pH from volumes of acid produced by hydrothermal processing

Experiment	pH measured	Volume acid produced (mol dm^{-3})	pH calculated
E1	5.02	1.65×10^{-3}	2.78
E2	2.70	2.00×10^{-3}	N/A
E3	2.51	3.09×10^{-3}	N/A
E4	4.25	9.70×10^{-3}	2.01
E5	4.72	3.29×10^{-3}	2.48
E6	4.01	9.77×10^{-5}	N/A
E7	3.85	1.41×10^{-4}	N/A
E8	4.75	3.07×10^{-3}	2.52
E9	7.29	8.84×10^{-6}	5.05
E10	3.27	5.37×10^{-4}	N/A
E11	2.97	1.07×10^{-3}	N/A
E12	6.93	2.02×10^{-5}	4.69

Aqueous phase pH values for each experiment give an interesting pattern (**Table 5.4**). As expected, reactions in the presence of 0.1M KOH (E1, E4, E5, E8, E9, E12) give pH values higher (less acidic) than reactions carried out in water (E2, E3, E6, E7, E10, E12).

For cellulose, calculated pH values from experimental data (E1 and E4) indicate the production of acid to be of a similar magnitude. Recalculating **Table 5.3** on this basis gives a more accurate account on the effects of catalyst on the amounts of acid produced by each reaction (**Table 5.4**). What this table now appears to show is that KOH catalyst increases the amount of acid produced by a small amount (pH0.2) for cellulose and by a much larger amount (pH 1.4) for xylan. It is this large increase in acid produced by xylan that is of most interest. What is unclear from this information is what effect each acid species produced has on this, as the assumption was made for acetic acid being the main acidic component. Formic acid has lower pK_a of 3.77 compared to acetic acid's pK_a 4.75. Given the higher portion of furan production, and with formic acid a known

degradation product of HMF, it could be argued that KOH increases the furan production for hydrothermal processing of xylan.

The use of catalyst in reactions involving lignin had the opposite effect than with xylan. Recalculated pH values with bias of buffer production removed (**Table 5.5**), produced a substantial increase from pH 3.1 in water to pH 4.9 using catalyst. This equates to a reduction of approx. 100 times acidity (pH being a log scale). The largest other lignin response that responded negatively to catalyst addition was oil production. Given that the oil mostly consists of phenolic components (**Chapter 4**), it is possible that reduction of these acid compounds, coupled with a retardation effect on organic acid concentration by an as yet unknown mechanism is responsible for this.

Reaction time was found to have little or no effect on acid production when production of buffer was taken into account for all compounds tested, indicating that the formation of acid is rapid, in agreement with literature sources (Jin et al. 2005). What other literature sources claim is that these compounds are further degraded via hydrothermal processing over time to either CO or by dehydration, but this would not appear to be the case as pH remains unchanged over the 10 minute – 5 hour timescale in this study, and also unlikely due to the stable nature of salt structures.

Table 5.5: Average response values and change in response for aqueous phase pH, taking into account buffer effect of potassium ethanoate

	pH cellulose	pH lignin	pH xylan		cellulose	lignin	xylan
$\overline{Water}$	2.6	3.1	3.9	Δ_{cat}	-0.2	1.8	-1.4
$\overline{10\ min}$	2.4	4.0	3.2	Δ_t	0	0	0.1
$\overline{200°C}$	2.7	4.2	3.2	Δ_T	-1.8	-0.4	0
$\overline{0.1M\ KOH}$	2.4	4.9	2.5				
$\overline{5hrs}$	2.4	4.0	3.3				
$\overline{250°C}$	4.5	3.8	3.2				

Results show that Δ_T had the largest effect on acid production for cellulose. From Jin et al. 2005, the following is quoted "*experimental results that the oxidation of all of cellulose, starch and glucose yielded a considerably high quantity of formic acid*". As

reaction temperatures increase, hydrolysis of cellulose produces glucose which further degrades via assumed oxidation pathways and cleavage of the $\alpha - C1$ or $\beta - C2$ carbonyl carbons of gluconic acid with the potential of producing 6 moles of formic acid from 1 mole of glucose or related sugars.

5.5   Conclusions

The study highlights many issues when hydrothermally processing lignocellulosic material in isolation. It is clear from the results that reaction temperature has the greatest single effect overall, but depending on the lignocellulosic species reacted and the reaction product in question, this can be negative or positive. Expected similarities with cellulose and xylan with regard to yields and related data are not observed and are in fact a degree of magnitude different, with less of an effect of process variables seen with xylan (in most cases).

Potassium hydroxide as the reaction catalyst had the biggest effect on cellulose, increasing char, oil and gas production and reducing levels of WSH and subsequently TOC. For biochar production, increased reaction temperature and residence time were found to have a negative effect on char production, with raised temperatures being the largest influence.

Problems faced when applying results from this set of analysis to real world biomass samples pose the obvious answer. Each lignocellulosic component including relative compositions of cellulose, hemicellulose and lignin in biomass effect not only liquefaction products, but even when taking into account the extraction procedure, behave differently under the same reaction conditions. It is still unknown what effect inorganic components contained within biomass samples will have on yields and fuel quality and if indeed these compounds have synergistic or catalytic effects in hydrothermal processing.

Chapter 6 will therefore be focused around hydrothermal liquefaction and carbonisation reactions of biomass, specifically *Miscanthus* and SRC Willow, fast growing energy crops. The purpose of this is to identify synergistic or non-synergistic effects of cellulose, lignin, hemicellulose and other compounds, when using biomass in its original state.

Chapter 6 – Hydrothermal Processing of *Miscanthus* and Willow, Biomass Energy Crops

6.1   Introduction

Chapters 4 and **5**, contain studies on a range of hydrothermal processing conditions (HTC and HTL) of biomass model compounds; cellulose, xylan and lignin. Variables studied include catalyst concentrations, reaction times and temperatures. Information gleaned from these chapters helps to build further understanding into the degradation of bio-polymers in hot, compressed water.

The most valuable biological compound in terms of conversion to fuel for hydrothermal processing is cellulose, due to the global abundance and the ease of processing. Production of hydrochar from cellulose is possibly the most efficient route for increasing energy density as reported thus far due to utilisation of the exothermic dehydration reaction and superior heat transfer from direct contact with water.

Lignin, as previously demonstrated in **Chapter 4** and **5**, when reacted in isolation and dependent on reaction conditions, can exhibit properties similar to the complex natural structure, or degrade under relatively mild reaction conditions; this empirical information is in some conflict, when compared to other literature sources that state degradation reactions start to occur under more extreme reaction conditions (higher temperatures and pressures). Also, due to the high carbon content, lignin gives attractive energy yields. Mechanisms for oxygen removal from lignin and cellulose are similar, with dehydration being the favoured route, preserving the majority of the carbon in the char.

Due to the ease of forming water soluble products from hemicellulose decomposition, in turn breaking the inter-connective bonds that bind the lignocellulosic structure together, hemicellulose is a key component in the initial stages of biomass breakdown under hydrothermal conditions.

The focus for this chapter is "real world" biomass, i.e. the high carbohydrate content energy crop samples, *Miscanthus* and Short Rotation Coppice (SRC) Willow.

Conversion is studied via hydrothermal processing in water at a range of temperatures, reaction times and a range of homogeneous catalysts.

Objectives for this chapter are as follows:

1. Produce a data set concerning the hydrothermal processing of biomass samples (Willow and *Miscanthus*) between 200 and 350°C and subsequent analysis

2. Determine whether biomass model compounds in their natural form behave differently to their isolated forms and investigate potential synergistic effects

3. Produce a set of recommendations for hydrothermal processing of lignocellulosic biomass, based on the relative proportions of biological compounds

Use of targeted, specific energy crops that do not compete for land or food production is seen by many as the best source of lignocellulosic material suitable for second and third generation bio-fuels. Ideally, energy crops that can be grown on land that not only is unsuitable for food production, but also that is uninhabitable would be an ideal choice. Obviously, with the advent of modern farming equipment, the job of planting, fertilising, and harvesting is mechanised. However, land currently unsuitable for food crop production may pose specific technical challenges for those wishing to grow energy crops. Another more serious consideration is the use of monocultures. Plants selectively bred for yield and drought/ pest resistance may fall foul of other diseases and microbes, which can decimate forests and crops alike, coupled with a decrease in biodiversity, increase the number of pests and give a greater requirement for fertiliser and lowering of soil quality (Naeem et al. 1994). That said, research into high yielding energy crops like *Miscanthus Giganticus*, Reed Canary Grass, SRC Willow and Switchgrass can provide not only high yields of biomass, but can be engineered to maximise suitability in areas unsuitable for food crops. UK research institutes such as the Institute for Biological, Environmental and Rural Sciences (IBERS), Rothamsted Research and the National Non – Food Crop Centre (NNFCC) are landed with the task of finding the most suitable plant species for energy production.

6.2   Experimental

Ultimate analysis of biomass raw materials Willow and *Miscanthus* including moisture and ash content is contained in **Table 6.1**. Approximate values of lignocellulosic content for each sample are taken as follows; Willow = 40% cellulose, 30% hemicellulose and 30% lignin (Bullard et al. 2002a; Bullard et al. 2002b). *Miscanthus* comprises of 44% cellulose, 24% hemicellulose and 17% lignin.(Price et al. 2004) Lignocellulosic content for willow is approximately 100%, whereas *Miscanthus* is 85% on average. Differences in chemical composition equate to *Miscanthus* having 8% less energy on a dry basis than willow (17 vs. 18.5 GJ/tonne)

Table 6.1: Analysis of willow and *Miscanthus* for moisture, ash and elemental content

	Moisture %	Ash %	N daf (% Wt.)	C daf (% Wt.)	H daf (% Wt.)	O daf* (% Wt.)
Willow	8.0	2.0	0.6	47.2	5.7	46.5
Miscanthus	7.4	2.5	0.1	48.6	5.5	45.7

*by difference

daf dry, ash free

6.3   *Miscanthus* reacted with a range of catalysts at HTL conditions – study 1

For the first comparative analysis, *Miscanthus* samples sourced from Rothamsted research with the code R/05/MISC/623/FH/W were processed at 350°C for 1 hour in solutions of a range of homogenous catalysts at a concentration of 1.0M and with a catalyst to sample ratio of 9:1. It is noted earlier in **Chapter 4** that the conclusions were that initial concentrations of catalyst at 1.0M KOH with model compounds were high and did not produce levels of oil expected. This work was carried out at a similar time, but on *Miscanthus*, hence the high level of catalyst employed here. Catalysts used were; sodium carbonate, acetic acid, formic acid, potassium hydroxide, and were chosen due to their low cost, abundance and quoted previous successes in literature sourced biomass experiments. It has to be noted that formic acid and acetic acid have a calorific value of 32.1 and 32.9MJ kg^{-1} respectively; therefore, when calculating yields, weights of these compounds in the reaction mixture must be taken into account. For 27ml of a

1.0M solution of acetic acid, this calculates to 1.62g and for 27ml 1.0M formic acid, 1.24g.

Reaction conditions, product yields and elemental analysis are presented in **Table 6.2**. Oil yields are lower than expected for all catalysts, particularly when using acetic acid. As discussed in previous chapters and as found from previous researchers, quoted oil yields are much higher for most kinds of lignocellulosic biomass at elevated temperatures. The biggest effect on reduction of oil yields is therefore the production of CO_2 rich gas. Combined oil and char yields for all reactions are in the region of 25-30%, which is low when compared to hydrothermal carbonisation products giving in excess of 60% char by weight. This is coupled with high levels of gas production, especially when looking at KOH (33.8%) and formic acid (22.9%).

Table 6.2: Reaction conditions, product yields and analyses for products from the hydrothermal processing of *Miscanthus*.

Reaction temperature (°C)	350	350	350	350	350
Dwell time	1hr	1hr	1hr	1hr	1hr
Solvent ratio	9:1	9:1	9:1	9:1	9:1
Catalyst	Na_2CO_3	CH_3COOH	HCOOH	KOH	N/A
Catalyst amount	27g	27g	27g	27g	N/A
Catalyst molarity	1M	1M	1M	1M	N/A
Residual pressure(Bar)	4	4	12	10	4
@ Temp(°C)	16	16	40	40	23
Oil (%)	14.9	5.0	10.1	12.8	7.9
Char / Solid (%)	8.8	20.1	19.1	12.4	26.6
Gas (%)	14.7	7.6	22.9	33.7	10.4
WSH (%)	61.6	67.3	47.9	41.2	55.1
%C (char)^{daf}	55.3	78.1	76.2	66.3	80.5
%H (char)^{daf}	5.1	5.1	5.0	5.3	4.9
%N (char)^{daf}	0.4	0.4	0.3	0.2	0.3
%O (char)^{daf}	39.2	16.4	18.5	28.1	14.3
%C (oil)	78.2	66.1	72.0	75.0	76.0
%H (oil)	8.4	7.0	7.2	8.1	8.2
%N (oil)	0.2	0.2	0.2	0.2	0.2
%O (oil)	13.2	26.8	20.6	16.6	15.6
HHV (MJ/Kg)(char)^{daf}	21.3	31.6	30.6	26.5	32.4
HHV (MJ/Kg)(oil)	35.8	28.5	31.5	34.1	34.6
TOC (g)	0.45	0.70	0.31	0.50	0.42

^{daf} dry, ash free. Molecular weights are Na_2CO_3:106, CH_3COOH:60, HCOOH:46 and KOH: 56

A control experiment using water alone with *Miscanthus*, gave the following yields; Oil – 7.9%, Char – 26.6%, Gas – 10.4% and WSH – 55.1%. This information is interesting as the combined yield of oil and char produced from using water at the same reaction conditions exceeded those produced using the various catalysts. Another observation for the control reaction is the calculated char HHV which was found to be 32.4MJ/kg. This brings the quality of the solid retained fuel to the same region as anthracite, with substantially reduced ash content in comparison.

Formation of organic acids during hydrothermal processing has been discussed in some detail in **Chapters 4** and **5**. By adding these acids prior to the start of the reaction it was hoped that they would produce a change in the reaction equilibrium and increase yields of oil, char or both. In fact, acid catalysts have produced a negative effect on the yields when compared to the control experiments.

Cellulose is hydrolysed forming glucose; fructose and furans and other small chain polymers (n1 to n3). These compounds then decompose forming acids. The acids then decompose to form CO_2. However, the addition of 1M acetic acid catalyst has reduced amounts of gas formation, whilst increasing the WSH content, compared to the control.
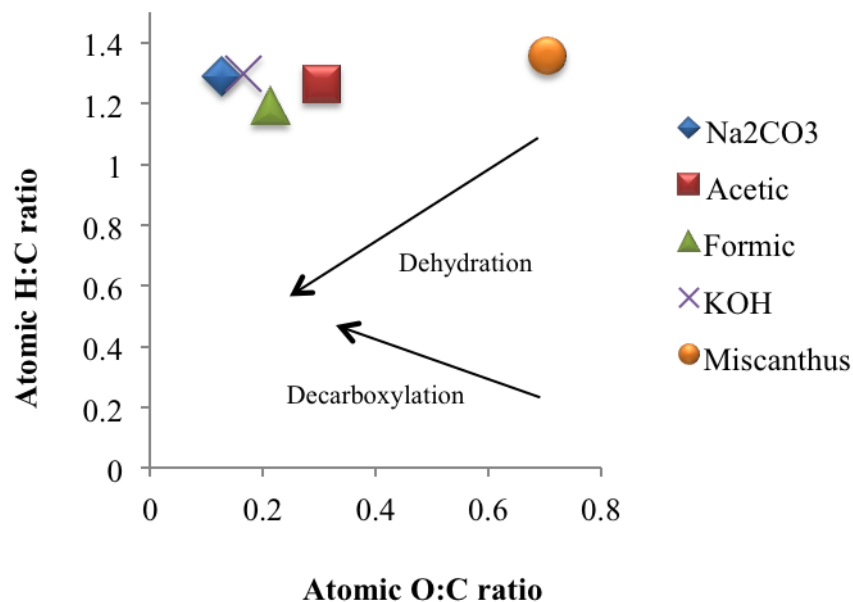
Figure 6.1: van Krevelen diagram for oil produced by hydrothermal processing of *Miscanthus* at 350°C for 1hour using a range of catalysts
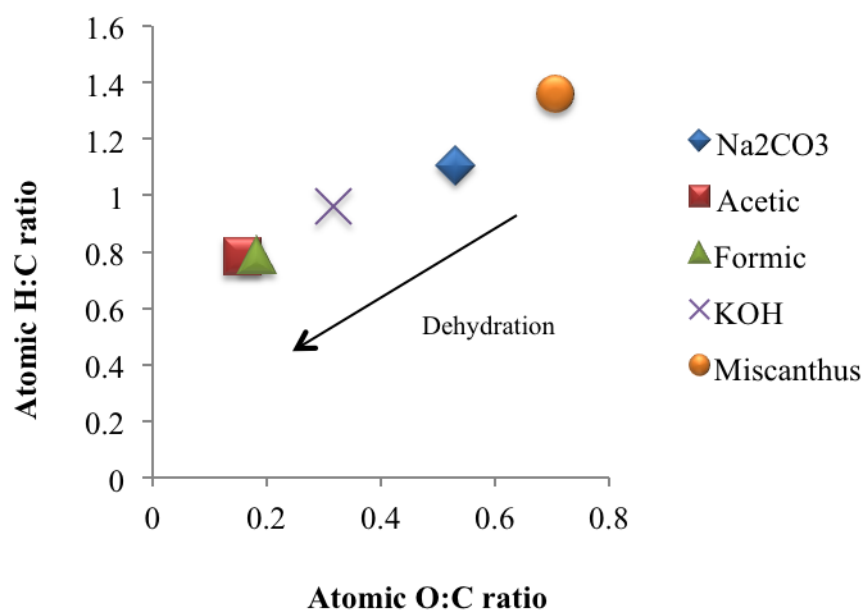
Figure 6.2: van Krevelen diagram for char produced by hydrothermal processing of *Miscanthus* at 350°C for 1hour using a range of catalysts

Van Krevelen diagrams for oil and char produced from the hydrothermal processing of *Miscanthus* at 350°C/ 1hour (**Figures 6.1** and **6.2**) highlight differences and changes in composition of products from each catalyst. It is clear from **Figure 6.2** that the main route of char production for all catalysts is via dehydration, corroborating analysis from previous chapters and from the literature (Sevilla and Fuertes 2009a, b). Decarboxylation is a minor reaction in comparison, causing a small shift toward a higher heating value in the region of coal currently used for energy production. Oil production however, is markedly different. **Figure 6.1** shows evidence for both dehydration and decarboxylation reactions; however, another possibility is the production of carbon monoxide.

It is the Na_2CO_3 catalyst reaction that is a surprising result. This reaction produced not only the highest amount of oil, but the highest quality oil compared to other catalysed reactions in terms of HHV, low oxygen content, and achieved with a relatively small gas production (14.7%) The expected result would be that the highest gas yield should produce oil with the highest heating value, but this is not the case. The explanation for this comes from degradation of each of the catalysts. Formic acid is known to decompose to CO_2 (Yu and Savage 1998) under hydrothermal conditions, whereas, under atmospheric heating, the products are CO and H_2O.(Barham and Clark 1951)

Balancing the reaction under hydrothermal conditions also produces an equimolar amount of H_2 ($HCOOH \rightarrow CO_2 + H_2$).
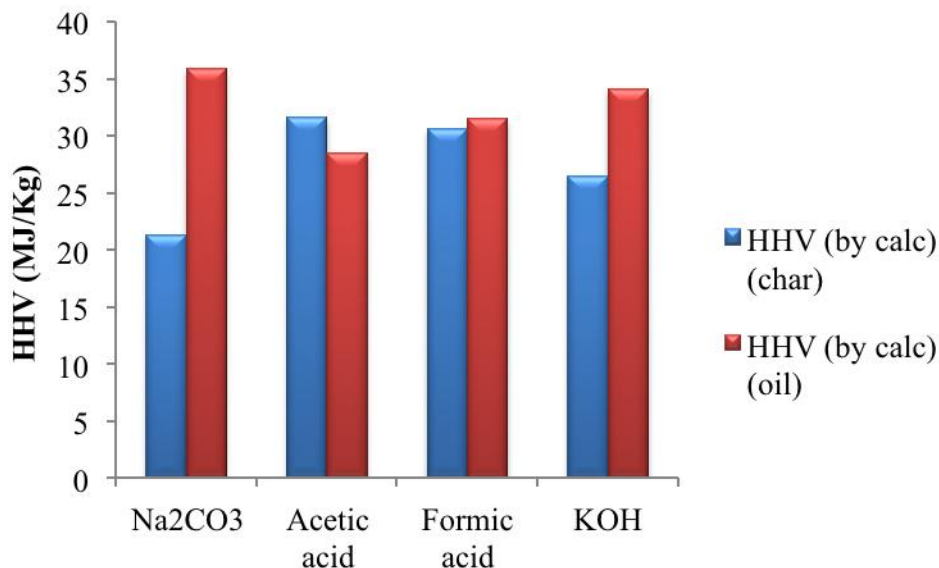
Figure 6.3: H HHV values of chars and oils produced via hydrothermal processing at 350°C for 1hr using a range of catalysts

Calculated HHV's for hydrothermally processed *Miscanthus* (**Figure 6.3**), highlight the changes in energy distribution when using acidic or basic catalysts. For Na_2CO_3 and KOH, HHV's of the resulting oils are greater than the corresponding chars, whereas, the chars formed from the use of acetic and formic acid are significantly higher in both mass and heating value.

The reaction temperature of 350°C itself is reported to produce greater oil product yields, and is stated in many literature sources. (Akhtar and Amin 2011; Burczyk 2007; Demirbas 1998a, b; Dileo et al. 2008; Garrote et al. 2003; Peterson et al. 2008) What may be a contributing factor to the reduced oil production of this set of samples is the relatively slow heating rate of approx. 10°C/ min and the long residence time of one hour. This gives a total reaction time, including heating and cooling, to be over 2 hours. Further polymerisation reactions taking place account for the increase in char, forming macrostructures from smaller molecular weight samples. (Sevilla and Fuertes 2009a, b).

Figure 6.4 graphically represents % conversion of *Miscanthus* catalysed reactions to oil, char, gas and WSH. What is apparent from viewing the graph is a lack of an obvious pattern between yields and large differences between catalysts. One might expect higher char yields to result in low WSH and vice versa or that the differences in product distribution when using slightly different organic acids would be minimal. Results show this would not appear to be the case.
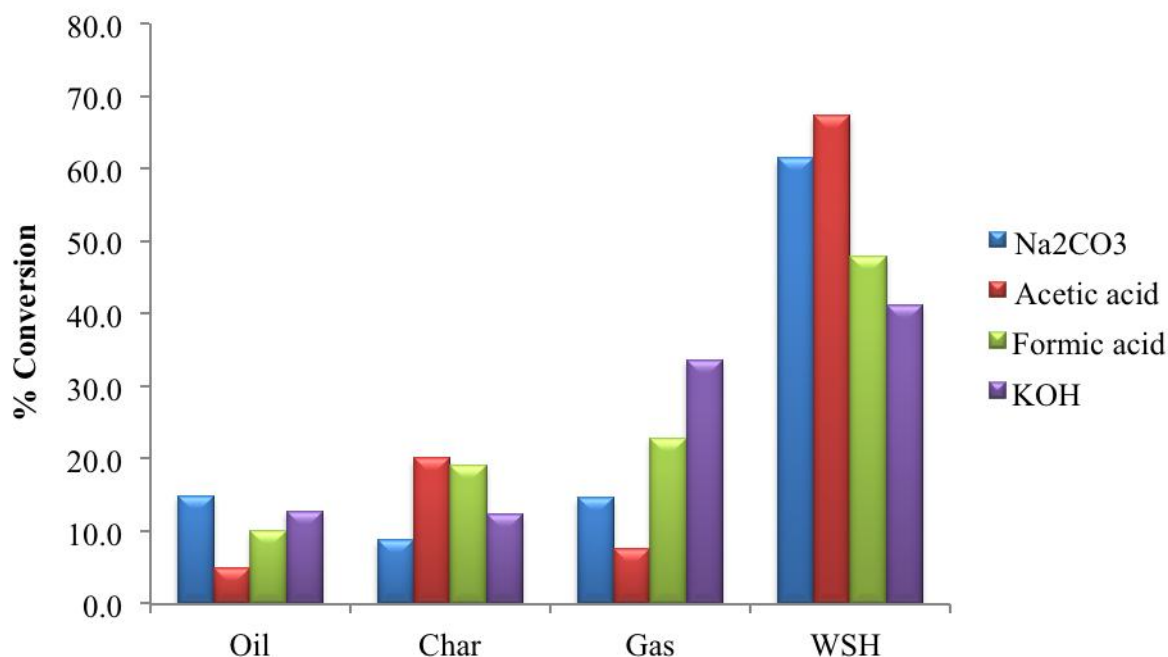
Figure 6.4: Oil, char, gas and WSH yields from hydrothermal processing of *Miscanthus* at 350° C for 1 hour using a range of catalysts

Energy (HHV), (**Table 6.2**) contained within the recoverable oil and char fractions is that which is deemed suitable for fuel use. Coupled with the respective weights of those fractions one can calculate the energy recovery using the formula:

$$\% \ Energy \ recovery = \frac{\left[HHV \ char \times char \ yield\,(g) \right] + \left[HHV \ oil \times oil \ yield\,(g) \right]}{\left[HHV \ sample \times sample \ weight\,(g) \right]} \times 100 \ ,$$

the results of which are tabulated in **Table 6.3**

Table 6.3: % energy recovery from char and oil yields for *Miscanthus* reacted with a variety of catalysts at 350°C

Catalyst	HHV combined oil and char (calc.) (MJ/Kg)	Energy recovered (%)
Formic acid	9.0	49.1
Acetic acid	7.8	42.3
Na_2CO_3	7.2	39.2
KOH	7.7	41.6
Water.	10.5	61.7

The obvious conclusion from this table is that, if a solid, char type material is required from hydrothermal processing of *Miscanthus* at 350°C for 1 hour, it is better not to use any additional reaction medium other than water. The continued and obvious problem with using homogenous catalysis is the cost and subsequent recovery of the compound used. In this case, it is clear that there is a breakdown of acids - acetic and formic - because of their organic nature, making the addition of these acids only desirable for specific product formation.

GC-MS analysis was carried out on the each oils produced from the various catalysts, using the experimental approach as described in **Chapter 2**. Chromatograms can be seen in **Figure 6.5** to **6.8** inclusive, with results for retention time, compound identification and proportional amounts of compounds measured via area% in **Table 6.3**. One observation is clear from looking at these graphs and from tabulated data, KOH and Na_2CO_3 produce similar types and amount of compounds, the most prominent of these being 2,3,4,5-tetramethyl-2-cyclopenten-1-one, 2,4-dimethyl-phenol, 2,3,4-trimethyl-2-cyclopenten-1-one, 2-ethyl-6-methyl-phenol and, 2-methoxy-phenol. These 4 compounds accounted for 35 area% for Na_2CO_3 and 39 area% for KOH.
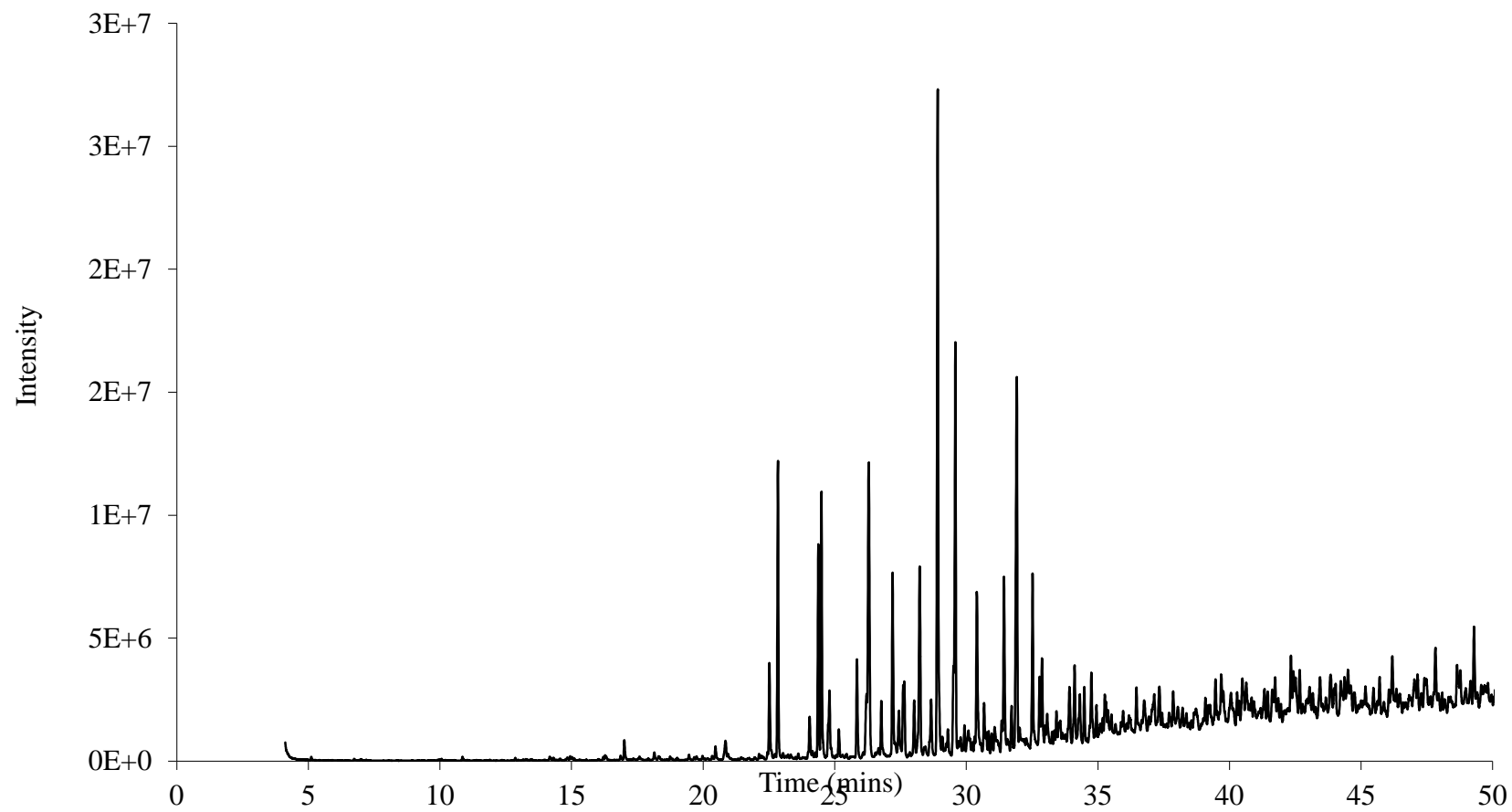
Figure 6.4: GC-MS chromatogram for oil produced from HTL of *Miscanthus* with 1M KOH catalyst at 350°C for 1 hour
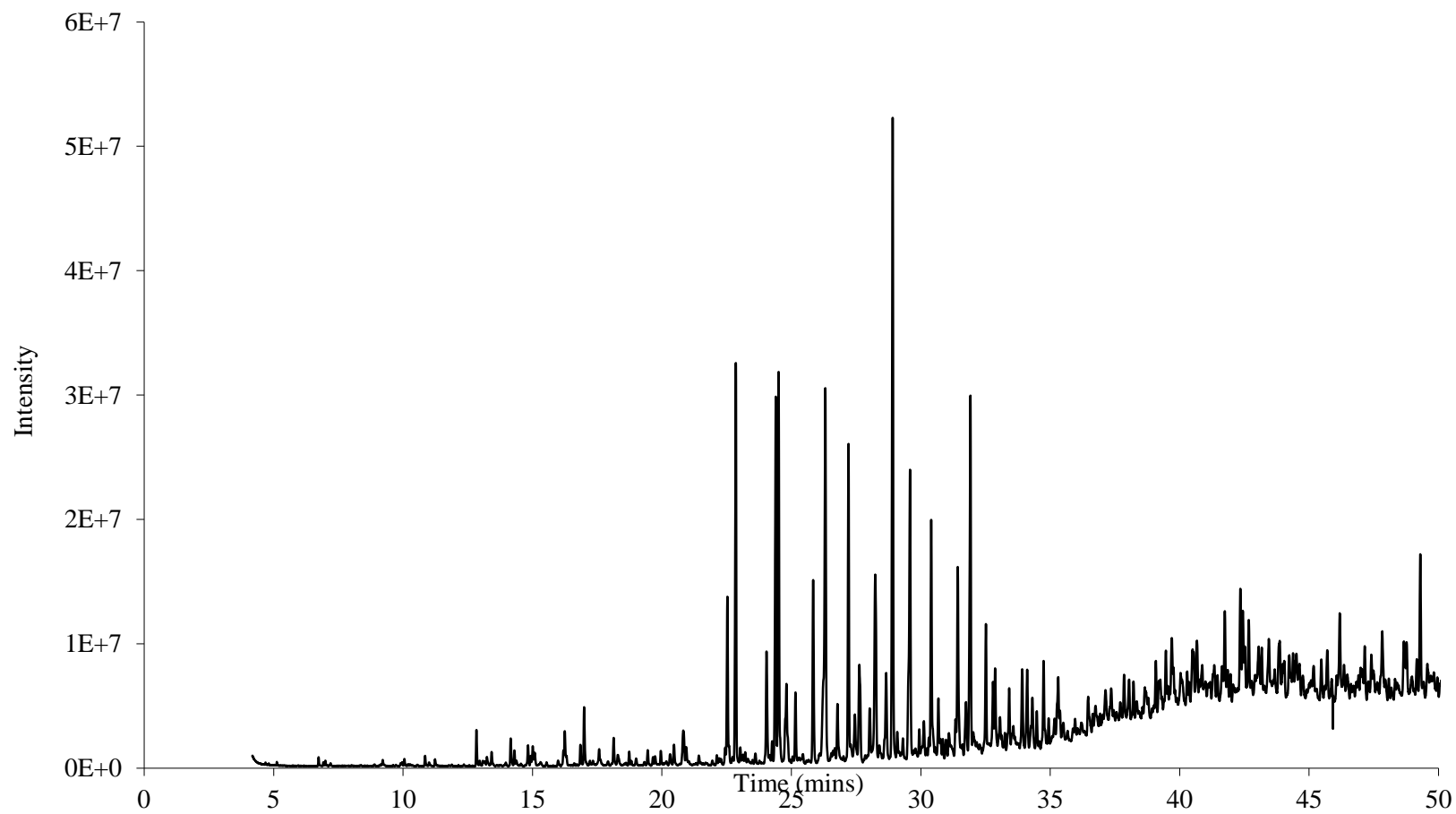
Figure 6.5: GC-MS chromatogram for oil produced from HTL of *Miscanthus* with 1M Na_2CO_3 catalyst at 350°C for 1 hour
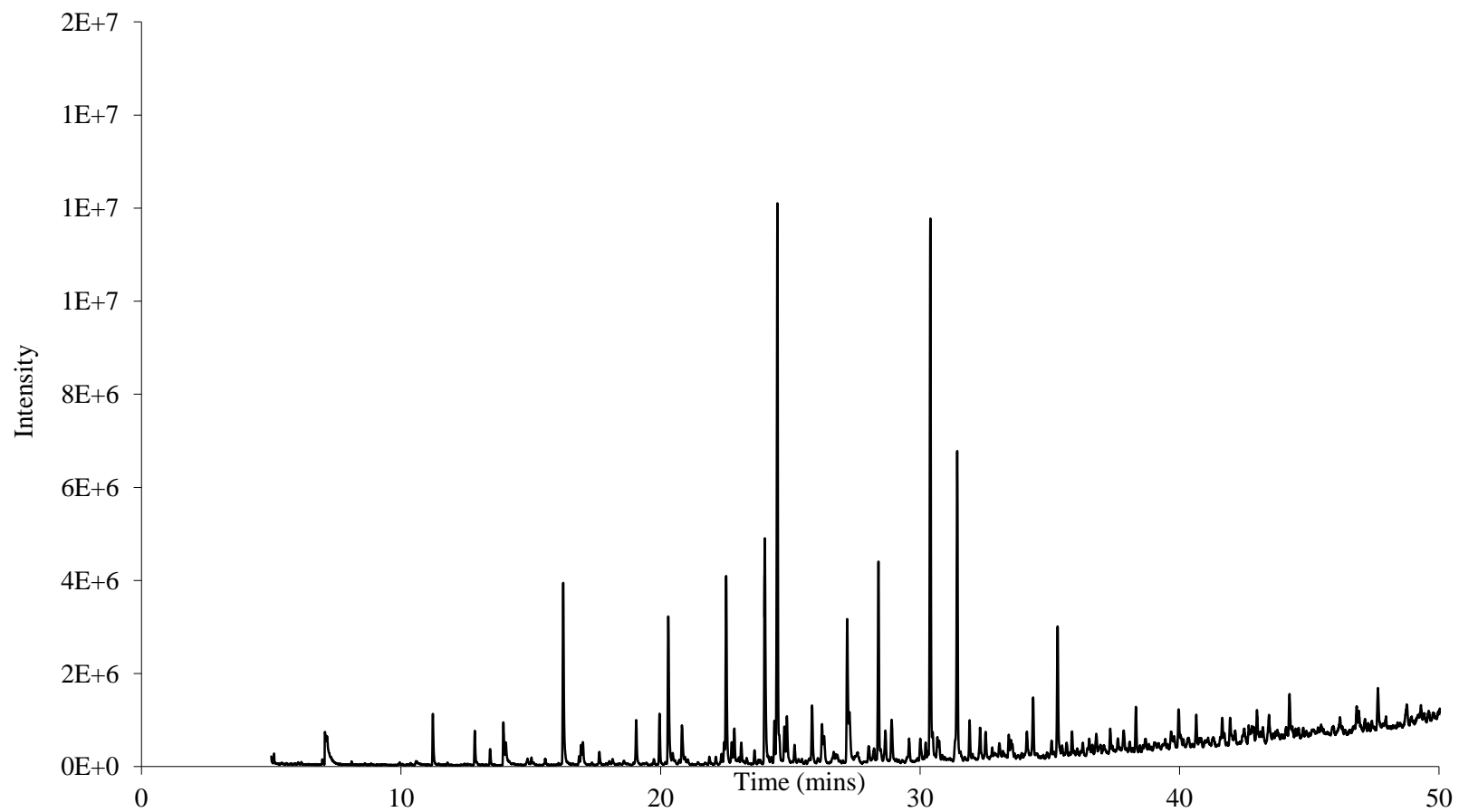
Figure 6.6: GC-MS chromatogram for oil produced from HTL of *Miscanthus* with 1M acetic acid catalyst at 350°C for 1 hour
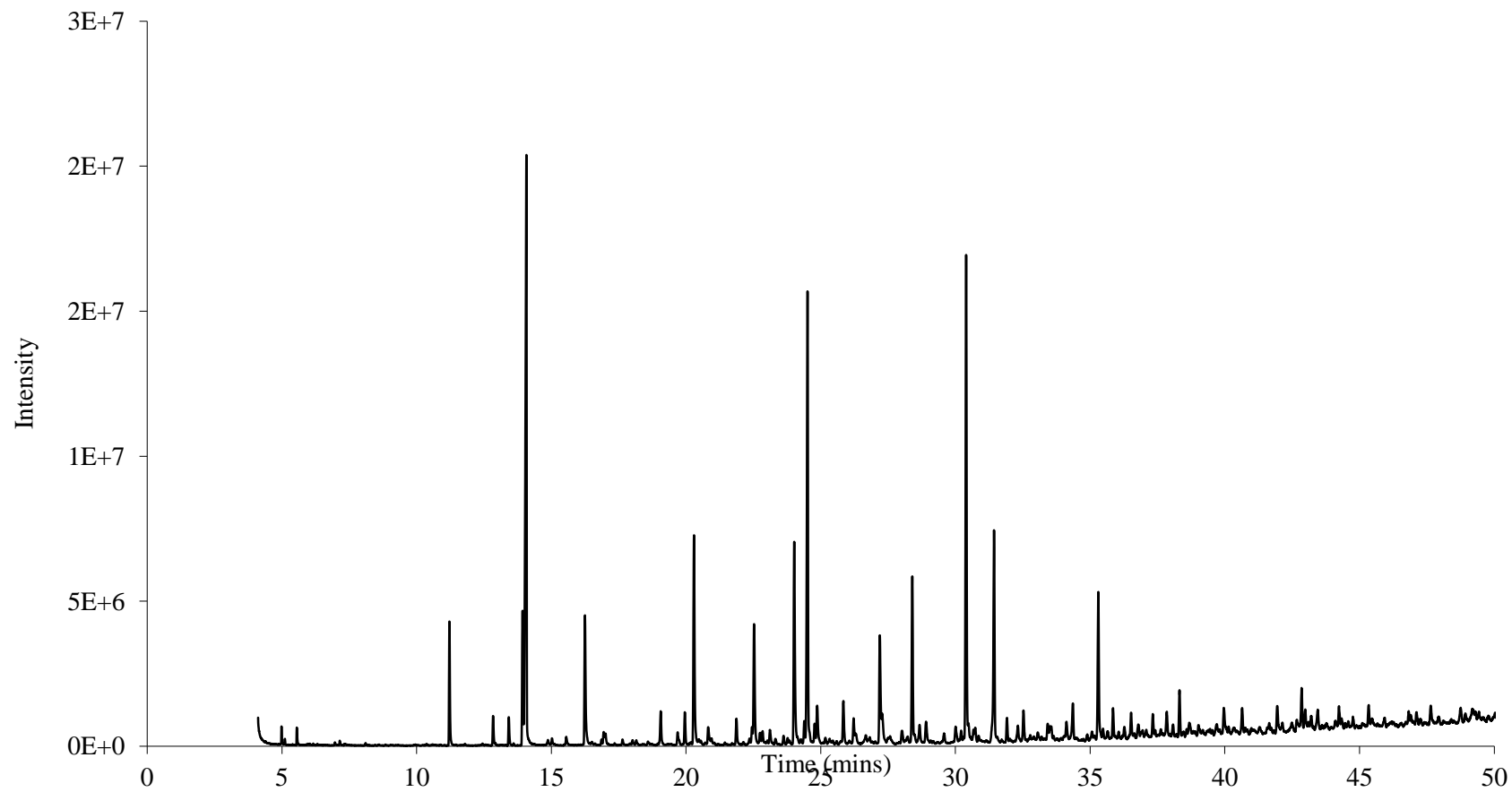
Figure 6.7: GC-MS chromatogram for oil produced from HTL of *Miscanthus* with 1M formic acid catalyst at 350°C for 1hour

Table 6.4: Compound identification from GC-MS analysis of oils produced from HTL of *Miscanthus* (Figure 6.5 to 6.8 inclusive)

RT (mins)	Compound name	Catalyst used (Area % of compound detected)			
		Formic	Acetic	Na2CO3	KOH
11.22	Cyclopentanone	3.10	1.30	-	-
13.93	2-Cyclopenten-1-one	3.63	0.95	-	-
14.08	Furfural	21.31	-	-	-
16.25	2-Cyclopenten-1-one, 2-methyl-	4.17	5.42	-	-
19.97	2-Cyclopenten-1-one, 2,3-dimethyl-	-	1.36	-	-
20.30	2-Cyclopenten-1-one, 3-methyl-	6.86	4.77	-	-
22.53	2-Cyclopenten-1-one, 2,3-dimethyl-	4.22	5.90	3.10	2.31
22.86	2-Cyclopenten-1-one, 2,3,4-trimethyl-	-	-	6.70	6.04
24.02	Phenol	7.11	7.20	1.99	-
24.40	2-Cyclopenten-1-one, 2,3,4-trimethyl-	-	1.19	6.62	4.44
24.51	Phenol, 2-methoxy-	14.78	16.87	7.07	5.77
24.81	2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-	-	1.66	2.31	2.12
25.84	Phenol, 2-methyl-	-	2.25	3.35	2.33
26.31	2-Cyclopenten-1-one, 2,3,4,5-tetramethyl-	-	-	10.00	8.79
27.20	Phenol, 4-methyl-	3.04	4.82	5.39	4.32
27.28	Phenol, 3-methyl-	-	2.03	-	-
27.61	1,3-Hexadiene, 3-ethyl-2,5-dimethyl-	-	-	2.62	0.21
28.23	2-Cyclohexen-1-one, 4-ethyl-3,4-dimethyl-	-	-	-	5.63
28.40	Phenol, 2-methoxy-4-methyl-	5.31	5.27	2.01	-
28.91	Phenol, 2,4-dimethyl-	-	1.64	11.38	14.96
29.58	Phenol, 2,4,6-trimethyl-	-	-	6.73	9.25
30.40	Phenol, 4-ethyl-	14.06	14.38	4.22	3.81
31.44	Phenol, 4-ethyl-2-methoxy-	7.42	9.58	3.59	4.02
31.92	Phenol, 2-ethyl-6-methyl-	-	1.10	6.68	9.53
32.52	3-Methyl-4-isopropylphenol	-	-	1.87	3.82
32.79	1H-Inden-1-one, 2,3-dihydro-2-methyl-	-	-	-	1.51
32.87	Phenol, 2,3,5-trimethyl-	-	-	-	1.99
34.12	3-Methyl-4-isopropylphenol	-	-	1.62	1.97
34.36	Phenol, 2-methoxy-4-propyl-	-	1.86	-	-
34.75	Benzene, 1-methoxy-4-propyl-	-	-	1.78	1.92
35.31	Phenol, 2,6-dimethoxy-	4.99	4.23	-	-
	Total	100.00	93.78	89.03	94.75

It is the use of formic acid that produced the most interesting result, i.e. the production of furfural at 21.31 area%. No other catalyst, not even acetic acid produced this product at such high yield. Routes of furfural manufacture are well understood and include treating various agricultural wastes such as oat spells, corncobs and rice husks with hot mineral acid (HCl). "*Pentosans (polypeptoses) are hydrolysed to pentoses, which then undergo dehydration and cyclization to form furfural*". (Morrison, Boyd 1992) (**Equation 6.1**)

$$(C_5H_8O_4)_n \xrightarrow{H_2O, H^+} C_5H_{10}O_5 \xrightarrow{-3\,H_2O} C_5H_4O_2 \qquad\qquad (6.1)$$
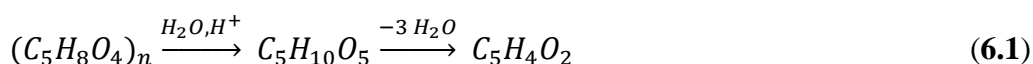
A reason why furfural may not be detected in hydrothermal reactions involving KOH could be due to the cannizzaro reaction – formation of salt and primary alcohol from an aldehyde reacting with a strong base. The products of the reaction of furfural and KOH following this reaction mechanism would be 2-furanmethanol and potassium furoate. These chemicals are not listed in **Table 6.3** for any catalyst, nor are further degradation products of furfural, perhaps indicating that the reaction pathway to furfural from pentosans, comprised from the hemicellulose fraction of *Miscanthus*, are avoided at the reaction conditions in the first part of this study. It is also possible that gaseous decomposition products of furfural and other cracked products may not be detectable with the column employed.

6.4   Hydrothermal reactions of *Miscanthus* and SRC willow in water – study 2

In the second set of comparative data using biomass samples, *Miscanthus* and SRC willow were hydrothermally reacted in water. The data from this set of experiments is included in (Unpublished work - Johnson and Ross 2011) and was reported as part of a comparative study with pyrolysis char. *Miscanthus* and willow were chosen because they are two high yielding energy crops, suitable for growth in the UK. As part of the Supergen research hub, they are some of the most studied plants and fully analysed samples could therefore be found.

Reaction conditions were chosen to represent moving up the scale from HTC reaction conditions (200°C, 16 Bar pressure max.) to HTL conditions (300°C, 100 Bar max.), with an intermediate temperature of 250°C included to see if the products were more

akin to either process. Reaction times were for 1hr, with addition of a 5hr reaction time (a1) for willow to check the rate of carbonization at 200°C. **Table 6.5** gives the list of reaction conditions, product yield and char analysis for willow and *Miscanthus*.

As can be seen in this table, there are a few predictable results relating to relative oil, char and gas yields; the general trend supporting what has already been discovered:

Higher temperatures/ HTL conditions (300°C) produce lower char, higher oil and higher gas yields. HTC (200°C) conditions produce higher char, lower oil and low gas yields.

There are a few anomaly's evident in the results. Earlier on in the chapter, **Table 6.1** contains ultimate analysis for the raw biomass samples. Ash contents are 2.0% and 2.5% with nitrogen contents 0.6% and 0.1% for willow and *Miscanthus* respectively.

It is interesting to note that, for both fuels, the nitrogen content in the char increases as the temperature of the experiment increases. The atomic N/C ratio in the daf willow is 0.011, and for the daf char from a4 is 0.018. Similarly, for *Miscanthus*, the atomic N/C ratio in the daf fuel is 0.0018, while for the char from a7 it is 0.0046. Clearly nitrogen is being enriched in the char in preference to being leached into the aqueous phase or by evolution of gaseous products.

Table 6.5: Reaction conditions, yield results and char analysis of willow and *Miscanthus*

	Willow				*Miscanthus*		
Experiment No.	a1	a2	a3	a4	a5	a6	a7
Reaction temp. (°C)	200	200	250	300	200	250	300
Dwell time	5hr	1hr	1hr	1hr	1hr	1hr	1hr
Ratio	20:1	20:1	20:1	20:1	20:1	20:1	20:1
Catalyst	water	water	water	water	water	water	water
Solvent amount (mL)	30	30	30	30	30	30	30
Residual pressure(Bar)	1	1	2	2	0	1	2
@ Temp.(°C)	29	30	26	19	28	27	14
Sample weight	1.5g	1.5g	1.5g	1.5g	1.5g	1.5g	1.5g
Oil (%)	3.6	4.5	9.2	15.5	6.1	5.1	28.4
Char / Solid (%)	62.9	63.3	40.5	24.6	61.8	36.8	12.4
Gas (%)	2.8	2.8	5.6	5.7	0.0	2.8	5.8
WSH (% by difference)	30.7	29.4	44.7	54.2	32.2	55.3	53.4
Moles gas	0.002	0.002	0.004	0.005	0	0.002	0.005
% C (char)^{daf}	56.1	51.3	63.1	73.4	53.3	71.2	74.4
% H (char)^{daf}	5.6	5.6	5.3	4.4	5.8	4.8	4.8
% N (char)^{daf}	0.6	0.6	1.0	1.5	0.1	0.2	0.4
% O (char)^{daf}	37.7	39.3	27.1	19.4	40.8	23.7	20.9
Char ash content (%)	0.6	0.9	0.7	1.3	0.4	0.3	0.6
% inorganic in aq. phase	81.1	71.5	71.7	57.2	87.2	89.0	74.3

^{daf} dry, ash free

Char ash contents are much lower than from their respective feedstocks. This data, together with the % inorganic content remaining in the water phase, show that hydrothermal processing effectively removes plant inorganic material. Leaching studies at room temperature have demonstrated that between 60 – 100% of individual inorganic components can be removed with water or HCl acid washing and may prove to be a useful biomass pre-treatment step before torrefaction (Saddawi 2011).
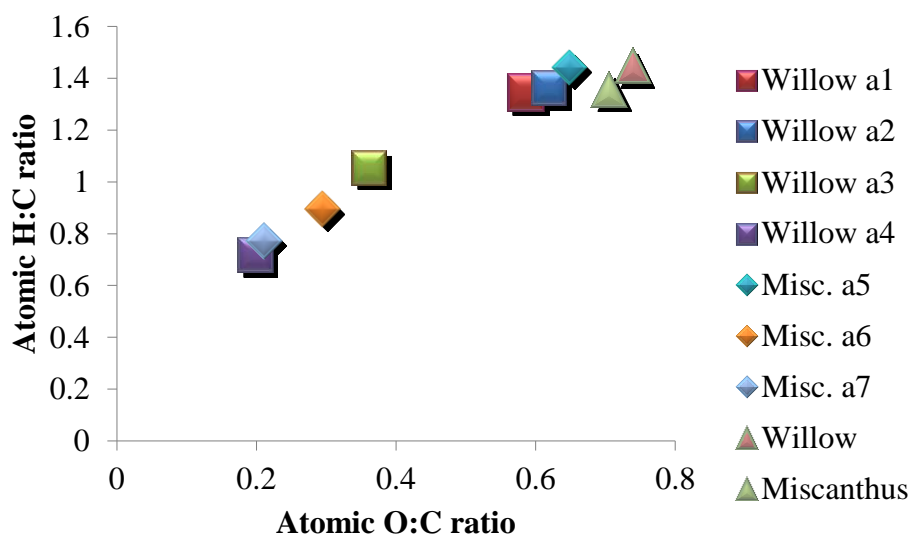
Figure 6.8: van Krevelen diagrams of hydrothermally processed willow and *Miscanthus* chars from study 2

The van Krevelen diagram, **Figure 6.9**, again gives the best evidence that dehydration is the main route for biomass degradation following the diagonal pathway previously discussed in **Chapter 4**. The loss of CO_2, though detectable by gas pressure, is not evident in this figure. This gives more weight to the theory that it is the oil components that degrade to gaseous products and not the chars.

Data for char and oil conversion from the second study is perhaps more succinctly presented in **Figure 6.10**. By isolating the more readily useful fractions of char and oil, a distinct pattern emerges between the two samples. Effect of reaction time on willow at 200°C has little effect on the char and gas yields. It would appear that formation of char at 1hr (a2) is slightly higher than for 5hrs (a1), however, HHV of a1 is slightly higher than a2, indicating an increased energy density of a1 char. This phenomenon is only slight at the reaction holding time measured, but is more pronounced for extended

reaction times. This also shows that dehydration is a relatively slow process at 200°C, with this being a rate limiting step.

As the reaction temperature increases from 200°C (a2 and a5), to 250°C, (a3 and a6) then to 300°C (a4 and a7), yields of oil increase for both willow and *Miscanthus* with the highest oil yield being that produced at 300°C for both substrates, due to the high combined amounts of cellulose and hemicellulose in both samples; and ties in with work in **Chapter 5** showing change in oil yield with increased reaction temperature (200 – 250°C) for both cellulose and lignin. Xylan oil yields are less affected by temperature. (**Figure 5.7**)

For *Miscanthus*, a reaction temperature of 250° gave a slightly lower yield of oil, compared to that produced at 200°C. More significant is the drop in char yield and large increase in the carbon content of the char at 250°C (53.3 to 71.2%), that is only slightly increased from 250 – 300°C (71.2 – 74.4%). Oil content for *Miscanthus* at 300°C reaches 28.4%, almost double that of willow which achieves 15.5%. This is at the cost of char production, which drops to 12.4%.

In **Chapter 5**, a negligible increase in oil yield with increased temperature was noted for xylan; however, the largest negative change in yield was the effect of 0.1M KOH catalyst on lignin (**Figure 5.7**). Published work has shown that the potassium content of *Miscanthus* ash can be up to 54% (as K_2O) (Baxter et al. 2012), this is evidence for the catalytic effect of potassium, forming oil from cellulose. Results from oil yields from model compounds in **Chapter 5** found increases for all with temperature, but significantly, yields of oil for lignin were found to drop with the addition of catalyst (**Figure 5.5**). Other researchers via TGA pyrolysis and combustion studies have suggested that alkali metals not only increase the rate of thermal degradation of all lignocellulosic compounds, but also lower the temperature at which it begins (Fahmi et al.).

A Mohamed et al. (Mohamed et al.) quote in their work on thermal degradation that "*Lignin decomposition starts at low temperatures (160 – 170°C) and this process continues at low rate until elevated temperature of 900°C. The second component which starts to decompose is hemicellulose, followed by cellulose. The decomposition of these*

two polymers takes place in a narrow temperature range of 200 – 400°C" The paper refers to pyrolytic conversion of biomass under slow heating rates for the production of carbon rich material and not hydrothermal conversion, however, the principle of lignin degradation at lower temperatures than quoted by other researchers is of obvious importance. Increasing aromatization of lignin chars while the macrostructure decomposes under heat and pressure accounts for the heavy, tar like material, soluble in acetone.

	Willow a1	Willow a2	Willow a3	Willow a4	Misc. a5	Misc. a6	Misc. a7
Oil (%)	3.6	4.5	9.2	15.5	6.1	5.1	28.4
Char / Solid (%)	62.9	63.3	40.5	24.6	61.8	36.8	12.4
Gas (%)	2.8	2.8	5.6	5.7	0.0	2.8	5.8
WSH (%)*	30.7	29.4	44.7	54.2	32.2	55.3	53.4
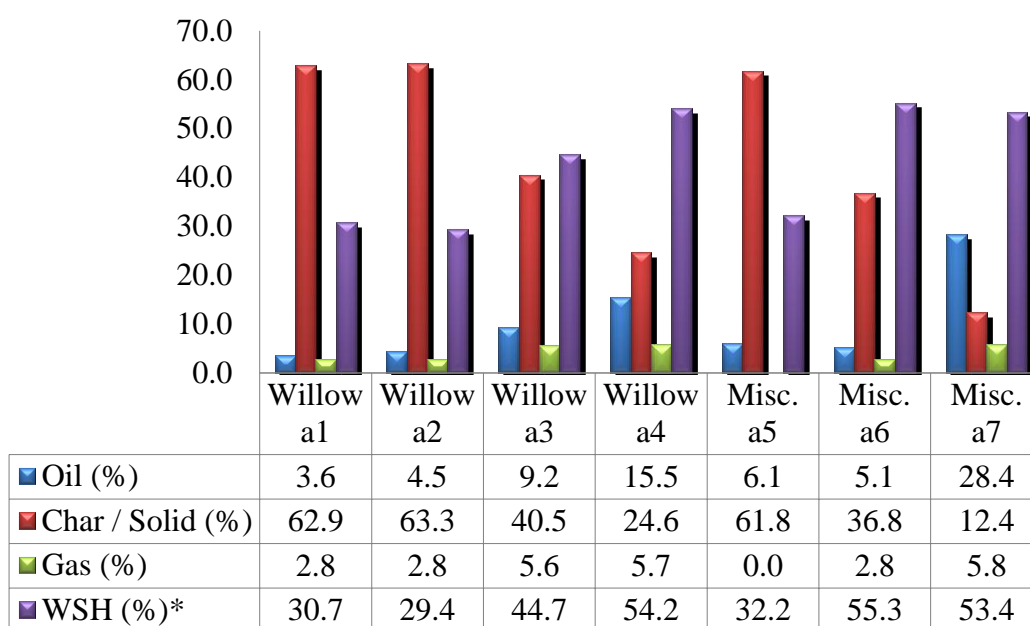
Figure 6.9: Weight % oil, char and gaseous products from hydrothermal processing of willow and *Miscanthus* at a range of temperatures. *by difference

The change in % conversion and char production displayed in **Figure 6.11** is broken down to the effect of temperature between the ranges 200 – 250°C, 250 – 300°C and the overall effect from 200 – 300°C. The results show that increased temperature have an overall effect of a reduction for % char for willow (**Figure 6.11**) and a similar, but greater decrease in % char for *Miscanthus* at 300°C (**Figure 6.12**). This result on first inspection is surprising, but actually can be explained from their lignocellulose composition, and is in agreement again with the findings in **Chapter 5**. The hemicellulose content of *Miscanthus* is higher than that of willow and hence there is a greater proportion of the substrate that breaks down rapidly, producing a larger WSH fraction at 200°C, consistent with **Figure 6.10**. This has the effect of a lower char amount produced at lower temperature.
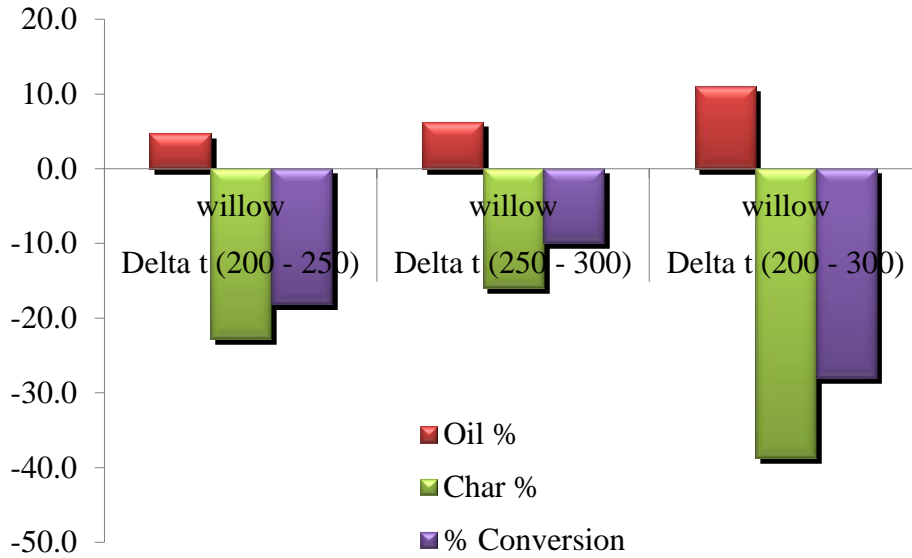
Figure 6.10: Change in product distribution with respect to temperature for willow

Temperature, being already highlighted as the most influential factor in product distribution is investigated by plotting changes in temperature (ΔT) against responses of % oil and char produced by each reaction, in this case the differences in yields brought about by respective changes in temperature from 200-250°C, 250-300°C and overall from 200-300°C. For willow, reactions a2 – a4 are seen in **Figure 6.11** and *Miscanthus* reactions a5 – a7, **Figure 6.12**.
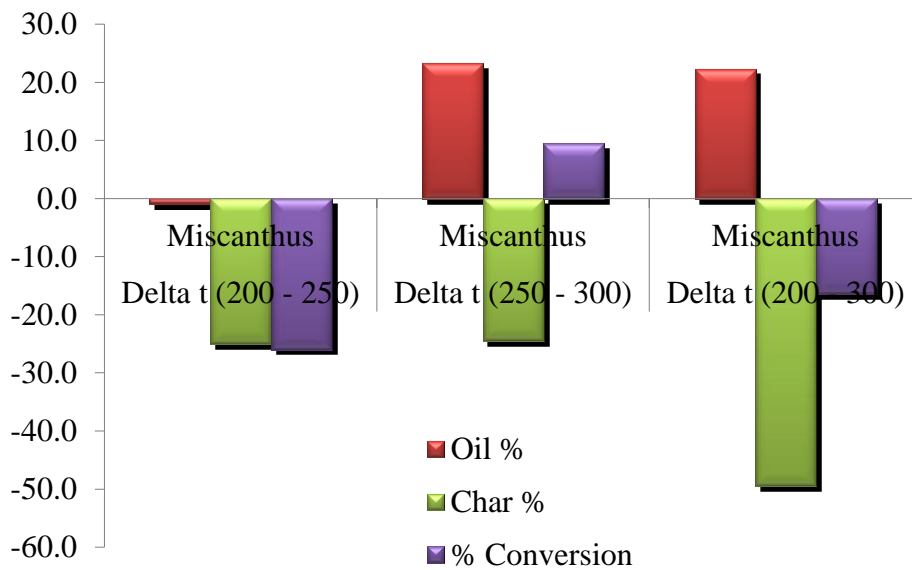
Figure 6.11: Change in product distribution with respect to temperature for *Miscanthus*

The two figures are in diametric opposition to each other with temperature changes from 200 – 250°C realise an increase in oil production for willow of >100% (4.5 – 9.2%), coupled with a 36% reduction in the amount of char produced. For the same temperature range, *Miscanthus* oil contents are maintained at a similar level, with a similar drop in char to willow.

Between 250 and 300°C, the oil yield increases by 68% for willow, but a huge rise of 450% is witnessed for *Miscanthus*. This has the effect of reducing the char content to 12.4%, but interestingly WSH contents are maintained. It is the availability of cellulose hydrolysis at this raised temperature and likely higher mineral content of *Miscanthus* (discussed later) that accounts for this significant increase in oil.

Calculated energy values for produced chars (HHV, MJ/Kg) and the percentage of energy recovered from those chars are contained within **Table 6.6**. What is interesting to note about the char HHVs, is those from both willow and *Miscanthus* rise by a similar amount as the temperature increases from 200 to 300°C. The energy recovery, as with the data for char yields, demonstrates a reduction overall for willow and *Miscanthus*.

This information is linked to cellulose and hemicellulose contents of both raw materials and reinforces the argument that the distribution of cellulose and hemicellulose found in *Miscanthus*, are the reason for the higher char yields after processing for longer periods of time at lower HTP conditions. What is perhaps not completely clear is the role of lignin in this phenomenon. The structure of lignin is often described as a polyphenolic macro structure, adding strength to the plant, but the formation and true composition for each individual plant is currently unknown. It would seem wholly possible from this research that plant containing lignin sources differ in their susceptibility to degradation, relative to the biological matrix in which they are found, also, with differing alkali metal contents of raw materials, the potential for metal catalysed degradation would increase with higher K or Na contents (discussed in **6.4.2**)

Table 6.6: Calculated HHV's of chars with % energy recovered

	HHV (calc.) (MJ/Kg)	Energy recovered from char.(%)
a1 Willow	22.3	75.8
a2 Willow	21.5	73.6
a3 Willow	26.7	58.5
a4 Willow	28.8	38.3
a5 *Misc.*	21.2	77.1
a6 *Misc.*	28.1	60.8
a7 *Misc.*	29.5	21.5

6.4.1 Recoverable minerals in the aqueous phase

This next section focuses on inorganic components of ash contained in the resulting hydrochar and compounds that have leached out during processing into the aqueous phase. Removal of metals from biomass via acid washing is well understood and has been undertaken, at least in the laboratory, as a method with which to improve the quality of biomass derived fuels. (Saddawi et al. 2011) Perennial grasses contain, on average, higher ash contents than woody biomass (2.8% Vs. 1.6%) (McKendry 2002b), but are reported to contain much lower levels of alkali metals (K, Na). The importance of this information is high when considering if the resulting products of HTC or HTL are suitable for use as fuels on an industrial scale. The main problems with ash content and composition during combustion in industrial scale boilers (i.e. for power stations) are with the alkali metal concentration (K^+ and Na^+). The amount of alkali per GJ of energy is referred to as the alkali index and has serious considerations from fouling of boilers and deposition on heat exchangers, causing mechanical failure, corrosion and turbine blade wear. Unfortunately, many biomass types from agricultural sources have high levels of alkali metals.

The calculation for alkali index is based on weight of alkali metals (assumed to be present as oxides) over the energy content of the fuel in GJ.

$$AI = \frac{Kg(K_2O + Na_2O)}{GJ}$$

Where; AI <0.17 – Safe combustion, AI>0.17<0.34 – fouling is probable and AI>0.34 – fouling is certain. (Taken from the subcontracted US National Renewable Energy Laboratory report TZ-2-1 1226-1) Miles et al, (1995).

The alkali index for raw willow is in the region of 0.16, allowing safe combustion. For *Miscanthus*, this increases to 0.31 with a likelihood of boiler fouling.

What must be stressed at this point is that high alkali index for industrial boilers is somewhat of an issue, but for domestic users using the end product in fires or stoves, this is not really a problem. In fact, there is evidence of potassium to catalyse char burn at lower temperatures under pyrolysis and combustion conditions (Nowakowski and Jones 2008; Nowakowski et al. 2007), which may provide a benefit to the end user, especially in the domestic solid fuel industry. Lower temperature ignitions for coal type products having some market advantage.

Figure 6-13 presents ppm concentrations of sodium, potassium, magnesium and calcium in HTC/HTL reaction aqueous phase measured by atomic absorption spectroscopy (AAS) using experimental procedures in **Chapter 3**. Water used in each reaction was deionised and therefore metal free. The same water source was used as a blank for the AAS response in between each analysis, therefore ensuring no contamination was present from the water. Calibration standards were made from dilutions of 1000ppm stock solutions, ensuring accurate measurements.
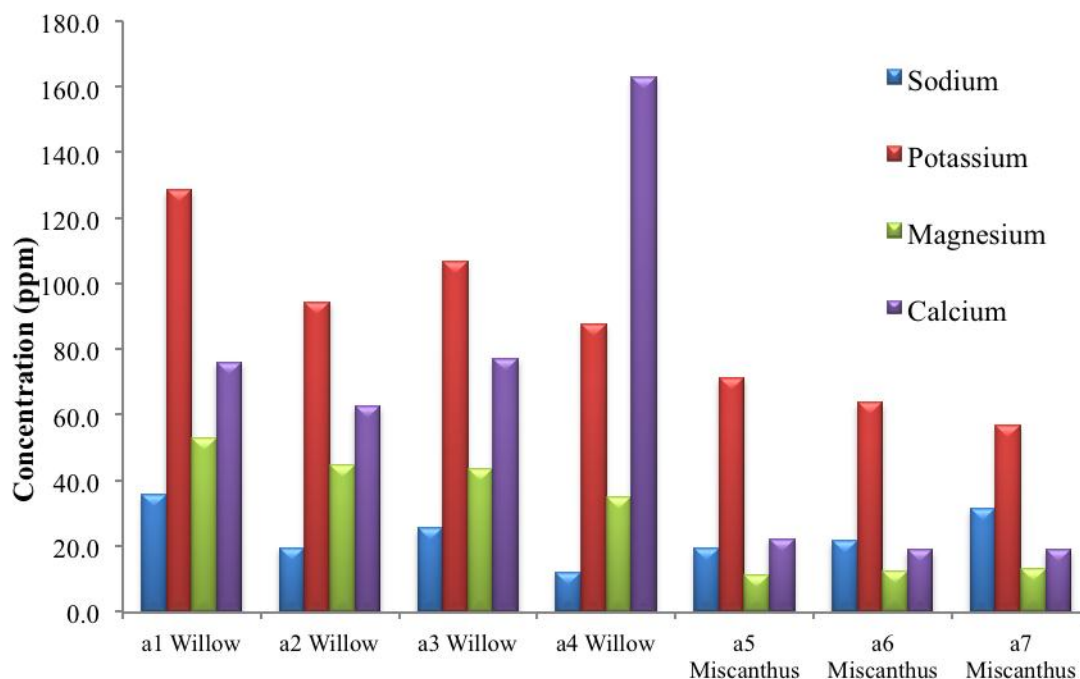
Figure 6.12: Metal analysis of aqueous phases via AAS from hydrothermal processing of willow and *Miscanthus*

As expected, there is leaching of the group 1 alkali metals, but also significant removal of magnesium and calcium from group 2. In the case of willow calcium removal seems to be facilitated with increasing temperature. *Miscanthus* does not share this phenomenon; a consistent amount of calcium is present after each experiment, despite increasing temperatures. The magnesium content of willow leachate is of a similar magnitude to the potassium concentration, and a longer reaction time produces a higher concentration (52.9 ppm) compared to a higher temperature (35.1 ppm). *Miscanthus* displays much more uniform leachate analyses, regardless of reaction conditions. Concentrations in the leachate from *Miscanthus* are also lower than those from Willow.

Aqueous phase potassium concentrations would be expected higher for *Miscanthus* than willow, as this has the higher AI of the two. Comparing the aqueous phase metal contents with those detected in the hydrochar (**Figure 6.14**) shows the inverse relationship, as expected. A decrease in metal concentration is observed with an increase in reaction severity from 200 to 300°C, such that the amounts of each metal detected in hydrochar mirror those from water leachate. Calcium is enriched in the char during hydrothermal reactions due to the loss of carbon, this result being also found by other researchers (Ross, 2012 – unpublished work). What this data set shows is that

increasing temperature during *Miscanthus* reactions removes more calcium from the solid than is observed in the corresponding willow reactions.
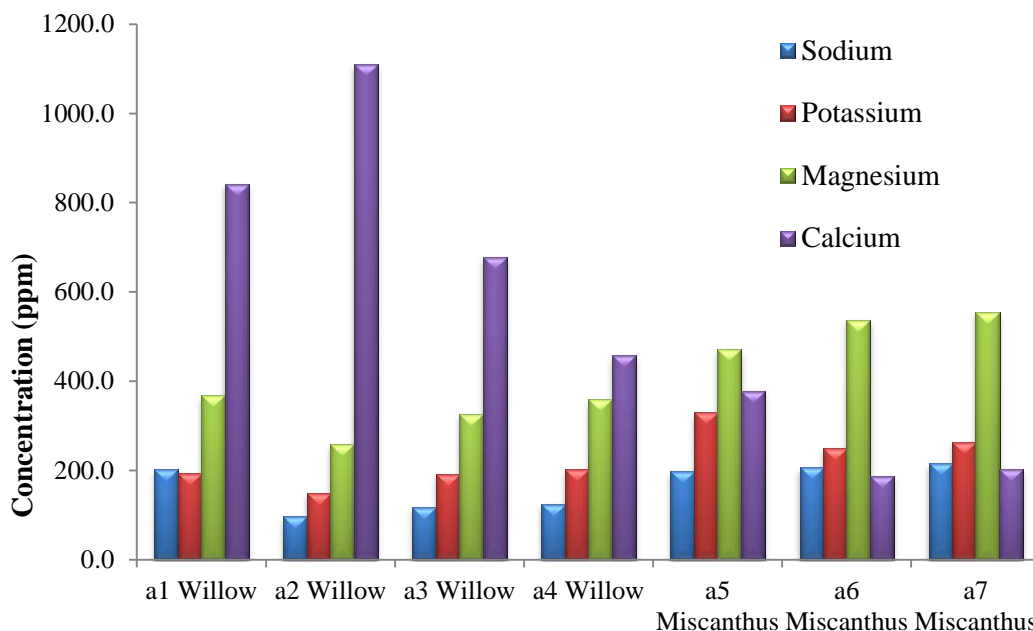
Figure 6.13: Metal analysis of chars via AAS from hydrothermal processing of willow and *Miscanthus*

Miscanthus sourced from Rothamsted Research (R/05/MISC/623/FH/W) [*Miscanthus* Cs/623 whole crop final harvest 2005/6 ppm in dry matter (dried at 80°C for 36hours] was analysed by ICP-OES for metals analysis and found to contain Ca 1003.7ppm, K 2689.7ppm, Mg 269.0ppm and Na 366.5ppm. Willow was also analysed by ICP-OES and found to contain Ca 1220ppm, K 2705ppm, Mg 254ppm and Na 304ppm.

For metals analysis of *Miscanthus* char it is magnesium alone that increases in concentration. This suggests magnesium is more tightly bound within the plant matrix for perennial grasses and may require further processing or more severe processing conditions (Saddawi 2011) for complete removal.

The results confirm that HTC is a suitable method to remove group I and II alkali metals from willow and *Miscanthus* with significant reductions in the metal concentrations in the resulting chars, and proportionally higher levels in the aqueous phases. Potassium

concentrations of <400ppm for *Miscanthus* chars indicate removal to be >80% effective, and with sodium ~40% efficient.

6.5   Hydrothermal carbonisation of *Miscanthus* and Willow – study 3

The following set of experiments deals specifically with the formation of high carbon solid material at 200°C for an extended reaction time of 18 hours. Literature sources for HTC vary in the reaction time from 0.3 to 50 hours (Funke and Ziegler 2010), so the timeframe chosen was to reflect the lowest reaction time for the highest char conversion, given the relatively high carbohydrate content of SRC Willow and *Miscanthus*. KOH at 0.1M concentration was used for comparison to water, to see what benefits there would be, if any, for use in extended batch reactions as opposed to the relatively short reaction times used in previous chapters.

6.5.1   Products

Reaction conditions, product yields and char analysis for HTC reactions of willow and *Miscanthus* can be seen in **Table 6.7.**

Table 6.7: Reaction conditions, product yields and char analysis of willow and *Miscanthus* reacted under HTC conditions - 18hrs at 200°C

Biomass type	Willow		*Miscanthus*	
Reaction temperature	200	200	200	200
Reaction time	18hrs	18hrs	18hrs	18hrs
Ratio	10:1	10:1	10:1	10:1
Catalyst	N/A	KOH	KOH	N/A
Catalyst amount (mL)	30	30	30	30
Catalyst molarity	-	0.1M	0.1M	-
Residual pressure(Bar)	3	3	3	3
@ Temp	20	22	14	18
sample weight	3g	3g	3g	3g
Oil (%)	0.8	2.6	2.9	0.9
Char / Solid (%)	57.4	49.2	44.1	52.1
Gas (%)	5.5	8.5	8.8	5.9
WSH (% by difference)	36.4	39.7	44.3	41.1
C (char)^{daf}	61.2	62.2	65.8	63.7
H (char)^{daf}	5.5	5.7	6.0	5.7
N (char)^{daf}	1	1.3	0.4	0.2
O (char)^{daf}	32.4	30.8	27.9	30.4
Char HHV(MJ/kg)	24.5	25.3	27.1	26.1
% Energy yield (from char)	76.1	67.7	70.3	72.5

^{daf} dry, ash free

Char yields in **Table 6.7** followed similar patterns to those obtained earlier in this chapter in **Table 6.5** with longer reaction times producing less oil and higher char carbon contents than reactions over 1-5 hrs. As expected, use of KOH decreased char levels in excess of 10wt%, but also increased the carbon content of the chars, previously seen in **Chapter 5**, **Figure 5.3**, this is reflected in *Miscanthus* having higher cellulose content. For uncatalysed HTC reactions, the higher lignin content of willow is reflected in the higher char yield, but calculated energy contents of char from *Miscanthus* are

greater than willow (26.1 vs. 24.5 MJ/kg), likely due to a greater degree of condensation polymerisation of hydrolysed hemi/ cellulose monomers.

At the time of writing, there are no direct comparisons with substrates in this study for extended reaction times as noted above. Using loblolly pine and in a similar reactor, (Yan et al. 2009) used 200, 230 and 260°C to thermally pre-treat biomass, achieving mass yields of 88.7, 70.6 and 57.0% and energy yields of 95.8, 79.8 and 77.5% at the respective temperatures. Reaction times for these experiments were only 5 minutes, with a ramp time from 15-30 minutes and rapid cooling in an ice bath. Oil contents were not determined, though it must be stressed that there is no direct comparison with literature sources on oil production from HTC processing as the object of the exercise is char formation. Exclusion of oils extraction in the data would therefore increase both char and water soluble TOC content.

Gas yields for base catalysed HTC reactions are greater than those observed for experiments performed in water alone. From Chapter 4 we know that this may be expected in alkali conditions because at short residence times reaction rates increase for the decomposition of cellulose and hemicellulose (**Chapter 4**), forming degradation products that are easily degraded to gases. HTC reactions under pH neutral and acid conditions are preferential in the breakdown of monosaccharaides (Bobleter 1994; Bonn et al. 1984).

Miscanthus contains a higher proportion of non-lignocellulosic hydrolysable material that is more readily degradable at lower temperatures, hence the lower char produced. For oil, in excess of 200% more is produced by KOH addition for both willow and *Miscanthus*. This would substantiate experimental work in all previous chapters, and appears a sensational increase, but the difference is still a small percentage of the total product yield overall. *Miscanthus*, having higher carbohydrate content, again produces more oil than willow when KOH is used, the sole reason being carbohydrate content. Oil production during HTC is not realised as a separate immiscible layer, or by the observation of a dark (black), opaque aqueous phase that becomes transparent when extracted by DCM solvent, as for HTL.

Uncatalysed reactions give higher char yield than the corresponding base catalysed reaction, equating to a 14-15% reduction. The reason for this is that more carbohydrate is dehydrated to solid product. *Miscanthus* has much lower yield than willow when using catalyst; it was lower for corresponding reaction in **Chapter 6.4** also, but not by the same magnitude. Char yields, when reacted for 1 hour at 200°C (**Section 6.4 – study 2**) were 63.3% and 61.8% for willow and *Miscanthus* respectively, but the corresponding carbon contents of the chars were 51.3 and 53.3% (**Table 6.5**), a small change from %C^{daf} of the raw material of 47.2 (w) and 48.6% (*M*) (**Table 6.1**). For willow, the presence of KOH produces a char with a slightly higher HHV than that produced when using water alone (25.3 vs 24.5 MJ/Kg), but this is not deemed to be significant. However, the energy recovered from water-only produced char is higher than when catalyst is added – 76% vs 68%. *Miscanthus* produces higher HHV char than willow, with much higher carbon content and with correspondingly low nitrogen content.

As discussed in **Chapter 4.5.7** and **Chapter 5 (Figure 5.1)**, the bulk of WSH concentration is made up of products from the hemicellulose fraction. However, willow has less hemicellulose than *Miscanthus* and a great deal more lignin. Other cell wall constituents make up approx. 15% of total mass of *Miscanthus*, leading to higher potential of WSH than willow, reflected in the amounts.

KOH had the effect of increasing WSH, and a synergistic relationship with gas production is perhaps present. To avoid potential issues that may arise from the disposal of process water, or by processing via aerobic or anaerobic means, it is proposed that this water may be reused over and over in the process. Additional work on the reuse of aqueous phase for HTL of willow at 300°C by the author has realised a significant increase (13.7 vs. 31.1%wt) in the amount of oil produced from the 2nd usage of this waste product. It must be noted that WSH content of the initial experiment was 44%, dropping to 25.8%wt in the second run, hence the second processing stage was able to convert a larger proportion of WSH to oil, while maintaining gas and char yields at a similar level. A third reaction with the same aqueous phase displayed a large drop in oil recovered down to 7.1%. Gas yields dropped to 3.7% and char increased slightly to 37.8%, leaving a larger portion of the initial material converted to WSH than in the previous 2 reactions (51.4%). It is therefore hypothesised that this cycle of high-low

WSH content and reciprocal low-high oil content will continue ad-infinitum with subsequent reactions and could be of benefit to future biomass processors wishing to utilise HTC technology. However, further work is needed to ascertain if this is the case. Energy recovery from char greatly increased for *Miscanthus* when residence time was increased. HHV of the corresponding char displayed a 100% increase when residence time increased from 1hr to 18hrs. Willow energy recovery increased from 70.4 to 76% with water as the reaction medium, but dropped to 67.2% when KOH was used.

In the literature, higher energy yields have been reported. For example, Sevilla and Fuertes reported 84.3% retention of carbon from cellulose HTP at 250°C, 160g/L cellulose concentration and 4 hours reaction time (Sevilla and Fuertes 2009b) Tsukashi reacted wood for 72hrs at 200°C to get a coal yield of 66% (Tsukashi.H 1966). Other researchers have not tried to remove oils from char material or recover them from the WSH. It is possible that a large portion of energy contained in hydrophobic higher molecular weight biopolymers were adhered to the char, giving an apparent higher yield and therefore energy content. This would be consistent with only a small portion of the energy therefore being contained in the aqueous phase in the form of polar compounds as reported in **Table 6.7**.

One of the aims of the work was to examine the relationship between model compound work on individual lignocellulose components and "real world" biomass samples, *Miscanthus* and willow. Evidence from previous chapters indicates rapid degradation of hemicellulose (xylan) at HTC conditions to a large proportion of WSH compounds, far in excess of those produced from cellulose or lignin in catalysed and uncatalysed reactions. Willow and *Miscanthus* contain ~30% and ~24% hemicellulose respectively and so willow is expected to be slightly more reactive, and hence lose a slightly higher mass under the same conditions. What has not been touched upon as yet are differences between hemicellulose compositions. In their 2004 report for ECN Biomass, Bergman et al., reprint a table from a primary source (Holzatlas 1974) to give a composition breakdown of hemicelluloses from deciduous and coniferous wood. For deciduous wood, 80-90wt% is 4-O methyl glucronoxylan, but coniferous wood is 60-70wt% glucomannan, with 15-30wt% aribinogalactan (Bergman et al. 10-14 May 2004)herbaceous biomass has a differing hemicellulose composition and could well account for the increased reactivity. However, lignin content is higher for willow (30%

compared to 17% for *Miscanthus*) and in **Chapter 5**, was found to be much less reactive than xylan under all HTP conditions.

Hydrothermal carbonisation is an exothermic reaction and past research in the field has offered values on heat energy produced from the exothermic reaction from a number of sources. Heat of reaction values have been quoted as being 0, i.e. non-existent to -5.8MJ/kg$_{feeddaf}$. **Table 6-8** is published from supplementary material supporting the 2011 paper by Funke and Zeigler. In their paper, they indicate and quantify heats of reaction determined experimentally as follows "*The heat released during hydrothermal carbonization at 240°C measured with the applied differential calorimetry setup is −1.06 MJ/kg$_{glucose,daf}$ with a standard deviation of 14%, −1.07 MJ/kg$_{cellulose,daf}$ with a standard deviation of 9%, and −0.76 MJ/kg$_{wood,daf}$ with a standard deviation of 32%.*" (Funke and Ziegler 2011) By doing so, they have significantly reduced the error associated with hydrothermal carbonisation. Original inventor of HTC, Fridrich Bergius back in 1913 calculated the expected heat of reaction and published this was an exothermic reaction. The lower heat of reaction of wood is explained by the lignin content, being more resistant to hydrothermal degradation. (Funke and Ziegler 2010) In this study, a crude method of electrical monitoring by use of a plug in energy meter was used to measure KW of electrical energy for the reaction over 18hrs vs a reactor with water alone. Over the course of the reaction, this was deemed to be 0.02KW or 20W less energy was used with biomass in the reactor, over the same conditions.

Table 6.8: Summary of reported values for the heat of reaction of hydrothermal carbonization. Supplemental material from (Funke and Ziegler 2011)

Feed	Temperature	Residence time	Heat of reaction	Reference
	[°C]	[h]	[MJ/kg$_{feed,daf}$]	
Cellulose	310	64	-1.8	Bergius,1913
Glucose	n. a.[a]	n. a.[a]	-5.8	Titirici et al., 2007
Peat	210-400	3-5	-0.5…-4.3	Oden and Unnerstad, 1924
Peat	280-300	n. s.	-1.7...-3.4	Terres, 1952
Peat	220	<0.3	0…-0.2 (±0.02…0.03)	Sunner, 1961
Lignite	165-310	1	0...-2.1	Könnecke and Leibnitz, 1955
Different	180	12	-4.3...-5.7	Ramke et al., 2010
Wood	200-260	0.08	0.3...0.6	Yan et al., 2010

n. a.: not applicable

n. s.: not specified

([a]) Theoretical reaction equation for dehydration, no experimental derivation

6.6 Conclusions

In Chapter 6, biomass samples willow and *Miscanthus* were reacted under HTL and HTC conditions in the presence and absence of catalysts. In study 1, HTL reactions of *Miscanthus* at 350°C for 1hour using acetic and formic acid, Na$_2$CO$_3$ and KOH catalysts at 1M concentration and water as control, resulted in large differences in product distribution. Oil yields were relatively meagre for all reactions with the greatest yield in the presence of Na$_2$CO$_3$ at 14.9%. The lowest oil yield was seen in the presence of acetic acid at just 5.0%. Char yields were also low, with a range of 8.8 − 20.1% for catalysed reactions and 26.6% for the control experiment. Aqueous phase TOC contents and high gas production - up to 33.7% explain the low solid and liquid yields, though the HHV of chars produced were in the region of high grade bituminous coals.

Data from study 2 concluded that differences between substrates exhibited greater differences in WSH, oil and char yields for 1hr processing times at a temperature range of 200-300°C. For *Miscanthus,* rapid conversion to WSH is observed, even at low temperatures and this can be explained from its relatively high extractives content (15%) and low lignin content. Condensation polymerisation reactions occur at elevated temperatures, observable from van Krevelen diagrams using elemental analysis of chars. Interestingly, no gas (or less than 1Bar) was produced at 200°C, this would indicate low carboxylic acid formation, low carboxylic acid degradation or a combination of the two. Willow retained the largest percentage of energy in char for all experiments in study 2. The conclusion for this is that it results from the high lignin content of willow and that this component is less reactive. Note that if this were due to resistance of cellulose degradation, then the higher carbohydrate content of *Miscanthus* would have resulted in equally high char yields.

HTC reactions of biomass samples with 18hr processing times in water and 0.1M KOH are covered in study 3. KOH increases oil yields, even after 18hrs processing, and expectations that oils would polymerise over time in aqueous media were not realised. Catalysed reactions also produced higher gas yields (and therefore more CO_2), which explains why the amount of char is lower, but not why % carbon in char increases. The other notable increase at long residence time is in the WSH for *Miscanthus.* This is explained from the reactive hemicellulose content of *Miscanthus*.

Increases in energy yields are possible at extended reaction times at low temperatures and can be seen from comparing results from study 2 to study 3. Gains are greater for high carbohydrate content biomass, as observed from the char yields for *Miscanthus* reacted for 1hour and 18hrs at 200°C (31.9 vs. 72.1%), and this is despite its low lignin content. Willow, with 30% lignin, returns greater yields with shorter residence time and lower temperature as hydrolysis is lower, but even though yields of char increase by a much smaller percentage, willow crucially still returns the largest energy yield over the same time period.

Upgrading of biomass via HTC in water is effective, not only from the view point of increasing energy density, but also in the removal of inorganic material via leaching, measured by the reduction in ash content of the char and by analysis of the water phase

for extracted metals. It is evident that any hydrothermal process will offer some degree of mineral extraction, but the findings are significant, not just for woody or plant biomass processing, but for unconventional materials with high moisture contents.

Chapter 7 – HTC and Torrefaction – A Comparison

Overview

Previous chapters have investigated processing of lignocellulosic biomass and their related model compounds in hot, compressed water at a range of temperatures, residence times and with differing types and amounts of homogeneous catalysts. The term 'wet' torrefaction for this type of process is used in many research texts to infer similarities with 'dry' torrefaction. This chapter will explain in more depth the dry torrefaction process, with current scientific understanding. The Chapter contains some new data on torrefaction from work conducted by the Author when employed at Argina Fuels, County Roscommon, Ireland from December 2010 to December 2011. The main aim of the Chapter is to compare results from hydrothermal processing studies in a general way, with those found from torrefaction on similar biomass products from literature sources. A simple comparison of the energy balances of the "wet" vs "dry" torrefaction is also made.

7.1   Introduction

Energy markets, in particular coal powered electricity generation already have targets for renewable fuels. Initiatives put forward by Eurozone countries have country specific targets to include varying proportions of renewables in their "energy mix". The targets are based on EU directives, and as such will purport to the reduction of fossil fuels over a 38 year period to 2050, whereby, depending on the country of origin, the reliance on non-renewable, carbon based energy will be in the region of 50% of today's levels. In the short term, some of this will be achieved by biomass combustion as a coal replacement. The levels at which current coal fired power stations co-fire biomass vary, as do the sources of biomass. To put this figure into perspective, Drax power station, the largest in the UK producing 7% of the electricity, burned 900,000 tons of biomass in 2010. This equated to approx. 10wt% of coal burned (ca. 9 million tons), but as biomass has roughly half of the heat, only 5% of the electricity output. This means of the electricity produced by Drax for the UK, 0.35% was from biomass.

Maximum biomass yields for the UK are estimated to be 16.6 million tons, with a further 7 million tons if unused agricultural land is used to grow energy crops. This is

still a large shortfall from the 50 million tons of biomass that need to be sourced annually if the government greenhouse gas emission targets are to be met.

As a result, the power industry is now looking for a better fuel than raw biomass for electricity generation. Torrefaction would seem to be a very promising replacement. The energy density is higher (ca. 22GJ/ton), bulk density higher, moisture contents are much lower (<2%) and the physical characteristics mean that both torrefied wood and their pellets are much more compatible with co-firing with coal, with the main benefits being due to energy densification and reduction in transport costs. There are other gains to be made from bulk transportation of torrefied wood; it makes more sense to increase energy density at the point of harvest and then transport with moisture removed. Off-gasses are greatly reduced when compared to biomass and the product is less prone to self-heating. This problem has been witnessed by fires suffered in biomass storage facilities in 2012. Also, with heat treatment, comes a reduction in irritancy caused by resin and terpines, suffered by process operators and immediate handlers of wood chip (Lachapelle 1986).

Novel products from biomass thermal processing are not covered under legislation from REACH, overseen by the European Chemicals Agency (ECHA). All EU member states are bound to guidelines, enforceable by government departments. All chemicals that enter the market has to be rigorously tested at the creator's expense and this applies to manufacture or import greater than a tonne per year. It is the author's belief that whoever is the first to submit an application will bear the brunt of these costs. Although there are numerous companies in The Netherlands that have produced allegedly large quantities of torrefied materials, a formal application for torrefied wood has yet to be received.

Machinery required for biomass torrefaction on an industrial scale is relatively straight forward. Dryers, rotating kilns and heated screw feeders can all be modified to fit the process. There are a couple of other manufactures that have developed novel processors – Toppel Energy BV utilize a hot air system with rapid heat transfer rates, whereas Rotawave favour microwave power to supplement the heat source. At the time of writing, technology to produce industrial quantities of biochar via HTC is limited to a handful of companies. In Europe there is only one – AVA-CO2.

It is for the following reasons that biomass torrefaction is receiving such scrutiny and investment;

- Technology required is readily available and relatively cheap
- Existing machinery (dryers/kilns/screw augers) can be adapted to torrefaction
- A large proportion of the energy contained in the biomass is preserved, when compared to other densification techniques i.e. pyrolysis
- Processing can be run continuously, reducing production costs
- Torrefied materials can be pelletised readily, reducing transport costs and greatly increasing bulk density
- End users (power stations etc.) can use existing boilers/ combustion equipment

7.2   Background

As explained in **Chapter 1**, torrefaction is best described as mild pyrolysis carried out in the temperature range of 200 – 300°C (Bergman et al. 10-14 May 2004). The purpose of torrefaction is to initially dry the feedstock and with further heating produce a carbon-enriched solid product with improved grindabilty (Arias et al. 2008; Bridgeman et al. 2010), hydrophobicity (Kim et al. ; Shang et al. 2012a) and with resistance to further degradation (Bridgeman 2008; Medic et al. 2012), providing a uniform product. This is achieved whilst simultaneously reducing the mass by up to a third on a dry basis and maintaining proportionally high carbon contents of ~90% (process and substrate dependent) (Uslu et al. 2008). The major route for increasing energy density is preferential loss of oxygen and hydrogen over that of carbon. Dehydration reactions (loss of H_2O) are favoured over CO_2 production, but as will be seen later, greatest calorific loss is through tarry compounds in torrefaction gas.

Although torrefied materials display degradation resistance in terms of heat and moisture, there is also claim to have superior resistance to microbial attack than their corresponding raw materials (Shah et al. 2012). It has been shown through fungal resistance studies carried out as part of an academic/ industrial partnership between Arigna Fuels and NUI Maynooth under the supervision of Prof. K. Kavanagh, an expert in fungal research, that this is not necessarily the case (internal report). In fact, torrefied materials produced by Arigna Fuels have been found to exhibit *less* microbial resistance than seasoned wood. Seasoning wood by reducing water content to less than 20% has

the effect of preserving it, resisting further degradation by microbes/fungi due to lowered water activity. The reasons for this have been investigated, and indeed answered by analysing fungal resistance of the torrefaction condensate. Neat condensate product was found to be a fungicide, offering fungal resistance for agar and having been tested under laboratory conditions, killing environmental fungi such as *penicillium*, *botrytis*, *mucor* and *geotrichum* species – all fungi types that can be found in wood. Other researchers found this condensate to be phytotoxic (Trifonova et al. 2009). Torrefaction samples sent for fungal resistance testing were measured at water contents of >3% (much lower than the water content of seasoned wood) and were found to support growth of the fungal species listed above. After torrefaction, loss of fungal resistant functional groups within the lignocellulosic matrix, through the formation of acids, furans and phenolic compounds actually makes the resulting material much more susceptible to fungal attack (internal report).

Stark differences in lignocellulosic decomposition have been reported by Melkior et al. In their 2012 paper, NMR analysis of torrefied "gently grinded", previously dried beech wood were carried out under reaction conditions of 200, 230,245 270 and 300°C. The susceptibility of hemicellulose to thermal degradation is noted. Also quoted in their paper and presented in **Figure 7-1**, is that demethoxylation of syringyl lignin components occurs at around 200°C, catalysed by production of organic acids (acetic and formic). (Melkior et al. 2012)
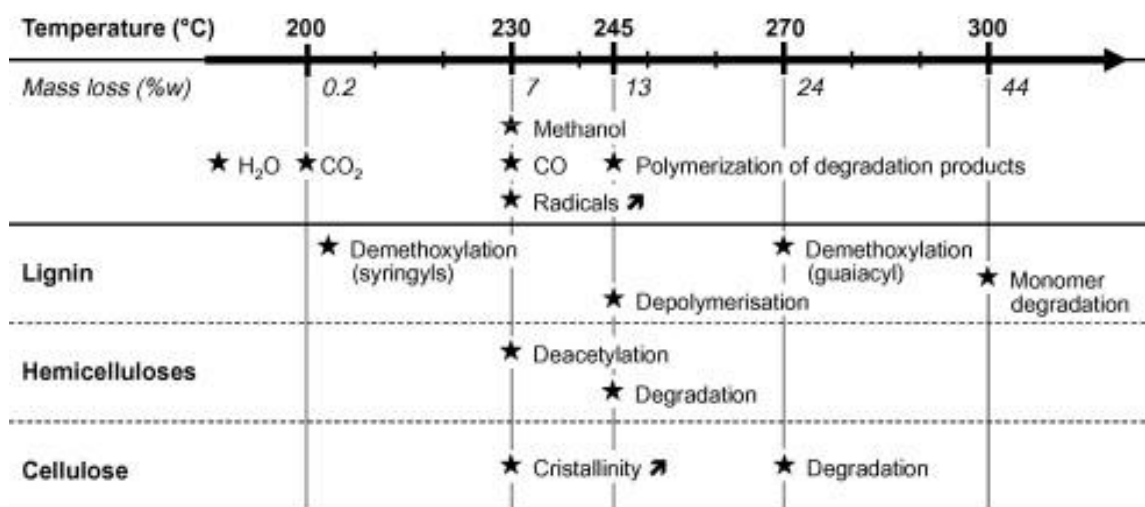
Figure 7.1: Overview of mass losses, produced volatiles and transformations of the wood polymers as a function of the torrefaction temperature. Stars indicate temperatures

at which the processes are clearly observed in the different measurements. From (Melkior et al. 2012)

Sources of organic substrates are varied and vast, with numerous types being researched, these include, but are not limited to; SRC Willow, *Miscanthus*, coniferous woods, deciduous woods, empty fruit bunch (EFB), straws, grasses, nut shells, agricultural wastes and other non-lignocellulosic wastes.(Bergman et al. 10-14 May 2004; Bridgeman 2008; Bridgeman et al. 2008; Bridgeman et al. 2010; Chen et al. 2011; Dhungana et al. 2012; Jones et al. 2012; Kim et al. ; Li et al. 2012; Medic et al. 2012; Melkior et al. 2012; Prins et al. 2006b; Shang et al. 2012a; Shang et al. 2012b; Uemura et al. 2011; Uslu et al. 2008; Wannapeera et al. 2011).
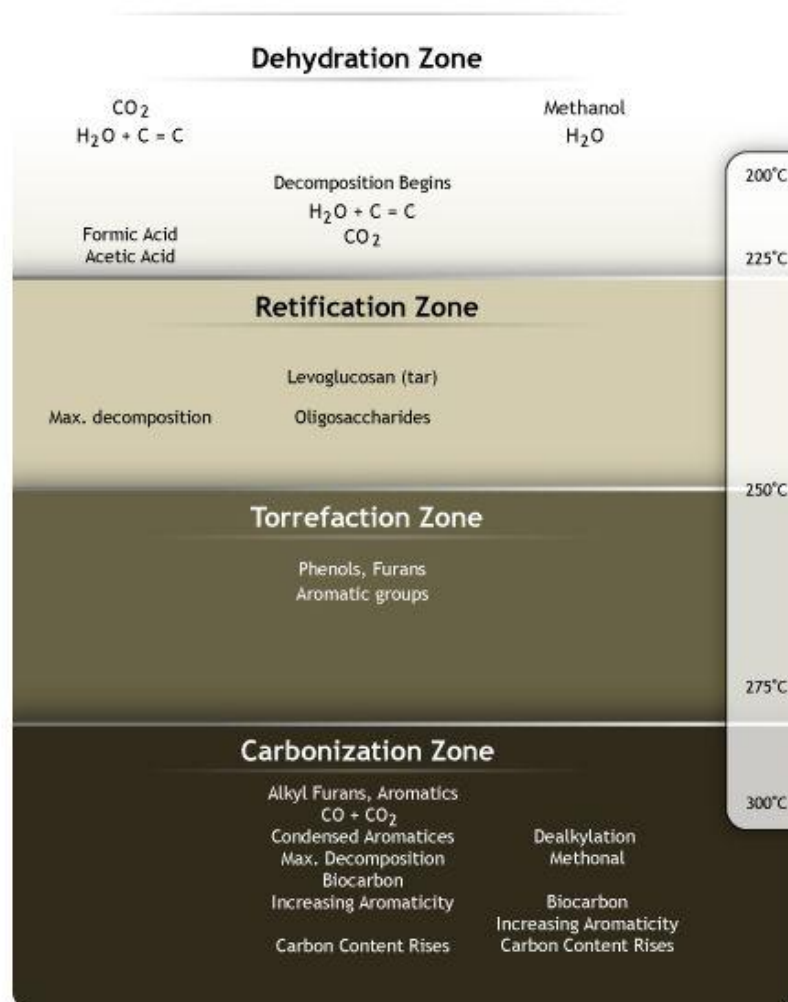
Figure 7.2: Defined zones for thermo-processing of lignocellulosic materials http://alternabiocarbon.com/carbonization/thermochemical-gradient

Torrefaction processes are more widely reputed to proceed mainly by hemicellulose degradation, beginning around 200°C (**Figure 7-2**), the largest portion of degradation products being water, produced during exothermic condensation reactions (discussed in more detail later), but also partial decomposition of cellulose beginning at ~240°C. Lignin, torrefied at temperatures <285°C is relatively unchanged, although there is plenty of evidence of phenolic compounds present in torrefaction condensates produced below this temperature (Bergman et al. 10-14 May 2004). The increase in energy density is also well documented and, dependent on substrate, reaction temperatures and residence times is of the order of 20-24MJ/kg from 17-19MJ/kg. This increase in energy does not necessarily correspond with an increase in surface area for unprocessed material. Jones et al. noted little change in surface area from torrefaction "*The surface area of the raw willows (10 W and 20 W) were measured as 3.9±0.8 m^2/g, and the surface areas of the torrefied willows were 3.4±0.4 m^2/g*" (Jones et al. 2012).

Checking for synergistic effects of torrefaction, Chen and Kho (2011) studied cellulose, lignin, hemicellulose, dextran, xylose and glucose. One of their findings in earlier work was that at 240°C, hemicellulose contained in biomass samples was '*influenced by light torrefaction, whereas cellulose and lignin were hardly affected*'. (Chen and Kuo 2011) This statement was then corroborated by examining TGA weight loss under nitrogen at temperatures of 230, 260 and 290°C for the 7 materials listed above, showing little change in weight loss for lignin at all temperatures. They conclude by comparing measured results to those predicted, and suggest that there is no synergistic effect of co-torrefaction.

As of April 2012, there are a number of industrial torrefaction plants operating in Europe. Most of these are situated in The Netherlands (Topell Energy B.V., Tor-Coal B.V., ECN, Fox-Coal B.V., BioLake B.V. etc.). Processing technology differs for each, but the basic flow chart for processing biomass is the same (**Figure 7.3**).
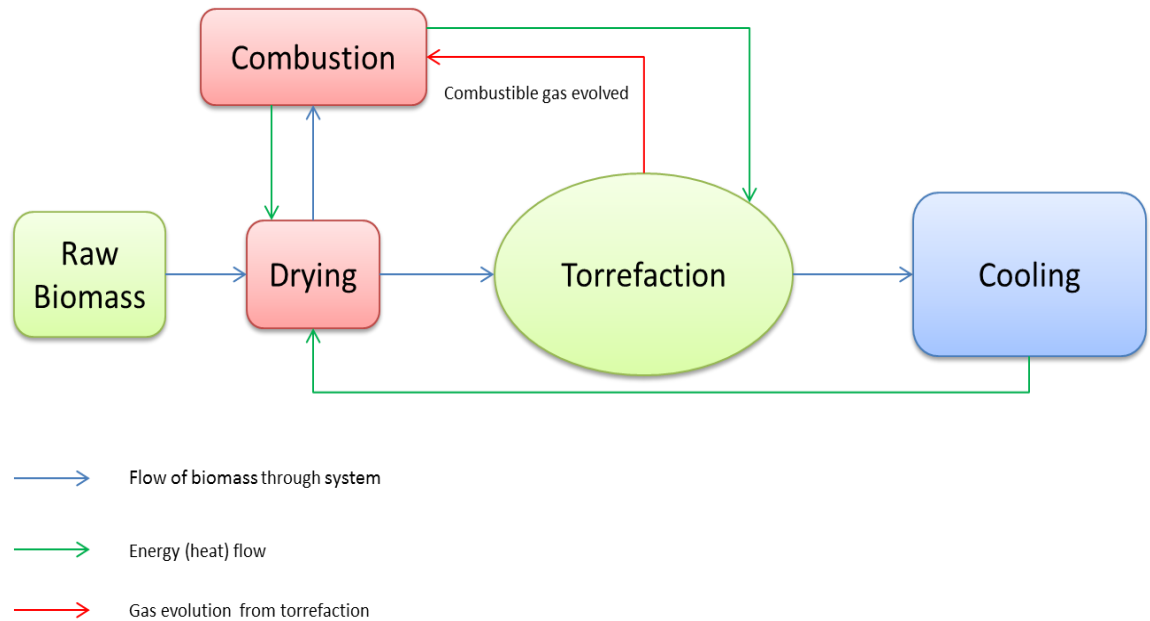
Figure 7.3: Basic torrefaction flow chart

Heat is required for the process, which can be provided either from burning either a portion of the raw, dried biomass, or from natural gas. Of course, the latter approach makes the process reliant on fossil fuels, and increases the amount of atmospheric CO_2 generated. The exothermic reaction resulting from thermal decomposition of biomass, measured at temperatures in excess of 200°C for torrefaction and 170°C for hydrothermal processing is also very similar. Hemicellulose decomposition accounts for a major part in this rise. Production of furfural, acetaldehyde, acetic and formic acid along with water and CO_2 in an oxygen depleted atmosphere is possible due to rearrangement reactions (Shen et al. 2010).

With all that said, torrefaction would seem to be the more suited technology for biomass upgrading. The largest negative surrounding this process is the production and reactivity of dust, having a high risk of dust explosions and auto-ignition. (Garcia-Torrent et al. 1998; Wilen and Rautalin 1993) It is likely that dust produced from the torrefaction process will be more reactive than biomass alone, making the system more prone to explosion. This is due to the process producing a drier and finer particle size dust, but may also be inherently more reactive than raw biomass. At the time of writing, there is no published data on the explosion risk from torrefied biomass, but work is being undertaken by a research group from the Energy Research Institute at Leeds University.

7.3 Batch torrefaction experiments in a 50L reactor at Arigna Fuels

This section details experimental work, providing empirical data for torrefaction in addition to literature sources. Samples of torrefied wood, other novel biomass types (palm kernel shell, citrus cattle feedstock etc.) and related condensate were produced by the author during employment at Arigna Fuels Ltd, County Roscommon, Ireland from December 2010 to December 2011. The reactor (**Figure 7.4**) used for the following torrefaction reactions was a 50L jacketed vessel, made from cast iron and modified with a long heated exhaust manifold to reduce condensation. Heating and cooling was provided by heating oil, maintained at temperature by a Tool-Temp oil heater with integrated water cooling. The reaction vessel was manually stirred at periodic intervals to ensure homogeneous substrate mixing. Condensable gases including moisture were collected in a cold trap at the end of the exhaust. Condensed liquid made a fairly homogeneous mixture similar in appearance to pyrolysis oil. The viscosity of the resulting mixture was more akin to water than oil, and had a pungent, aroma of smoked wood and fat. Mass loss on drying for condensate at 105°C was 72%.
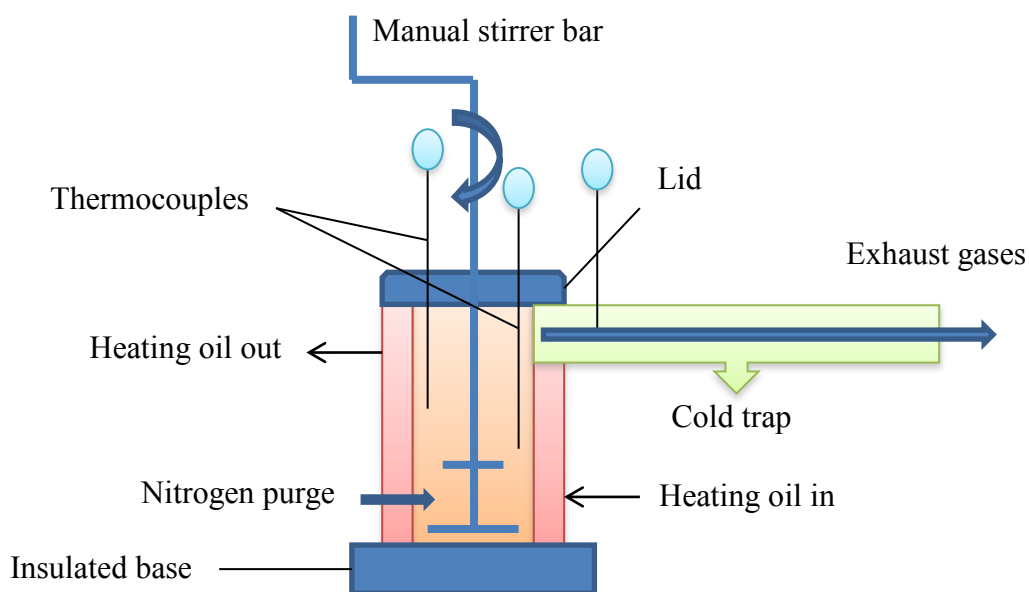
Figure 7.4: Schematic of pilot scale torrefaction reactor at Arigna Fuels

For some of the unique biomass sources torrefied, oil was either present as an immiscible layer, or as high moisture content, dark, opaque liquid, akin to HTC aqueous phase prior to oil removal. Oil extraction was either by separation or DCM extraction, as described in **Chapter 3**.

Combustible gases produced by the system, dependent on the method of process, substrate and the torrefaction temperature, have a heating value in the range of 4.0 – 20.0 MJ/Nm^3 (Bergman et al. 10-14 May 2004). This is despite possessing high moisture contents of anything between 50 and 80% mass. Most of the energy contained in the vapours is from lipids, primarily fatty acids with carbon chain lengths C8 – C18, but also with other organics, CO and by CO_2 (**section 7.4.1**). the resulting condensate was analysed by GC-MS (**Figure 7.5**), but contains mainly the lipid portion as the samples were evaporated to dryness at 105°C meaning some volatile organic products (acetic acid, furfural etc.) were evolved and lost. Dried condensate was dissolved in DCM prior to injection into the GC-MS. (Experimental details can be found in **Chapter 3**).
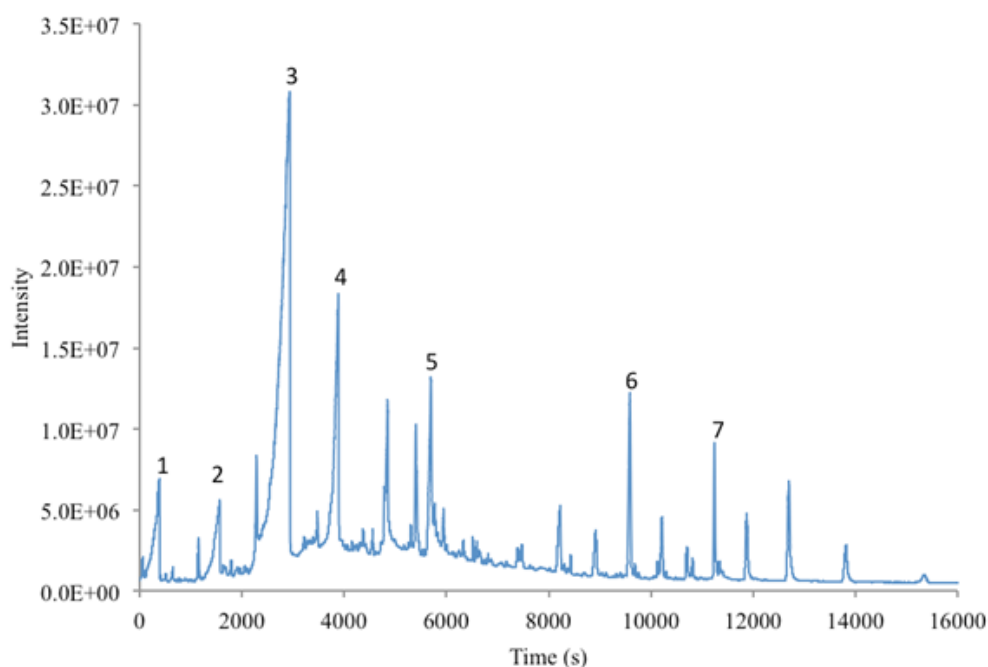
Figure 7.5: GC-MS spectra of torrefaction condensate produced from palm kernel shell, dried at 105°C. Main peaks are; 1, n-Decanoic acid 2, Nonanoic acid, 3, Nonanoic acid 4, n-Decanoic acid, 5, Undecanoic acid 6, 1-Hexadecanol, 7, 4-Dibenzofuranamine.

Products were identified from NIST database comparisons, with individual peaks manually checked.

On an area % basis, over 70% of the total peak area in the GS-MS spectra was identified as fatty acids. The production of torrefaction gas poses interesting choices for the producer. Currently, all torrefaction plant designs burn this gas, using the resulting heat in the process. The other option would be to condense these gases, and separate to get higher value chemicals. In the open chemical market, medium chain fatty acids increased in value from 2010 to 2011 (Source – ICIS.com). Asian markets in particular saw rises of 150% ($1000 to $2500 per tonne) over the same time period. This would make a much more attractive use of the condensate, even factoring in processing costs. The problem with condensing gases is the subsequent condensation products and the cost of separation. The tar-like, higher molecular weight compounds stick to surfaces and have the potential to cause blockages. Heating of pipework and addition of a temperature controlled distillation/ fractionating column would help prevent this.

Table 7.1: Torrefaction gas mass and composition data for reburner/ safety flare design

Biomass feed to reactor			400	kg	
Moisture Content			8	%	
Weight Loss in Reactor			30	%	
(Wt of dry biomass)			368	kg	
Wt of Gas to burner*			120	kg	
Wt of Water from moisture			320	kg	
Therefore 'reaction ' Gas			880	kg	
(wt loss on dry biomass)			24	%	
Reaction Gas Constituents[1]					
Permanent Gases		11%	99	kg	(see split below)
Organics		14%	120	kg	(see split below)
lipids		11%	99	kg	
Reaction Water		64%	563	kg	(50 to 80 %
	Total	100%	880	kg	
Permanent Gases[1]					
Carbon Dioxide		87%	86	kg	
Carbon Monoxide		12%	12	kg	
Other		1%	1	kg	
	Total	100%	99	kg	
Organics[1]					
Acetic Acid		68%	81	kg	
Methanol		15%	18	kg	
2- Furalhehyde		4%	5	kg	
Others		13%	16	kg	
	Total	100%	120	kg	
Summary Gas Analysis					
			kg	%	
Inert	Total		883	74%	
	CO2		86	7%	
Reactive	Acetic		81	7%	
	Methanol		18	1%	
	Lipids		99	8%	
	CO		12	1%	
	Other		21	2%	
		Total	120	100	
Carrier	Nitrogen		125	kg	
		Grand	132	kg	

Table 7.1 Additional information/ assumptions
Note 1: Lipids are listed as containing the following: terpenes, phenols, fatty acids, waxes, tanins
Note 2: CV of Gas (excluding moisture content of biomass and Nitrogen Carrier) = 5.3 to 16.2 MJ/NM^3)
Note 3: Adiabatic Flame Temperature for biomass at 15% Moisture (above calculated at 10%) is calculated at 986C to 1473C
Note 4: Lipids are given as contributing 65% of CV
Note 5: On our test rig gas temperature never rose above 110 C using thermocouple in SS pocket.
*Gas weight was 30% of 4000kg (1200kg)
[1]Data taken from combined STA-GC-MS analysis

Table 7.1 contains data produced from Arigna Fuels as part of a torrefaction gas re-burner and safety flare design calculation with throughput of 4000kg hr^{-1} wood chip at 8% moisture content. Torrefaction reaction temperature was 270°C. Data was taken from mass loss calculations, and sequential STA-GC-MS analysis, giving detected levels of lipids, organics, permanent gases and reaction water. The total reactive portion of the gas is 19% and the total mass loss from gas evolution is 24% on a dry biomass basis. For 1000kg dry biomass, this gives;

$$1000kg \times \left(\frac{24}{100}\right) \times \left(\frac{19}{100}\right) = 45.6kg \tag{7.1}$$

45.6kg or 4.56% total reactive gas produced. Carbon lost through decarboxylation (CO_2 formation) is 7% of the total gas produced and is therefore;

$$1000kg \times \left(\frac{24}{100}\right) \times \left(\frac{7}{100}\right) = 16.8kg \tag{7.2}$$

16.8kg or 1.68% CO_2 formed.

Similar calculations can be made for CO and the organic vapours such that the composition of the reaction gas can be estimated as given in **Table 7.1**.The above calculations (**7.1** and **7.2**) show that the mass of reactive gas available for combustion is

46.6kg, with 16.8kg unrecoverable gas produced as CO_2 containing 4.58kg carbon. Most energy losses that arise from gaseous product formation during torrefaction are recoverable and can be reused within the system, through re-burning.

7.3.1 Solid torrefied material

Literature sources for chars produced from torrefaction give energy contents from 19 – 23 MJ/kg (Prins et al. 2006b; Uslu et al. 2008) or an increase of between 5 – 28% compared to the raw material on a w/w basis. Most of the torrefaction chars produced in Arigna Fuels have energy contents higher than these. This is due to the batch reactor employed and as such, no accurate control of the runaway exothermal reaction that occurs. **Figure 7.6** highlights this reaction in some detail and shows that temperature in the reactor exceeds that from the heat input from the heating oil jacket, but only for a brief time. This phenomenon occurs simultaneous with water production from dehydration mechanisms of hemicellulose and cellulose and CO_2 formation from decarboxylation described earlier in **Chapters 4**, **5** and **6**. Overall in the reactor, this has the dual effect of cooling and decreasing the oxygen content within the reactor, meaning self-ignition of torrefied material is unlikely.
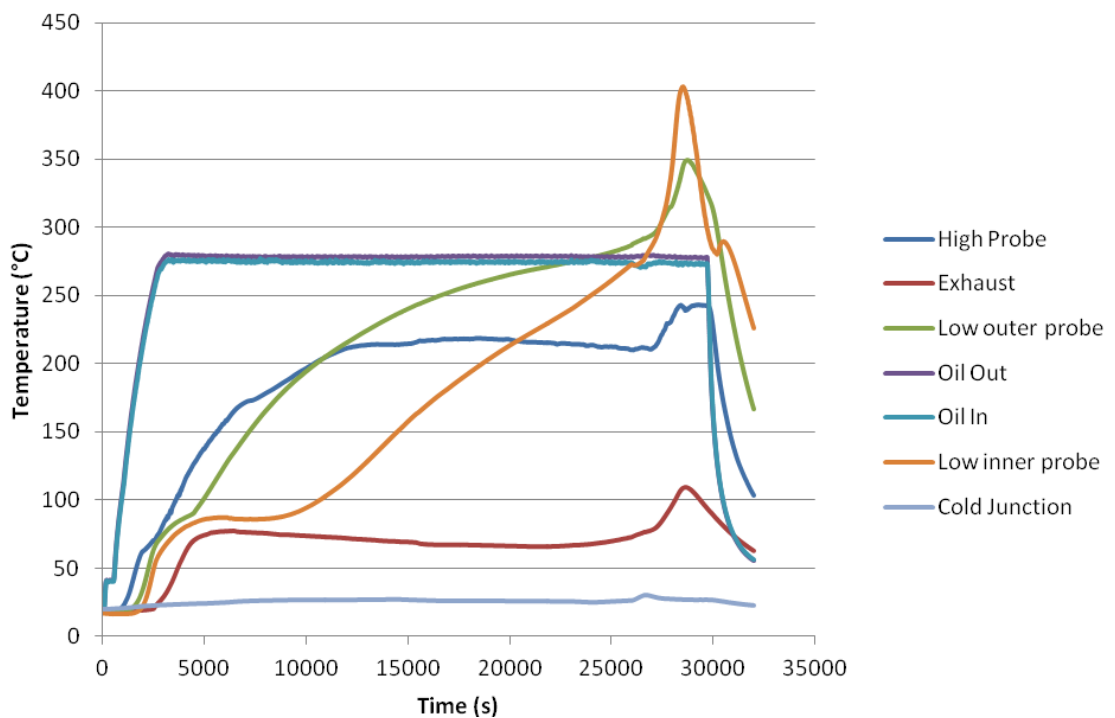

Figure 7.6: Typical batch torrefaction temperature data from jacketed reactor using wood chip as substrate

A low nitrogen flow through the reactor (<2L/min) helps with gas removal. What is apparent by studying **Figure 7.3** are differing heating rates of wood chip depending on their physical location within the reactor. The oil that supplies heat to the reactor is marked as 'Oil Out' and 'Oil In' and shows a fairly rapid heating of the reactor to 275°C, this takes approx. 3000 seconds or 50 minutes. The three probes positioned in the reactor are 'High probe', 'Low outer probe' and 'Low inner probe', coming into direct contact with the biomass. The fastest heating rate is observed initially by the high probe. This is positioned close to the reactor sidewall, where the heating oil is circulated, at the same distance from the heated jacket wall as the Low outer probe. It takes 2.7 hrs. for these probes to register 200°C. The low inner probe is located only 10 cm closer to the center of the reactor, but heats up at a much slower rate, taking 5.3 hrs. to reach 200°C, a clear indication as to the insulating properties of wood resulting in largely reduced heat transfer rates through the mass. The evidence of condensing moisture at the initial stages of heating prevents the temperature of the wood from achieving over 100°C for over 2.7 hrs. from the start of the reaction.

Temperatures of biomass within the reactor, even at the apex of the exothermic reaction differ largely. There is over 150°C difference at the peak temperature observed between the 3 probes; this shows that the heat transfer properties of the torrefied wood chip also results in a temperature gradient through the bed.

7.4 HTC vs. Torrefaction

Chapters 4, 5 and 6 present work on the hydrothermal processing of lignocellulosic biomass and their related model compounds. The HTC process has been found to be most efficient when reacting for long periods at relatively low pressures and temperatures to produce a carbon rich char. The technology for this process is in its infancy, but is within the grasp of process engineering on a large scale. As HTC is more suited to batch reactions, reducing batch times via catalysis or progressing to a semi/continuous process will improve profitability in the future.

The major challenge for HTL is overcoming a large technological barrier to provide products that are cost effective when all equipment and processing energy is taken into account. Continuous processing of biomass under HTL conditions (>100 Bar, >300°C) will require an engineering feat and large investment and may only be suitable for

geographical areas with abundant, cheap heat, ideally from renewable sources. Potential energy benefits for processing high moisture content/ wet biomass types i.e. algae and food wastes by hydrothermal processing rather than by torrefaction are discussed later.

There are evidently a number of similarities between products derived from HTC and torrefaction. Each processing method gives char, oil, gas and water soluble hydrocarbons with water and CO_2 as by-products. The oils and chars produced have a similar composition and calorific value, if water is removed. Activation energies required to initiate decomposition reactions differs only by the use of the environment in which it is surrounded, i.e. water, for hydrothermal processing and nitrogen (or an oxygen deficient atmosphere) for torrefaction. Activation energies for initial torrefaction degradation for willow have been quoted as 76.0kJ/mol (Prins et al. 2006a), attributable to hemicellulose. Post torrefaction, E_A for willow have been experimentally calculated as being 81.6 – 87.4kJ/mol (Jones et al. 2012)

7.4.1 Reaction efficiencies - torrefaction

With any processing system the amount of energy required to make a product can be calculated from either electricity, liters of oil or kilograms of coal consumed. For an over-engineered lab-scale reactor this cost can seem extortionately high. It is only when scaling up that the true cost of energy can be calculated. For torrefaction, the design for most systems requires a portion (around 10%) (Prins et al. 2006b) of biomass to be burned to facilitate the removal of water and for the subsequent torrefaction reaction.

Kinetics for heat transfer using gases are relatively poor, compared to water, although the energy required to heat water by 1°C is 4.18kJ/kg from 0 – 100°C, enthalpy of water vaporisation under atmospheric conditions (Δ_{Hvap}) is 2257kJ/kg, thus the total energy required to convert 1kg water to steam is 2675kJ. For 1000kg biomass at 50% moisture content, this would equal 1337.5MJ or 1.34GJ of energy required for 500kg water removal, assuming no losses. The specific heat capacity (cP) of biomass is reported to be in the region of 1.3 – 2.5J.g^{-1}.K or approx. 0.002MJ.kg^{-1}.K adding a further 90MJ (90°C increase). If assumptions are made that the drying process is 65% efficient (Shah et al. 2012), this gives an energy requirement of approx. 2.2GJ for the drying portion. To this is added the energy required for torrefaction, again, after drying, the 500kg of dried biomass needs to be raised to 280°C at a specific heat capacity of 0.002MJ.kg^{-1}.K.

This is 180MJ. Assuming 60% torrefaction efficiency, further 300MJ heat energy is needed. At the end of the process, a small portion of retained heat from the torrefied wood can be collected, and combustible gases are re-burnt, but due to the high gas moisture, energy contents are relatively low (4.56% reactive gas is produced) (**Table 7-1**). This gives an adjusted figure of 2185MJ (2.19GJ) or a reaction efficiency based on raw materials of ~77% (500kg dry biomass = 9.5GJ energy)

7.4.2 Reaction efficiencies - HTL

To reach the saturation point of water at 200°C in a HTC system, 1kg water would require 858.54kJ energy to rise from 0 to 200°C. Again, assuming a high pressure reactor contains 1000kg biomass at 50% moisture content, but with 2000kg additional water, making a ratio of 1:5 biomass: water (lower than all HTC reactions in this study). For the whole process, keeping biomass cP at 0.002MJ.kg^{-1}.K, 190MJ heat is required to raise the temperature of biomass 190°C from 10 to 200°C, but to heat the water for reaction, 2146.4MJ (2.15GJ) energy is needed. Efficiencies can be assumed to be higher as the batch system can be better insulated with fewer losses associated with movement of gases through the system. Assuming 85% heating efficiency, this gives 2753MJ (2.75GJ) energy required. Though to be removed from this figure is heat from the exothermic reaction at 0.76MJ.kg^{-1} (Funke and Ziegler 2011) or 380MJ to give a revised total of 2373MJ (2.37GJ) for the process. Overall, reaction efficiencies based on raw material energy content are ~75%.

These simple calculations imply that there is very little difference in the reaction efficiencies for torrefaction and HTL when considering a biomass feedstock at 50% moisture content (77 to 75%). Indeed, plant design may be able to utilise more energy by employing heat exchangers, rapid heat transfer in the case of torrefaction and thermal storage in the case of HTC, ideally obtained from renewable sources i.e. solar/ geothermal. In the case of HTC, utilisation of these technologies will enable large reductions in operating costs, but the price of large, high pressure reactors being tied up for 1-2 days, will inevitably increase production costs, though economies of scale may indeed prove the process to be worthwhile. The real difference in process suitability for all biomass types will in future depend on moisture content. With biomass sources being so varied and unusual, there is plenty of interest in hydrothermal conversion of high moisture and lipid content algae (Biller and Ross), and high moisture/ high mineral

content seaweeds (Anastasakis and Ross 2011). For a pure energy basis, those biomass types up to and including 50% moisture content and depending on physical characteristics, torrefaction would be the most suited thermal conversion technique for energy densification. For those raw materials >60% moisture and for slurries, HTC would be more suited.

Considerations not included above would be initial drying of material for the purpose of torrefaction, to a level <30%. If wood chip were used, timber would have to be seasoned under cover for a year at least as raw timber (especially spruce) can be as high as 60% moisture when freshly cut. Coppiced willow is harvested annually and chipped at source, with the chips stored in piles and left to dry over months. Biomass mass loss also occurs at this point from natural processes, self-heating and microbial/fungal degradation. Storage of materials prior to and after torrefaction is still an important consideration as they remain weather dependent. Though hydrophobicity has been claimed for torrefied wood, this is a relative term when compared to raw wood, but the reality of making torrefied wood pellets (e.g TOP) is that these cannot at present be stored outside, despite manufacturers claims to the contrary, as they absorb water and disintegrate over time, thus storage and transportation are still similar to costs realized for wood pellets. (Penmetsa and Steele 2012) One large scale producer, Torpell Energy BV, loads torrefied wood pellets into dry, sealed containers for shipping via barge to a RWE power station up-river. Friability of the material and the requirement to keep dry at all times also increases risks associated with dust production. Biocoal, being produced in water and with higher carbon content is more hydrophobic than torrefied wood, but there are no sources to cite regarding weathering capabilities in briquetted or in its raw form.

Table 7.2: Comparison of HTC and torrefaction processes

	HTC	Torrefaction
Capital expenditure for new processing plant capable of processing 50,000 TPA of dry biomass with 6 year life	>500M$[est]	>20M$[1]
Processing costs ($ per metric tonne)	Unknown	17.5[1]
Energy to react 500kg biomass at 50% moisture	2.37GJ[2]	2.15GJ[1]
Product yield (dry basis)	60% (200°C)[2]	77% (280°C)[3]
Energy yield	75%[2]	78-90%[4]
Typical HHV of products	24-28MJ/kg[2]	20-22
Ash contents of solid	Typically >40% reduction in inorganic content[2]	Proportional increase depending on reaction severity pre-treatment methods

[est]Estimated, [1](Shah et al. 2012), [2](this work), [3](Lipinsky et al. 2002), [4](Bergman et al. 10-14 May 2004)

Data contained in **Table 7-1** allows comparisons to be drawn between HTC and torrefaction. Many of the physical properties and yields are obviously dependent on reaction conditions and in some way can be tunable to fit the end user. Process energy requirements for HTC are independent of biomass moisture content and therefore of the same magnitude regardless. Use of different biomass substrates will have little change to the overall figure in this case.

7.4.3 Physical and chemical properties of reaction products

Ash content is dependent on uniformity of sample source. Torrefaction increases ash content proportionately compared to the starting material as all inorganic material remains within the product. This, as explained in **Chapter 6,** causes problems for subsequent combustion in boilers as ash contains alkali earth metals, contributing to slagging and fouling. Additional pre-treatment steps to remove/ leach inorganic materials, have been found to achieve high levels of extractable metals/ silica and chlorine with high extraction efficiencies (Saddawi et al. 2011), but additional pre-

treatment processing steps to include saturating with water or acid, on an industrial scale will inevitably increase processing costs. As HTC is a self-contained 'one pot reaction', if carried out in water only (or with stable, removable heterogeneous catalysts) overall ash is reduced by 70-80% (**Chapter 6, section 6.4.2**). Recovery of inorganics or treatment of solubilized material from the aqueous phase could include inline processing of batch water via ion exchange. There would be no requirement for removal of WSH as the process water would simply be recycled.

Gas compositions vary largely between the two processes. For woody products, HTC reactions produce mostly CO_2 with smaller amounts of H_2, CH_4 and CO (Funke and Ziegler 2010) (see Appendix for GC-FID/TCD analysis of HTP gases). Torrefaction gas is moisture rich (~64%) with permanent gases comprising of ~11%.(Wannapeera et al. 2011) Organic content is ~14% with lipids making the remainder of ~11%. Of the permanent gases, 87% is CO_2 and 12% CO. Organics comprise acetic acid (68%), methanol (15%) furfural (4%) with others making the remainder (13%) (Medic et al. 2012). Lipids are listed as containing terpenes, phenols, fatty acids, waxes and tannins. (This study) Regarding energy content of reactive gas, lipids have the highest portion of energy. This will be discussed in more detail in **section 7.4**

Levels of WSH in HTC are found to rise at short residence time due to hemicellulose breakdown (**Chapter 5**). Concentrations then lower with longer residence time as condensation polymerization takes place within degraded monomers, forming macromolecular structures as carbonisation reactions progress and also as gaseous products are evolved. For torrefaction, WSH are related directly to temperature and are mentioned twice as they are also evolved as vapours. Compounds are in terms of abundance - acetic acid, 2-methoxy phenol, phenol, 4,6-dimethyl- pyrimidine, 2-furanmethanol and 2-furanmethanol acetate (Johnson, 2012 – unpublished work).

Lipid (oil) content for HTC reactions are low in uncatalysed water (typically <0.9%), raising to 2-3% with KOH catalyst (**Chapter 6** section **6-5**). If obtaining oil from HTC is not the desired outcome, the likely fate of this oil, consisting of polar hydrocarbons, is to be recycled within the system as explained earlier on in the chapter, potentially increasing char yields. Water saturated with organic oils/compounds may serve to catalyse HTC reactions further due to the acidic pH content, as noted in **Chapter 4**.

Thus, reuse of HTC water would be an interesting study and worthy of further research. Torrefaction oils derived from higher nitrogen sourced materials contain a greater proportion of nitrogen heterocyclic compounds, combined with fatty acids, and a lower proportion of furfural/ phenolic compounds as detected in the water phase only. Other lipids found in condensed torrefaction gases include C8 to C12 fatty acids (**Figure 7.2**). Torrefied biomass would not usually be described as a char, more as an intermediate material lying between wood and charcoal. The appearance of unprocessed torrefied wood is a darker brown version of the raw material from which it derived. The different stages of torrefaction or degrees of torrefaction progression depends mainly on the temperature to which the raw material is heated and not residence time. Torrefied material char contents are in the region of 50 – 56% carbon quoted in literature sources, with 65 – 70% carbon enriched product obtained from the on-site reactor at Arigna (see **section 7.3**). Biomass HTC chars are 60-70% (200°C, 18hrs reaction time, no catalyst) (**Chapter 6, section 6.5**)

Raw wood chip has high volatile content and low fixed carbon content. Torrefied wood has reduced volatile content and increased fixed carbon content (Bridgeman et al. 2008; Dhungana et al. 2012). HTC char has the highest amount of fixed carbon coupled with low ash, indicating that this would be a more suitable fuel as a direct coal replacement. Torrefying biomass reduces moisture content to approx. 2% or less (Bridgeman et al. 2008). Although the material is dried to <0.1% during production, there is a propensity to absorb atmospheric moisture (though torrefied material is not hygroscopic), with also the possibility of moisture generation from condensation reactions occurring during the cooling process. The physical composition of the material changes so that it is less fibrous in nature, allowing easier grinding. (Arias et al. 2008; Bridgeman et al. 2010; Shang et al. 2012a; Shang et al. 2012b) This also has an effect of a reduction in bulk density to around 200 Kg /m^3 from ~220 Kg/ m^3. The effect on processing is great as the torrefied wood is easily ground and pressed into pellets. This increases the bulk density and there are even reports of a 1200Kg/ m^3 pellet being made, though not in any scientific journals.

Closer inspection of chars by SEM microscopy highlights other phenomenon. Hydrothermal processing has been used to produce functionalised carbons, such as

nanofibres and microspheres (Funke and Ziegler 2010; Sevilla and Fuertes 2009a, b; Titirici and Antonietti 2009), the exploitation of which is still under study.

7.5   Conclusions

In this chapter, HTC was compared with torrefaction from data present in literature sources and from empirical experiments carried out at Arigna Fuels.

Processing equipment to make torrefied wood is technologically easier, gives good yields and increases energy density. These are all attractive qualities for companies wishing to exploit this limited natural resource. In addition, torrefaction condensate contains high value chemicals including acetic acid, methanol, fatty acids and methoxy phenols. Separation of these compounds from the aqueous solution could provide additional revenue streams, with a value far in excess of combustible wood alone – the current price of wood chip is around £50 per tonne at 45% moisture (Source – www.biomassenergycentre.org.uk)

Both processing technologies, HTC and torrefaction, can avail of the observed exothermic reactions to their advantage, but reaction control for torrefaction is much more critical due to the risk of fire and explosion from runaway exothermic reactions and oxygen ingress. Heat dissipation in a batch reactor for HTC is far easier to control, especially as the reaction media is water and has a large specific heat capacity. Fire risks are removed, but obvious precautionary measures need to be taken with large vessels operating under 16Bar+ pressure.

HTC has a much greater time penalty related to reaction time and requires much more sophisticated processing equipment that can currently only be achieved in a batch process. The resulting bio-coal has fuel qualities in excess of torrefied wood with lower ash, much higher carbon and lower oxygen content. The greatest technological hurdles to overcome are processing time reduction and introduction of a continuous (semi-continuous) processing system.

Chapter 8 – Conclusions and Future Work

8.1 Conclusions

During this study, hydrothermal liquefaction and hydrothermal carbonisation reactions in the presence of homogenous catalysts/ water were used to degrade two different biomass types and their related model compounds to gaseous, liquid and solid products. The differences between torrefaction and hydrothermal carbonisation were also studied.

Hydrothermal liquefaction reactions undertaken using catalysts did not produce the quantities of oil as found by other researchers in the field. The reasons for this are likely due to faster heating rates than those in this study; achieving rapid degradation of the macro lignocellulosic structure to their related monomer compounds, organic acids and gases, but also increased rate of vessel cooling, preventing subsequent polymerisation by quenching further reactions. Chars from catalysed reactions at high catalyst concentrations were found to contain high inorganic contents relative to the staring material, indicating catalyst retention within; and retard, to some extent, oil production from hemicellulose and cellulose. Reactions in water were found to be just as effective converters of biomass to fuels with the system employed, giving lower ash contents of respective oils and chars. Overall, energy recovery from solid and liquid fuels was low, with greater emphasis on solubilisation in the aqueous phase.

It is the neutralisation of KOH under hydrothermal conditions that provides a significant finding. This discovery would suggest that production of organic acids increases linearly with the addition of alkali, and would also explain not only low oil and char yields, but increased inorganic content of chars resulting from catalyst uptake.

Hydrothermal carbonisation, being a lower temperature and longer reaction time process was found to be much more suited to the formation of char from biomass, giving much higher energy yields and availing of the exothermic reaction produced by dehydration of carbohydrates. Oil contents were expectedly low, but present indicating levels of WSH in the aqueous phase resisting conversion to higher molecular weight materials, even after 18hrs processing time. Lower temperature ranges, 200°C were sufficient to degrade lignin, the presence of lignin monomers/ substituted phenolic compounds in the aqueous phase being evidence of this. Reaction mechanisms for chars

from HTP are all via the dehydration route. From the factorial study in Chapter 5, temperature was found to have the greatest effect on all responses overall, be they positive or negative.

For HTC reactions at 200°C, reaction time has the greatest bearing on char yields and energy recovery. Initial solubilisation of hemicellulose, preferentially forming WSH, re-polymerise over extended periods to produce insoluble chars. There is seemingly no benefit in the case of HTC to use KOH as catalyst; however, mild catalytic effects may arise from high potassium/ sodium contents of raw biomass. Removal of plant inorganic material is also a large benefit of HTC, this could overcome problems associated with combustion of high alkali metal content biomass following thermal conversion. Reducing levels of not only these metals, but also silicates would help provide cleaner burning; naturally low sulphur fuels, making industrial use much more attractive, whilst avoiding expensive pre-treatment steps.

HTC was found to be the most efficient hydrothermal method of biomass conversion to fuels, reaching a similar solid product return to those produced via torrefaction at 50% moisture content. By comparing the two thermal conversion systems, torrefaction is most suited method for biomass types <45% moisture content, with HTC more suited for those biomass types in excess of 50% moisture content (algae, seaweed, municipal sludges and waste slurries). Energy required for water removal is by far the largest motivator for this technique over torrefaction for high moisture containing biomass.

8.2 Future work

The data presented in this study, though comprehensive, could be embellished upon to increase understanding in the hydrothermal conversion of biomass to upgraded fuels. As touched upon earlier in this work, a number of research paths could be employed:

- HPLC/ LC analysis of the aqueous phase from HTP of the full range of model compounds and biomass types to correctly assess water soluble compounds from their parent.
- Full metals analysis of HTC/ Torrefaction chars and aqueous phases via ICP-OES to determine leaching qualities of both systems. Torrefaction is reported to retain all inorganic material, is this true?

- HTP of various homogeneous and heterogeneous catalysts in water only to see how each compound behaves under the same system.
- Expand torrefaction and HTC to include novel biomass types currently unexploited as fuel sources e.g. Olive press cake/ Rushes

Bibliography

Adhikari, S., S. Fernando, S. R Gwaltney, S. D. Filip To, R. M Bricka, P. H. Steele and A. Haryanto, 2007. "A thermodynamic analysis of hydrogen production by steam reforming of glycerol." *International Journal of Hydrogen Energy* 32:2875-2880.

Akhtar, J. and N. A. S. Amin. 2011. "A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass." *Renewable & Sustainable Energy Reviews* 15(3):1615-1624.

Anastasakis, K. and A. B. Ross. 2011. "Hydrothermal liquefaction of the brown macro-alga Laminaria Saccharina: Effect of reaction conditions on product distribution and composition." *Bioresource Technology* 102(7):4876-4883.

Annee, J.H.J and H.P Ruytter. 1986. "Process for producing hydrocarbon containing liquids from biomass." Shell International Research.

Antal, M. J., W. S. L. Mok and G. N. Richards. 1990. "Kinetic-Studies of the Reactions of Ketoses and Aldoses in Water at High-Temperature .1. Mechanism of Formation of 5-(Hydroxymethyl)-2-Furaldehyde from D-Fructose and Sucrose." *Carbohydrate Research 199*(1):91-109.

Ardrey, B. 2003. *Liquid Chromatography Mass Spectrometry*: Wiley.

Arias, B., C. Pevida, J. Fermoso, M. G. Plaza, F. Rubiera and J. J. Pis. 2008. "Influence of torrefaction on the grindability and reactivity of woody biomass." *Fuel Processing Technology* 89(2):169-175.

Barham, H. N. and Louis Watts Clark. 1951. "The Decomposition of Formic Acid at Low Temperatures 1." *Journal of the American Chemical Society* 73(10):4638-4640.

Baxter, X. C., L. I. Darvell, J. M. Jones, T. Barraclough, N. E. Yates and I. Shield. 2012. "Study of *Miscanthus* x giganteus ash composition - Variation with agronomy and assessment method." *Fuel* 95(1):50-62.

Beesley, L., E. Moreno-Jiménez and J. L. Gomez-Eyles. 2010. "Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil." *Environmental Pollution* 158(6):2282-2287.

Bergman, P.C.A., A.R. Boersma, J.H.A. Kiel, M.J. Prins, K.J. Ptasinski and F.J.J.G. Janssen. 10-14 May 2004. "Torrefaction for Entrained-Flow Gasification of Biomass." In The 2nd World Conference and Technology Exhibitionon Biomass for Energy, Industry and Climate Protection. Rome, Italy.

Berlin, A., N. Gilkes, D. Kilburn, V. Maximenko, R. Bura, A. Markov, A. Skomarovsky, A. Gusakov, A. Sinitsyn, O. Okunev, I. Solovieva and J. N. Saddler. 2006a. "Evaluation of cellulase preparations for hydrolysis of hardwood substrates." *Applied Biochemistry and Biotechnology* 130(1-3):528-545.

Berlin, A., M. Balakshin, N. Gilkes, J. Kadla, V. Maximenko, S. Kubo and J. Saddler. 2006b. "Inhibition of cellulase, xylanase and [beta]-glucosidase activities by softwood lignin preparations." *Journal of Biotechnology* 125(2):198-209.

Bhaskar, T., A. Sera, A. Muto and Y. Sakata. 2008. "Hydrothermal upgrading of wood biomass: Influence of the addition of K2CO3 and cellulose/lignin ratio." *Fuel* 87(10-11):2236-2242.

Biller, P. and A. B. Ross. "Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content." *Bioresource Technology* In Press, Corrected Proof.

Bobleter, O. 1994. "Hydrothermal degradation of polymers derived from plants." *Progress in Polymer Science* 19(5):797-841.

Bonn, G., P. J. Oefner and O. Bobleter. 1988. "Analytical determination of organic-acids formed during hydrothermal and organosolv degradation of lignocellulosic biomass." *Fresenius Zeitschrift Fur Analytische Chemie* 331(1):46-50.

Bonn, G., R. Pecina, E. Burtscher and O. Bobleter. 1984. "Separation of wood degradation products by high-performance liquid-chromatography." *Journal of Chromatography* 287(1):215-221.

Box, G.E.P, W.G. Hunter and J.S. Hunter. 1979. *Statistics for Experimenters - Introduction to Design, Data-Analysis, and Model-Building*: Wiley.

Bridgeman, T. 2008. "Torrefaction of biomass." In *SPEME*. Leeds: University of Leeds.

Bridgeman, T. G., J. M. Jones, I. Shield and P. T. Williams. 2008. "Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties." *Fuel* 87(6):844-856.

Bridgeman, T. G., J. M. Jones, A. Williams and D. J. Waldron. 2010. "An investigation of the grindability of two torrefied energy crops." *Fuel* 89(12):3911-3918.

Bullard, M. J., S. J. Mustill, P. Carver and P. M. I. Nixon. 2002a. "Yield improvements through modification of planting density and harvest frequency in short rotation coppice Salix spp. - 2. Resource capture and used in two morphologically diverse varieties." *Biomass & Bioenergy* 22(1):27-39.

Bullard, M. J., S. J. Mustill, S. D. McMillan, P. M. I. Nixon, P. Carver and C. P. Britt. 2002b. "Yield improvements through modification of planting density and harvest frequency in short rotation coppice Salix spp. - 1. Yield response in two morphologically diverse varieties." *Biomass & Bioenergy* 22(1):15-25.

Burczyk, B. 2007. "Water - a useful and environmentally friendly reaction medium." *Przemysl Chemiczny* 86(3):184-194.

Channiwala, S. A. and P. P. Parikh. 2002. "A unified correlation for estimating HHV of solid, liquid and gaseous fuels." *Fuel* 81(8):1051-1063.

Chen, S. F., R. A. Mowery, V. A. Castleberry, G. P. van Walsum and C. K. Chambliss. 2006. "High-performance liquid chromatography method for simultaneous

determination of aliphatic acid, aromatic acid and neutral degradation products in biomass pretreatment hydrolysates." *Journal of Chromatography* A 1104(1-2):54-61.

Chen, W. H., W. Y. Cheng, K. M. Lu and Y. P. Huang. 2011. "An evaluation on improvement of pulverized biomass property for solid fuel through torrefaction." *Applied Energy* 88(11):3636-3644.

Chen, Wei-Hsin and Po-Chih Kuo. 2011. "Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass." *Energy* 36(2):803-811.

Correia, M. A. S., K. Mazumder, J. L. A. Bras, S. J. Firbank, Y. P. Zhu, R. J. Lewis, W. S. York, Cmga Fontes and H. J. Gilbert. 2011. "Structure and Function of an Arabinoxylan-specific Xylanase." *Journal of Biological Chemistry* 286(25):22510-22520.

Czernik, S., R. French, C. Feik and E. Chornet. 1999. "Fluidized bed catalytic reforming of pyrolysis oils for production of hydrogen." In Proceedings of the Forth Biomass Conference of the Americas eds. R.P. Overend and E. Chornet: Elsevier Science Ltd.

Czernik, S., R. French, C. Feik and E. Chornet eds. 2000. *Production Of Hydrogen From Biomass By Pyrolysis/ Steam Reforming*. New York: Kluwer Academic/ Plenum Publishers.

Czernik, S., R. French, C. Feik and E. Chornet. 2002. "Hydrogen by catalytic steam reforming of liquid by-products from biomass thermoconversion processes." *Industrial & Engineering Chemistry Research* 41:4209-4215.

D.J. Cuff and W. J. Young. 1980. *U.S. Energy Atlas.* New York: FreePress/McMillan Publishing Co.

Dehkhoda, A. M., A. H. West and N. Ellis. "Biochar based solid acid catalyst for biodiesel production." *Applied Catalysis a-General* 382(2):197-204.

Demirbas, A. 2001a. "Biomass resource facilities and biomass conversion processing for fuels and chemicals." *Energy Conversion and Management* 42:1357-1378.

Demirbas, A. 2007a. "The influence of temperature on the yields of compounds existing in bio-oils from biomass samples via pyrolysis." *Fuel Processing Technology* 88:591-597.

Demirbas, A. 2008. "Biofuels sources, biofuel policy, biofuel economy and global biofuel projections." *Energy Conversion and Management* 49:2106-2116.

Demirbas, A. 1998a. "Aqueous glycerol delignification of wood chips and ground wood." *Bioresource Technology* 63(2):179-185.

Demirbas, A. 1998b. "Yields of oil products from thermochemical biomass conversion processes." *Energy Conversion and Management* 39(7):685-690.

Demirbas, A. 2000. "Effect of lignin content on aqueous liquefaction products of biomass." *Energy Conversion and Management* 41(15):1601-1607.

Demirbas, A. 2001b. "Biomass to charcoal, liquid, and gaseous products via carbonization process." *Energy Sources* 23(6):579-587.

Demirbas, A. 2007b. "The influence of temperature on the yields of compounds existing in bio-oils obtained from biomass samples via pyrolysis." *Fuel Processing Technology* 88(6):591-597.

Dhungana, A., A. Dutta and P. Basu. 2012. "Torrefaction of non-lignocellulose biomass waste." *Canadian Journal of Chemical Engineering* 90(1):186-195.

Dileo, G. J., M. E. Neff, S. Kim and P. E. Savage. 2008. "Supercritical water gasification of phenol and glycine as models for plant and protein biomass." *Energy & Fuels* 22(2):871-877.

Goudriaan, F., B. Van de Beld, F. Boerefijn, and G. Bos. 2001. "Thermal Efficiency of the HTU® Process for Biomass Liquefaction." (*Progress in Thermochemical Biomass Conversion*).

Fahmi, R., A. V. Bridgwater, L. I. Darvell, J. M. Jones, N. Yates, S. Thain and I. S. Donnison. 2007. "The effect of alkali metals on combustion and pyrolysis of Lolium and Festuca grasses, switchgrass and willow." *Fuel* 86(10-11):1560-1569.

Fang, Z. and C. Fang. 2008. "Complete dissolution and hydrolysis of wood in hot water." *Aiche Journal* 54(10):2751-2758.

Fang, Z., T. Minowa, R. L. Smith, T. Ogi and J. A. Kozinski. 2004. "Liquefaction and gasification of cellulose with Na2CO3 and Ni in subcritical water at 350 degrees C." *Industrial & Engineering Chemistry Research* 43(10):2454-2463.

Fang, Z., T. Sato, R. L. Smith, H. Inomata, K. Arai and J. A. Kozinski. 2008. "Reaction chemistry and phase behavior of lignin in high-temperature and supercritical water." *Bioresource Technology* 99(9):3424-3430.

Fu, D., G.Mazza and Y. Tamaki. 2010. "Lignin Extraction from Straw by Ionic Liquids and Enzymatic Hydrolysis of the Cellulosic Residues." *Journal of Agricultural and Food Chemistry* 58(5):2915-2922.

Funke, A. and F. Ziegler. 2010. "Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering." *Biofuels Bioproducts & Biorefining-Biofpr* 4(2):160-177.

Funke, A. and F. Ziegler. 2011. "Heat of reaction measurements for hydrothermal carbonization of biomass." *Bioresource Technology* 102(16):7595-7598.

Garcia-Torrent, J., E. Conde-Lazaro, C. Wilen and A. Rautalin. 1998. "Biomass dust explosibility at elevated initial pressures." *Fuel* 77(9-10):1093-1097.

Garrote, G., M. E. Eugenio, M. J. Diaz, J. Ariza and F. Lopez. 2003. "Hydrothermal and pulp processing of Eucalyptus." *Bioresource Technology* 88(1):61-68.

Crabtree, G. W., M. S. Dresselhaus, and M. V. Buchanan. 2004. "The Hydrogen Economy." *Physics Today*.

Glaser, B., L. Haumaier, G. Guggenberger and W. Zech. 2001. "The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics." *Naturwissenschaften* 88(1):37-41.

Hartley, W., N. M. Dickinson, P. Riby and N. W. Lepp. 2009. "Arsenic mobility in brownfield soils amended with green waste compost or biochar and planted with *Miscanthus*." *Environmental Pollution* 157(10):2654-2662.

Hashaikeh, R., Z. Fang, I. S. Butler, J. Hawari and J. A. Kozinski. 2007. "Hydrothermal dissolution of willow in hot compressed water as a model for biomass conversion." *Fuel* 86(10-11):1614-1622.

Fleming, I. and D. Williams. 1995. *Spectroscopic Methods in Organic Chemistry*. 5 Edition: McGraw Hill.

Ingram, J. S. I., P. J. Gregory and A-M Izac. 2008. "The role of agronomic research in climate change and food security policy." *Agriculture, Ecosystems and Environment* 126:4-12.

Jenkins, B. M., L. L. Baxter, T. R. Miles Jr and T. R. Miles. 1998. "Combustion properties of biomass." *Fuel Processing Technology* 54(1–3):17-46.

Jin, F. M. and H. Enomoto. 2008. "Application of hydrothermal reaction to conversion of plant-origin biomasses into acetic and lactic acids." *Journal of Materials Science* 43(7):2463-2471.

Jin, F. M., Z. Y. Zhou, T. Moriya, H. Kishida, H. Higashijima and H. Enomoto. 2005. "Controlling hydrothermal reaction pathways to improve acetic acid production from carbohydrate biomass." *Environmental Science & Technology* 39(6):1893-1902.

Jin, F., Z. Zhou, A. Kishita and H. Enomoto. 2006. "Hydrothermal conversion of biomass into acetic acid." *Journal of Materials Science* 41(5):1495-1500.

Jones, J. M., T. G. Bridgeman, L. I. Darvell, B. Gudka, A. Saddawi and A. Williams. 2012. "Combustion properties of torrefied willow compared with bituminous coals." *Fuel Processing Technology* 101(0):1-9.

Kabyemela, B. M., T. Adschiri, R. M. Malaluan and H. Ohzeki. 1997. "Rapid and selective conversion of glucose to erythrose in supercritical water." *Industrial & Engineering Chemistry Research* 36(12):5063-5067.

Karagoz, S., T. Bhaskar, A. Muto and Y. Sakata. 2005a. "Comparative studies of oil compositions produced from sawdust, rice husk, lignin and cellulose by hydrothermal treatment." *Fuel* 84(7-8):875-884.

Karagoz, S., T. Bhaskar, A. Muto, Y. Sakata, T. Oshiki and T. Kishimoto. 2005b. "Low-temperature catalytic hydrothermal treatment of wood biomass: analysis of liquid products." *Chemical Engineering Journal* 108(1-2):127-137.

Karagöz, S., T. Bhaskar, A. Muto, and Y. Sakata. 2004. "Effect of Rb and Cs carbonates for production of phenols from liquefaction of wood biomass " *Fuel* 83(17-18): 2293-2299.

Karagöz, S., T. Bhaskar, A. Muto, and Y. Sakata. 2005a. "Comparative studies of oil compositions produced from sawdust, rice husk, lignin and cellulose by hydrothermal treatment." *Fuel* 84(7-8):875-884.

Karagöz, S., T. Bhaskar, A. Muto, Y. Sakata, T. Oshiki, and T. Kishnmoto. 2005b. "Low-temperature catalytic hydrothermal treatment of wood biomass: analysis of liquid products" *Chemical Engineering Journal* 108(1-2):127-137.

Kelley, S.S, X. Wang, M. D. Myers and D. Johnson, K eds. 1997. *Use of Biomass Pyrolysis Oils for Preparation of Modified Phenol Formaldehyde Resins.* London: Blackie Academic & Professional.

Young-Hun, K., S.-M. Lee, H.-W. Lee and J.-W. Lee. "Physical and chemical characteristics of products from the torrefaction of yellow poplar (Liriodendron tulipifera)." *Bioresource Technology*(0).

King, M. D. 2007. "The carbon cycle." Available from http://earthobservatory.nasa.gov/Library/CarbonCycle/carbon_cycle4.html. Acc essed 8th October 2007.

Klinke, H. B., A. B. Thomsen, and B. K. Ahring. 2004. "Inhibition of ethanol-producing yeast and bacteria by degradation products produced during pre-treatment of biomass." *Appl Microbiol Biotechnol* 66:10-26.

Kothari, V. and M.J. Antal. 1985. "Numerical studies of the flash pyrolysis of cellulose." *Fuel* 64(1487-1494).

Kronholm, J., J. Kalpala, K. Hartonen, and M-L Riekkola. 2002. "Pressurized hot water extraction coupled with supercritical water oxidation in remediation of sand and soil containing PAHs." *J. Supercrit Fluids* 23:123-134.

Kruse, A., P. Maniam and F. Spieler. 2007. "Influence of proteins on the hydrothermal gasification and liquefaction of biomass. 2. Model compounds." *Industrial & Engineering Chemistry Research* 46(1):87-96.

Kumar, S. and R. B. Gupta. 2009. "Biocrude Production from Switchgrass Using Subcritical Water." *Energy & Fuels* 23:5151-5159.

Lachapelle, J. M. 1986. "Industrial airborne irritant or allergic contact-dermatitis." *Contact Dermatitis* 14(3):137-145.

Lal, Rattan. 2008. "Black and buried carbons' impacts on soil quality and ecosystem services." *Soil and Tillage Research* 99(1):1-3.

Lede, J., F. Verzaro and J. Villermaux. 1980. Le cyclone: un nouveau réacteur chimique solaire gaz-solide Application à la mise en oeuvre en continu de la pyrolyse flash de sciure de bois. *Rev. Phys. Appl.* 15:535-543.

Lee, J. W., M. Kidder, B. R. Evans, S. Paik, A. C. Buchanan, C. T. Garten and R. C. Brown. "Characterization of Biochars Produced from Cornstovers for Soil Amendment." *Environmental Science & Technology* 44(20):7970-7974.

Li, C. Z. and Z. K. B. Zhao. 2007. "Efficient acid-catalyzed hydrolysis of cellulose in ionic liquid." *Advanced Synthesis & Catalysis* 349:1847-1850.

Li, F., L. P. Chang, P. Wen and K. C. Xie. 2001. "Simulated distillation of coal tar." *Energy Sources* 23(2):189-199.

Hui, L., X. Liu, R. Legros, X. T. Bi, C. J. Lim and S. Sokhansanj. 2012. "Pelletization of torrefied sawdust and properties of torrefied pellets." *Applied Energy* 93(0):680-685.

Lipinsky, E. S., J. R. Arcate and T.B. Reed. 2002. "Enhanced wood fuels via torrefaction." *Abstracts of Papers American Chemical Society* 223(1-2):171.

Maschio, G. 1992a. "Pyrolysis, a promising route for biomass utilisation." *Bioresource Technology* 42:219-231.

Maschio, G. 1992b. "Pyrolysis, a promising route for biomass utilisation." *Bioresource Technology* 42:219-231.

McKendry, P. 2002a. "Energy production from biomass(part 1): Overview of biomass." *Bioresource Technology* 83:37-46.

McKendry, P. 2002b. "Energy production from biomass (part 1): overview of biomass." *Bioresource Technology* 83(1):PII S0960-8524(0901)00118-00113.

McKendry, P. 2002c. "Energy production from biomass (part 2): conversion technologies." *Bioresource Technology* 83(1):PII S0960-8524(0901)00119-00115.

Medic, D., M. Darr, A. Shah, B. Potter and J. Zimmerman. 2012. "Effects of torrefaction process parameters on biomass feedstock upgrading." *Fuel* 91(1):147-154.

Meier, D., D. R. Larimer and O. Faix. 1986a. "Direct liquefaction of different lignocellulosics and their constituents .1. fractionation, elemental composition." *Fuel* 65(7):910-915.

Meier, D., D. R. Larimer and O. Faix. 1986b. "Direct liquefaction of different lignocellulosics and their constituents .2. molecular-weight determination, gas-chromatography, IR spectroscopy." *Fuel* 65(7):916-921.

Melkior, T., S. Jacob, G. Gerbaud, S. Hediger, L. Le Pape, L. Bonnefois and M. Bardet. 2012. "NMR analysis of the transformation of wood constituents by torrefaction." *Fuel* 92(1):271-280.

Xiaoling, M., Q. Wu and C.Yang. 2004. "Fast pyrolysis of microalgae to produce renewable fuels." *Journal of Analytical and Applied Pyrolysis* 71(2):855-863.

Minowa, T., F. Zhen, T. Ogi and G. Varhegyi. 1997. "Liquefaction of cellulose in hot compressed water using sodium carbonate: Products distribution at different reaction temperatures." *Journal of Chemical Engineering of Japan* 30(1):186-190.

Mohamed, A. R., M. Mohammadi and G. N. Darzi. 2010. "Preparation of carbon molecular sieve from lignocellulosic biomass: A review." *Renewable & Sustainable Energy Reviews* 14(6):1591-1599.

Mohan, D., C. U. Pittman and P. H. Steele. 2006. "Pyrolysis of wood/biomass for bio-oil: A critical review." *Energy & Fuels* 20(3):848-889.

Mok, W., S. Lai and M. J. Antal. 1992. "Uncatalyzed solvolysis of whole biomass hemicellulose by hot compressed liquid water." *Industrial & Engineering Chemistry Research* 31(4):1157-1161.

Moore, A. 2008. "Biofuels are dead: long live biofuels(?) - part two." *New Biotechnology* 25(2-3):96-100.

Naeem, S., L. J. Thompson, S. P. Lawler, J. H. Lawton and R. M. Woodfin. 1994. "Declining biodiversity can alter the performance of ecosystems." *Nature* 368(6473):734-737.

Nowakowski, D. J. and J. M. Jones. 2008. "Uncatalysed and potassium-catalysed pyrolysis of the cell-wall constituents of biomass and their model compounds." *Journal of Analytical and Applied Pyrolysis* 83(1):12-25.

Nowakowski, D. J., J. M. Jones, R. M. D. Brydson and A. B. Ross. 2007. "Potassium catalysis in the pyrolysis behaviour of short rotation willow coppice." *Fuel* 86(15):2389-2402.

Ozcimen, D. and A. Ersoy-Mericboyu. "Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials." *Renewable Energy* 35(6):1319-1324.

Parkinson, G. 2006. "BG's North Sea discovery raises hopes for UK gas production." *The Independent*, London, UK, September 2.

Penmetsa, Venkata K. and Philip H. Steele. 2012. "Preliminary findings for the production of water repellent torrefied wood pellets with pyrolysis oil." *Environmental Progress & Sustainable Energy* 31(2):235-239.

Peterson, A. A., F. Vogel, R. P. Lachance, M. Froling, M. J. Antal and J. W. Tester. 2008. "Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies." *Energy & Environmental Science* 1(1):32-65.

Price, L., M. Bullard, H. Lyons, S. Anthony and P. Nixon. 2004. "Identifying the yield potential of *Miscanthus* x giganteus: an assessment of the spatial and temporal variability of M-x giganteus biomass productivity across England and Wales." *Biomass & Bioenergy* 26(1):3-13.

Prins, M. J., K. J. Ptasinski and F. Janssen. 2006a. "Torrefaction of wood - Part 1. Weight loss kinetics." *Journal of Analytical and Applied Pyrolysis* 77(1):28-34.

Prins, M. J., K. J. Ptasinski and F. J. J. G. Janssen. 2006b. "More efficient biomass gasification via torrefaction." *Energy* 31(15):3458-3470.

Ptasinski, K. J., M. J. Prins and A. Pierik. 2007. "Exergetic evaluation of biomass gasification." *Energy* 32(4):568-574.

Qian, Y. J., C. J. Zuo, H. Tan and J. H. He. 2007. "Structural analysis of bio-oils from sub-and supercritical water liquefaction of woody biomass." *Energy* 32(3):196-202.

R. M. Mackaya and S. D. Probert. 2001. "Forecasting the United Kingdom's supplies and demands for fluid fossil-fuels " *Applied Energy* 69(3):161-189.

S. Adhikari, S. Fernando, and A. Haryanto. 2007. "Production of hydrogen by steam reforming of glycerin over alumina-supported metal catalysts." *Catalysis Today* 129(3-4):355-364.

Saddawi, A., J. M. Jones, A. Williams and C. Le Coeur. 2011. "Commodity fuels from biomass through pretreatment and torrefaction: effects of mineral content on torrefied fuel characteristics and quality." *Energy & Fuels*.

Saddawi, A. 2011. *The Role of Alkali Metals in Biomass Thermochemical Conversion*. Leeds,: University of Leeds (Energy and Resources Research Institute, School of Process, Environmental and Materials Engineering).

Sakaki, T., M. Shibata, T. Miki, H. Hirosue and N. Hayashi. 1996a. "Decomposition of cellulose in near-critical water and fermentability of the products." *Energy & Fuels* 10(3):684-688.

Sakaki, T., M. Shibata, T. Miki, H. Hirosue and N. Hayashi. 1996b. "Reaction model of cellulose decomposition in near-critical water and fermentation of products." *Bioresource Technology* 58(2):197-202.

Sarma, A. K, Ryder, A. G. 2006. "Comparison of the Fluorescence Behavior of a Biocrude Oil and Crude Petroleum Oils" *Energy & Fuels* 20:783-785.

Sasaki, M., Z. Fang, Y. Fukushima, T. Adschiri and K. Arai. 2000. "Dissolution and hydrolysis of cellulose in subcritical and supercritical water." *Industrial & Engineering Chemistry Research* 39(8):2883-2890.

Sasaki, M., K. Goto, K. Tajima, T. Adschiri and K. Arai. 2002. "Rapid and selective retro-aldol condensation of glucose to glycolaldehyde in supercritical water." *Green Chemistry* 4(3):285-287.

Scott, D. and J. Piskorz. 1984. "The continuous flash pyrolysis of biomass." *Can. J. Chem. Eng*. 62:404-412.

Sevilla, M. and A. B. Fuertes. 2009a. "Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides." *Chemistry-a European Journal* 15(16):4195-4203.

Sevilla, M. and A. B. Fuertes. 2009b. "The production of carbon materials by hydrothermal carbonization of cellulose." *Carbon* 47(9):2281-2289.

Shabtai, J. S, W. Zmierczak and E. Chornet. 1997. "Conversion of lignin to reformulated gasoline compositions." In *Third Biomass Conference of the America*s, eds. R.P. Overend and E. Chornet: Elsevier Science Ltd.:Oxford, U.K.

Shafizadeh, F., G. D. McGinnis and C. W. Philpot. 1972. "Thermal degradation of xylan and related model compounds." *Carbohydrate Research* 25(1):23-33.

Shah, A., M. J. Darr, D. Medic, R. P. Anex, S. Khanal and D. Maski. 2012. "Techno-economic analysis of a production-scale torrefaction system for cellulosic biomass upgrading." *Biofuels Bioproducts & Biorefining-Biofpr* 6(1):45-57.

Shahriar, S., and Topala, E. 2007. "An econometrics view of worldwide fossil fuel consumptionand the role of US." *Energy Policy* 36:775-786.

Shang, L., J. Ahrenfeldt, J. K. Holm, A. R. Sanadi, S. Barsberg, T.Thomsen, W. Stelte and U. B. Henriksen. 2012a. "Changes of chemical and mechanical behavior of torrefied wheat straw." *Biomass and Bioenergy* 40(0):63-70.

Shang, L., N. P. K. Nielsen, J. Dahl, W. Stelte, J. Ahrenfeldt, J. K. Holm, T. Thomsen and U. B. Henriksen. 2012b. "Quality effects caused by torrefaction of pellets made from Scots pine." *Fuel Processing Technology* 101(0):23-28.

Shaw, R. W., T. B. Brill, A. A. Clifford, C. A. Eckert and E. U. Franck. 1991. "Supercritical water - a medium for chemistry." *Chemical & Engineering News* 69(51).

Shen, D. K., S. Gu and A. V. Bridgwater. 2010. "Study on the pyrolytic behaviour of xylan-based hemicellulose using TG-FTIR and Py-GC-FTIR." *Journal of Analytical and Applied Pyrolysis* 87(2):199-206.

Chen, S.-F. R. A. Mowery, V. A. Castleberry, G. P. Van Walsum and C. K. Chambliss. 2006. "High-performance liquid chromatography method for simultaneous determination of aliphatic acid, aromatic acid and neutral degredation products in biomass pretreatment hydrolysates." *Journal of Chromatography* A 1104:54-61.

Sinag, A., S. Gülbay, B. Uskan and M. Canel. "Biomass decomposition in near critical water." *Energy Conversion and Management* 51(3):612-620.

Sohi, S. P., E. Krull, E. Lopez-Capel and R. Bol. "A review of biochar and its use and function in soil." In *Advances in Agronomy*, Vol 105. San Diego: Elsevier Academic Press Inc.

Soltes E. J., A. T. Wiley and S. C. K. Lin. 1981. "Biomass pyrolysis towards an understanding of its versitility and potentials." *Biotechnology and Bioengineering Symp. Ser.* 11:125-136.

Srokol, Z., A. G. Bouche, A. van Estrik, R. C. J. Strik, T. Maschmeyer and J. A. Peters. 2004. "Hydrothermal upgrading of biomass to biofuel; studies on some

monosaccharide model compounds." *Carbohydrate Research* 339(10):1717-1726.

Steinbeiss, S., G. Gleixner and M. Antonietti. 2009. "Effect of biochar amendment on soil carbon balance and soil microbial activity." *Soil Biology and Biochemistry* 41(6):1301-1310.

Takeuchi Y., F. Gin, H. Enomoto and K. Tohji. 2007. "Application of acid catalytic hydrothermal reaction to conversion of carbohydrate biomass into valuable substances." *Water dynamics* 898:190-192.

Taner, F., A. Eratik and I. Ardic. 2005. "Identification of the compounds in the aqueous phases from liquefaction of lignocellulosics." *Fuel Processing Technology* 86(4):407-418.

Titirici, M.-M. and M. Antonietti. 2009. "Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization." *Chem Soc Rev* 39(1):103-116.

Trifonova, R., J. Postma, M. T. Schilder and J. D. van Elsas. 2009. "Microbial enrichment of a novel growing substrate and its effect on plant growth." *Microbial Ecology* 58(3):632-641.

Tsukashi. H. 1966. "Infrared spectra of artificial coal made from submerged wood at Uozu Toyama Prefecture Japan." *Bulletin of the Chemical Society of Japan* 39(3):460-&.

Uemura, Y., W. N. Omar, T. Tsutsui and S. B. Yusup. 2011. "Torrefaction of oil palm wastes." *Fuel* 90(8):2585-2591.

Uslu, A., A.P. C. Faaij and P. C. A. Bergman. 2008. "Pre-treatment technologies, and their effect on international bioenergy supply chain logistics. Techno-economic evaluation of torrefaction, fast pyrolysis and pelletisation." *Energy* 33(8):1206-1223.

Van Zwieten, L., S. Kimber, S. Morris, K. Y. Chan, A. Downie, J. Rust, S. Joseph and A. Cowie. 2010. "Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility." *Plant and Soil* 327(1-2):235-246.

Vassilev, S. V., K. Kitano and C. G. Vassileva. 1996. "Some relationships between coal rank and chemical and mineral composition." *Fuel* 75(13):1537-1542.

Wahyudiono, T. Kanetake, M. Sasaki and M. Goto. 2007a. "Decomposition of a lignin model compound under hydrothermal conditions." *Chemical Engineering & Technology* 30(8):1113-1122.

Wahyudiono, M. Sasaki and M. Goto. 2007b. "Noncatalytic liquefaction of tar with low-temperature hydrothermal Treatment." *J Mater Cycles Waste Manag* 9:173-181.

Wang, C., J. X. Pan, J. H. Li and Z. Y. Yang. 2008. "Comparative studies of products produced from four different biomass samples via deoxy-liquefaction." *Bioresource Technology* 99(8):2778-2786.

Wang, D, S. Czernik and E. Chornet. 1998. "Production of hydrogen from biomass by catalytic steam reforming of fast pyrolysis oils." *Energy Fuels* 12:19.

Wang, D., S. Czernik, D. Montane and E. Chornet. 1997. "Biomass to hydrogen via pyrolysis and catalytic steam reforming of the pyrolysis oil and its fractions." *Industrial & Engineering Chemistry Research* 36:1507.

Wannapeera, J., B. Fungtammasan and N. Worasuwannarak. 2011. "Effects of temperature and holding time during torrefaction on the pyrolysis behaviors of woody biomass." *Journal of Analytical and Applied Pyrolysis* 92(1):99-105.

Wereko-Bobby, C. Y. and E. B. Hagen. 1996. *Biomass Conversion and Technology.* Chichester: John Wiley & Sons Ltd.

Wilen, C. and A. Rautalin. 1993. "Handling and feeding of biomass to pressurized reactors - safety engineering." *Bioresource Technology* 46(1-2):77-85.

Williams, P. T. and J. Onwudili. 2005. "Composition of products from the supercritical water gasification of glucose: A model biomass compound." *Industrial & Engineering Chemistry Research* 44(23):8739-8749.

Yan, Wei, Tapas C. Acharjee, Charles J. Coronella and Victor R. Vasquez. 2009. "Thermal Pretreatment of Lignocellulosic Biomass." *Environmental Progress & Sustainable Energy* 28(3):435-440.

Yan, W., J. T. Hastings, T. C. Acharjee, C. J. Coronella and V. R. Vasquez. 2010. "Mass and Energy Balances of Wet Torrefaction of Lignocellulosic Biomass." *Energy & Fuels* 24:4738-4742.

Yesodharan, S. 2002. "Supercritical water oxidation: an environmentally safe method for the disposal of organic wastes." *Curr Sci* 82:1112-1122.

Yip, J., M. J. Chen, Y. S. Szeto and S. C. Yan. 2009. "Comparative study of liquefaction process and liquefied products from bamboo using different organic solvents." *Bioresource Technology* 100(24):6674-6678.

Yu, J. and P. E. Savage. 1998. "Decomposition of Formic Acid under Hydrothermal Conditions." *Industrial & Engineering Chemistry Research* 37(1):2-10.

Zhang, B., M. von Keitz and K. Valentas. 2008. "Thermal effects on hydrothermal biomass liquefaction." *Applied Biochemistry and Biotechnology* 147(1-3):143-150.

Zhang, M., W. Qi, R. Liu, R. Su, S. Wu and Z. He. "Fractionating lignocellulose by formic acid: Characterization of major components." *Biomass and Bioenergy* 34(4):525-532.

Zhong, C. L. and X. M. Wei. 2004. "A comparative experimental study on the liquefaction of wood." *Energy* 29(11):1731-1741.

Appendix

Hydrothermal liquefaction observations

Initially, the choice of sample, catalyst and ratio of solid to liquid was decided by studying the literature. The heating method was devised using the settings present in the PID. The PID settings and the controller ramp rate could not be fixed at a certain value (°C/min), but merely monitored via a temperature vs. time plot.

Due to the latent heat capacity of the stainless steel reactor and the initial heating of the mantle, there was also an approximate 2 minute lag at the start of the temperature ramp, with a reduction in the heating rate when the temperature reached 100-150°C. To this point, heating commenced at a rate of ~10°C/min. After this, the rate dropped to ~8°C/min until the final temperature was reached and held for 10 minutes.

The volume of the reactor is 75 ml, but it was found early on that filling the reactor with more than 30ml of sample and catalyst gave rise to high residual pressures and product escaping when venting the gas at the end of the reaction. Lowering the temperature of the reactor for gas venting proved to be unsuccessful in eliminating this problem, so a smaller amount of sample and catalyst was used.

Cellulose

Most work commissioning the reactor used cellulose as this is the largest constituent component of biomass. Note that HTP reactions at 200°C and under for less than 1 hour reaction time produced material very similar to that at the start. Reactions carried out at 300°C, <1 hour with varying ratios of sample: catalyst produced oil and char and a total reduction of un-reacted cellulose contained in the aqueous phase, indicating an increase in solubility and the formation of water soluble products. Residual pressures remained high, indicating a greater volume of gas produced.

Lignin

Lignin reactions using 1M KOH produced on the whole, opaque, viscous, black liquids that were difficult to extract water from. Reactions in lower KOH concentrations were much easier to separate.

Xylan

Xylan reactions proved to be the most difficult to convert to liquid products and produced brown solution with un-reacted particles in suspension. Recovery of product from the aqueous phase was high.

Cellulose model compounds

Cellulose liquefaction products showed GC-MS chromatograms that contained many compounds with trace amounts. The chromatograms also showed a column bleed in the baseline, following the temperature ramp. This information, coupled with the low-scale reading indicated only tiny amounts of compounds were extracted.

The greatest amounts of compounds detected were saturated and unsaturated cyclic alcohols and ketones; many similar products were detected in all the cellulose extracts with the most significant being cyclopentanone, 2-methyl-cyclopentanone, 2-cyclopenten-1-one, tetrahydro-2-furanmethanol, , 2-methyl-2-cyclopenten-1-one, , 2-2,3-dimethyl-cyclopenten-1-one, 3-methyl-2-cyclopenten-1-one, 4-hydroxy-butanoic acid, 3,4-dimethyl-2-Cyclopenten-1-one and 2,3-dimethyl-2-Cyclopenten-1-one.

Lignin model compounds

Lignin liquefaction products detected included mainly phenols, consistent with the findings from the analysis of lignin in the literature.(Wahyudiono. et al 2007) There was a marked difference in the amounts of compounds detected with lignin than with cellulose, in that the response was higher, with many fewer peaks. Comparing the peak areas with those of cellulose shows the lowest amounts of the most significant peaks of lignin correspond with the highest amounts found in cellulose. Explanations for this could be the amount of higher molecular weight oxygenated hydrocarbons and sugars present in the cellulose extract, with detection of the mass spec. detector only measuring compounds with a molecular weight less than 550. Sugars would also not be separated by the GC and may not be detected by MS.

GC-MS data did not correlate however with results seen from the work carried out at IBERS. GC-MS data showed the highest proportion of the extract to be substituted phenolic compounds with a molecular weight of 124 (2-methoxyphenol) to 168 (1, 2, 3 tri-methoxy benzene), with molecular weights detected via LC-MS being >200.

HPLC analysis

Following a simplified version of the method parameters described in (Karagoz S. et al 2005b) it was possible to achieve separation between the compounds found within the aqueous phase of the liquefaction products. Identification of the individual compounds proved much trickier, even when standard solutions were made and run. Even when identifying relatively simple compounds such as formic and acetic acid, the UV profile taken from the standards did not match exactly peaks in the chromatogram, at the retention time and at the levels previously detected in the literature.(Karagoz S. et al 2005b)

A great deal of time and effort was put into trying to get accurate standard preparation by using compounds such as 4-hydroxy benzoic acid, 4-hydroxy benzoate, guaiacol (2-methoxy phenol), eugenol, *ortho, meta* and *para*-crescol, all compounds reported to have been detected in the aqueous phase. Standard preparation of these compounds was difficult as the water solubility of a number of the standard compounds was low.

As a result of the above issues, to date, qualitative and quantitative analysis of the liquefaction products contained in the aqueous phase has not been entirely successful. It is proposed for future work that both sample and standard preparation are carried out using solid phase extraction (SPE) under strict pH conditions.