The Microwave Activation of Cellulose

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Abstract

The aim of this project was to determine a fundamental understanding of the parameters affecting a microwave pyrolysis and microwave hydrolysis process of microcrystalline cellulose, providing a fundamental insight into the processes of cellulose degradation.

A systematic investigation into the microwave pyrolysis of cellulose was performed in which the fundamental parameters of microwave power, microwave duration, sample density, sample pre-heating and maximum pyrolysis temperature were studied. About 65wt.% decomposition of microcrystalline cellulose could be achieved, resulting in the formation of ~44wt.% bio-oil or ~26wt.% gas under their optimum microwave pyrolysis conditions. The maximum temperature/heating rate attained during the microwave pyrolysis processes and moisture content played a critical role in the overall extent of decomposition.

The temperature of decomposition under microwave activation was ~120°C lower than that of the thermal decomposition, with initiation of the decomposition process occurring at ~180°C. This coincides with the phase change of cellulose structure.

However, the resulting pyrolysis bio-oil largely consisted of levoglucosenone, 1,4:3,6-dianhydro-α-D-glucopyranose, levoglucosan and 1,6-anhydro-β-D-glucofuranose. Due to limitations in use of these products, a hydrolysis process to produce simple fermentable sugars was developed.

It proved possible to achieve ~80wt.% decomposition of cellulose with ~30-40wt.% fermentable sugars formed. Further to this, the new microwave specific reaction pathway of cellulose decomposition was determined and the degree of freedom of the cellulose enclosed -CH$_2$OH groups were found to be crucial. This mechanism helped explain the key experimental observations such as: high efficiency of microwave treatment; the dependence of the selectivity yield of glucose on the applied microwave density; the observed high glucose to HMF ratio and the influence of the degree of cellulose crystallinity on the results of the hydrolysis.

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<u>Acknowledgements</u>

Declaration

Some of the results presented in this thesis were obtained by, or in collaboration with other workers, who are fully acknowledged in the list below. All other results are the work of the author.

Jiajun Fan

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Work	Collaborator (based in Green Chemistry Centre of Excellence, University of York. Unless otherwise stated.)
Chapter 4	
4.4.2 Pre-heating temperature	Dr. P. Shuttleworth, Dr. V. Budarin
4.4.2.1 Mass Balances	Dr. V. Budarin
Chapter 5	
5.2 Results	Dr. V. Budarin
Chapter 6	
6.3.1 Comparison of conventional thermal and microwave hydrolysis of cellulose	Dr. V. Budarin, Dr. M. De Bruyn
Chapter 7	
7.1.2.2 Solvent extraction	Dr. A. Hunt, Dr. V. Budarin
7.1.2.4 Microwave pyrolysis	Dr. V. Budarin

Elemental (CHN) analysis, ESI-MS were carried out through University of York chemistry department services.

All other results are the work of the author. Aspects of work presented in this thesis have been included in publications, references as follows:

- Budarin, V. L., Shuttleworth, P. S., Dodson, J. R., Hunt, A. J., Lanigan, B., Marriott, R., Milkowski, K. J., Wilson, A. J., Breeden, S. W., Fan, J., Sin, E. H. K. & Clark, J. H. (2011). Use of green chemical technologies in an integrated biorefinery. Energy & Environmental Science, 4, 471-479.

- Fan, J., De , M., Budarin, V., Gronnow, M., Shuttleworth, P., Breeden, S., Macquarrie, D., & Clark, J. (2013)Direct Microwave-Assisted Hydrothermal Depolymerization of Cellulose, Journal of the American Chemical Society 135 (32), 11728-11731

- Fan, J., De , M., Zhu, Z., Budarin, V., Gronnow, M., Gomez, L. D., Macquarrie, D. & Clark, J. (2013) Microwave-enhanced formation of glucose from cellulosic waste. Chemical Engineering and Processing: Process Intensification.

The work presented in this thesis has not previously been submitted for a degree at this or any other university.

Chapter 1:

Introduction

1 Introduction and Literature Review

The twentieth century saw a major emphasis in the development of petroleum, coal and natural gas based fuels, exploiting cheap readily available fossil feedstocks. These could be used to produce a variety of high value products such as fine chemicals, pharmaceuticals, detergents, plastics, pesticides, asphalt, low value fuels etc.

Fossil fuels account for ~80% of primary energy consumption worldwide, followed by biomass, ~9.3% and nuclear ~6.9% (Goldemberg, 2006). Oil resources are estimated to be sufficient in supporting the projected growth in demand until the year 2030, with supplies predicted to escalate from 36 million barrels per day in 2006 to 46 million barrels per day in 2015, reaching 61 million barrels per day by 2030. In addition to this it is estimated that 850 billion tonnes of recoverable coal is also available (World Energy Council, 2007, Shafiee and Topal, 2009). With these figures in mind it begs the question, why should we change the current situation which has enabled the human race to progress leaps and bounds in the past 100 years.

The answer to this comes quite simply in the form a number of issues arising from energy supply and is not only limited to global warming, but also include the concerns of air pollution, acid precipitation, ozone depletion, forest destruction and the utilisation of radioactive substances. All of these must be considered if we are to achieve a sustainable energy future. Fossil resources are no longer regarded as sustainable with respect to ever declining petroleum reserves, economic, ecological and environmental viewpoints. It is now recognised that in using these sources an increasing loading of the atmosphere with anthropogenic gasses such as CO_2 (carbon dioxide), N_2O (nitrous oxide) and CH_4 (methane). This is increasing global temperatures due to their green house effects with many effects to the global climate (Bender, 2000, Carroll and Somerville, 2009).

The largest negative effects of fossil fuels can be summarised as follows:
- Environmental damage relating to the emissions of combustion products of fossil fuels.
  - On a local scale most damage occurs from sulfur oxides, nitrogen oxides, carbon monoxide, particulate matter and volatile organic compounds, which

are widely associated with urban air pollution and attributed to hundreds of thousands of deaths worldwide every year from respiratory diseases (Molina and Molina, 2004).

- o On a regional level emissions from combustion can be deposited hundreds to thousands of kilometres from the source of origin. These emissions result in acidification of lakes and soils, resulting in damage to natural systems, crops and human-made structures over time.

- o The global scale presents the critical environmental issue of the "greenhouse effect". This is a result of the release of carbon dioxide and other greenhouse gases into the atmosphere as a result of combustion and extraction of fuels

- The location of oil reserves results in problems with external dependency and security of supply for many countries, with political ties and many markets depend upon oil producing countries. This has the result of severely hampering many non-oil producing countries in the developing world, causing political tensions and unrest. As such a diversification away from, and development of new sources of fuels is desirable for a number, if not all countries.
(Molina and Molina, 2004, Goldemberg, 2006)

Solving these problems requires a new approach to energy production and usage that considers impacts at a local and global scale, which considers a wider variety of fuels, cleaner technologies, increases efficiency and considers the needs of the present and future generations.

As part of this move towards sustainability, it is necessary to consider the whole life process of generating fuels, reducing their environmental impact. In order to achieve this it is necessary to abide by the twelve principles of greener chemistry as set out by Anastas and Warner (2000).

The principles are defined as:

1. Prevention: prevention of waste generation is better than retroactive cleanup.
2. Atom Economy: maximisation of resource efficiency, with minimisation of chemical use not incorporated into the final product
3. Less Hazardous Chemical Syntheses: when possible, steps should be taken to use chemicals with little or no toxicity to humans and the environment.
4. Designing Safer Chemicals: chemical products should have minimal toxicity whilst satisfying their chemical/material requirements.
5. Safer Solvents and Auxiliaries: the use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Design for Energy Efficiency: energy requirements should be minimised, reducing environmental impact and improving economic viability. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. Use of Renewable Feedstocks: a raw material or feedstock ought to be renewable rather than depleting at whatever time technically and economically feasible.
8. Reduce Derivatives: unnecessary derivatisation should be minimised or avoided if possible, as such steps necessitate additional reagents and can produce waste.
9. Catalysis: catalytic reagents are superior to stoichiometric reagents.
10. Design for Degradation: chemical products should be designed so that at the end of their life they break down into innocuous degradation products and do not persist in the environment.
11. Real-time analysis for Pollution Prevention: real-time in-process monitoring and control is required to prevent the formation of hazardous substances.
12. Inherently Safer Chemistry for Accident Prevention: substances and the form of a substance used in a chemical process should be chosen to reduce the potential for chemical accidents, together with releases, explosions, and fires.

(Anastas and Warner, 2000)

When considering the ways in which the intrinsic link can be broken between energy production and fossil resources, a number of options have been suggested, as both transitional and final. These have included, but are not limited to:

- Renewable energy technologies
- Energy conservation
- Cogeneration of electricity and district heating
- Energy storage technologies
- Alternative energies for use in transportation, e.g. hydrogen fuel cells and bio-fuels
- Coal cleaning technologies
- Optimum monitoring of energy use and evaluation of energy indicators
- Policy integration
- Recycling
- Acceleration of forestation
- Carbon or fuel taxes
- Materials substitution
- Promoting public transport
- Changing life styles
- Increasing public awareness
- Education and training

(Dincer, 2000)

Of these changes new renewable technologies have been constantly developed. These technologies produce marketable energy by converting natural energy forms which are derived from direct and indirect impact of sunlight on the earth; wind, falling water, heating effects and plant growth. There are also a number of technologies developed which utilise non-solar energy forms, these being tidal and geothermal energy. These sources, present untapped sources of energy which dwarf those available from fossil fuels. However, these are generally diffuse, not fully accessible, have large regional variations and are intermittent (Barton and Infield, 2004, Panwar *et al.*, 2011, Abbasi and Abbasi, 2011).

Of all energy sources biomass presents itself as the most readily available across the world. Biomass can be converted into most modern energy carrier types; these being heat,

electricity and transportation fuels (biofuels). Biofuels offer the potential to solve, in part, the issues surrounding the use of oil; lack of diversity of resources and the reduction of green house gas emissions from the transportation sector (International Energy Forum, 2010). However, it has been recognised that conventional thermal means (pyrolysis and gasification technologies) of biofuel production are still in their infancy and require much further development to produce fuels of a reasonable quality and at a viable economic cost (Hoekman, 2009, Mettler *et al.*, 2012).

1.1 Biorefinery Concept

The biorefinery concept has emerged in recent years in response to growing concerns over:

- decreasing fossil fuel reserves
- rising crude oil prices
- issues arising around security of supply
- negative environmental impacts
- a shift towards sustainable technology

(Stöcker, 2008b, Budarin *et al.*, 2011a)

This has led to the development of both local and global policies, pushing economies towards biomass based fuels. In achieving this, two strategic goals must be met. Firstly, the replacement of imported petroleum by domestically sourced renewable feedstocks and secondly, by the establishment of a versatile bio-based industry (Stöcker, 2008b, Taylor, 2008, Budarin *et al.*, 2011a).

In undertaking this, significant efforts have been placed in developing bio-fuels that displace the conventional sources of transportation fuel, with advances in the production of ethanol, butanol and biodiesel (Olson *et al.*, 2004). However, the low value of liquid fossil fuels still hampers the development of these new bio based fuel sources, with little or no return on investment attainable in their development within current market conditions (Bozell and Petersen, 2010). As a result, a diversification from the production of fuels has occurred with increased focus on the development of high value chemicals (Kaparaju *et al.*, 2009).

The efforts placed in the development of bio-fuels and bio-derived chemicals are advancing the development of new zero-waste bio-refinery technologies. This has resulted in three

main technologies; 'extraction' of high value compounds, 'biological treatment' focusing on the production of alcohols and 'thermochemical' for recovery of organic compounds and production of bio-char (Fadeev and Meagher, 2001, Yazdani and Gonzalez, 2007, Carroll and Somerville, 2009).

Nevertheless, significant limitations are yet to be overcome with the issues arising from geographical distribution, high moisture content and low bulk density of biomass resources, resulting in expensive transportation and processing costs (Hess *et al.*, 2007). These can be overcome through pre-treatment and densification of biomass at source or through the development of localised processing and energy production facilities (Deswarte *et al.*, 2007). However, all options require significant investment and changes in national infrastructure; hence, a unified strategy requiring government backing must be adopted for these to become viable (Tyner and Taheripour, 2007, Londo and Deurwaarder, 2007). But with continual research, development of new processes and technology the reality of the bio-refinery becomes ever closer.

1.2 Biomass Composition

Biomass is a large group of materials derived from organic matter either terrestrial or marine and typically includes, trees, crops and algae but can be derived from animals and waste resulting from food and industry (Lin and Tanaka, 2006). Of these, plant derived biomass is of particular interest to the renewable energy sector as it provides a potentially carbon neutral source of energy which is non-depleting (Klass, 1998). These are subdivided in to a number of overarching groups/sources, as summarised in Figure 1-1.
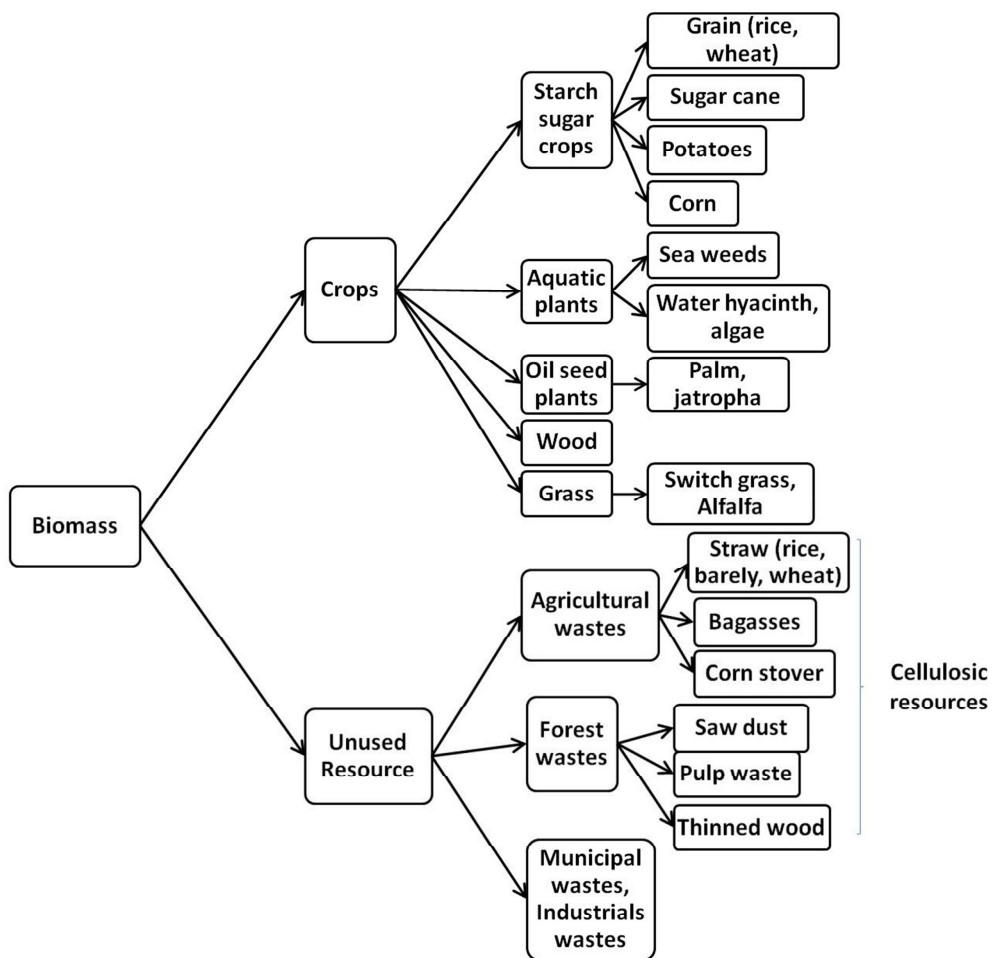
Figure 1-1   Breakdown of available biomass resources (Naik *et al.*, 2010)

Of these, the composition of material found within vary with three distinct components: lignin, hemicellulose and cellulose (see Figure 1-2), with further content of non structural compounds such as wax and inorganic components including silicates. It is the composition of the biomass, which ultimately dictates the choice of conversion process employed and the difficulties that may be encountered, thereafter. As such, it is important to understand the composition of biomass being used and its primary building blocks(McKendry, 2002).

A.
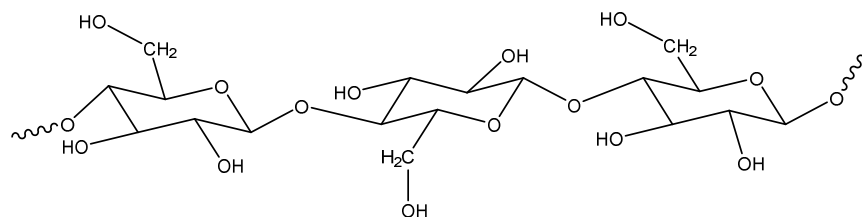
B.
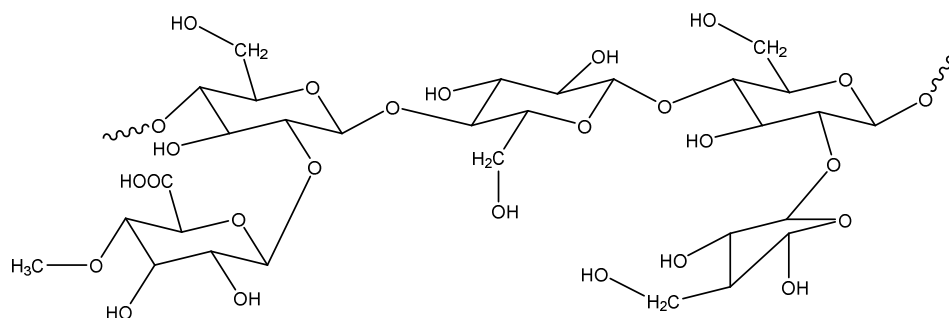
C.
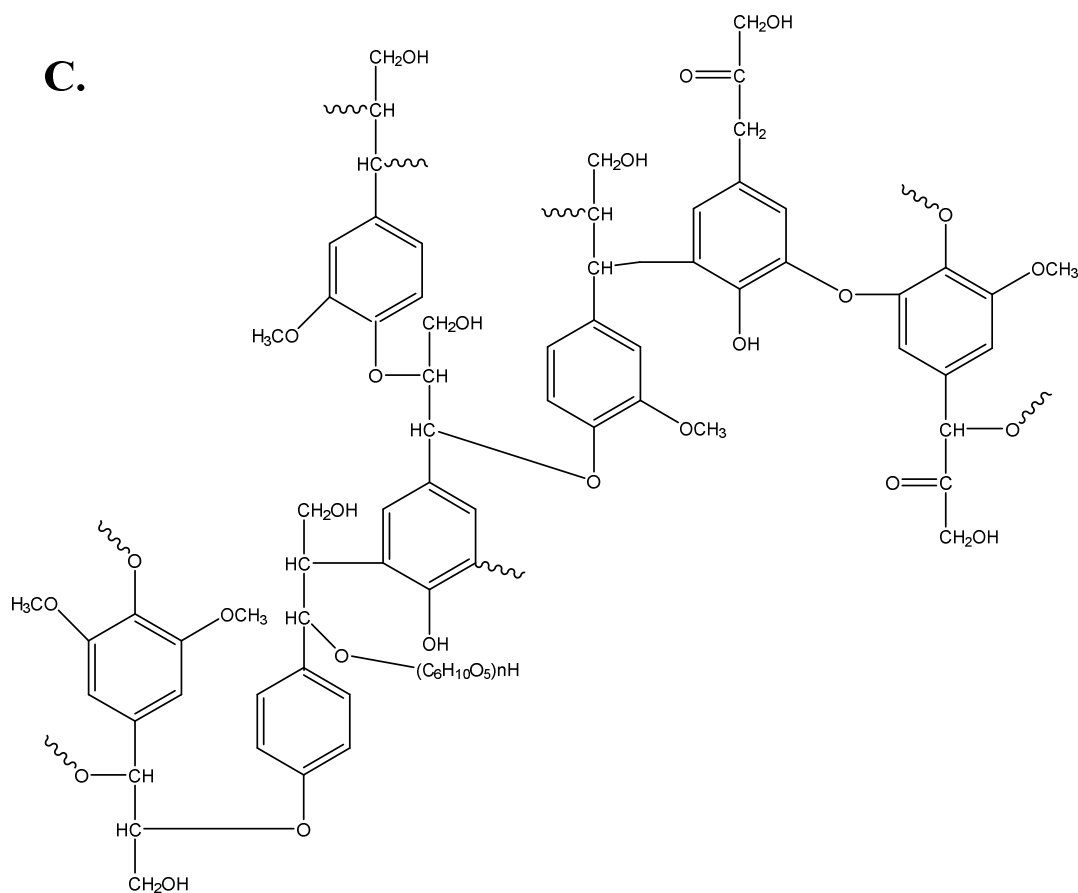
Figure 1-2   **Chemical structure of a.) cellulose, b.) hemi-cellulose and c.) lignin (O'Sullivan, 1997)**

1.2.1 Cellulose

Cellulose is a polymer of repeating D-glucose units connected in a β-(1,4) configuration, with chains consisting of hundreds to tens of thousands of D-glucose molecules (O'Sullivan, 1997) (see Figure 1-2). As a result of the long un-branched structure of cellulose with the intra- and inter- molecular bonds, cellulose has a high thermal stability and mechanical strength. The hydrogen bonding between cellulose chains acts to promote the formation of crystalline structure, with the degree of polymerization and crystallinity making cellulose structure have varying degrees of resistance to chemical and enzymatic attack.

The crystalline structure of cellulose is seen to take two crystal phases I_α and I_β. The relative proportions of each form vary depending on the sources of cellulose, with lower organisms such as bacteria displaying higher proportions of I_α and higher organisms such as plants and trees displaying greater portions of I_β(Sannigrahi $et\ al.$, 2010). There is little work examining the relative proportions of these components, hence the effect that they might have on a later process are no understood. However, the degree of crystallinity and conversely the degree of amorphous (cellulose lacking long range ordered structure) structure is found to have a significant effect on the ability of cellulose to resist chemical attack. Furthermore, the hydrophobic crystalline face of cellulose makes it increasingly resistant to acid attack as it forms a dense layer of water at the interfacial boundary (Himmel $et\ al.$, 2007).

1.2.2 Hemicellulose

Hemicellulose is a mixture of polysaccharides containing xylose, glucose mannose, arabinose, methylglucuronic and galacturonic acids as its structural units; this is discussed at length in Puls (1997). The structure is heterogeneously branched dependent upon the composition of the polysaccharides contained and their relative abundances; which are known to vary with species (McKendry, 2002). However, it is understood that it has a low thermal stability with the branches volatilising easily to CO, CO_2, and lower molecular weight hydrocarbons (McKendry, 2002).

1.2.3 Lignin

Lignin is commonly defined as an amorphous, polyphenolic material arising from the enzymatic polymerisation of three phenylpropanoid monomers, with a three carbon chain attached to six carbon atom ring structures called phenyl-propanes. Further to this it can have up to two methoxy groups present (McKendry, 2002). The resulting polymer is highly

resistant to degradation and forms nature's greatest sink of aromatic structures. The ultimate structure of the lignin formed is dependent upon the species, from which it is derived (Bonawitz and Chapple, 2010).

1.2.4 Summary

The relative abundances of these three components determine the physical properties of the resulting biomass. These three sources of naturally occurring organic compounds can be considered a renewable energy source, providing

- secured, local access to energy
- mitigation of the effects of climate change
- development and maintenance of agricultural activities

Hence, the increasing focus on conversion of biomass to satisfy our need for renewable sources of fuel.

1.3 Biofuels

Traditional biomass such as wood, charcoal and animal dung represents the largest proportion of energy for a large number of people in developing countries who use it mainly for cooking and heating.

However, advanced efficient conversion technologies can now generate biofuels from materials such as wood, crops and waste materials (Stöcker, 2008b, Demirbaş, 2001). Biofuels can be of solid, liquid or gaseous forms, although scientific literature often refers to 'biofuels' in the narrow sense of liquid biofuels for transportation.

For a fuel to be called a biofuel it must have been derived from recently living organisms, whether it is agricultural, forestry, fisheries or municipal waste derived. There are two different types of biofuel, primary, which consists of wood, wood chips and pellets, or other organic materials, which are used in an unprocessed form, and secondary, which result from the processing of biomass via chemical, biological or thermal means. Traditionally, secondary biofuels have been produced in a number of methods; extraction of oils, fermentation of sugars to produce alcohols, pyrolysis/gasification and chemical synthesis and are normally sourced from traditional biomass sources as shown in Figure 1-1.

From these, technologies have been developed to utilise them, with sources of methanol, ethanol, synthetic diesel, biodiesel, bio oil and hydrogen derived: all of which have significantly different properties and uses. These biofuels are currently categorised into 1st and second generations (Jansen, 2012).

1.3.1 First Generation

First generation biofuels are largely made from sugar, starch, vegetable oils, or animal fats using conventional technology. They are often produced from crops such as grains, sugar beet and oil seeds. Their production is limited due to competition with food crops and is unable to achieve targets for oil-product substitution, climate change mitigation and economic growth. The production of first generation biofuels is commercial today, with approximately 50 billion litres produced annually (Naik *et al.*, 2010). Other biofuels are also commercially available but are not sold in sufficient quantities make a significant impact on the world fuel market, an example of these being biogas (methane) derived from anaerobic treatment of manure (Holm-Nielsen *et al.*, 2009).

Two main types of fuel have been developed in the first generation and currently available on a commercial scale:

- Biodiesel
- Ethanol

(Fatih Demirbas, 2009, Lin and Tanaka, 2006, Naik *et al.*, 2010)

Biodiesel and bioethanol are derived from different resources, with biodiesel mainly from vegetable oils and bioethanol from sugars and starch (see Figure 1-3).
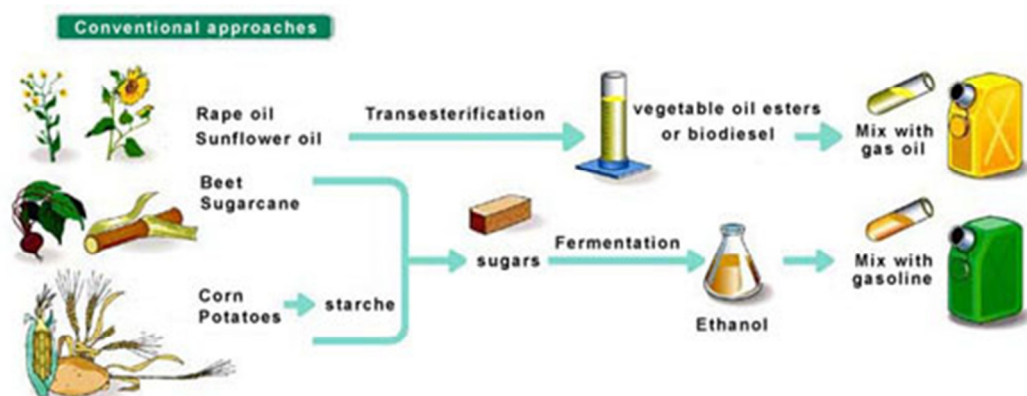
Figure 1-3   Conventional routes of biodiesel and bioethanol production

1.3.1.1 Bio-diesel

Biodiesel has mainly been produced through the transesterfication of vegetable oils and is generically summarised through the transesterfication reaction shown in Equation 1-1

$$RCOOR^1 + R^2OH \overset{catalyst}{\Longleftrightarrow} RCOOR^2 + R^1OH$$

Ester + Alcohol   Ester + Alcohol
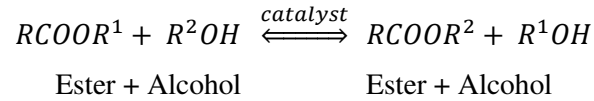
Equation 1-1   The transesterfication reaction (Meher *et al.*, 2006)

The resultant quality of the biodiesel is such that it can be used as a direct substitute for diesel (Fukuda *et al.*, 2001). Nevertheless, special care is required when storing biodiesel as they are susceptible to changes in viscosity and Rancimat Induction Period (oxidation period), determined by the nature of the starting material used (Meher *et al.*, 2006). These have major implications for the set-up, storage and supply chain.

The starting material also has significant implications on the type of process used in the production of the diesel. Oils with a high free fatty acid (FFA) content hinder the process, with the saponification reaction taking place preferentially over the conversion to methyl ester (Kulkarni *et al.*, 2006). For this to take place the addition of solid catalysts are required to simultaneously catalyse transesterfication of triglycerides and the esterfication of FFA to methyl ester. Hence, the biodiesel production process requires consistent feedstock and careful process control to ensure product quality (Naik *et al.*, 2010).

1.3.1.2 Ethanol

The production of bioethanol has until now, been dominated by the process of fermentation of sugars derived from starch (Alvira *et al.*, 2010). The resulting ethanol has the potential to be used as a partial or full replacement of gasoline. The ethanol itself can also be further converted to ethyl tertiary butyl ether (ETBE) for blending with gasoline to form gasohol (Malça and Freire, 2006).

The ethanol production reaction is most simply described by the following reaction as shown in Equation 1-2.

$$C_6H_{12}O_{6\,(aq)} \overset{yeast}{\Longrightarrow} 2CH_3CH_2OH_{(aq)} + 2CO_{2\,(g)}$$

Glucose   Ethanol   Carbon Dioxide
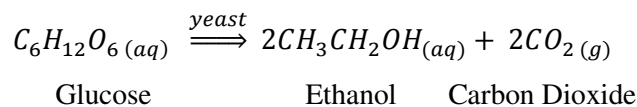
Equation 1-2   Typical ethanolic fermentation reaction of glucose

Nevertheless, ethanol production is derived from two differing sources of material. The first of which are sugar-containing crops such as wheat, sugarbeet, fruits and starch containing crops such as potatoes, corn, barley etc. The starch from these is not readily fermented to ethanol by normal formation practices, but by addition of specialist species such as *saccharomyces cerevial*, *saccharomyces uvarum*, *schizosacaharomyces pombe* and *klayveromyces* conversion is possible (Naik *et al.*, 2010). The alcohol produced from these is referred to as grain alcohol (Agarwal, 2007).

The second process involves conversion of cellulose to ethanol. This is used for materials such as wood and agricultural residues. The alcohol produced is referred to as biomass ethanol (Wyman, 1999). This process is significantly more complicated than that of the grain ethanol, requiring pre treatment of biomass to render the cellulosic content amenable to the hydrolytic enzymes required for fermentation to occur (Lynd, 1996). The pre-treatment process is required to open the lignocellulosic structure of the biomass, making both glucan and xylan accessible to enzymatic attack (Baugh and McCarty, 1988). As such, it is critical that the combination of substrate, pre-treatment type and enzyme dosage have a great effect on the digestability of the biomass. Pre-treatment is critical, and can make the difference of less than 20% ethanol yield without and greater than 90% ethanol yield with (Alvira *et al.*, 2010).

Nevertheless, a balance between the severity of pre-treatment and the cost implication are required for a viable biomass ethanol process. In this, it is usually observed that if pre-treatment severity is reduced, increased or differing enzyme combinations will be required to achieve similar concentrations of sugar. Hence, factors influencing the level of substrate pre-treatment are of significant interest to the biomass ethanol community; with the main factors having been recognised as:

- Cellulose crystallinity (Chang and Holtzapple, 2000)
- Degree of cellulose polymerisation (Puri, 1984)
- Available surface area (Alvira *et al.*, 2010)
- Lignin content and distribution (Mansfield *et al.*, 1999)
- Hemicelluloses content (Chandra *et al.*, 2007)
- Feedstock particle size (Sun and Cheng, 2002)
- Feedstock porosity (Chandra *et al.*, 2007)
- Cell wall thickness (Alvira *et al.*, 2010)

1.3.1.2.1 Pre-treatment

From an understanding of the factors, a number of pre-treatment technologies have been developed which can be generically classified as biological, physical, chemical and physio-chemical (Galbe and Zacchi, 2007).

Biological treatments often involve the use of fungi to degrade lignin and hemicelluloses found within wood derived. The process is often advantageous requiring little capital cost, low energy requirement, no addition of chemicals and a passive effect on the surrounding environment. However, the process is limited by the resulting low rates of hydrolysis and large land requirements (Sánchez, 2009, Wan and Li, 2012)

Physical pre-treatments involve subjecting the feedstock to particle size reduction and/or disruption to the fibrous structure. This most commonly takes the form of mechanical comminution and extrusion (Alvira *et al.*, 2010).

The mechanical comminution involves particle size reduction of feedstock and subsequent reduction in crystallinity of lignocellulose, with a resulting increase in specific surface area and decrease in extent of polymerisation. Nevertheless, the process requires significant energy input (dependent upon particle size), often rendering the process economically unfeasible (Taherzadeh and Karimi, 2008). The second process, extrusion, involves the heating, mixing and shearing of the biomass through a screw auger. The process achieves much the same result as comminution with the added advantages that screw speed and barrel temperature are believed to interrupt with the lignocellulosic structure, rendering it more accessible to enzymatyic attack (McMillan James, 1994, Zheng, 2009)

The third group of pre-treatment methods involves the use of chemical pre-treatments to alter the structure of the constituent components of biomass to make them more accessible to chemical attack. These are generically classified into five chemical treatment routes, acidic, alkali, ozonolysis, organosolv and ionic liquids. Of these the alkali and acid processes are most commonly used; the benefits of each are summarised as follows:

- Alkali treatment –
  - o increases cellulose digestibility
  - o effective for cellulose solubilisation, however, is less able to solubilise hemicelluloses/cellulose than an acid process

- o is performed at room temperature
- o more effective than other processes in treating agricultural residue and wood
- o reduction in formation of HMF or furfural when alkaline peroxides are used, favouring the fermentation pathway in an ethanol production process

(Mosier *et al.*, 2005, Cheng *et al.*, 2010, Ramirez *et al.*, 2013)

- Acid treatment -
  - o increase cellulose digestibility
  - o effective solubilisation of hemicellulose fractions
  - o increases accessibility of cellulose to enzymatic attack
  - o retention time at elevated temperatures results in solubilising hemicellulose to xylan and fermentable sugars
  - o however, elevated temperatures often result in degradation of hemicellulose to furfural and HMF
  - o results in high operating costs due to equipment damage resulting from use of acid

(Sun and Cheng, 2002)

The final group of pre-treatments are the physio-chemical routes. These include such processes as steam explosion, hydrolysis, ammonia fibre explosion, ultrasound and CO_2 explosion (Alvira *et al.*, 2010).

1.3.1.3   Criticisms and Drawbacks

There are a significant number of concerns and limitations surrounding the use of first generation biofuels with regard to environmental impacts and carbon balances, these are summarised below:

1. Competition for use of crops for food or fuel production, giving rise to the possibility of food price rises and/or shortages in many countries. This is a significant factor in the argument against biofuels as there are an estimated 854 million people classified as undernourished in the world (Escobar *et al.*, 2009). As the amount of agricultural land available globally is limited there is an ethical debate whether the production of biofuels using this land can be justified whilst the undernourishment of these peoples occur. A further complication also arises when using food crops for the biofuel production as it increases the price of these foods.

Hence, inflating the market and pushing further swathes of populations in to food poverty (Ajanovic, 2011).

2. Only limited greenhouse gas emission savings when taking into account emissions from production (due to increased use of fertilisers) and transportation. This is as a result of cultivating crops requiring significant energy input from the use of petroleum products and energy in farm machinery/transportation, but also the indirect energy impacts accumulated from using fertilisers and chemicals (Janulis, 2004).

3. Reduction of biodiversity due to land requirements and use of chemicals. High nitrogen inputs from crops can lead to the reduction of oxygen in water and result is increased hypoxic conditions. Furthermore, large scale agriculture adopted by most biomass production facilities results in greater levels of water usage, nitrogen and pesticide pollution, all resulting in increased pressure on natural ecosystems and reduction in overall biodiversity (Groom *et al.*, 2008).

4. Current non-competitive pricing with fossil fuel derived oils. The cost of feedstocks is the single largest proportion of biofuel production, however, significant costs are also incurred as a result of increased difficulty of deconstructing these materials and the further processing required improving fuel quality. As such, current biofuel technologies are largely non-economically viable without subsidies (Tao and Aden, 2009).

As a result of these limitations further developments have been made to alleviate them, this has resulted in the second and third generations of biofuels (United Nations – Energy, 2007).

1.3.2 Second Generation

Second generation biofuels are derived from truly sustainable sources of biomass, which are carbon neutral/carbon negative and have less social impact than that of the first generation (Timilsina *et al.*, 2010). As such, they derive their feedstocks from non-food parts of current crops e.g. stems, leaves, and husks, or, from non-food crops such as switchgrass, miscanthus and/or the residue from industrial activity e.g. woodchips, pulps, pips (Simmons *et al.*, 2008). The sources of biomass used for second generation biofuels are plentiful but largely unutilised, as they are lignocellulosic and pose significant technological challenges in their conversion (Sims *et al.*, 2010).

However, a number of technologies have been developed and are currently in use, these being:

- physical conversion – mechanical extraction, briquetting and distillation
- thermo-chemical conversion – combustion, gasification, liquefaction and pyrolysis

(Damartzis and Zabaniotou, 2011)

1.3.2.1 Physical Conversion

Physical conversion processes involve the physical destruction of biomass to enable extraction of oils or the densification/re-shaping of material for easier transport and use.

The first method most commonly used is the mechanical extraction of oils through the application of pressure. This most commonly involves the use of screws to press the biomass and collect the oil. This process can be used to partially press biomass to extract part of the oil, followed by further processing by solvent extraction. In total between 30-40wt.% oil can be recovered by this process (Naik *et al.*, 2010).

Briquetting is also a commonly used method in the physical conversion of biomass. The method is most commonly used on agricultural and forestry residues, which would otherwise be difficult to transport due to the irregularity of sizes and shapes (Grover and Mishra, 1996). The process utilises maceration and pressing, often in conjunction with each other, to produce regular shapes, of increased density (Grover and Mishra, 1996). This makes the material easier to handle and transport. The method is used more extensively now that a number of large-scale power production facilities are moving away from the combustion of fossil fuels to that of biomass.

The final, most commonly used physical conversion method is steam distillation. This quite simply involves the maceration or chopping of material followed by exposure to steam to force the volatilisation of oils, which are subsequently condensed and separated.

1.3.2.2 Thermo-chemical Conversion of Biomass

The thermo-chemical conversion of biomass to energy is largely dependent upon the constituent components and the physical structure of the biomass used. As such, it is important that an understanding of the decomposition of the three major components of

cellulose, hemicellulose and lignin is considered when investigating a thermal upgrading process.
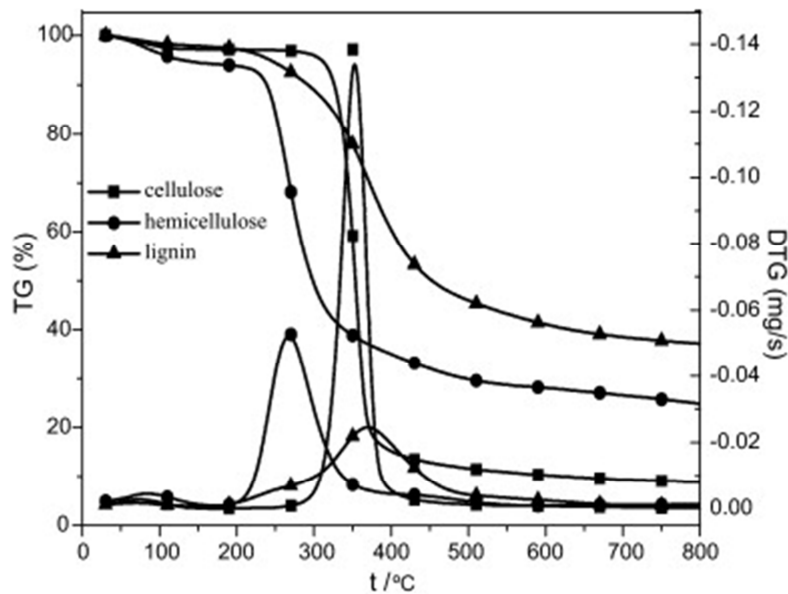
Figure 1-4   TGA/DTG of cellulose, hemicellulose and lignin (Wang *et al.*, 2011)

The decomposition of the three biomass components is shown in Figure 1-4. Of these, hemicellulose is observed to decompose first, with initiation occurring at 220°C and peak loss occurring at 260°C (Yang *et al.*, 2005, Wang *et al.*, 2011). During this phase, the rearrangement of the glucosidic ring structure occurs resulting in hemicellulose depolymerisation.   At temperatures of approximately 300°C oligosaccharides and monosaccharides predominantly decompose to form char, CO, CO_2 and H_2O.

Cellulose decomposition occurs at significantly greater temperatures than that of hemicellulose, with initial decomposition taking place at 315- 390°C and a maximum loss rate occurring at 355°C (see Figure 1-4). During this phase, cellulose is thought to undergo several reactions consisting of dehydration, elimination, condensation and fragmentation reactions. Several models have been proposed for the decomposition including that of the Waterloo Model, the Diebold Model and the Varhegyi-Antal Model (Wooten *et al.*, 2003)
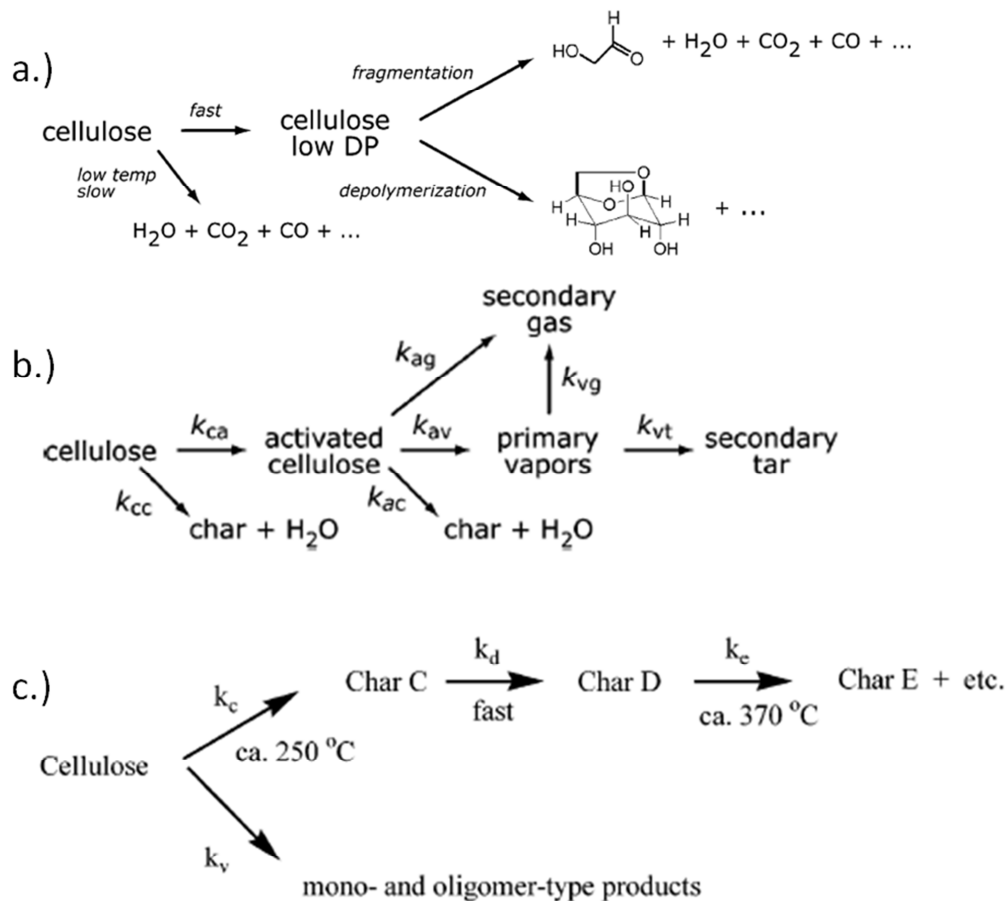
Figure 1-5 **Proposed cellulosic decomposition pathways: a.) Waterloo Model, b.) Diebold Model and c.) the Varhegyi-Antal Model (taken from Wooten *et al.* (2003))**

However, it is recognised that a number of compounds are commonly formed during the decomposition of cellulose, including levoglucosan, 5-hydromethylfurfural, furfural, hydroxyacetone, hydroxyacetaldehyde and some C1−2 compounds (Shen and Gu, 2009).

Lignin is the final organic component of the lignocellulosic materials. Its' decomposition occurs over a wide range of temperatures with softening of the structure below 200°C and char formation and volatilisation occurring up to temperatures of 600°C (see Figure 1-4).

1.3.2.3   *Gasification, Fischer-Tropsch and Pyrolysis*

The thermo-chemical conversion of biomass takes place by the processes of direct combustion, gasification and pyrolysis. The latter two methods involve heating of biomass in conditions lacking oxygen of varying extents. Gasification and pyrolysis results in the

partial oxidation and/or decomposition of the biomass with the ensuing production of syngas (H_2, CO, CO_2, CH_4 and N_2) and hydrocarbon species (Mohan *et al.*, 2006). These routes are summarised in Figure 1-6, with the end uses indicated.
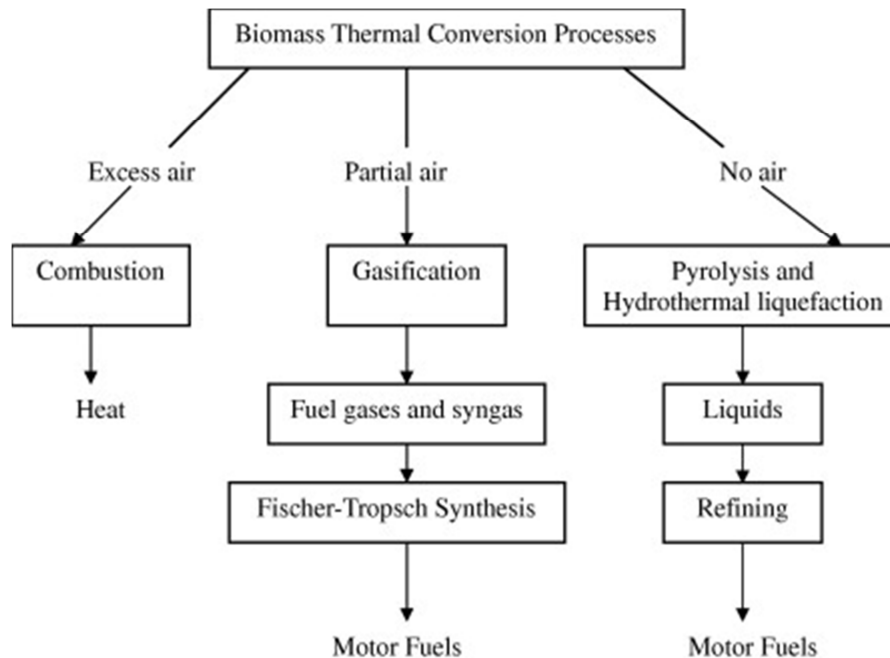
Figure 1-6   Biomass thermal conversion routes (Fatih Demirbas, 2009)

1.3.2.3.1   Gasification

Gasification technology has been used extensively within the biomass industry over the past 30 years. The process relies upon partial oxidation of biomass at high temperatures ($>1300^{\circ}C$) in the presence of oxygen or steam. The oxidation largely results in production of syngas, composed of CO, CO_2, H_2, CH_4 and N_2, with small proportions of heavy organic components and inorganic gases.

The gas produced is often used for the production of fuels with calorific values varying from ~5 – 20 MJ/m^3 (Bridgwater, 2006) or chemical intermediates. Historically the process has been utilised to produce fuels by the Fischer-Tropsch process (Fatih Demirbas, 2009) and methanol by thermo-catalytic conversion (Lavoie *et al.*, 2013). Currently, many areas of research surround the gasification process with authors such as Castello *et al.* (2013), Zhang *et al.* (2013), Hanaoka *et al.* (2013) looking at using subcritical and supercritical water, hot gas cleaning and the gasification of aquatic biomass, respectively, to name but a few.

1.3.2.3.2 Fischer-Tropsch

The Fischer-Tropsch process is used extensively in the current biofuels production market. The process utilises a series of chemical reactions to produce a variety of aliphatic hydrocarbons through the addition of single units of hydrogen and carbon, as summarised in Equation 1-3.

$$(2n + 1)H_2 + nCO \xrightarrow{catalyst} C_nH_{(2n+2)} + nH_2O$$
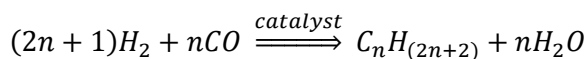
Equation 1-3   Generalised Fischer-Tropsch addition reaction

The process involves the conversion of CO to alkanes through hydrogenation of the CO, the hydrogenolysis of the C-O and the formation of C-C bonds. Most products produced using this process are within the diesel range, however a small number of alkenes, alcohols and other oxygenated compounds are formed during the process. Depending on the desired product outcome differing catalysts and temperatures are used typically between 200-240°C or 300-350°C, with either iron or cobalt catalysts (Wright *et al.*, 2008).

This process can be extremely useful in the conversion of biomass to useful hydrocarbons as it can be used to produce high purity fuels which can otherwise not be achieved through other thermal chemical conversion pathways. However, in order to utilise the Fisher-Tropsch process a five step process is required to be performed on biomass, this includes comminution, gasification, gas cleaning, water gas shift and then Fischer-Tropsch reaction. Comminution, is used to reduce the biomass feedstock size to increase its surface area to volume ratio. Gasification takes place to convert the biomass to syngas (as described in Section 1.3.2.3.1), which is subsequently cleaned to remove particulate matter and trace contaminants such as sulphur, chlorine, and ammonia. The water gas shift reaction is then utilised to adjust the H$_2$:CO ratio as required by the final catalyst used in the Fischer-Tropsch reaction (Demirbas, 2007, Luque *et al.*, 2012a, Stöcker, 2008a).

Recent advances in the Fischer-Tropsch process and the ever increasing price of crude oil mean that the process is increasing in popularity, with its advantage of producing high quality biofuel making it of significant interest over other thermal processes. The ability to produce diesel range fuels also mean that it can be integrated with current infrastructure. Nevertheless challenges still require overcoming surrounding biomass gasification and

catalyst design, hence the large scale commercial application of the Fischer-Tropsch process has not been fully realised (Luque *et al.*, 2012a).

1.3.2.3.3 Pyrolysis

Pyrolysis is the process in which the thermal degradation of a material occurs in the absence of an oxygen-containing atmosphere (inert). When used in the decomposition of lignocellulosic materials three products are formed; bio-char, bio-oil and bio-gas (Maschio *et al.*, 1992). To date the pyrolysis process to recover the bio-oil component only produces liquid biofuels of medium to low calorific value (Demirbaş and Şahin, 1998). Oil typically progresses through a number of steps, these being:

1. Transfer of heat from its source to the material undergoing pyrolysis
2. Initiation of pyrolysis reactions at higher temperatures releasing volatiles and forming char
3. Hot volatiles travel through cooler regions of solid and transfer heat to un-pyrolysed material
4. Condensation of some volatiles, followed by secondary reactions to form tar
5. Secondary autocatalytic pyrolysis reactions occur alongside initiation reactions in a simultaneous competitive process
6. Continuing thermal decomposition occurs alongside water gas shift reactions, radicals recombination, and dehydrations, dependent upon process parameters

(Mohan *et al.*, 2006)

The pyrolysis process is of significant interest in the production of biofuels as through adjustment of the parameters of feedstock type, maximum temperature, heating rate and dwell time, products of particular interest can be favoured. Hence, from this three types of pyrolysis have been developed and are often referred to, being; conventional pyrolysis, fast pyrolysis and flash pyrolysis (Maschio *et al.*, 1992, Ranzi *et al.*, 2008).

Parameters	Conventional Pyrolysis	Fast Pyrolysis	Flash Pyrolysis
Pyrolysis Temperature (^{o}C)	277 – 677	577 – 977	777 – 1027
Heating Rate (^{o}C/s)	0.1 – 1.0	10 – 200	≤1000
Particle Size (mm)	5 – 50	< 1	< 0.2
Solid Residence Time	450 – 550	0.5 – 10	< 0.5

Conventional pyrolysis (slow pyrolysis), is typically used for formation of charcoal. The long residence times used mean that volatile products do not escape readily, hence, undergo secondary reactions to form heavier products such as oil and tar or undergo further carbonisation reactions (Bridgwater, 2006, Mohan *et al.*, 2006).

Fast pyrolysis is used when liquid and gaseous products are favoured. A short (1s) residence time is used to favour the formation of vapours and aerosols which can subsequently be condensed to form bio-oil; this typically makes up 60-75wt.%. The remaining mass comprises of 10-20wt.% gas and 15-25wt.% char. Increasing residence time (10-20s) during fast pyrolysis can have a pronounced effect on the product distribution, with ~50wt.% bio-oil/water, ~30wt.% gas and ~20wt.% char formed (Bridgwater, 2006). The bio-oil produced during fast pyrolysis contains several hundred chemicals, ranging from phenols to anhydrosugars, dependent upon the feedstock used and the proportions of hemicellulose, cellulose and lignin present. As such, bio-oil typically has higher heating value of 16-19MJ/kg, with moisture contents of 15-30wt.% (Mohan *et al.*, 2006)

The flash pyrolysis process is significantly different to that of conventional and fast pyrolysis, requiring small particle size, high heating rates and short contact time. It mainly results in the production of CO, CO_2, CH_4, C_2H_4 and C_2H_6 gases with the final product split of approximately 44wt.% gas, 33wt.% oil, 8wt.% char and 13wt.% water (Scott *et al.*, 1985).

As such, by varying operating parameters it is possible to attain differing product yields through biomass pyrolysis, with the general rule:

- Char formation requires low temperatures and low heating rate.

- Bio-oil require low temperature, high heating rate and short gas residence time
- Gases require high temperatures, high heating rates and short gas residence time

1.3.2.4 *Limitations of Thermal Pyrolysis*

Products produced from pyrolysis technologies are often hugely variable, dependent on the process used. As such, much research has been performed to ascertain the conditions which produce the highest value product yields. However, current technology appears limited in its feasibility. This is due to a number of factors:

- Organic materials have a low thermal conductivity – this results in greater amounts of time required to heat the material sufficiently to recover useful liquid and gaseous fractions. Further to this, heating is often slow and wide product distributions are formed requiring further processing to make a useful product (Kriegerbrockett, 1994)

- Heteroatom content is detrimental to fuel quality and contaminate chemical intermediates (Mullen *et al.*, 2009)

- Large volumes of fuel need to be stored on site for heating of the reactors (Jones *et al.*, 2002)

- The thermal process often has a large land footprint due to the nature of the process storage of large amounts of fuel (Jones *et al.*, 2002)

1.1.1 Conclusion

Although thermo-chemical conversion routes are a viable option in the processing of biomass, limitations arise when large scale sustainable production of liquid biofuels is attempted. Further research and knowledge are required to overcome the current social, political and technical challenges, specifically the problems of feedstock supply and the re-engineering of technology and distribution networks to accommodate the newly evolving fuels (Nigam and Singh, 2011).

As such, pyrolysis based bio-oils require compatibility with current technology, whilst these challenges are faced and resolved. Hence, optimisation and development of the current pyrolysis technology is required to overcome the technical and economic challenges faced by current technology. These currently result from pyrolysis being highly energy intensive, resulting from the low thermal conductivities of biomass, wide product distributions in oil

and the requirement for large land footprints. With this, the quality of oil produced is such that the significant processing (refining) is required before they can be utilised in engines (Mohan *et al.*, 2006).

Further research needs to be applied in ascertaining suitable biomass types and process engineering, in particular in the field of more highly efficient conversion processes of lignocellulosic materials to higher quality bio-oil. As a first step in achieving this, a revolution is required in the way that energy is transferred to biomass and increased selectivity of thermo-chemical decomposition pathways. Hence, a move from conductive heat transfer mechanisms to the direct application of energy would form one of the first logical steps.

To achieve this, the utilisation of electromagnetic radiation, heating the biomass on a molecular level, would be one approach. Hence, the application of microwave energy would present itself as a possible avenue of investigation.

1.4 Fundamentals of Microwaves

Microwaves are electromagnetic waves lying between radio and infrared (see Figure 1-7), with the specific frequencies of 0.3 – 300GHz and correspond to wave lengths of 1mm to 1m (Lidström *et al.*, 2001). They are mainly used for telecommunication and radar equipment, but are also employed in the heating of materials.
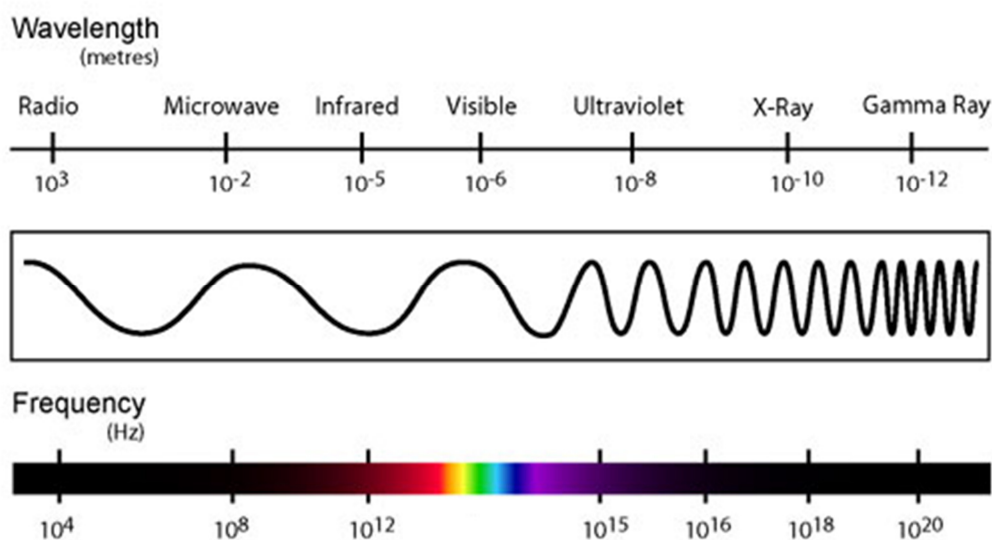
Figure 1-7   The electromagnetic spectrum

All frequencies used are strictly regulated and controlled, with designated frequencies for 'Industrial, Scientific and Medical' (ISM) applications. Of these, microwave frequencies assigned for the purposes of heating include 896 MHz or 2450MHz within the UK (Lidström *et al.*, 2001, Mingos and Baghurst, 1991). Of these frequencies 896 MHz is used predominantly within industry and the latter within the domestic sector (Will *et al.*, 2004).

1.4.1   Microwaves and Materials

Microwaves, like any other electromagnetic wave, obey the basic laws of optics but differ, as they are coherent and polarising (Xia and Picklesi, 2000). As such, a microwave consists of the electric field and the magnetic field component (see Figure 1-8). Of these, the electric field component is responsible for the heating of materials, with the response of charged particles by the two mechanisms of dipolar polarisation and/or ionic conduction (Clark and Sutton, 1996, Lidström *et al.*, 2001).

ε = electric field
ℋ = magnetic field
λ = wavelength (12.2 cm for 2450 MHz)
c = speed of light (300,000 km/s)
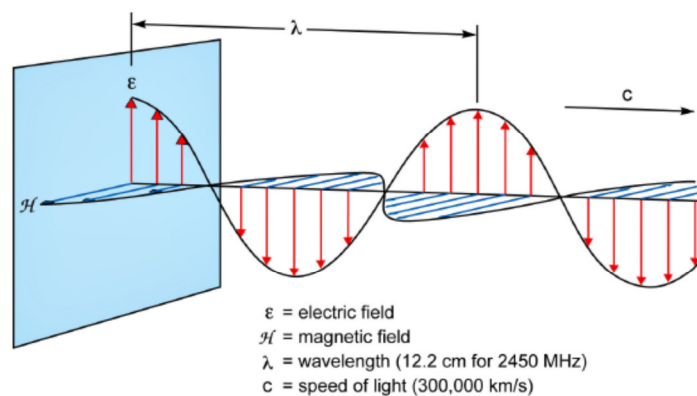
Figure 1-8   Microwave Components (CEM Corporation, 2013)

1.4.1.1   Dipolar Polarisation Mechanism

The dipolar polarisation mechanism requires a materials to have a positive and negative charge which is separated over a distance (see Figure 1-9). When placed in an electric field they will become polarised through the formation and rotation of dielectric dipoles or magnetic dipoles, if present (Clark and Sutton, 1996).
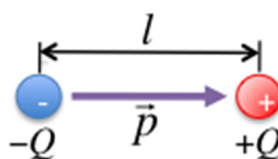
Figure 1-9   Electric Dipole

The dipole moment is described as a vector from the negative to positive charge on the molecule(Gabriel *et al.*, 1998). Dipoles take either two forms, permanent or temporary, with a permanent uneven distribution of charge or induced when in an electric field; respectively (Bolton, 1992).

Upon application of an electric field, the dipoles rotate, attempting to align with the passing electric field. When at extremely low frequencies, molecules are able to align themselves precisely with the field, with little energy being gained in the process. At high frequencies the molecules are unable to follow the oscillating electric field and do not rotate, hence little or no transfer of energy occurs. However, at intermediary frequencies, dipoles are able to rotate following the electric field but the frequency is sufficient that full rotation cannot be achieved; as such a phase difference arises, known as relaxation time. When this occurs, energy is lost through molecular friction/collisions and is dissipated as heat throughout the

material (Clark and Sutton, 1996, Katz, 1992, Lidström *et al.*, 2001, Thostenson and Chou, 1999). This is illustrated in Figure 1-10.

Figure 1-10   Dipolar polarisation mechanism (taken from Lidström *et al.* (2001))

The dielectric properties of a material are described through the following equation:

Equation 1-4   Material dielectric properties (Gabriel *et al.*, 1998)

Where: ε^* = the complex dielectric constant

ε' = the relative dielectric constant

j = $\sqrt{-1}$

ε'' = the relative dielectric loss factor

The relative dielectric constant represents the microwave energy density within a material, which is an imaginary component that considers the internal loss mechanisms within a material, hence governs the efficiency that absorbed energy can be converted to heat.

Equation 1-5   The Loss Tangent (Gabriel *et al.*, 1998, Kappe, 2013)

The loss tangent is given through Equation 1-5. It is a measure of the ability of the electric field to penetrate the material and convert the electromagnetic energy into heat energy, at a specified frequency and temperature; hence also known as the dissipation factor. The higher the value of tanδ the greater the materials ability to couple with the microwave radiation (Chen *et al.*, 1993, Clark and Sutton, 1996, Lidström *et al.*, 2001).

Finally, the heating of a material originates from the dielectric power absorption, as described in Equation 1-6.

Equation 1-6   Dielectric Power Absorption

Where: P = the power dissipation (W/m^3)

f = the applied frequency (Hz)

E = the electric field strength (V/m)

For this equation to apply the field is assumed to be uniform throughout, hence is only applicable to thin materials, due to field strength depleting as it is absorbed whilst passing through the material undergoing irradiation (Thostenson and Chou, 1999).

1.4.1.2   Ionic Conduction Mechanism

The ionic conduction mechanism is the second mechanism of microwave heating but is normally only applicable to the heating of solutions containing ions. The mechanism involves the long range transportation of charge, when a charge carrier is exposed to an electric field, inducing a current (as illustrated in Figure 1-11) (Lidström *et al.*, 2001).
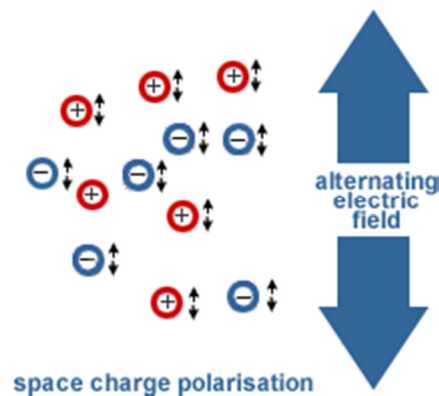
Figure 1-11   Conduction Mechanism (Puschner Microwave Power Systems, 2013)

The conduction mechanism has a much greater interaction with the microwave field than that of the dipolar polarisation mechanism, hence is able to generate greater levels of heat (Lidström *et al.*, 2001).

1.4.2   Microwave Technology

There are two forms of microwave heating equipment available, utilising the same frequencies and similar power densities:

- single mode
- multimode

However, their applications are very different relating to the design of their microwave cavity and the field distribution attained thereafter. Hence, it is important to understand the principles governing their design before use.
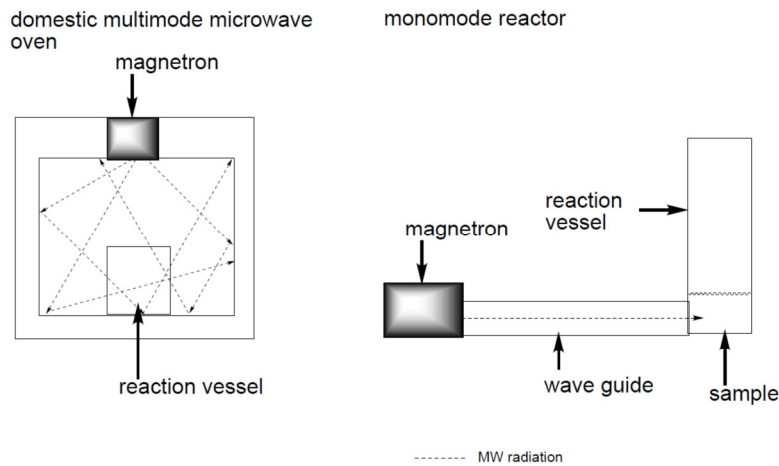
Figure 1-12 **Wave paths in multimode and single mode microwave chambers (Kuhnert, 2002)**

A single mode microwave utilises a solution to the Maxwell equations (Thostenson and Chou, 1999), creating a standing wave within the microwave chamber and forming a single resonant node (see Figure 1-12). The microwave field produced is predictable yet non-uniform.
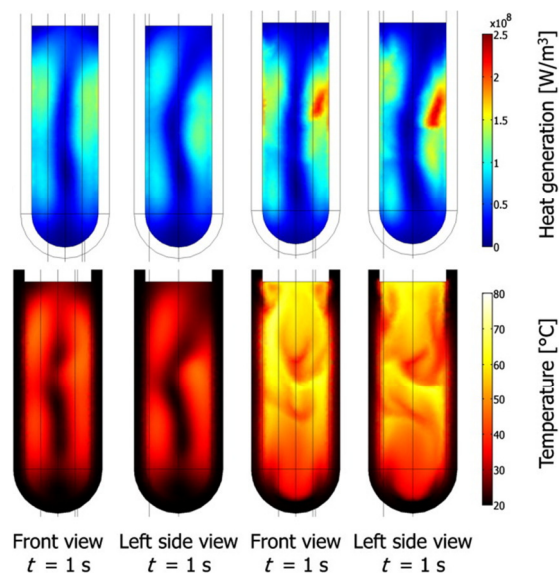
Figure 1-13 **Thermal distribution of water within a single mode microwave cavity after 1 seconds microwave exposure: modelled (top) and measured (bottom) (Sturm *et al.*, 2012).**

Hence, a nodal point can be focused within the centre of a sample undergoing irradiation, with greatest coupling occurring at this point. This in turn generates a point within the sample undergoing irradiation in which the temperature is greater than the surrounding material, otherwise referred to as a "hot spot"(Kriegsmann, 1997). This is of greatest use within laboratory scale investigations, whereby the specific action of microwave and their effect on a material require investigating (Robinson *et al.*, 2010, Thostenson and Chou, 1999). Nevertheless, the field distribution is not always uniform when a material of high dielectric properties is heated within a single mode cavity, resulting in increasingly uneven electric field distribution and the generation of thermal gradients (Sturm *et al.*, 2012).

A multimode microwave utilises a cavity of much greater dimensions than that of a single mode, generating a field with multiple modes and the resulting numerous resonant nodes. With this constructive and destructive wave patterns are also formed because of reflected waves (see Figure 1-14).
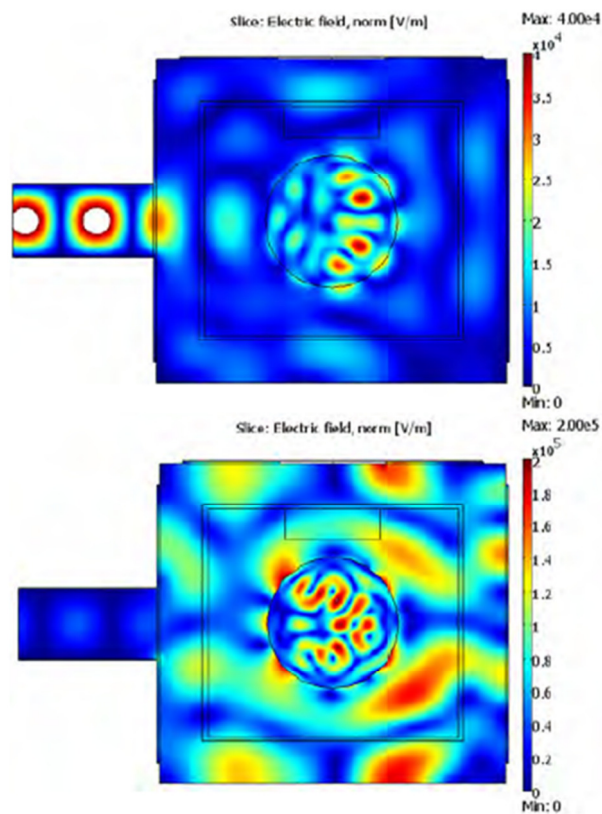
Figure 1-14 **Microwave field distribution within a multimode cavity (from Santos *et al.* (2010))**

However, the nodal point and formation of hot spots within a sample can be overcome through:

- Sample movement – moving the sample through areas of high and low field intensity, achieving time based exposure uniformity
- Mode stirring – disturbing waves travelling through the chamber causing continual redistributions of the microwave field, achieving time based field uniformity.

(Kimrey and Janney, 1988)

1.4.3 Advantages and disadvantages of a microwave process

The principle advantage of using a microwave electromagnetic field is through the mode of interaction of the material undergoing heating, whereby the material heats volumetrically. This is in contrast to that of conventional heating in which energy is transferred through the means of conduction, convection and radiation (Kappe *et al.*, 2013, Sutton *et al.*, 1988, Thostenson and Chou, 1999).

The result of volumetric heating is the formation of inverted temperature profiles within the sample undergoing irradiation, thus the interior of the sample is hotter than the exterior: as shown in Figure 1-15

.
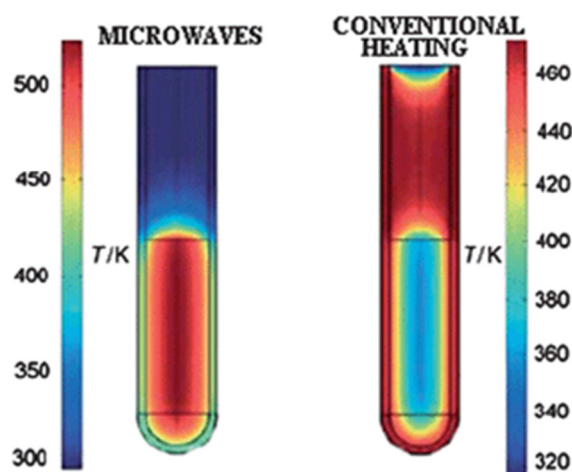
Figure 1-15   Temperature profiles of conventional vs. microwave heating (Schanche, 2003)

This is thought to result in volatiles released from the internal of the sample not passing over a hot exterior region (as in conventional pyrolysis) and thus undergoing secondary reactions, producing a cleaner char structure and smaller product distribution (Miura *et al.*, 2004,

Luque *et al.*, 2012b). It is thought that the potential benefits of microwave heating for a pyrolysis process are numerous, with the major advantages envisaged as:

- efficient heating
- rapid heating times
- increased energy efficiency
- selective heating
- enhanced product quality

(Zong *et al.*, 2003, Luque *et al.*, 2012b)

However, a number of microwave specific anomalies hamper the use of microwave in material processing; these include thermal runaway and self limiting heating.

Thermal runaway is a significant problem in microwave processing. It occurs when localised variations in temperature occur within a material undergoing irradiation due to power dissipation exceeding the rate at which energy is transmitted to its surroundings. If this is accompanied by a thermally dependent increase in the dielectric constant then thermal runaway will be entered and non-uniform sample heating will ensue. This anomaly is more pronounced in multimode cavities in which differing intensities in the electromagnetic field vary with position (Kriegsmann, 1992, Moriwaki *et al.*, 2006, Santos *et al.*, 2010).

Self-limiting heating is also a problem in microwave heating. At a given temperature the dielectric constant can decrease, resulting in decreased conversion of microwave energy to heat within the material, hence heating becomes self-limiting. If this were to happen during a pyrolysis process it could pose the problem of hindering the decomposition of the material, or, require significantly increased power input to overcome the plateau, making the process more energy intensive (Wallace *et al.*, 2006).

1.4.4   Summary

Microwaves present a different way of heating and decomposing a material to that of traditional pyrolysis. This is largely due to the effect of highly polar regions of a molecule (which tend to decompose first). Super and self limited heating, accelerated heating and inverted temperature profiles result in product distributions that are likely to differ from conventional thermal pyrolysis. As such, they offer an opportunity for research into

alternative methods of generating bio-oils/biofuels because of the potentially beneficial differences in the reactions and hence products generated.

1.5   Microwave Pyrolysis of Lignocellulosic Biomass

A number of studies have been performed investigating the microwave heating and pyrolysis of lignocellulosic feedstocks. These have included studies into wood (Miura *et al.*, 2004), coffee hulls (Domínguez *et al.*, 2007), rice straw (Huang *et al.*, 2008), waste tea (Yagmur *et al.*, 2008), wheat straw (Budarin *et al.*, 2009), sewage sludge (Domínguez *et al.*, 2005, Menéndez *et al.*, 2002) and corn stover (Yu *et al.*, 2007). These studies encompass the microwave pyrolysis of the structural components of cellulose, hemi-cellulose, and lignin, but not in their pure form.

However, the first study of significance was undertaken by Allan *et al.* (1980) in which the microwave pyrolysis of cellulose was investigated. In this it was found that water content had a significant effect on the heating profile of the material. This was clearly demonstrated in Allan *et al.* (1980) work in which vacuum dried cellulose resulted in lower heating rates at temperatures below 100°C. This was followed by a rapid absorption of microwaves and heating beyond this. If water was present this profile was not observed with a significantly increased heating rate below 100°C; conducive with significant microwave absorption due to the strongly absorbing moisture.   Nevertheless, pyrolysis was achieved in those circumstances with the formation of char, tar and condensate. Tar was found to contain high levels of levoglucosan, but low levels of other products.   This is conducive with the decomposition and dehydration of cellulose and glucose, respectively.

It is found that little research has been performed on the pure compounds of cellulose, hemi-cellulose and lignin with most investigations undertaking pyrolysis of biomass. Of these previously mentioned studies Miura *et al.* (2001) investigated the pyrolysis of wood block. During this investigation samples of 60 to 300 mm and up to 12 kg were exposed to microwaves in a multi-mode system. From this investigation it was found that char yield was high due to the slow pyrolysis conditions, however upon examination under electron microscope, residual structure of wood block was found to be much cleaner with the mechanism of heating the sample from the internal to the external allowing for the escape of volatile compounds without them undergoing secondary reactions or cracking. This was thought to be as a result of lack of contact with hot surfaces. This displayed a clear

difference over that of a conventional process, in which blockage and condensate was observed on the residual structure of the wood block post pyrolysis. Furthermore, condensate formed during the pyrolysis of wood block was largely found to comprise of lower molecular weight acids, furfural, phenolics and levoglucosan, all being the decomposition products of lignin.

Tea waste and coffee hulls were investigated by Yagmur *et al.* (2008) and Domínguez *et al.* (2007), respectively. In the former, phosphoric acid was used as a pre-treatment and the activated carbons were produced by heating to temperatures from 300°C to 700°C, over a 30 second duration. The results were subsequently compared against 12 hour conventional pyrolysis at 350°C. After microwave exposure it was found that he surface area of 1157 metres square programme could be achieved at a maximum temperature of 350° C, displaying a significant time saving over that of a conventional process.

From the study of coffee hulls it was found when a char was used as a microwave absorber substantial yields of gaseous products could be formed between the temperatures of 500°C and 1000°C. This was compared against conventional pyrolysis in which gas yields were less, char yields were similar and oil yields were less. This suggested that under microwave conditions significant cracking of oils occurred. This was evidenced by substantial increase in the production of hydrogen gas. This is an accepted finding during microwave pyrolysis in which carbon additive is used, thought to be a result of the emission of π-electrons from the surface of the char, cleaving bonds in decomposition products, resulting in the formation of lighter molecular weight species (Lam and Chase, 2012).

Studies have also been published which have utilised the straw from rice and wheat. These were performed by Huang *et al.* (2008) and Budarin *et al.* (2009), respectively. From the microwave pyrolysis of rice straw under single mode conditions it was found that increased microwave power cause increased heating rate and final temperature. As such, the microwave pyrolysis process was described as being predictable. Similar patterns of microwave absorption were observed as those presented by Allan *et al.* (1980), in which water played a significant role in the heating below 100°C. However, in contrast they found that low microwave powers only resulted in drying of the biomass and pyrolysis was not achieved. However, at high microwave powers drying and pyrolysis occurred. From the

pyrolysis products it was found that alkanes, polycyclic aromatic hydrocarbons and phenols were the main components of the oils formed.

Wheat straw was heated under microwave conditions with vacuum but only to temperatures below 200°C. Two fractions of condensate were formed during this process, the first comprising of water and organic acids and the second of levoglucosan as the largest component benzoic furan and phenol (Budarin *et al.*, 2009).

A number of further studies have been performed as previously mentioned but with no significant deviations from the trends produced in the ones mentioned. As such, it is evident that of a small body of work has been performed on a number of selected biomass types. However, limited work has been performed on the pure biomass components of cellulose, hemi-cellulose and lignin. As such, it would seem relatively apparent that a gap in the knowledge is present in the microwave pyrolysis of biomass. Hence, an investigation on a parametric basis would appear logical in investigating the microwave decomposition process and products from cellulose, hemi-cellulose and lignin.

1.6   Aims and Objectives

Many research establishments have explored biological and thermal processes extensively for conversion of biomass to liquid biofuels. From these, it has been established that thermo-chemical route of pyrolysis provides one of the simplest paths for the production of chemicals that can be adapted for use with current liquid fuel based technology. However, the products produced from these processes face significant challenges in their application, as they possess significant undesirable properties, such as, wide product distributions, high oxygen content, high water content, low pH and the presence of significant levels of alkali metals (Babu, 2008, Fatih Demirbas, 2009, Mohan *et al.*, 2006).

As such, it is necessary to establish technologies, which are able to convert biomass through cleaner, more efficient methods to liquid biofuels. Hence, the application of microwave energy poses a potential route for the conversion of biomass, with a number of authors having explored the high temperature microwave pyrolysis of a number of lignocellulosic materials. However, little work has been performed to establish if the conversion of biomass can be achieved through the use of low temperature ($<350^{o}C$), especially on the individual components of cellulose, hemi-cellulose and lignin (Menéndez *et al.*, 2006).

Hence, the work primarily undertaken sets out to explore the effect of low temperature microwave processing on the most basic unit found within biomass; cellulose. As part of this, the work performed sets out to establish the following:

Objective 1:   "Perform Research to compare and contrast different types of biomass, establishing their potential quantities, availability and finally the prospective sources of cellulosic material available within the UK"

Very little is known about the microwave decomposition processes of cellulose. However, a number of pieces of work have demonstrated the key principles of the process and the resulting high value energy products, these being Miura *et al.* (2001) and Budarin *et al.* (2010) to name but two.

Previous research found that cellulose decomposes to a greater extent at temperatures greater than 180°C with larger yields of char and oil, of which both displayed increased calorific values (Budarin et al., 2010).

With this in mind, it is deemed necessary to explore these established effects further. As such, it is necessary to explore and possibly identify the fundamental microwave decomposition process occurring. Hence, the following objectives were established to explore this effect further:

Objective 2:   "Investigate the effect of microwave power exposure on the decomposition process"

Objective 3:   "Investigate the effect of pre-heating temperature on the microwave decomposition process."

Objective 4:   "Investigate the effect of heating rate on the microwave decomposition process"

Objective 5:   "Investigate the effect of microwave final temperature on the decomposition products"

Objective 6:   "Investigate the effect of density on the decomposition process and final products"

From these investigations it is hoped that the correlation between individual parameters and final products can be established, furthering our knowledge of the microwave decomposition process.

Chapter 2: Preliminary Sources Study

Published Work

Budarin, V. L., Shuttleworth, P. S., Dodson, J. R., Hunt, A. J., Lanigan, B., Marriott, R., Milkowski, K. J., Wilson, A. J., Breeden, S. W., Fan, J., Sin, E. H. K. & Clark, J. H. (2011). Use of green chemical technologies in an integrated biorefinery. Energy & Environmental Science, 4, 471-479.

2   Preliminary Biomass Sources Study Review

2.1   Introduction

In order to understand fully the potential of bio-fuels within the UK, an assessment of potential feedstock sources was required. For this, two possible assessments could be undertaken;

- demand driven – an estimation of the competitiveness of bio energy with current conventional sources and/or a target; with a required amount to meet this need given.
- resource focused – a compilation of an inventory of biomass resources based on assumptions over resource availability and competition between markets

(Berndes *et al.*, 2003).

The primary aim of this investigation is to determine the current resources of biomass available within the UK that are non-competitive with food production but not to assess the competition between markets. As such, a resource assessment has been undertaken for biomasses within the UK, ignoring collection/transportation and market forces. To achieve this, a systematic review of the literature was undertaken, identifying data sources that could be used to compile estimates of the current UK biomass potential resources and quantities. Further estimates of the potential energy that could be attained from these were calculated from calorific values collected from academic literature. On this basis the following six major sources of biomass have been identified from academic literature as possible sources of feedstock, these being:

- Virgin Wood
- Energy Crops
- Agricultural Residues
- Wet Food Waste
- Dry Food Waste
- Industrial Waste

(Scott *et al.*, 1985, Maschio *et al.*, 1992, Downing and Graham, 1996, Hague, 1997, McKendry, 2002, Klass, 2004, Bridgwater, 2006, Demirbas, 2008, Field *et al.*, 2008)

2.2 Results

It was found from the study that round softwood provides a large prospective resource for energy production, with 35.89 TWh/Yr potentially available at a cost significantly lower than any other wood source at £1.22 per GJ. With its high calorific value of 19,600kJ/Kg (Demirbaş, 1997), the round softwood gives one of the greatest quantities of energy per kilo of all biomass sources studied, making it a potentially good source of bio-fuel for electrical power stations and/or communal heating systems. The density of the material also makes it attractive for storage and transportation.

Wood chip and pellets appear to be the least economically viable at £6.39 per GJ but provides the second largest available resource of energy after round softwood in the virgin wood group. This may prove a potential source of energy for the domestic market, but is unlikely to be used as an industrial source for the production of bio-fuel.

However, both sources of wood based biomass lend themselves in particular to a pyrolysis based conversion to bio-oils, as the largely lignocellulosic nature of wood lends itself to be converted to a significantly aromatic rich oil. Nevertheless, this process still has significant limitations as outlined in section 1.3.2.4.

Comparison of agricultural residues was also performed, looking at both arable and livestock farming. The results of this identified a number of potential sources, two of which displayed a high calorific yield, these being straw and poultry litter.

Of the straw types, wheat straw presented itself as an interesting source of biomass. With it being a co-product of food production, its current usage is little when compared with other types of straw, which are be used as cattle fodder or bedding. Further to this, the high volumes of wheat straw produced on an annual basis are a potentially substantial resource on the UK biomass market. However, a number of disadvantages present themselves, being related to its density. This has the net result of increasing the cost of transportation.

Poultry litter is a readily available source of carbonaceous matter which is easily collected and transported. It has a high calorific value when dry, with a low cost of £0.74 per GJ giving it great potential as a possible source of energy (Biomass Energy Centre, 2013).

The potential energy derived from straws and poultry litter alone, is equal to the generation of 27.73 TWh/year of electricity.

However, four biomass sources stand out as providing the greatest potential of energy; paper waste (49 TWh/year), sugar crops (45 TWh/year), round softwood (36 TWh/year) and starch crops (33 TWh/year). This could possibly provide ~7% of the total energy demand in the UK from 2011 (Department of Energy & Climate Change, 2012).

Nevertheless, with the focus of the research being performed in this study, the two sources of largely cellulosic biomass, paper waste and straws (14TWh/year); make up a potential 63TWh/year of energy. If this were to be converted to liquid bio fuels of the same calorific value it has the potential to provide ~10% of energy required the transportation sector (Department of Energy & Climate Change, 2012). As such, it would seem logical to look at cellulose first in any conversion process to establish its potential conversion.

Chapter 3:

Thermal Degradation

3   Conventional Thermal Decomposition

In order to determine the characteristics of the cellulose used and provide a comparative baseline for microwave experiments, it was necessary to investigate its thermal decomposition behaviour.
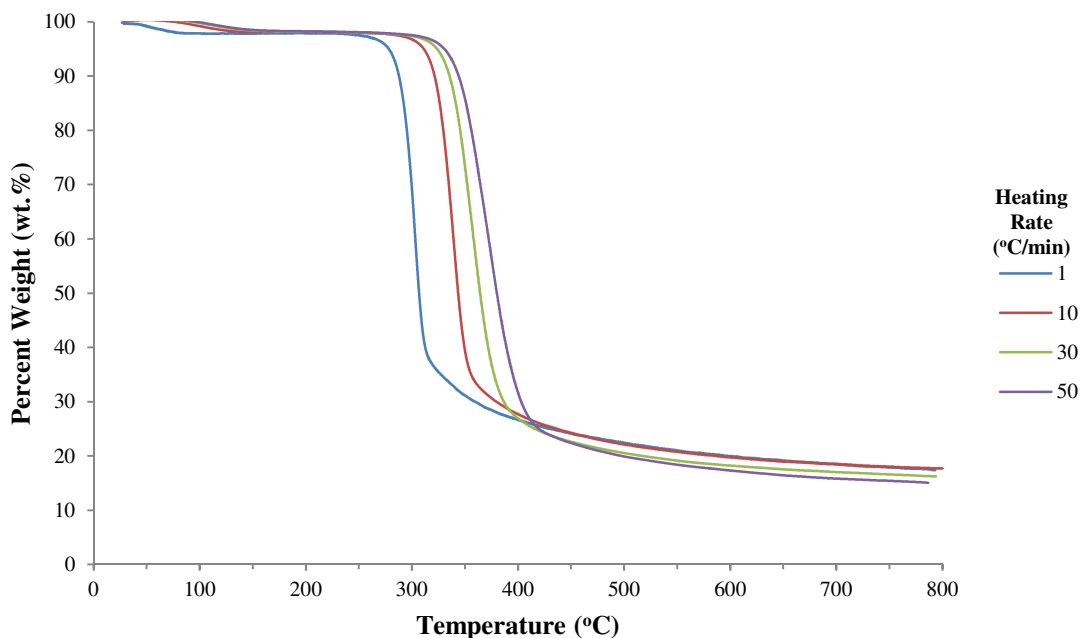
Figure 3-1   Thermal degradation of cellulose at 1, 10, 30 and 50°C/min to 800°C
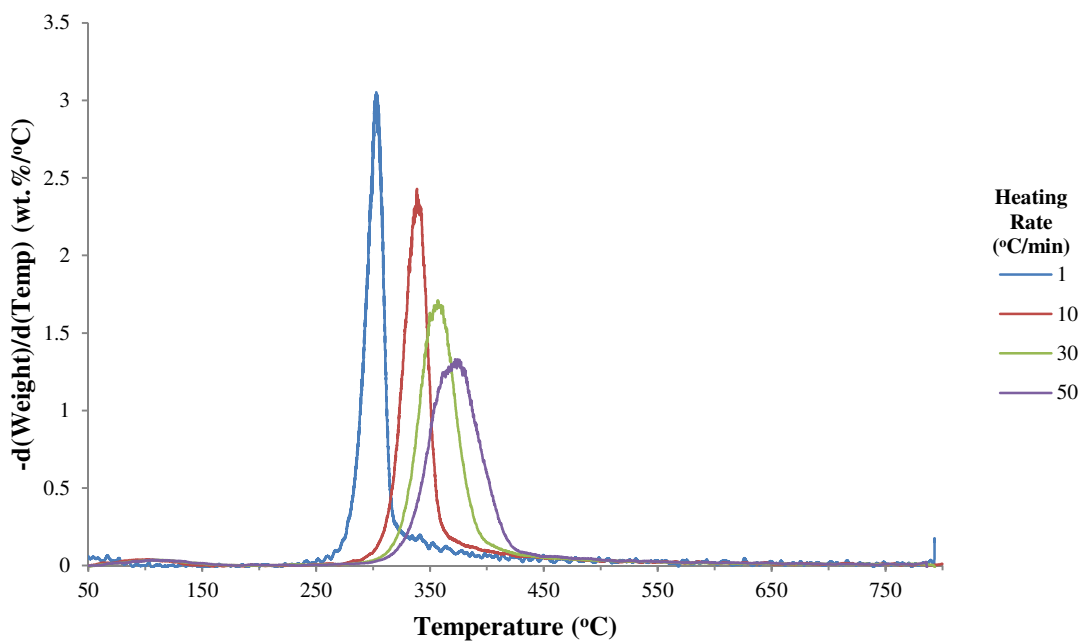
Figure 3-2   Differential Thermal Gravimetric (DTG) Analysis of cellulose at 1, 10, 30 and 50°C/min to 800°C

To determine this, cellulose was first tested for its thermal decomposition behaviour by thermal gravimetric analysis (TGA) at heating rates of 1,10,30 and 50°C/min to a maximum temperature of 800°C, the results of which are shown in Figure 3-1and Figure 3-2. From Figure 3-1 it is observed that cellulose decomposition takes place over a single decomposition step in which up to ~75wt.% of cellulose can be lost at heating rates of 30°C/min and above. However, at heating rates lower than this it is observed that less mass is lost over this first initial step, with a second phase of gradual decomposition continuing to 800°C, whereby ~17.4wt.% remains at 1 and 10°C/min, with 16.3 and 15.1wt.% remaining for 30 and 50°C/min, respectively. It was further determined by oven drying to constant weight that 5.0wt.% of the microcrystalline cellulose corresponded to free water.

The variation in residual weight is also reflected in the initiation of cellulose decomposition, with this occurring at 274, 305, 322 and 326°C for the heating rates of 1, 10, 30 and 50°C/min respectively. Alongside this, it is also observed from Figure 3-2 that over all heating rates the DTG curves were symmetric with greatest mass loss occurring at 302, 338, 356 and 371°C for the heating rates of 1, 10, 30 and 50°C, respectively. This was also accompanied by a decrease in peak height and broadening of peak half-height width with increasing heating rate.

These changes in DTG peak shape and position are consistent with those observed by Lin *et al.* (2009), which were attributed to thermal lag within the instrument. Changes in pyrolysis residue with heating rate also imply a change in the pyrolysis chemistry, which is in agreement with Várhegyi *et al.* (1997) and Lin *et al.* (2009), however, the solid phase decomposition pathway of cellulose is still poorly understood. It is theorised by Mok *et al.* (1992) that char formation occurs only as a result of solid/vapour interactions, hence experiments which favour greater contact times between evolved pyrolysis vapours and solid result in greater char yields. It has also been proposed that the formation of char is as a result of competitive degradation mechanisms, whereby depolymerisation reactions form no char and yet dehydration reactions favour char formation (Broido and Nelson, 1975); as illustrated in Figure 1-4. It can be concluded that high temperatures and high heating rates favour the formation of hydroxyacetaldehyde, with less char and low temperatures and low heating rates favour the formation of levoglucosan and bio-char (Wooten *et al.*, 2003).

The phase transition temperature of cellulose is important in the microwave decomposition process, as previously determined by Budarin *et al.* (2010). As such, the thermal properties of the microcrystalline cellulose were determined by Modulated Differential Scanning Calorimetry (MDSC). This testing was conducted by Dr Peter Shuttleworth of the Green Chemistry Centre of Excellence, University of York by DSC Q2000, TA instruments; see Figure 3-3.
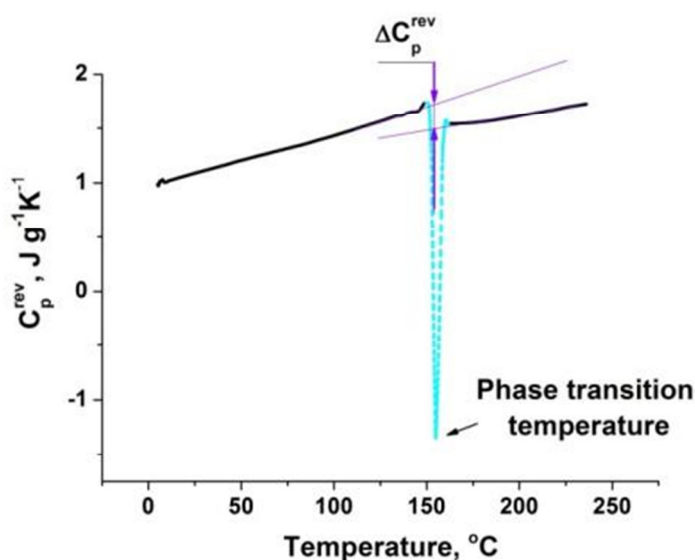
Figure 3-3   MDSC Reverse Heat Capacity Traces for unprocessed Microcrystalline Cellulose.

The use of MDSC was employed so that the structural changes of crystallisation and melting could be determined. The technique offers increased sensitivity over that of conventional Differential Scanning Calorimetry (DSC) (Gill *et al.*, 1993, Reading *et al.*, 1994). Like DSC, MDSC determines phase changes by measuring the difference in heat flow between a sample and a reference, quantifying endothermic and exothermic events from this. MDSC modulates the heating rate the sample is exposed to allowing for the simultaneous detection of both endothermic and exothermic events. This is subsequently mathematically corrected so that reversing and non reversing heat flows can be derived. (Boller *et al.*, 1995, Simon, 2001).

From the MDSC trace, it was possible to determine the phase transition temperature (T_{phase}) and the reverse heat capacity (ΔC_p^{rev}). The MDSC shows the reverse heat flow trace, which does not directly show the phase transition temperature, but rather the change from a

metastable to the thermodynamically stable crystalline state, hence the reverse heat flow. This is the reverse phase transition.

Further tests were performed on samples that had undergone heating to temperatures between 120 and 200°C for 5 minutes, then allowed to cool to room temperature; see Figure 3-4.
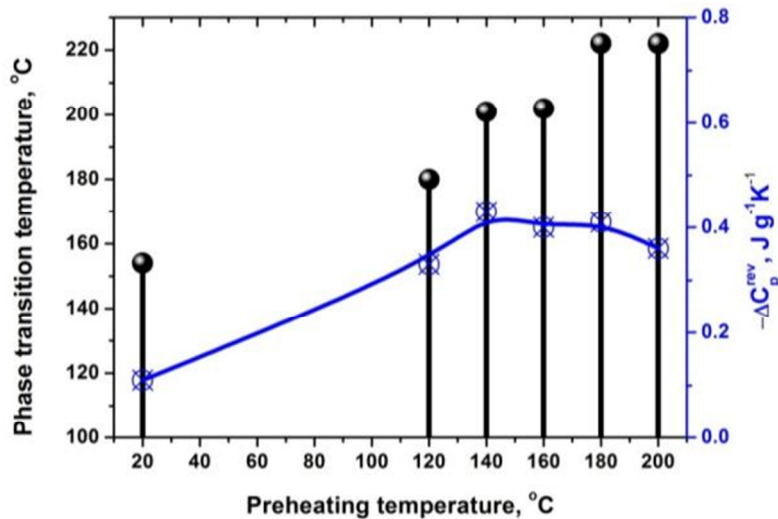
Figure 3-4   Influence of conventional preheating temperature on the phase transition characteristic of cellulose.

From the results it was found that with no pre-heating the microcrystalline cellulose underwent its phase transition temperature at ~160°C. This is lower than expected from the results of Budarin *et al.* (2010) by 20°C, but is consistent with the results of Szcześniak *et al.* (2008), which indicate that a higher degree of crystalinity with moisture present, rapidly translates into a reduction in phase transition temperature.

Nevertheless, it can be observed that the phase transition temperature of cellulose increases to ~180, ~200 and ~220°C for the pre-heating temperatures of 120, 140 and 180°C, respectively. This is most likely to result in pre-heating at significantly elevated temperatures removing free and freezing-bound water from the cellulose structure, pushing the phase transition temperature up (Hancock and Zografi, 1994), with the added effect of reducing cellulose dielectric properties. It is noted that the $-\Delta C_p^{rev}$ of cellulose shows little variation, signifying that pre–heating conventionally does not cause significant changes to

the crystalline/amorphous ratio, hence giving more evidence to support the hypothesis that water content is causing the shift in phase transition temperature. This is supported by Roig *et al.* (2011), whom hypothesised that the increase in water content interfered with existing hydrogen bonds between polymer chains, increasing the free volume between polymers and reducing the hindrance of local chain mobility.

Since cellulose is pre-heated to a given temperature and then microwaved without any cooling taking place, this should have littel effect on the pyrolysis process as the removal of this water would occur during the microwave heating itself.

Chapter 4:

The Small Scale Microwave Induced Decomposition of Microcrystalline Cellulose

Conference Posters

BITs 1ˢᵗ World Congress of Bioenergy - "The Microwave Biorefinery", April 2011, Dalian, China

NORSC– "Transportation fules from biomass: Microwave pyrolysis of cellulose", October 2010, York, UK

BIOTEN – "Microwave pyrolysis of the structural components of biomass", September 2010, Birmingham, UK

4 The Small Scale Microwave Induced Decomposition of Microcrystalline Cellulose

4.1 Introduction

Diversification away from fossil fuels and the search for new sources of chemicals, has led to significant interest in thermo-chemical conversion of biomass (Bridgwater and Cottam, 1992). Of these technologies, pyrolysis has received a great deal of interest, with the potential yields of liquid and gaseous fuels making it an attractive route for production of bio-fuels which can be easily transported and used with current technology (Czernik and Bridgwater, 2004, Demirbas, 2007).

The technical challenge of understanding and developing conventional pyrolysis based bio-fuels, has been largely based on the basic principles, with products being controlled to the greatest extent by manipulating reaction conditions such as heating rate, maximum temperatures and product residence times (Lin *et al.*, 2009).

However, this is but half the challenge with the composition of biomass playing a significant role in the products formed. Hence, with cellulose forming the most abundant component of plant derived biomass (generally 50% dry weight (Antal and Varhegyi, 1995)), it is necessary to understand its behaviour under pyrolysis conditions for developing efficient technologies in its conversion to bio-fuels and chemical feedstocks. As such, the microwave pyrolysis of cellulose has been investigated on a parametric basis.

4.2 Temperature Measurement

In past studies, it has been observed that specific microwave effects occur giving advantages over that of a thermal process; these include rate accelerations, altered product distributions and/or change in material properties. (Durka *et al.*, 2010, Herrero *et al.*, 2007, Kappe, 2013). As such, in distinguishing these from thermal/kinetic effects or that of experimental inaccuracy, it is necessary to measure sample temperature to a high degree of precision. However, temperature measurement during a microwave process is inherently difficult owing to the unique properties of microwaves and the effect of dielectric heating (Kappe *et al.*, 2013).

Hence, it is important to consider the technologies employed in temperature measurement and their method of application in a microwave investigation. Of these methods three major types of measurement have been applied in previous studies; thermocouples, fibre optic thermometers and infrared pyrometers (Pert *et al.*, 2001).

Thermocouples are not appropriate for use in microwave chambers due to their construction utilising metal. The first most obvious problem that arises from a thermocouples use is that of induction (Kappe, 2013, Pert *et al.*, 2001). Induction of current within the metallic element of the thermocouple results in false high temperature readings, but also the potential for electrostatic discharges (Pert et al., 2001). Further to this, the metallic component results in distortion of the electromagnetic field, often resulting in the concentration of the field around the tip of the thermocouple (see Figure 4-1). This can result in increased deposition of microwave energy. Therefore, the use of thermocouples is not advisable in microwave experimentation.
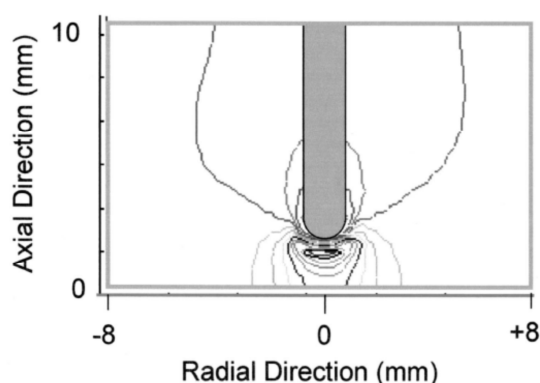
Figure 4-1   Distortion of electric field lines within a microwave field by a thermocouple (Pert *et al.*, 2001)

Fibre optic thermometers are the most widely accepted and utilised technique in the microwave synthesis community (Herrero *et al.*, 2007, Pert *et al.*, 2001). Their direct contact with the material undergoing investigation makes the measurement accurate, assuming the reaction media is well stirred and no thermal gradients are permitted to form. However, when used in a solid phase reaction they become limited in their use, as thermal gradients form due to hot spotting within the sample can be seen. Hence, multiple monitoring points are required to ascertain a representative temperature (Herrero *et al.*, 2007). Further problems arise from the use of aggressive reactants or formation of reactive species (Kappe

et al., 2013). This renders fibre optic thermometres of limited use in microwave pyrolysis experimentation.

The final method of temperature measurement is by infrared pyrometer. This relies on the measurement of infrared radiation emitted from the surface under observation. The inference of sample temperature by this method is limited by the temperature of the surface being monitored, hence in the application of a microwave reactor it is necessary to determine the relationship between external surface temperature of a reactor and actual temperature of the sample (Kappe *et al.*, 2013).

It is important to note that upon increasing reactor size thermal gradients can become significantly greater within the sample and external temperature measurement becomes limited (Fernández *et al.*, 2011). Hence, in all circumstances extensive efforts must be made to ascertain the relationship between sample temperature and external temperature prior to using this method. Due to the microwaves used in this experimentation utilising infrared pyrometers, calibrations were performed.

4.2.1   Calibration of CEM Microwave System

The CEM microwave system is the standard system that was used in the initial investigation of the microwave decomposition of cellulose. As such, it was necessary to ascertain the temperature of the microwave reactor and the sample contained within, so that the microwave temperature could be both measured and controlled, accurately through the feedback loop with the IR sensor; similar to that of the process described by Kappe (2013).

The methodology used to achieve this was as follows:
1.) 5mL ± 0.01mL of ethylene glycol was placed in the microwave reactor
2.) The test tube was heated to the desired temperature by the pre-heating block
3.) The test tube was inserted in to the microwave.
4.) A thermocouple was then inserted into the test tube.
5.) Readings were recorded at 10 second intervals simultaneously from the microwave IR sensor and the thermocouple.
6.) Readings were plotted on an XY scatter graph and results compared
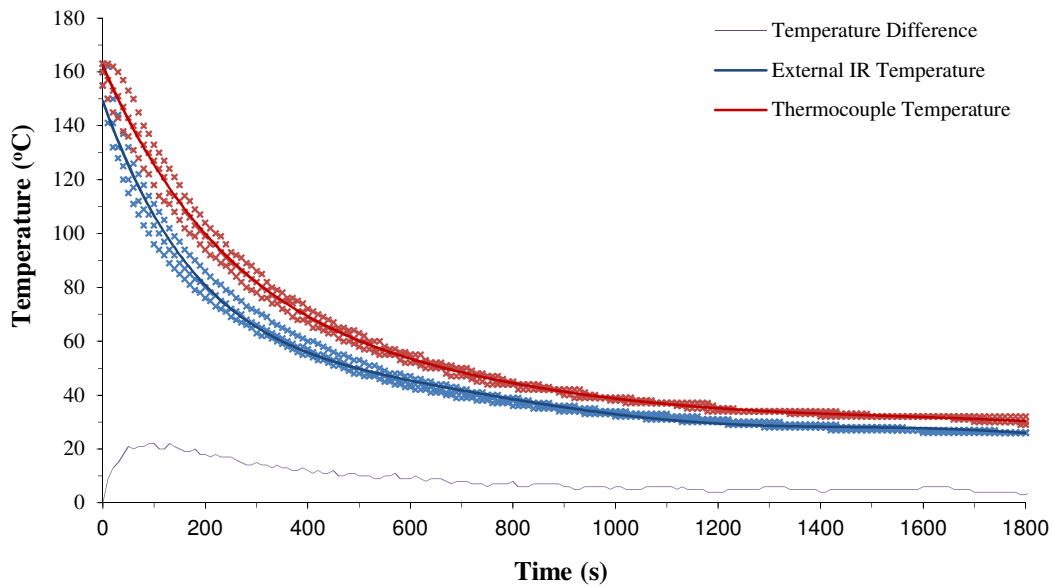
Figure 4-2   Comparison of readings from Microwave IR and Thermocouple

After analysis of the results, it was found that the mean temperature difference between the two temperature readings came to 7.9°C, with a standard deviation of 5.3. This indicates that the IR sensors readings were significantly different to that of the actual temperature. As such, the microwave IR sensor was recalibrated at higher temperatures, using a silicone oil sample, which had been heated to 250°C. The reliability of the temperature readings have been seen to be accurate for the higher temperatures used, although it is expected to be less accurate for the lower end of the scale. This is as a result of the CEM microwave allowing for a single point calibration method only (Kappe *et al.*, 2013).

4.3   Microwave Processing of Cellulose

The dielectric properties of cellulose were initially examined by Stoops (1934), whereby he examined as part of his work the dielectric response of cellulose acetate and cellophane in relation to temperature (-50 – 100°C) and frequency (0 – 1MHz); see Figure 4-3.
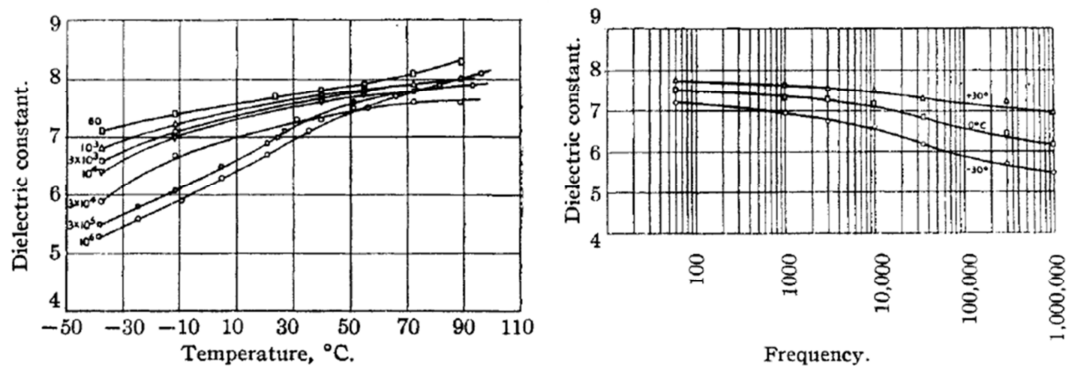
Figure 4-3   Dielectric constant of cellophane under differing temperatures and frequencies as determined by Stoops (1934)

From this, Stoops (1934) was able to determine that cellulose did possess dielectric properties, and surmised they were most likely as a result of the –OH groups. The paper further suspected that each glucose molecule in the chain was free to move about the suspected –O– bond that held them together and that due to this, the dielectric constant would increase with greater temperature.

This has subsequently been examined by a number of authors Budarin *et al.* (2010), Ishida *et al.* (1959), Khan and Pilpel (1987), Montès and Cavaillé (1999) and Rachocki *et al.* (2005) to name but a few and the dielectric properties of cellulose proven to be as originally suspected. However, it was found that the dielectric properties of cellulose are also dependent upon moisture content, with significant changes occurring when water is not present. This was demonstrated clearly in the work of Ollivon *et al.* (1988), whereby the dielectric behaviour and heating of cellulose was examined with no moisture and 6wt.% moisture, the results of which are demonstrated in Figure 4-4.
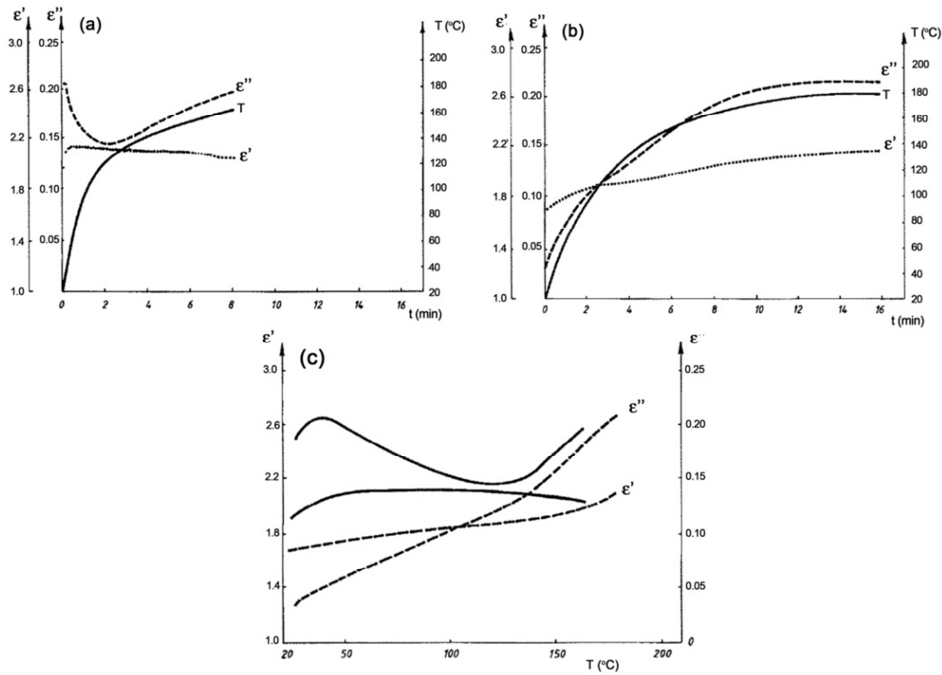
Figure 4-4 **Changes in dielectric constant (ε') and loss factor (ε'') with temperature when 6wt.% moisture (a) and no moisture is present (b) and comparison of their dielectric properties (c) (unbroken line = with 6% moisture, broken line = no moisture) under for a 12mg sample under 2450MHz 6W (as taken from Ollivon _et al._ (1988))**

From this (Figure 4-4) it can be seen that when moisture is present, three stages of dielectric change occur:

1. The sample is heated with no moisture being lost until approximately 110°C, during which the dielectric constant increases to a plateau which finishes at 100°C, then decreases; whereas the dielectric loss factor increases to 40°C then progressively decreases to 110°C.

2. The removal of water occurs after 110°C and an increase in dielectric loss factor occurs.

3. The completely dried sample continues to heat whilst a continual increase in dielectric loss factor persists.

(Ollivon _et al._, 1988)

However, when a dried sample is irradiated it is found to experience continual increases in both dielectric constant and dielectric loss factor, as temperature increases to a maximum of 180°C. The major difference that occurs as a result of the presence of moisture, is a reduction in the time required for a cellulose sample to reach a given temperature below 100°C; as seen from the top two graphs in Figure 4-4.

An important aspect of these experiments was the determination of moisture at 6wt.% has not left the sample until in excess of 100°C. This is thought most likely due to the interaction of hydroxyl groups and water through varying degrees of hydrogen bonding (see Figure 4-5), with the resulting progressive breakage through increasing temperatures. This most likely effected the dielectric properties of the cellulose due to the rotation of hydroxyl groups being restricted, potentially resulting in the increased loss factor (Ollivon *et al.*, 1988).
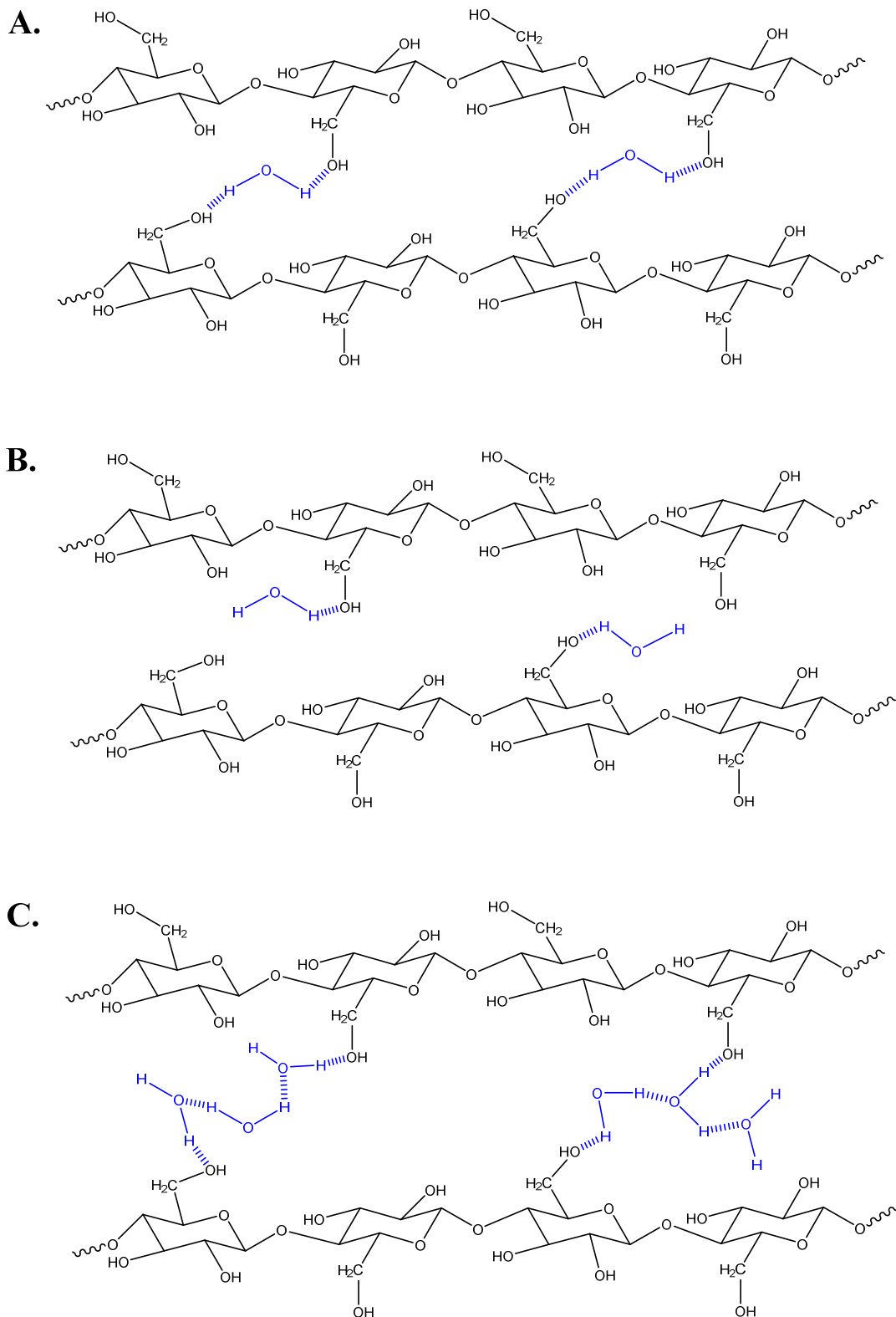
Figure 4-5 **Hydrogen bonding of hydroxyl groups and water between cellulose chains a.) double hydrogen bonded water b.) single hydrogen bonded water c.) multi layer hydrogen bonding between water molecules and cellulose (from Khan and Pilpel (1987))**

Nevertheless, the investigation of utilising dielectric heating to decompose cellulose in a pyrolytic process have not been investigated in a parametric fashion. The last significant attempt made to do this was by Allan *et al.* (1980), however, limitations in technology used have left significant gaps in the understanding of the interactions and resultant products formed in the microwave pyrolysis process. Initial attempts have been made by Budarin *et al.* (2010), but require further examination to build a fundamental understanding of the cellulose microwave pyrolysis process.

Hence, the following investigations have been designed to establish the effects of:
- Microwave Power
- Microwave Time
- Maximum Temperature
- Sample Pre-Heating
- Sample Density

These are presented herein.

4.3.1   Power and Duration

4.3.1.1   Thermal Profiles

The response of cellulose to microwave radiation was investigated through the method outlined in Section 9.2.3. During this, microwave powers of between 50 and 300W were investigated, over durations of 0-60 seconds. The moisture content of cellulose was found to be approximately 5wt.%, hence, throughout this section of experimentation the moisture content was maintained at this value. This moisture was not removed as it assisted in maintaining a higher dielectric loss factor for cellulose during the low temperature region (0-110$^{\mathrm{o}}$C) of the decomposition; as discussed by Allan *et al.* (1980) and Ollivon *et al.* (1988). After this temperature range had been exceeded, the dielectric response of cellulose was such that the polymer heated readily; increasing in its response as temperature increased.

This is an important consideration of any microwave investigation and requires the understanding of the model proposed by Hill and Marchant (1996), whereby the response of any material can be described by the change in microwave power, sample temperature and

the multi-valued changes in its dielectric response. This leads to the generic model as shown in Figure 4-6.
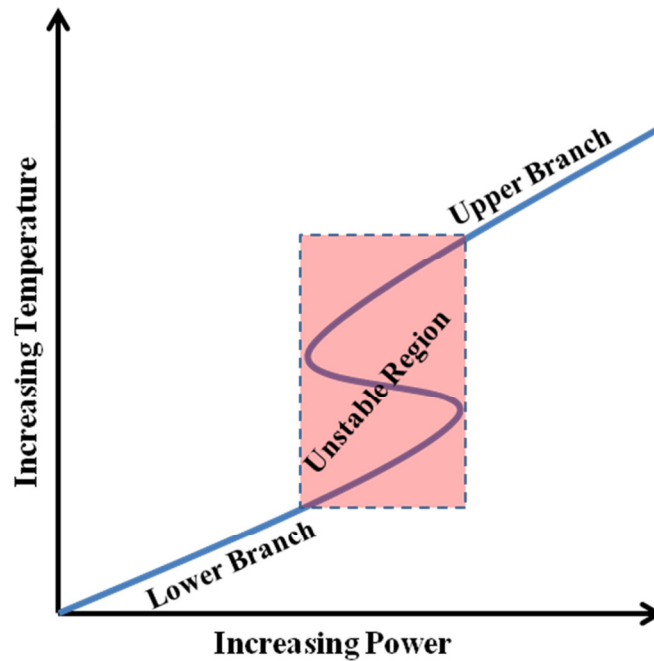
Figure 4-6   Generic model of the relationship between microwave power and sample temperature (adapted from Hill and Marchant (1996))

From this model, it can be seen that the extent a sample will heat under microwave radiation is largely dependent on the branch of the curve that the sample conditions fall within. Steady state conditions being achieved on either the upper or lower branch; whereby thermal losses are equal to energy input/conversion.

However, if the temperature of the sample enters the unstable region in which dielectric properties of the sample changes it is possible for the sample under irradiation to jump from one branch to another.

As such, when we examine the thermal profiles attained from the microwave irradiation of cellulose (see Figure 4-7), we can see the relationship between microwave power and changes in dielectrics occurring. This is most evident from the shape of each thermal profile and the heating rates derived from it (see Figure 4-8).
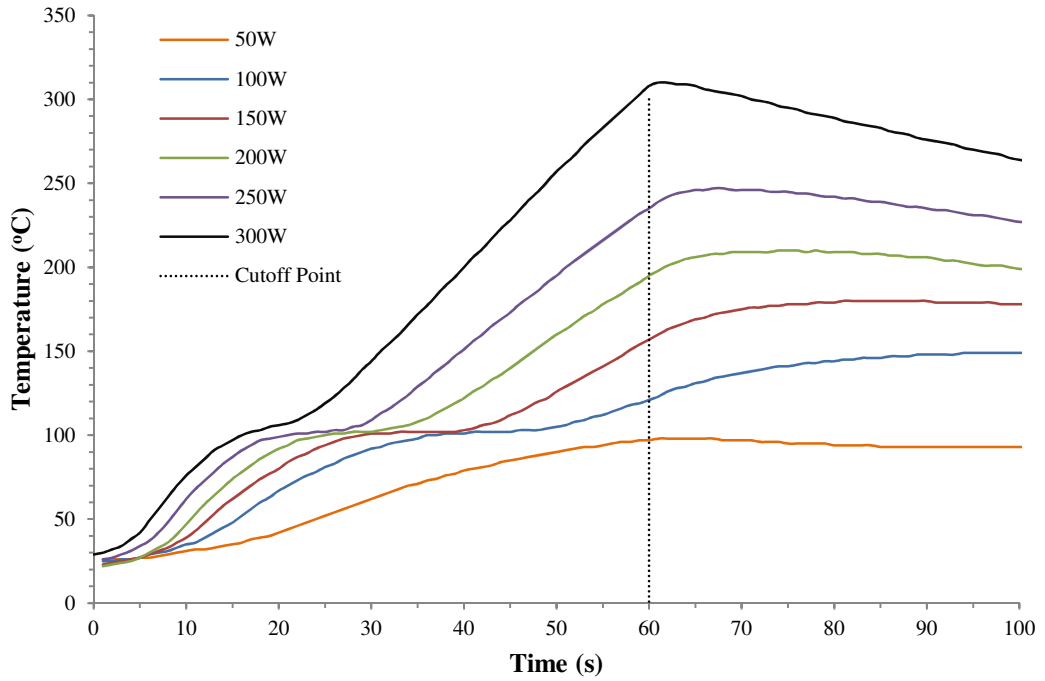
Figure 4-7   Thermal profiles of cellulose under microwave irradiation of 100-300W for a duration of 60 seconds
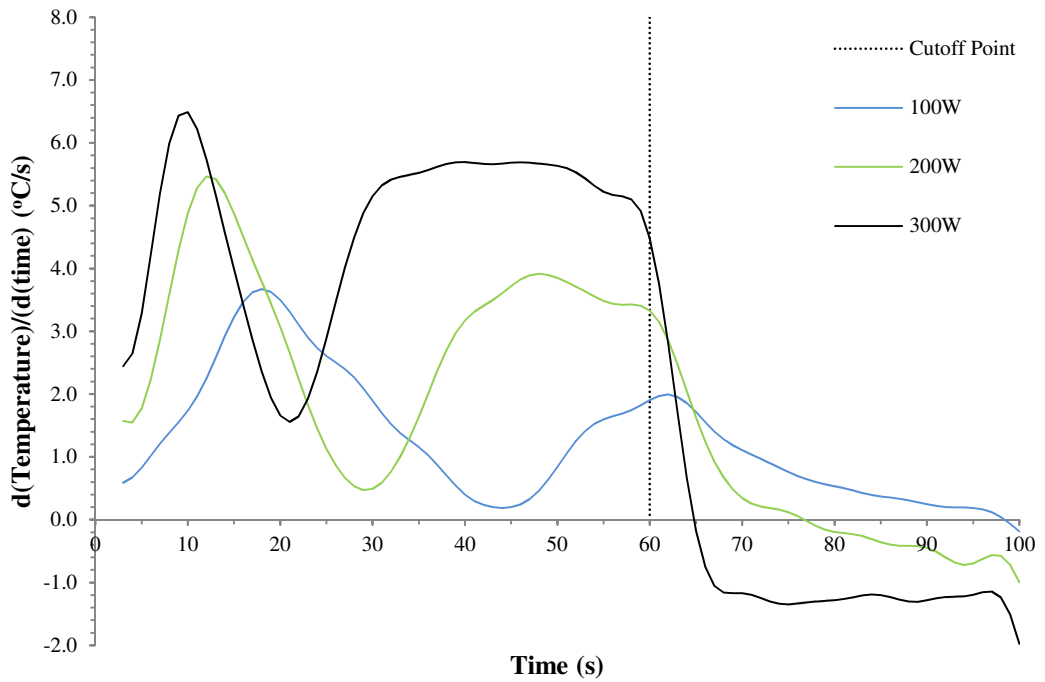
Figure 4-8   Heat rates of cellulose under microwave irradiation of 100, 200 and 300W for a duration of 60 seconds

The initial rapid heating of the sample between the temperatures of 0 and 100°C relates to the conductive heating provided by water molecules to the cellulose, with the water content giving a dielectric response up to 200% greater than that of dry cellulose (Allan *et al.*, 1980). This was recognised by Metaxas and Driscoll (1974), whereby the dielectric loss factor of cellulose was observed to increase as a function of moisture content. This is reflected in peak heating rates (see Table 4-1) of 420°C/min at 300W reducing to 120°C/min at 50W during this first phase.

Table 4-1   Peak heating rates observed between the temperatures of 0-100°C during microwave irradiation between 50-300W

Microwave Power	Peak Heating Rate (^{o}C/min)
50	120
100	228
150	300
200	348
250	414
300	420

This is further supported by work performed by Budarin *et al.* (2011a) (see Figure 4-9), where significant portions of water were detected alongside organic acids whilst cellulose underwent microwave pyrolysis.
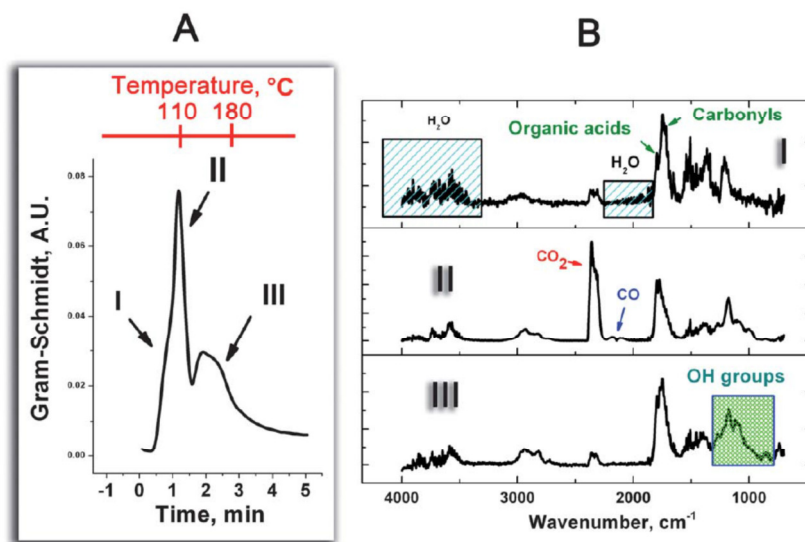
Figure 4-9   In situ FT-IR analysis of volatiles produced during the microwave decomposition of cellulose (from Budarin *et al.* (2011a))

When examined in terms of average heating rate from ambient temperature to $100^{o}C$, a more complex relationship appears with microwave power; see Figure 4-10.

$$y = 85.33\ln(x) - 264.39$$
$$R^2 = 0.9948$$
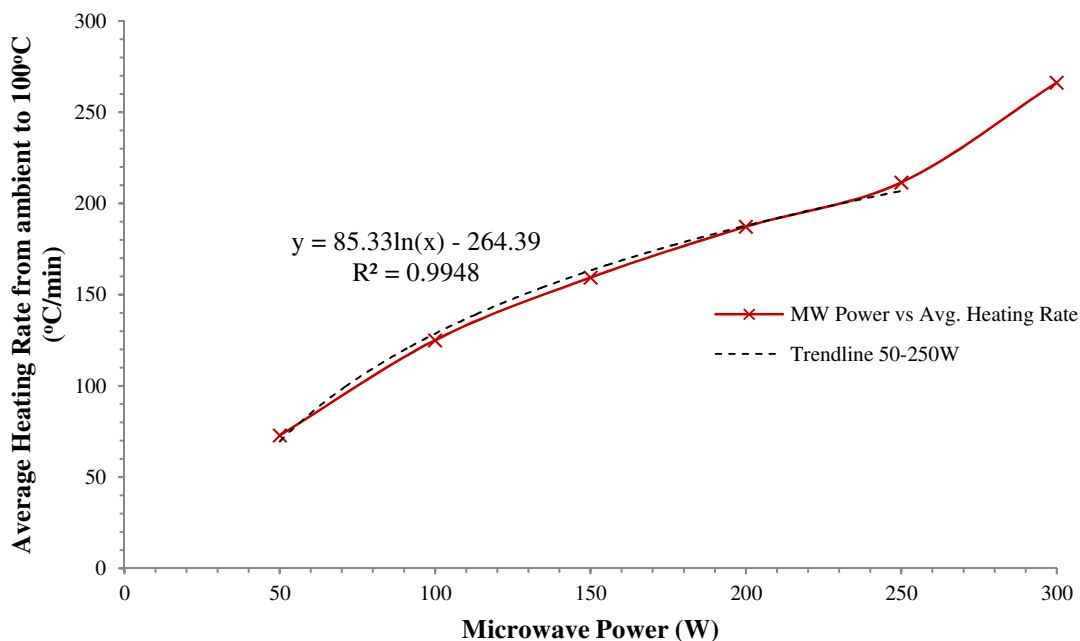
Figure 4-10   Average heating rate from ambient temperature to $100^{o}C$ when cellulose is exposed to 50-300W at 50W intervals

At microwave powers of 50-250W, a logarithmic trend appears between microwave power and average heating rate to 100°C. However, when 300W is used a significant shift in response occurs with an unexpected increase in heating rate. This is also accompanied by a much reduced plateau within its thermal profile at 100°C (see Figure 4-7). The precise reason for this occurrence is unknown but may be as a result of uneven heating patterns or the rate of heating being sufficient that portions of cellulose are able to achieve such temperatures on a local scale that they become microwave responsive, adding to the overall absorption of microwave energy.

For 300W experiments it is also possible that the rapid heating of cellulose, affects the degree of crystallinity, opening new areas (amorphous structure) for high frequency interaction with the electromagnetic field. This can also be accompanied by a significant proportion of chemical dehydration, with diffusion of moisture being sufficiently slow that both the additional water content adds to the ability of the sample to absorb microwave energy (Allan *et al.*, 1980), acting as a 'molecular radiator' (Kappe, 2004). Nevertheless, the precise reason for this anomaly cannot be directly measured due to limitations of instrument use within a microwave field.

For 50-250W experiments (Figure 4-7), after heating to 100°C a plateau forms with the apparent duration corresponding to the input of microwave power. The plateau duration decreases with greater power input. However, at a power of 50W the sample is not seen to progress past this stage, with minimal temperature increases recorded. This is most likely due to the loss of the microwave responsive water and insufficient energy being applied to the less responsive cellulose to enable the sample to heat further; the thermal losses from the reactor equalling the rate at which microwave energy can be absorbed by cellulose. This follows the model proposed in Figure 4-6, whereby steady state conditions are achieved falling on the lower branch. This is further seen in Figure 4-10, as the sample is microwaved for a further 60 seconds and little increase in temperature occurs.
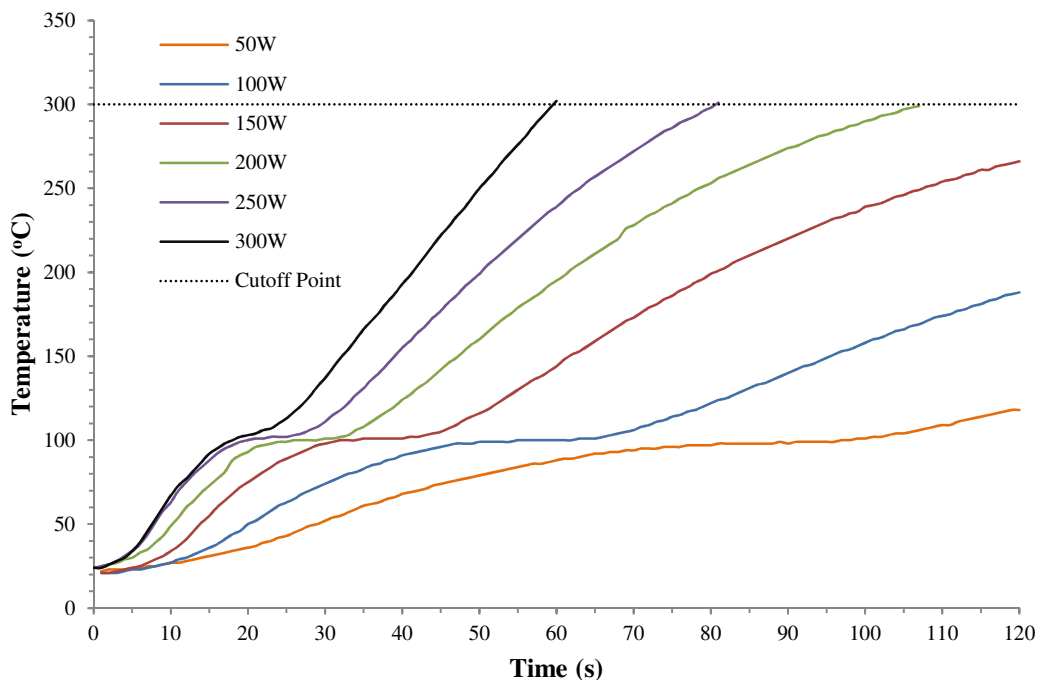
Figure 4-11   Thermal profiles of cellulose under microwave irradiation of 100-300W for a duration of 120 seconds

When microwave exposure durations are extended (see Figure 4-11) it is found that the microwave power of 50W is not as previously suggested, with sufficient energy input to heat the cellulose in excess of 120°C, nevertheless, the thermal profile does suggest that there is insufficient power to attain a temperature significantly greater than 120°C , with a plateau in temperature forming. This pattern is also observed for powers up to and including 150W, whereby the thermal profile indicates that a plateau in temperature will be reached. This follows the trend outlined in Figure 4-6, whereby steady state conditions occur as thermal losses equal absorbed microwave energy.

This is also evident from the profiles of 200 and 250W, however, cannot be inferred as dielectric changes in excess of 300°C may occur. A resulting greater dielectric response and further heating of the residual structure may arise with thermal runaway taking place, with the samples dielectrics increasing further on the upper branch of Figure 4-6. Nevertheless, this cannot be explored, due to limitations of the microwave technology used only being capable of withstanding temperatures of up to 300°C.

4.3.1.2 Mass Balances

The yields of solid, oil and gas for microwave decompositions are presented in Figure 4-12 to Figure 4-15. From these experiments it was found that from the microwave exposure of cellulose it was possible to achieve up to 66wt.% decomposition, yielding a maximum of 44.8wt.% oil and 26.5wt.% gas, under optimal conditions for each component.

When we examine the solid yields in Figure 4-12, it is possible to observe the removal of 5wt.% for all microwave powers relating to that of moisture content. This correlates well with the thermal profiles presented in Figure 4-7, whereby the change in dielectric corresponds to the timings of this mass loss. Nevertheless, the removal of the water is highly dependent upon the power input, with 50W taking a full 60 seconds to achieve this and 300W requiring approximately 15 seconds. This does demonstrate that the lower application of power resulted in improved efficiency of removal with a total of 3000J as compared to 4500J for the removal of 0.1g water. The inference of this decreased efficiency in the removal of water, may further indicate that at 300W the simultaneous decomposition of cellulose and heating of water molecules occurs.
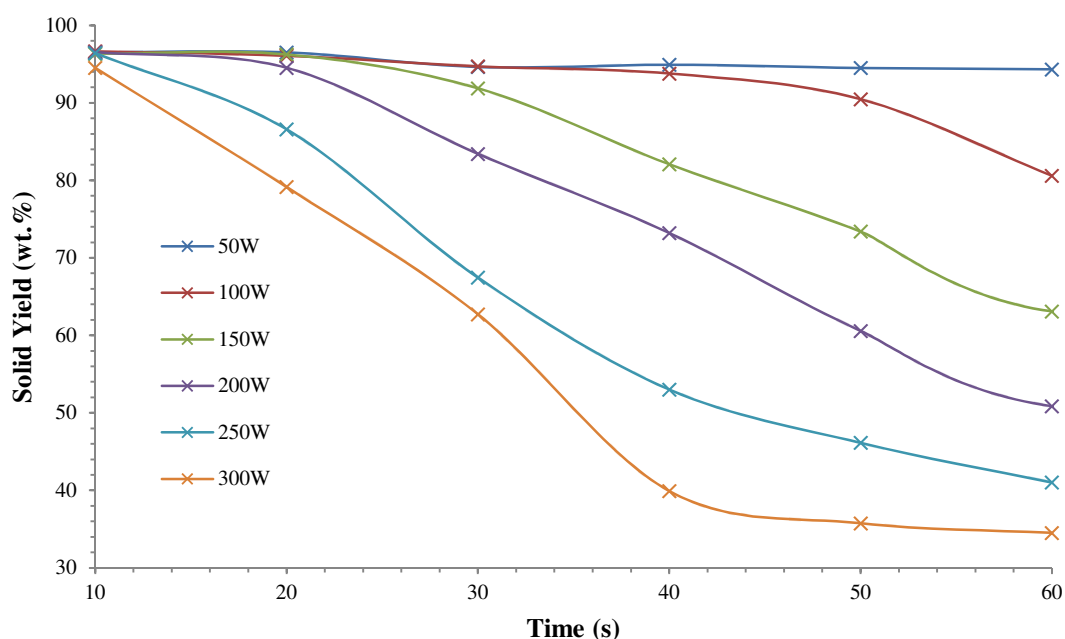
Figure 4-12   Solid yield for microwave durations of 10-60 seconds and microwave powers of 50-300W
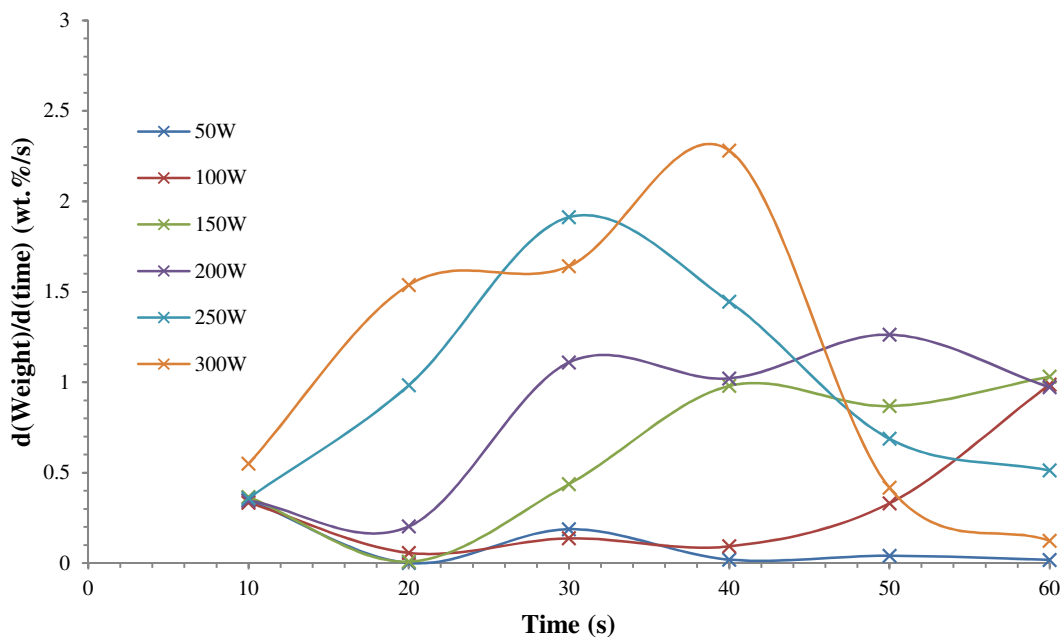
Figure 4-13   Rate of solid mass loss for the microwave powers of 50-300W

The continual decrease in sample mass is observed for each power (see Figure 4-12) with increasing microwave exposure. The slowest rate is reflected by the lowest power and the greatest rate with the highest power. Based on other power inputs, all decomposition rates fall within these in ascending order. This is further reflected in Figure 4-13, whereby the rates of decomposition are represented as wt.%/s.

However, from Figure 4-13 it is possible to observe that the rate of decomposition is maintained at the greatest rate for the longest duration for the microwave power of 300W. Whereas at 250W a maxima is seen at 30 seconds with rates diminishing to 60 seconds, indicating that the decomposition takes place over a greater period of time but at a reduced rate. This is also reflected to a similar extent in the decomposition achieved as seen in Figure 4-12.

Nevertheless, when compared with the heating rates as presented in Figure 4-7 and Figure 4-11, it appears that a differing mechanism is occurring in the decomposition, with no decrease in the rate of heating for 300W experiments. Whereas, a gradual diminishing rate is observed for less than or equal to 250W experiments.

As mass loss is almost constant by 50 seconds for 300W, it would indicate that the dielectric of the residual material is high, with the potential for thermal runaway to occur. This is likely due to the charring of the residual cellulose and the formation of the highly dielectrically responsive polyaromatic structure. This is conducive with the results observed in Figure 4-14 and Figure 4-15 whereby it is evident that the further breakdown or carbonisation of bio-oils occurs between 50-60 seconds microwave duration. With this a further elimination of approximately 1.2wt.% of mass from the solid and a reduction of approximately 5.8wt.% bio-oil, resulting in an increase in approximately 7.0wt.% gas.

For samples at 200 and 150W a plateau in mass loss was formed (see Figure 4-13) from 40-60 seconds and 30-60 seconds for 150 and 200W, respectively, showing no sign of decomposition rates diminishing. However, at 100W the rate of decomposition is seen to climb from 50 to 60 seconds, indicating that sufficient temperature has been attained for the decomposition of cellulose to occur.
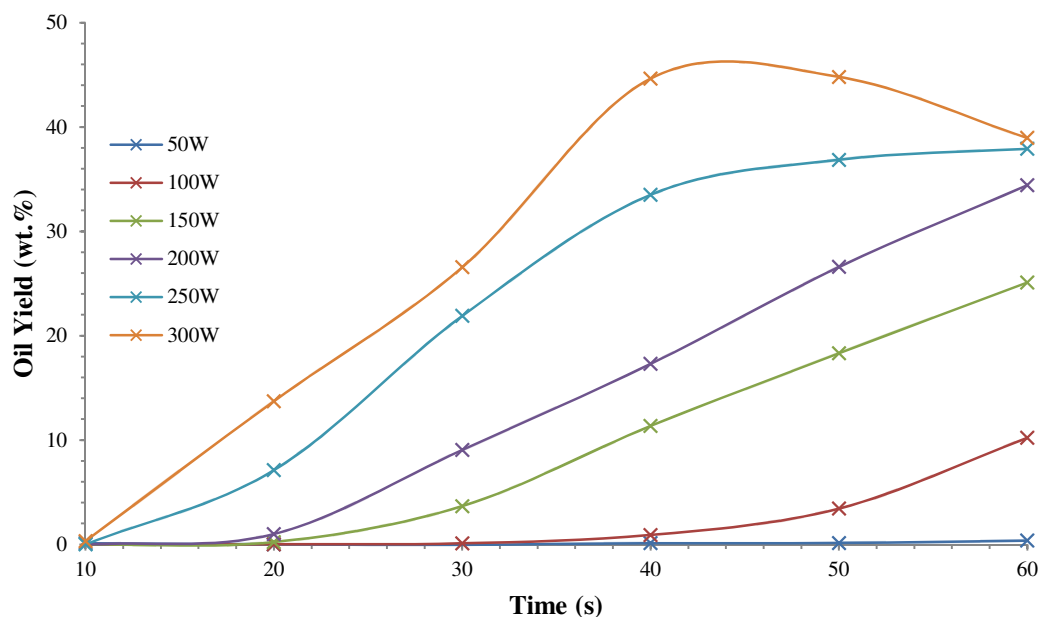
Figure 4-14   Bio-oil yield for microwave durations of 10-60 seconds and microwave powers of 50-300W
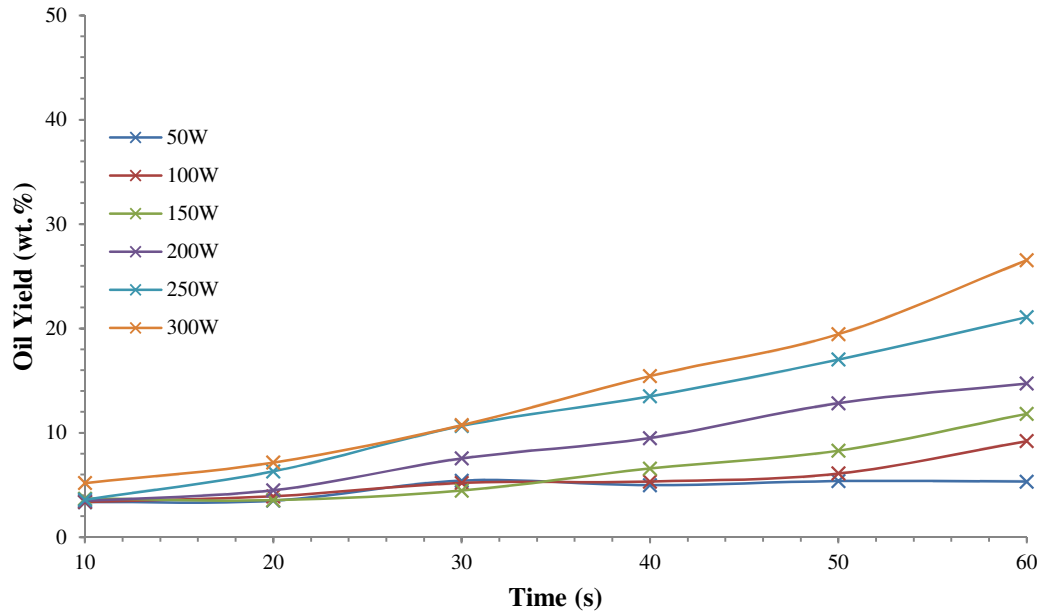
Figure 4-15 Gas yield for microwave durations of 10-60 seconds and microwave powers of 50-300W
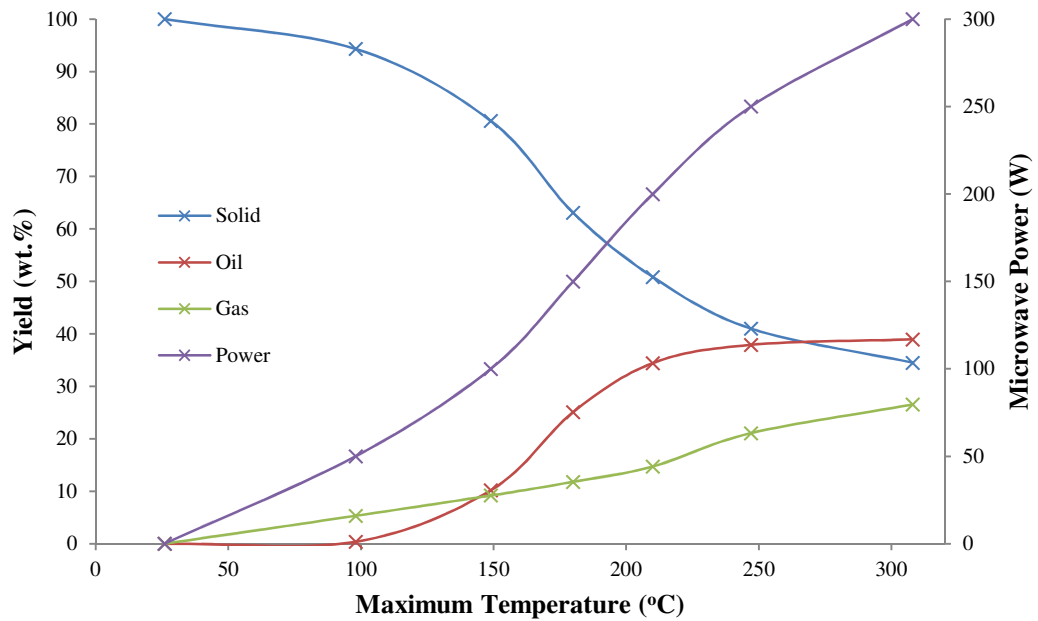
Figure 4-16 Yields of solid, oil, and gas from cellulose under microwave irradiation of 100-300W compared to maximum temperatures achieved

A similar pattern is observed for gas yield, as for oil. Nevertheless, when we examine the relationship between yields of solid, oil and gas with maximum temperature (see Figure 4-16), a connection appears with each component. This being reduction in solid and increase in oil/gas with greater temperature. This would indicate that if conditions were sufficient for each power to attain similar temperatures to that of 300W, that the same yields of each component could be achieved.

The relationship between maximum temperature and the extent of pyrolysis can be seen from Figure 4-16. From this it is possible to further build on the information gained from thermal profiles presented in Figure 4-7, with the evidence presented from both solid and gas yields indicating the 5wt.% loss of water by 100°C. By 150°C approximately a 10wt.% yield of oil is formed along with a further 4wt.% increase in gas yield. This continues to rise and by 210°C the yield of oil has reached 34.4wt.% with a small increase in gas yield to 14.7wt.%. After this point yields of oil does not increase dramatically up to the maximum temperature of 300°C whereby a maximum of 38.9wt.% is formed. Although throughout the full decomposition an anomaly is seen in gas production between 210 and 247°C, in which greater proportions are formed. When this is examined as rate of decomposition a much clearer picture of the process appears, as shown in Figure 4-17.
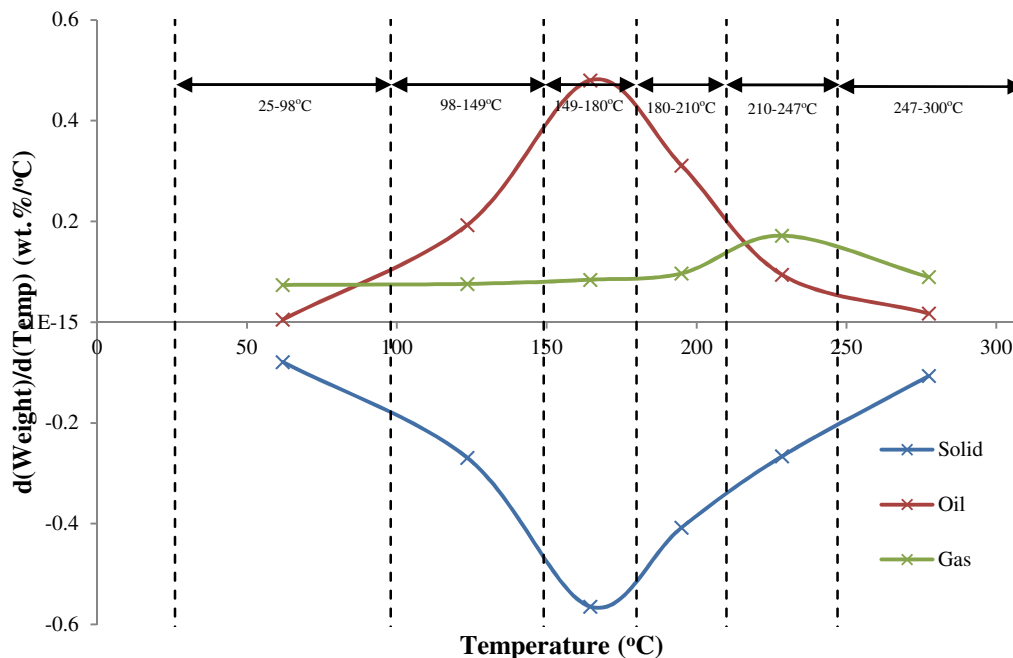
Figure 4-17 **Average rate of cellulose decomposition per degrees Celsius for temperature periods indicated: as derived from data in Figure 4-16**

From the average decomposition rates, it can be clearly seen that the greatest rate of decomposition per degrees Celsius occurs between the temperatures of 149-180°C. This is of significant importance and demonstrates a clear difference to that of a thermal decomposition process (see Figure 3-1), in which the major decomposition of cellulose occurs at approximately 300°C. It was also observed by Budarin *et al.* (2010) that a significant decomposition occurred at this temperature in the microwave decompositions they performed, however the rate at which decomposition occurred had not been quantified.

The data presented in Figure 4-17 shows that between the temperatures of 149 and 180°C an average cellulose decomposition rate of ~0.56wt.%/^{o}C occurs, which corresponds to a peak production rate of oil (~0.48wt.%/^{o}C). This rate of decomposition for oil rapidly decreases by 210-247°C, but is reflected by the sudden increase in gas production with ~0.17wt.%/^{o}C seen over this period. The rate at which cellulose decomposes and oil/gas are formed both decrease in the temperature region of 247-300°C.

The difference in peak decomposition and oil production from the microwave decomposition process is of significant interest as it represents a 120°C decrease in the temperature required for the decomposition of cellulose to occur compared to a conventional process.

Budarin *et al.* (2010) investigated the changes in crystallinity of fibrous cellulose after microwave irradiation between these temperatures, proposing that the depolymerisation and decomposition coincided with the phase transition temperature (~180°C) of cellulose. Hence, during this period an increase in molecular motion would occur within the amorphous regions of the cellulose and cooperative stress is induced on the crystalline region, resulting in reduction of overall crystallinity; accounting for the >100°C reduction in decomposition temperature.

However, it is also possible that within these amorphous regions of cellulose, the freer rotation of molecules with the chain result in localised microscopic heating and although not reflected in the bulk temperature reading, areas of the polymer may reach significantly elevated temperatures than those recorded. This is referred to by Obermayer *et al.* (2009):

".....selective interactions of the electromagnetic field with specific substrate molecules, reagents, or catalysts not connected to a macroscopic bulk temperature effect ... so called "specific" or "non-thermal effects"."

(Obermayer *et al.*, 2009)

However, both explanations have their merits, but due to limitations in temperature measurement on a microscopic scale and within a microwave cavity, it is not possible to prove the mechanism either way.

4.3.1.3 Bio-oil Composition

Analysis of oils was performed by the methods of GC-MS and FT-IR; as described in Sections 9.3.5 and 9.3.6, respectively.

The infrared spectra of bio-oils produced during the microwave decomposition of cellulose at both 200 and 300W are presented in Figure 4-18 and Figure 4-19. From these it was possible to determine the potential functional groups present in the bio-oils and determine likely characteristic changes.
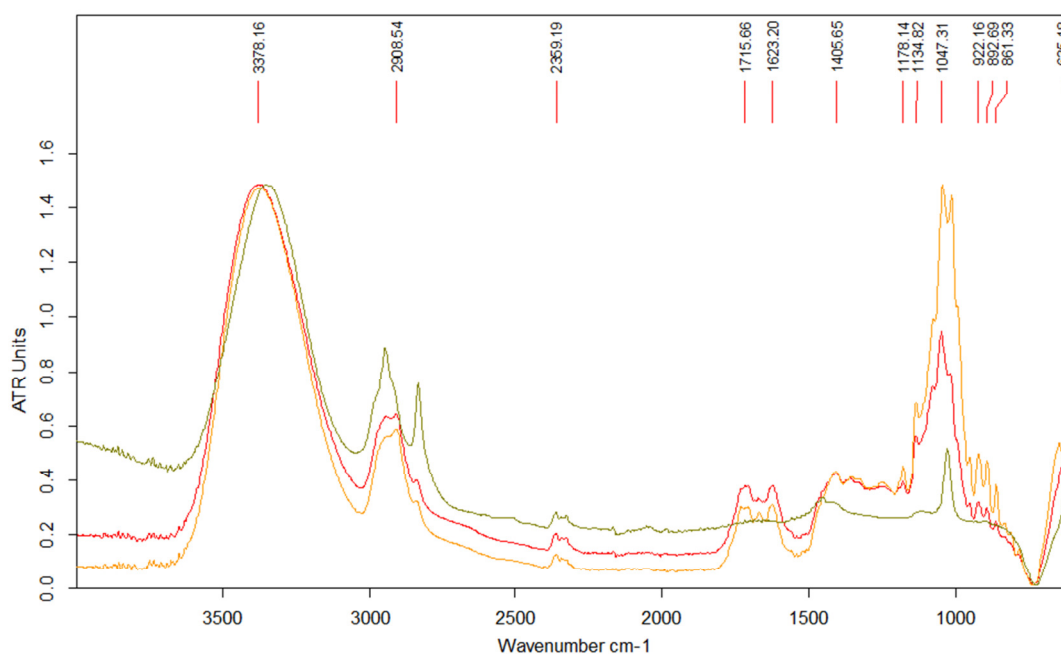
Figure 4-18   FT-IR spectrum of bio-oils of cellulose pyrolysis oils from 200W microwave exposures for 20(green), 40 (orange) and 60 (red) seconds
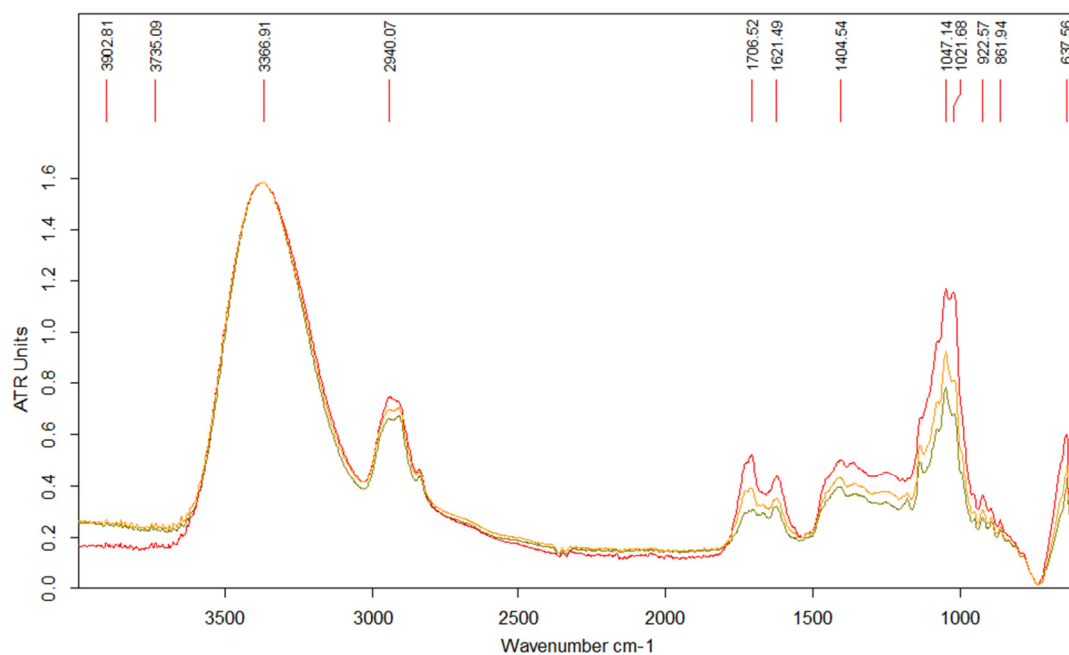
Figure 4-19 **FT-IR spectrum of bio-oils of cellulose pyrolysis oils from 300W microwave exposures for 20 (green), 40 (orange) and 60 (red) seconds**

From approximately 3000 to 3600cm^{-1} –OH stretching vibrations are present indicating the presence of residual water, alcohols or phenols. Peaks from 2860-2970cm^{-1} alongside those at 1402cm^{-1} show stretching and bending vibrations (respectively) of C-H$_n$, demonstrating the presence of alkyl, aliphatic or aromatic structures. The peaks at 1706 and 1621cm^{-1} are characteristic of aromatic stretching and benzene ring stretching, respectively. However, the peak at 1706cm^{-1} can also be characteristic of C=O stretching vibrations, corresponding to the presence of ketones, aldehydes or carboxylic acid groups present within the mixture.

The significant peaks present at 1047cm^{-1} are most likely to correspond to C-O stretching and C-O deformation. The peaks arising at 635, 861 and 922cm^{-1} correspond to C-H deformation of aromatic hydrogen.

When Figure 4-18, is examined further we are able to determine that the functional groups seen in oils produced at a 20 second exposure at 200W radiation mainly consist of weak C-O, strong -OH and strong C-H stretching signatures, indicating most likely the presence of water and a small fraction of organic compounds. The overall spectrum increases at 40 and 60 second experiments, indicating the much greater presence of organic compounds, particularly aromatic structures containing oxygen. However, the diminishing signatures of 1000-1200cm^{-1} for the 60 seconds microwaving, are indicative of loss of oxygen containing groups from the bio-oil.

Upon examining Figure 4-19, little difference can be observed in the spectrum, indicating the composition of the oil is very similar regardless of the microwave duration. This is of particular interest as when viewed in conjunction with bio-oil yields presented in Figure 4-14, as it would indicate that the decomposition of cellulose is progressive, with the volume of oil produced gradually building as more cellulose is decomposed. This in turn would support the theory presented in Section 4.3.1.2, that localised microscopic heating is occurring not reflected by the bulk temperature of the sample.

For GC-MS results an adapted method to that presented by Ludlow-Palafox and Chase (2001) was utilised to semi-quantify and identify trends in production of differing components by integration of Total Ion Chromatograms (TiC). The method does not rely upon the quantification of components by calibration but rather uses changes in the relative percentage ion count (%TiC) of each chromatographic peak after integration to approximate changes in composition.

The semi-quantitative GC-MS performed on the bio-oils produced, with the compounds m/z ion spectra produced, compared against the National Institute of Standards and Technology Database '08. From this, it was possible to tentatively identify the peaks present within the chromatogram.

A typical chromatogram from cellulose microwave pyrolysis oils is presented in Figure 4-20. It was quickly determined that all oils consisted of relatively few compounds, with approximately 8 major peaks present in each chromatogram. A number of smaller peaks were present just above baseline noise, but were of insufficient magnitude for integration and identification of the component.

Figure 4-20   **Typical chromatogram from GC/MS trace of microwave produced bio-oil**

Figure 4-21   **Typical cellulosic pyrolysis oil GC/MS trace from conventional pyrolysis oils performed to 400-600°C at 20°C/min, Hajaligol *et al.* (2001)**

This is in contrast to bio-oils produced by a conventional thermal degradation process as presented in the results of Hajaligol *et al.* (2001) (see Figure 4-21), in which the complexity of the oil and the number of products present are significant. It is noted that the temperatures attained to gain these oils are greater than that of the microwave process, hence likely that a free radical processes will dominate. However, the lower temperatures indicated in the microwave process do not yield any pyrolysis oils when applied to a conventional thermal

process, hence, have no thermal pyrolysis oils of the same temperature decomposition to compare against.

This is further supported by the works Shen and Gu (2009), whereby a minimum of 16 compounds were identified by GC/MS of conventional cellulose pyrolysis oils. It must be noted that the analysis of such complex mixtures by GC methods has its limitations due to the volatility of the products under analysis and further analytical technologies must be employed to enable the full characterisation of the complex mixtures of the oils produced (Hosoya *et al.*, 2007, Shen and Gu, 2009).

Nevertheless, on analysis and identification of components present in bio-oils produced from the 200 and 300W microwave experiments, it is found that the compounds present are consistent, with no further compounds produced when differeing experimental conditions are applied; these are summarised in Table 4-2 and Table 4-3.

Table 4-2   Composition of bio-oils produced during microwave pyrolysis runs at 200W from 20-60 seconds microwave irradiation

%TiC = Percentage Total Ion Count ***B.D.L = Below Detection Limits***			Microwave Duration (s) and Maximum Temperature Achieved (°C)				
		Duration	20	30	40	50	60
		Max. Temp.	100	112	145	195	299
Retention Time (Cm)	**Compound Name**	**Empirical Formula**	**%TiC**	**%TiC**	**%TiC**	**%TiC**	**%TiC**
5.01	Hexylene Glycol	$C_6H_{14}O_2$	1.40	2.12	2.12	2.67	2.99
8.39	Levoglucosenone	$C_6H_6O_3$	1.95	1.91	2.33	1.94	5.89
10.08	1,4:3,6-Dianhydro-.A.-D-glucopyranose	$C_6H_8O_4$	2.23	3.03	3.29	4.67	8.52
11.65	4,5-Dimethyl-3-heptanol	$C_9H_{20}O$	4.09	3.23	3.39	4.39	2.61
11.75	3-Butenyl pentyl ether	$C_9H_{18}O$	2.39	2.93	3.13	7.22	10.15
13.90	D-Allose	$C_6H_{12}O_6$	2.65	1.97	1.16	1.80	B.D.L
14.79	Levoglucosan	$C_6H_{10}O_5$	79.52	81.08	80.26	72.32	64.87
16.19	1,6-Anhydro-.B.-D-glucofuranose	$C_6H_{10}O_5$	7.17	5.85	6.45	4.89	7.96

Table 4-3   Composition of bio-oils produced during microwave pyrolysis runs at 300W from 20-60 seconds microwave irradiation

%TiC = Percentage Total Ion Count ***B.D.L = Below Detection Limits***			Microwave Duration (s) and Maximum Temperature Achieved (°C)				
		Duration	20	30	40	50	60
		Max. Temp.	98	122	191	247	308
Retention Time (Cm)	**Compound Name**	**Empirical Formula**	**%TiC**	**%TiC**	**%TiC**	**%TiC**	**%TiC**
5.01	Hexylene glycol	$C_6H_{14}O_2$	1.92	2.58	1.66	2.37	3.53
8.39	Levoglucosenone	$C_6H_6O_3$	1.44	1.13	1.64	2.15	2.56
10.08	1,4:3,6-Dianhydro-.A.-D-glucopyranose	$C_6H_8O_4$	1.38	2.26	2.85	2.67	5.42
11.65	4,5-Dimethyl-3-heptanol	$C_9H_{20}O$	2.10	1.89	2.83	2.28	0
11.75	3-Butenyl Pentyl Ether	$C_9H_{18}O$	3.70	4.06	2.67	4.07	9.76
13.90	D-Allose	$C_6H_{12}O_6$	2.75	1.46	1.05	1.84	0.84
14.79	Levoglucosan	$C_6H_{10}O_5$	79.17	80.18	80.34	77.72	70.31
16.19	1,6-Anhydro-.B.-D-glucofuranose	$C_6H_{10}O_5$	7.53	6.44	6.95	6.89	7.58
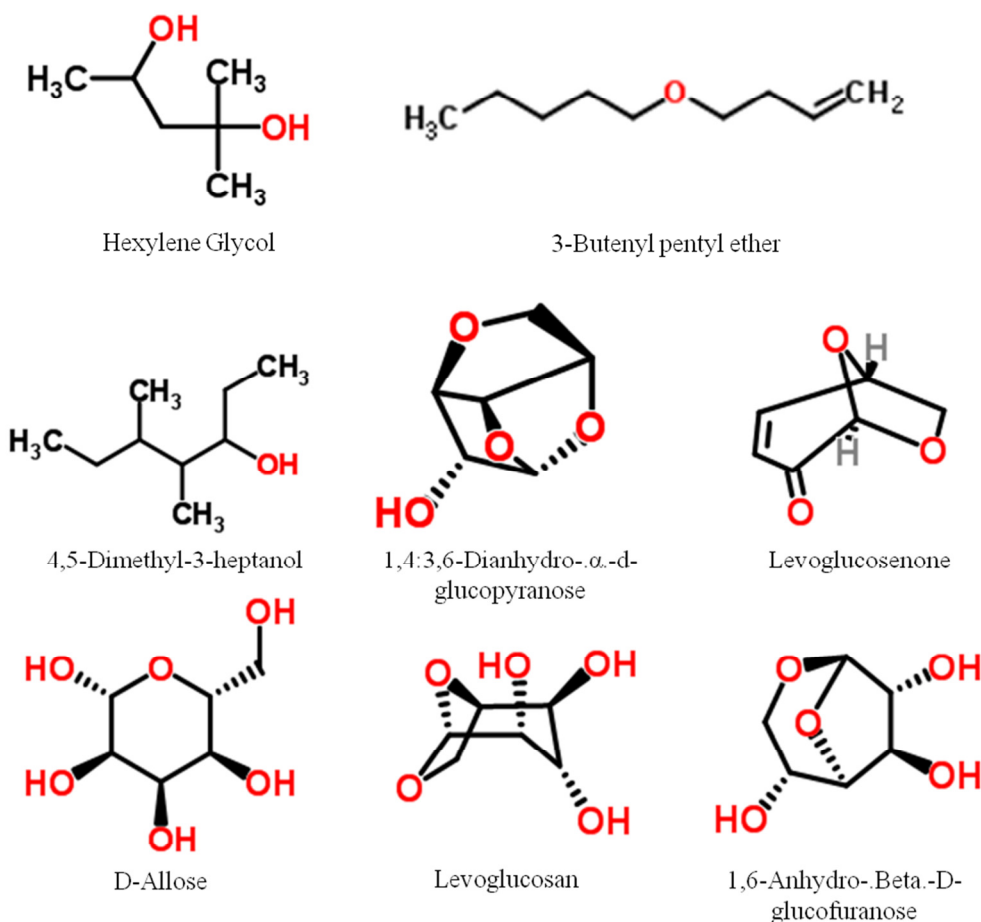
Figure 4-22   Chemical structures of compounds produced during the microwave pyrolysis of cellulose; as defined in Table 4-2 and Table 4-3

Four major components of the bio-oil are immediately of interest from the microwave pyrolysis process. These being, levoglucosan, 1,6-anhydro-.β.-D-glucofuranose, 1,4:3,6-dianhydro-.α.-D-glucopyranose and levoglucosenone. The presence of these compounds is supported by Figure 4-18 and Figure 4-19, with little evidence of aromatic products and the indication of C=O relating to the presence of levglucosenone. These have been recognised as the major decomposition products of cellulose pyrolysis from a conventional thermal process by Shafizadeh and Fu (1973), Shafizadeh (1982), Antal and Varhegyi (1995), Shen and Gu (2009) and Lin *et al.* (2009), to name but a few. As previously motioned in Section 1.3.2.2, the mechanism of cellulose pyrolysis is still widely debated, but the generalised model as presented in Figure 4-23 is widely accepted.
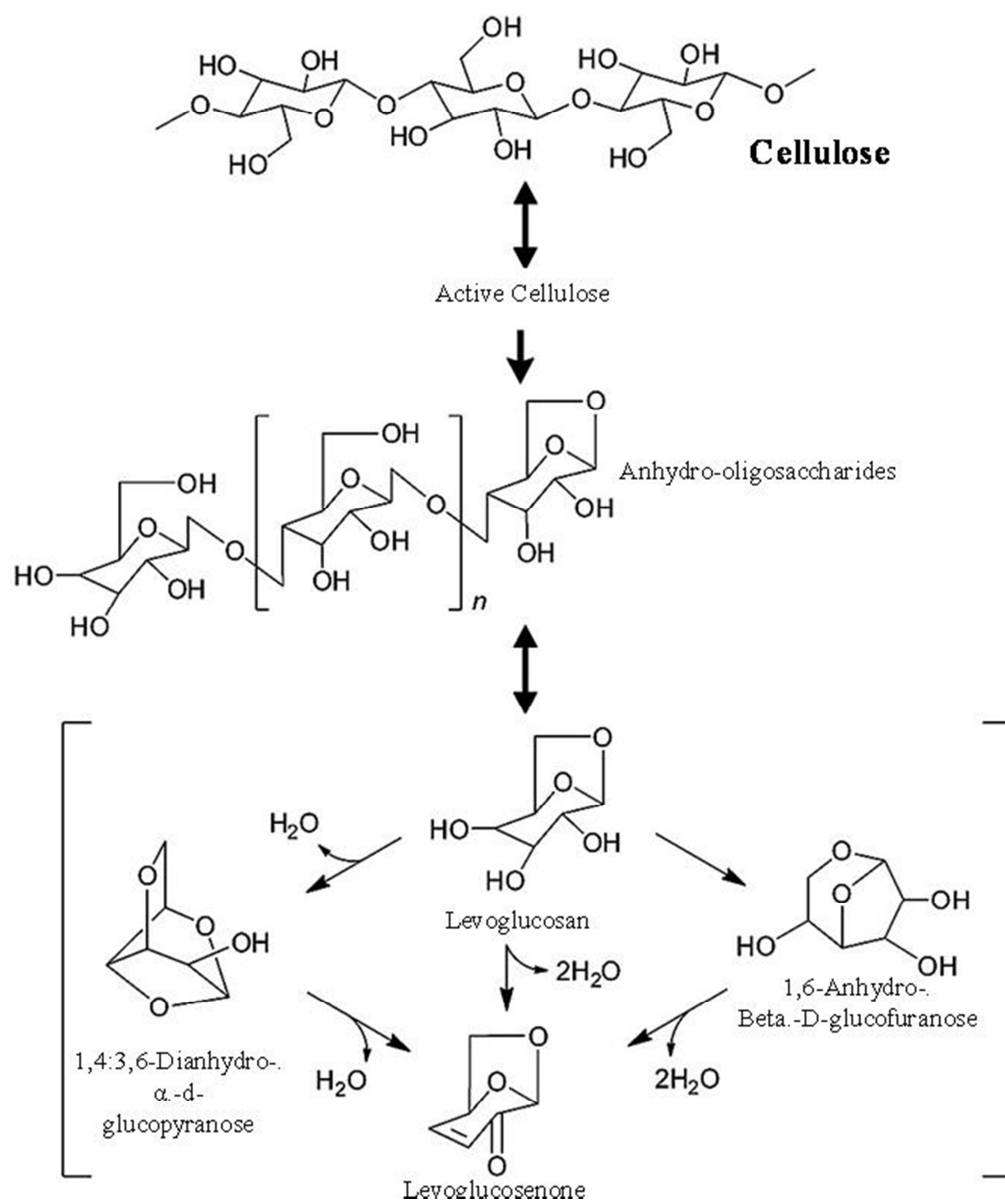
Figure 4-23   Proposed route of cellulose pyrolysis

The celluloses first stage in the decomposition process is to form active cellulose, undergoing depolymerisation to oligosaccharides. These undergo further depolymerisations until individual sugar units are formed. The first of these is levoglucosan, which is thought to be formed through the cleavage of 1,4-glycosidic linkage in polymer followed by intramolecular rearrangement of monomer units (Shen and Gu, 2009). levoglucosan can undergo further dehydration reactions to form 1,4:3,6-dianhydro-α-D-glucopyranose with the loss of one water and levoglucosenone from the loss of two waters. The route that this decomposition takes is unclear with simultaneous competing pathways forming both products directly, however it is also possible to form levoglucosenone from further dehydration of 1,4:3,6-dianhydro-α-D-glucopyranose. Nevertheless, the isomer of levoglucosan, 1,6-anhydro-β-D-glucofuranose is also present during this decomposition process and is thought to go through dehydration losing two waters to form leveglucosenone.

Nevertheless, it was found from the bio-oils produced that levoglucosan formed a significant proportion of the TiC signal (approximately 80% TiC), indicating that it was present in significant quantities in comparison to other components. This is consistent with the results presented from Allan *et al.* (1980). This was thought to be as a result of the mechanism of microwave heating, from the inside to the outside, hence the relatively unstable product of levoglucosan does not pass through regions of significantly elevated temperature whilst it escapes from the sample; not undergoing further decomposition.

When Figure 4-24 and Figure 4-25 are examined we find a distinct trend in the changes of the four components of levoglucosan, 1,6-anhydro-β-D-glucofuranose, 1,4:3,6-dianhydro-α-D-glucopyranose and levoglucosenone. Initial decomposition temperatures of 112°C and 191°C for 200W and 300W, respectively result in gradual increase of levoglucosan to ~80%TiC. After these temperatures the signal is observed to diminish, with a reduction to ~65 and 70%TiC for microwave powers of 200 (299°C) and 300W (300°C), respectively. Whilst this occurs the increase in 1,4:3,6-dianhydro-α-D-glucopyranose and levoglucosenone occurs at corresponding temperatures. This would indicate that temperature plays a vital role in the microwave decomposition process, similar to that of the thermal decomposition process.
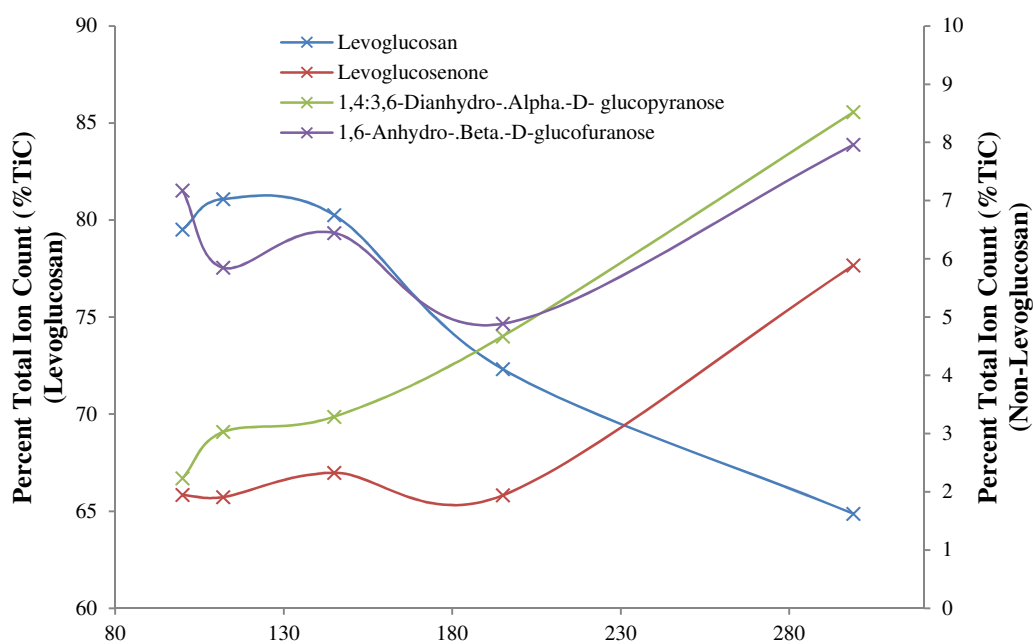
Figure 4-24 **Changes in TiC signal for the four major bio-oil components of Levoglucosan (left axis), Levoglucosenone, 1,4:3,6-Dianhydro-α-D-glucopyranose and 1,6-Anhydro-β-D-glucofuranose (right axis) for 200W experiments with increasing maximum temperature**
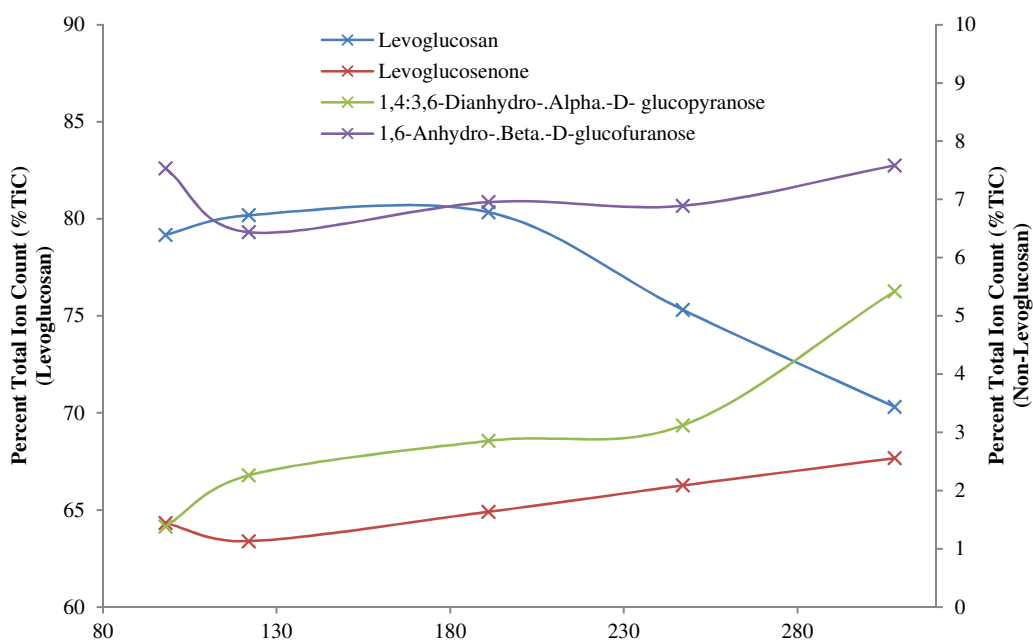
Figure 4-25 **Changes in TiC signal for the four major bio-oil components of Levoglucosan (left axis), Levoglucosenone, 1,4:3,6-Dianhydro-α-D-glucopyranose and 1,6-Anhydro-β-D-glucofuranose (right axis) for 300W experiments with increasing maximum temperature**

A marked difference in the temperatures at which this pattern of component formation is achieved is recognised between the powers of 200 and 300W (see Figure 4-24 and Figure 4-25). This is most likely attributable to the transfer of microwave energy to the whole cellulose volume and the resultant thermal gradients present within the sample indicating a much lower temperature than that actually achieved. It might also be possible that the differing heating rates introduced by the amount of power put into the system have a distinct effect on this process, but this is not able to be examined from the current microwave technology available.

A number of further decomposition products are present during the microwave decomposition process, with hexylene glycol and 3-butenyl pentyl observed to build in their relative %TiC as temperature increases. The structure of these compounds (see Figure 4-22) demonstrate that they are aliphatic fragments. These are most likely formed as increase residence times and temperatures open the ring structure of anhydrosugars and partial fragmentation occurs (Kawamoto *et al.*, 2009, Shen and Gu, 2009). This is most notable in 300W experiments in which by 60 seconds 3-butenyl pentyl has built from 3.70 to 9.76%TiC. Nevertheless, the specific reaction pathway for these compounds formation is not yet determined.

4.4 Microwave Decomposition of Cellulose: The Effect of Sample Pre-Heating

4.4.1 Introduction

Changes in the microwave dielectrics with temperature have been observed and documented originally by Stoops (1934) and further investigated by Allan *et al.* (1980) in which microwave pyrolysis of cellulosic materials was first performed. However, dielectric changes with temperature have been investigated to the greatest extent by Ollivon *et al.* (1988). From Allan *et al.* (1980) and Ollivon *et al.* (1988) (see Figure 4-26) it is possible to determine that by a temperature of 180°C the dielectric properties of cellulose are at their maximum values (Figure 4-26:A), whereby the rate at which temperature increases is at its greatest. After this, a reduction in the dielectric properties of cellulose occurs as the temperature increases and the sample undergoes decomposition.
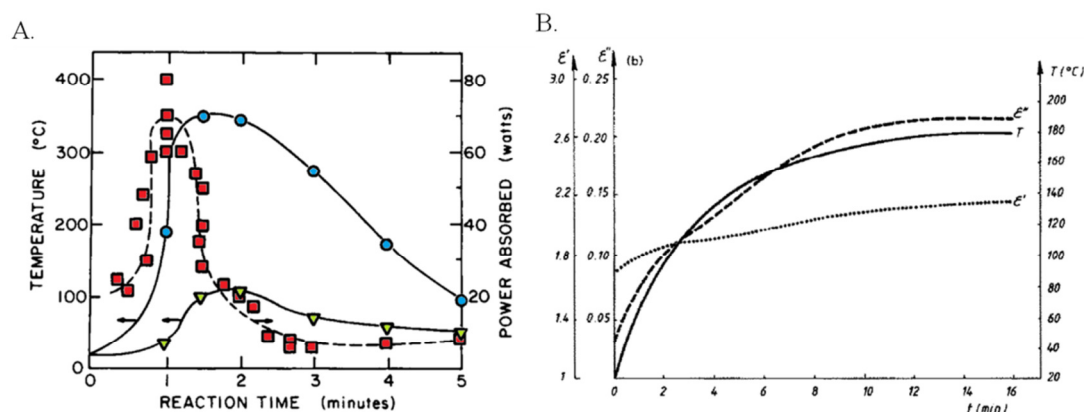
Figure 4-26   The changes in absorbed power (left: red = absorbed power, blue = internal sample temperature, green = evolved gas temperature) and dielectric properties (right: T = Temperature, ε' and ε'') of cellulose with increasing temperature; from Allan *et al.* (1980) and Ollivon *et al.* (1988), respectively

The change in the dielectric properties of cellulose is accompanied by its phase transition temperature; the point at which cellulose undergoes a phase transition from a glass state to an elastic state (Szcześniak *et al.*, 2008). This occurs at approximately 220-250°C for dry cellulose (Kalashnik *et al.*, 1991). This is extremely high, close to the temperatures at which initiation of conventional thermal decomposition of cellulose occurs, at approximately 250°C (see Figure 3-1 and Figure 3-2).

Nevertheless, for cellulose containing moisture the phase transition temperature is reduced, dependent upon the crystallinity index of the original polymer with the effect being more pronounced for cellulose of greater crystallinity (Szcześniak *et al.*, 2008). This is considered to be a result of the moisture content reducing the interactions between polymer chains on a macroscopic scale, acting as a plasticiser, lowering the phase transition temperature of cellulose (Roig *et al.*, 2011).

Budarin *et al.* (2010) examined the crystalline changes of cellulose with temperature, finding that a significant reduction in crystallinity occurred at $180^{\circ}C$. This was subsequently linked with major dielectric changes when the sample underwent microwave heating. Budarin *et al.* (2010) proposed that it was the changes in crystallinity within the regions undergoing phase transition that gave the increased dielectric response. The author further proposed cellulose was considered to have greater molecular freedom as the structure became amorphous, resulting in the increasing numbers of CH_2OH groups within the intra-molecular arrangement to undergo microwave heating by dipolar polarisation (see Figure 4-27).
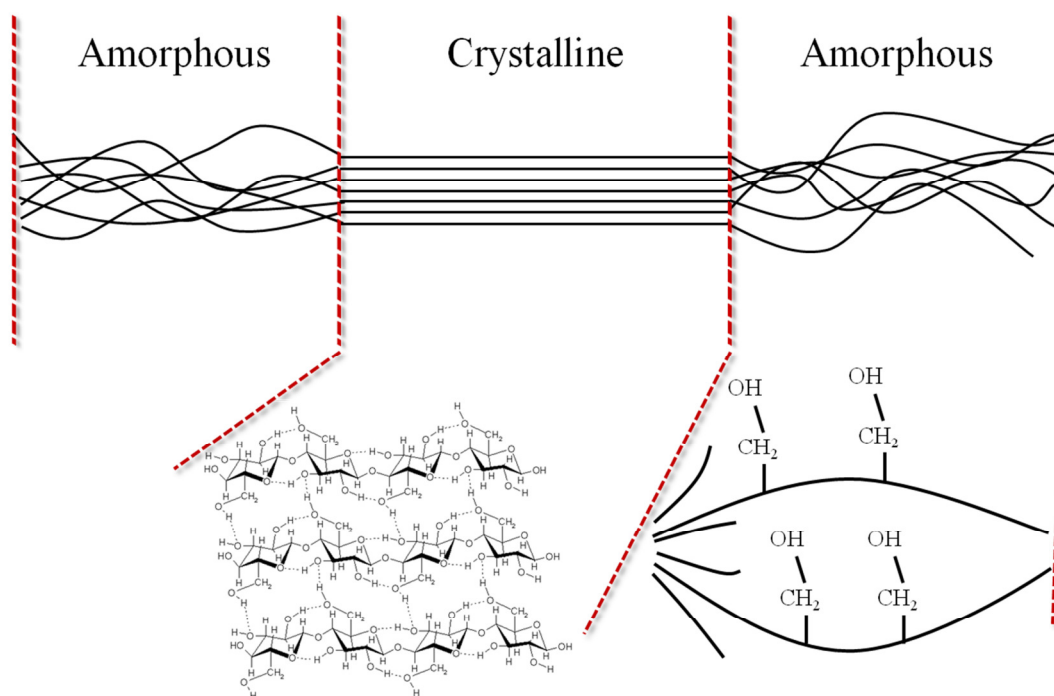
Figure 4-27   Crystalline and amorphous regions of cellulose

From this, it is possible that preheating of cellulose, to temperatures closer to that of its phase transition temperature, could ensure that greater portions of cellulose interact with the microwave field, at the point of microwave exposure. An enhanced rate of decomposition and greater product yields could potentially be achieved as a result.

Hence, an investigation was undertaken to investigate the effect of cellulose pre-heating before microwave exposure, determining its effect on microwave response and product yields.

4.4.2 Pre-Heating Temperature

Before preheating experiments were performed, it was necessary to calibrate the conventional heating block utilised, so that accurate temperatures could be attained. This was achieved through recording the temperature by thermocouple of the microwave tube filled with 5ml ± 0.01ml of Silicone oil (Sigma-Aldrich Co. LLC). The heating block temperature was set to a given temperature and the oil-filled tube allowed to equilibrate. The subsequent temperature was recorded. The results of this are presented in Figure 4-28.
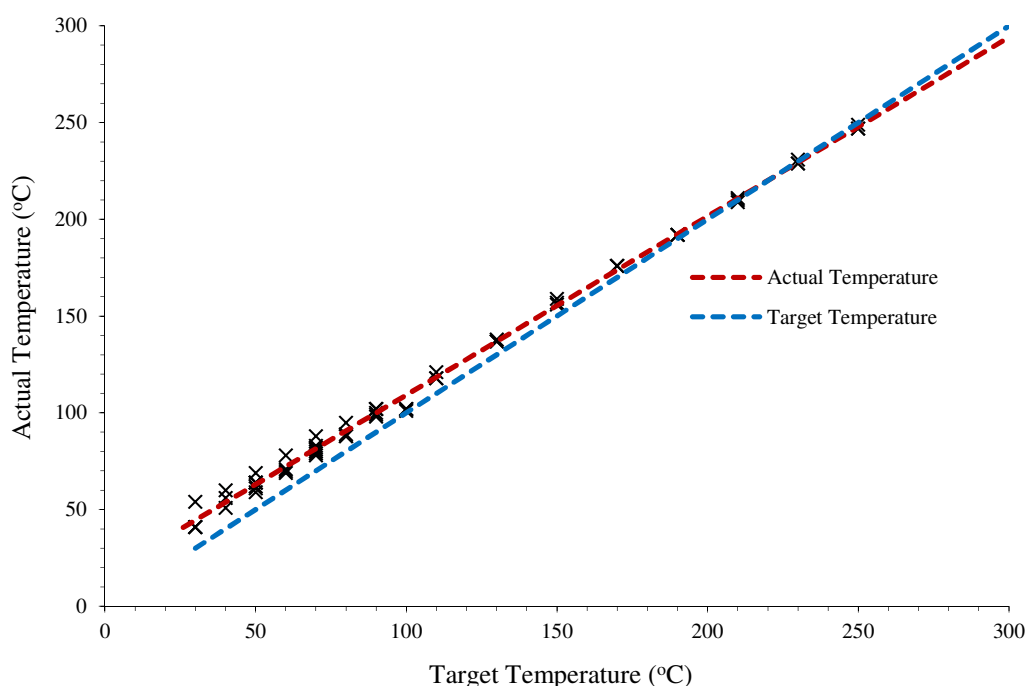
Figure 4-28   Pre heating block testing Target Temperature

The results demonstrated that the temperatures of the heating block were significantly different to that of the set temperature at temperatures between 40 and 170°C. This was shown by a maximum difference in the pre-set and actual temperature of +15°C at a set temperature of 40°C. This temperature difference decreased with increasing preset temperature to 170°C, at which point a difference of +3°C of the set temperature. From the data gained it was possible to calibrate the heating block so that temperature of ±2°C could be achieved.

It was also necessary to determine the time required for a 2g cellulose sample to reach uniform temperature when placed in the heating block. As such, a thermocouple was placed at the centre of cellulose samples and heated at temperatures of 50, 100, 150, 200, 250 and 300°C. From this it was found that a duration of 5 minutes would be sufficient. Hence, for all experiments the sample was allowed to equilibrate within the heating block for 5 minutes before microwave exposure. The resulting pre-heating experiment procedure is described in Section 9.2.2.

Table 4-4   Effect of Microwave Pre-Heating on Phase Transition Characteristics

MW Preheating Temperature (^{o}C)	$-\Delta C^{rev}_{p}$ ($Jg^{-1}K^{-1}$)	Phase transition temperature (^{o}C)
120	0.29	182
140	0.32	181
160	0.29	188
180	0.50	173

Experiments were performed to determine the effect that microwave heating has on the phase transition temperature of cellulose, with results presented in Table 4-4. In comparison to those results presented in section 3, it can be seen from the data that the microwave heating has no effect on the phase transition temperature of microcrystalline cellulose nor on the $-\Delta C^{rev}_{p}$ below 180°C. However, when the phase transition temperature (180°C) of cellulose is reached a noticeable but not substantial rise in the $-\Delta C^{rev}_{p}$ is observed to 0.50Jg^{-1}K^{-1} within the cellulose, indicating that an increased level of crystallinity has occurred upon cooling. These results give strong evidence to suggest that during the microwave heating of cellulose, water within its structure cannot escape, as dissociated (polarised) water interacts more strongly with the cellulose polymers. This is consistent with the results presented by Szcześniak *et al.* (2008) and Roig *et al.* (2011). As such, it can be concluded that, in contrast

to conventional preheating, (see Figure 3-4), microwave preheating does not significantly change the temperature range and intensity of the phase transition (See Table 4-4).

4.4.2.1   Mass Balances

The degradation of pre-heated cellulose samples upon exposure to 300W microwave radiation is presented in Figure 4-29 to Figure 4-33.

From Figure 4-29 it is evident that pre-heating temperature has a significant effect on the extent of decomposition that cellulose undergoes, with increasing pre-heating temperature resulting in increased extent of decomposition.

For pre-heating temperatures between 60 and 140°C with no microwave exposure, it is evident that the free water contained within the cellulose is driven off (Roig *et al.*, 2011), with a reduction of approximately 5wt.% (see Figure 4-29 and Figure 4-31). This correlates well with MDSC results (see Figure 3-3), in which the increase in phase transition temperature occurs as moisture content decreases. However, from Figure 4-31, for pre-heating temperatures of 180°C or greater, cellulose begins to undergo thermal decomposition. This is reflected in a further 1.5wt.% loss for the temperatures up to 220°C. Above 220°C, substantial mass losses occur, with a total 10 and 19wt.% for the pre-heating temperatures of 260 and 300°C respectively. This is conducive with the results of Szcześniak *et al.* (2008), Zhang *et al.* (2010a) and those presented in Figure 3-1, whereby thermal decomposition of microcrystalline cellulose undergoes initial degradation from 220°C onwards.
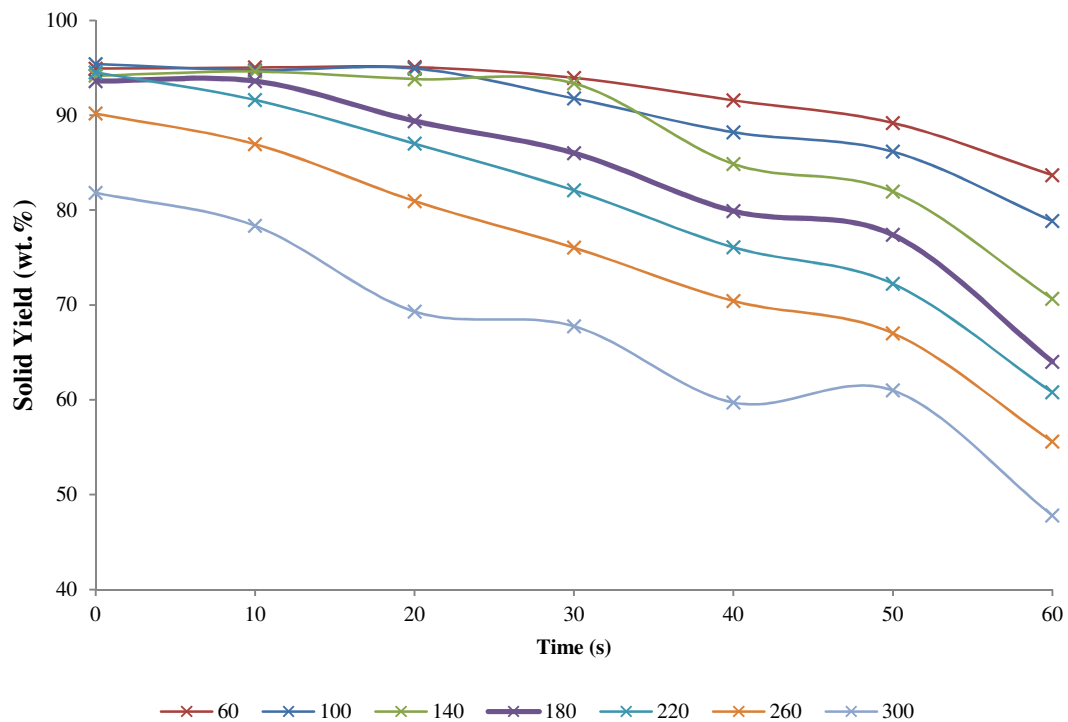
Figure 4-29 **Residual solid yield for cellulose samples preheated to 60-300°C for 5 minutes before microwave irradiation of 300W for durations of 0-60 seconds**

Upon microwave irradiation, samples are observed to decompose progressively with increased microwave duration, with the resultant extent of decomposition following the pre-heating temperature the sample was exposed to, with least decomposition and greatest decomposition for the minimum and maximum pre-heating temperatures.

However, the rate of decomposition (see Figure 4-30) of pre-heated cellulose samples reveals that the pre-heating temperature plays a critical role in microwave decomposition process. For the pre-heating temperature of 180°C (the temperature at which microcrystalline cellulose becomes most responsive to microwave irradiation in an un pre-heated process) it is found that the decomposition rate is negligible, requiring 20 seconds microwaving before the decomposition rate increases substantially. This is reflected in Figure 4-30:D, in which the initial rate of decomposition is found to be much less than the temperatures bounding it. This would appear to support MDSC results (see Figure 3-3), as when pre-heating the cellulose sample to 180°C, the phase transition temperature will increase to ~220°C, requiring a further ~40°C before thermal runaway can occur within the cellulose than a purely microwave process (without pre-heating).
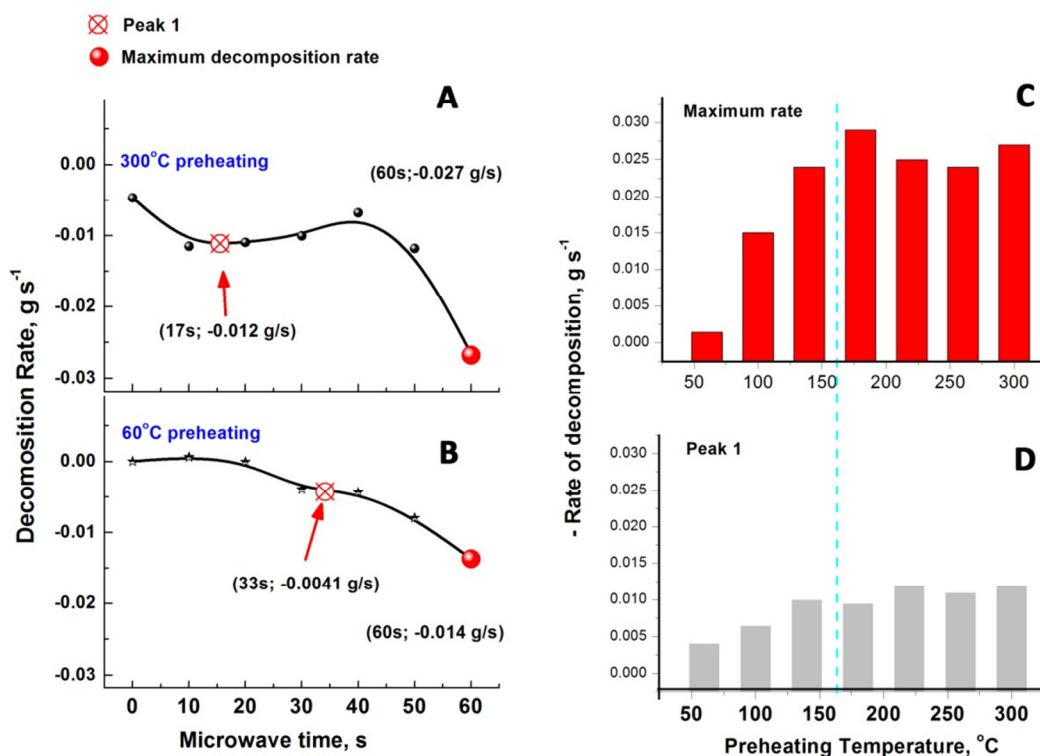
Figure 4-30 Solid yield decomposition rate A) for 300°C pre-heating, B) for 60°C pre-heating, C) indicated maximum rate of decomposition and D)rate of decomposition at first peak for cellulose samples microwave irradiated at 300W for durations of 0-60 seconds

Nevertheless, the maximum rate of decomposition is greatest at 180°C pre-heating with the next greatest at 300°C. It was also found that at lower pre-heating temperatures (see Figure 4-30:B) a less pronounced first peak (see Figure 4-30:C and D) was observed, indicating a gradual decomposition of cellulose. This would indicate the that bulk of the cellulose undergoing microwave irradiation was not undergoing simultaneous decomposition, suggesting the possibility that hot spotting and the gradual decomposition from a hot spot might be arising. Nevertheless, by 140°C pre-heating and above, little difference could be observed in the first peak decomposition rates.
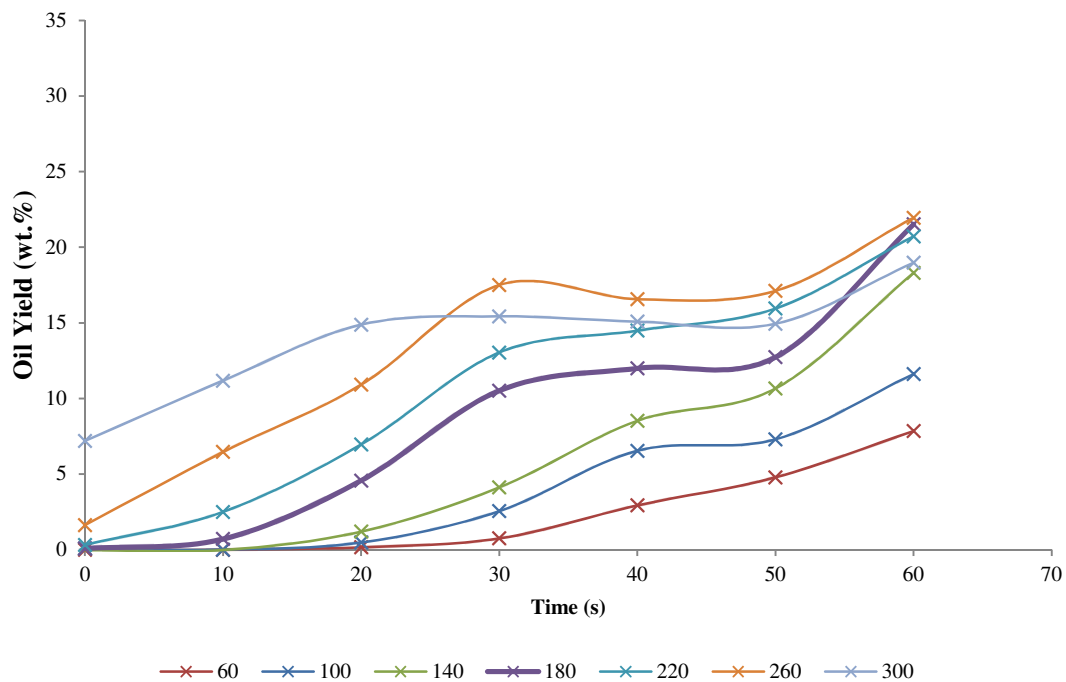
Figure 4-31   Bio-oil yield for cellulose samples preheated to 60-300°C for 5 minutes before microwave irradiation of 300W for durations of 0-60 seconds

Bio-oil yields for pre-heating only, were conducive with total mass loss (see Figure 4-31), with the mass loss over and above that of free water for samples pre-heated to 260 and 300°C producing, 1.6 and 7.9wt.% respectively. For all samples which are pre-heated to between 180 and 260°C, bio-oil production was seen to rise rapidly up to 30 seconds microwave duration, at which point the production of oil reached a plateau. This is seen in Figure 4-31 and Figure 4-32, where for the pre-heating temperatures of 180, 220 and 260°C the production of bio-oil is seen to follow the same pattern of decomposition rate, with peaks occurring at 30 and 60 seconds.

For pre-heating temperatures of 100 and 140°C a similar pattern of oil production is observed, but with 140°C demonstrating bio-oil production rates similar to that of 180°C at 60 seconds (see Figure 4-32). The overall weights of bio-oil produced for pre-heating temperatures of 140 to 300°C displayed little variation with all producing between 18.9 to 21.9wt.% (see Figure 4-31).
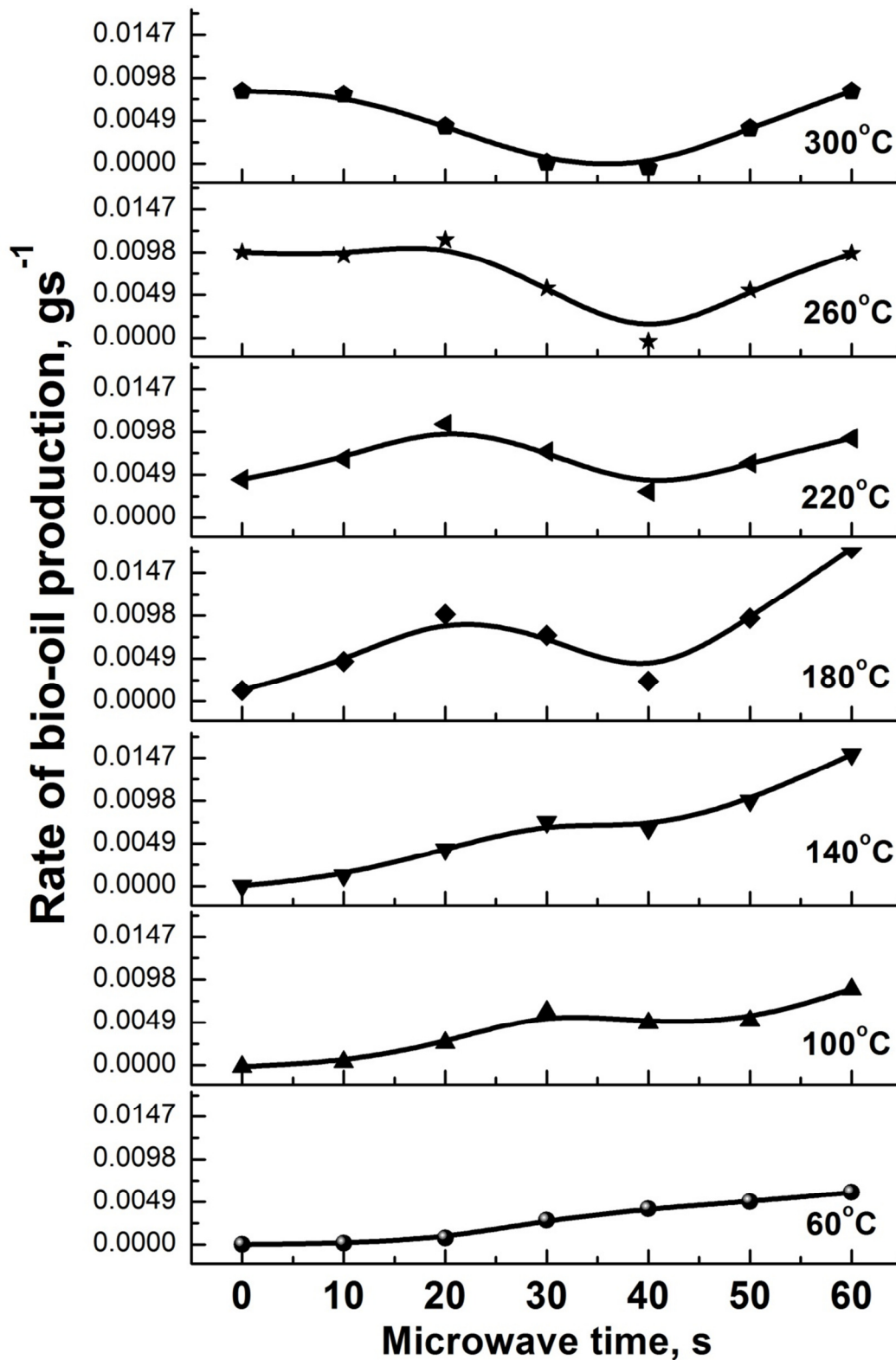
Figure 4-32 **Bio-oil yield d(Weight)/d(time) for cellulose samples preheated to 60-300°C for 5 minutes before microwave irradiation of 300W for durations of 0-60 seconds**

Nevertheless, for a pre-heating temperature of 300°C a differing pattern of oil production is observed with initial rate being the greatest of all temperatures at 10 seconds microwave duration. This quickly drops until the rate of oil production becomes negative. When this is examined in conjunction with Figure 4-29, Figure 4-31 and Figure 4-33 it becomes clear that between 30 and 50 seconds the majority of mass is converted to gas rather than bio-oil, with a proportion of bio-oil also being converted to gas.

However, at 50 seconds the proportion of solid is seen to increase, clear evidence that oils and gas are undergoing secondary reactions to form solids (see Figure 4-29). This is likely as reaction temperatures and residence times within the microwave reactor increase and charring occurs. Yields of gas are significant in cellulose decomposition, with greater yields of gas than oil for pre heating temperatures in excess of 260°C (see Figure 4-31 and Figure 4-33). For those less than 260°C, the yield of gas was comparable to that of oil with similar patterns in the rates of production for both components.
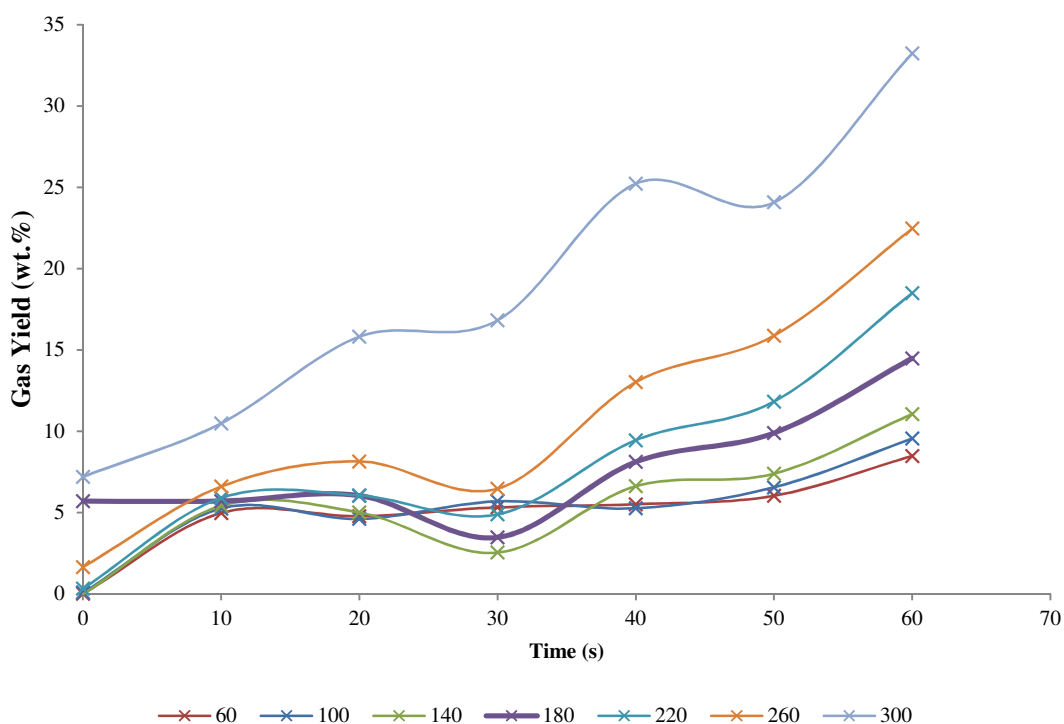
Figure 4-33   Gas yield for cellulose samples preheated to 60-300°C for 5 minutes before microwave irradiation of 300W for durations of 0-60 seconds

Nevertheless, the rate at which gas production occurs is similar for the pre-heating temperatures of 140 – 300°C, indicating that similar reactions are occurring dependent on

microwave exposure time rather than a given temperature, with the extent to which each of these reactions occurs being dictated by the pre-heating temperature the cellulose was exposed to.
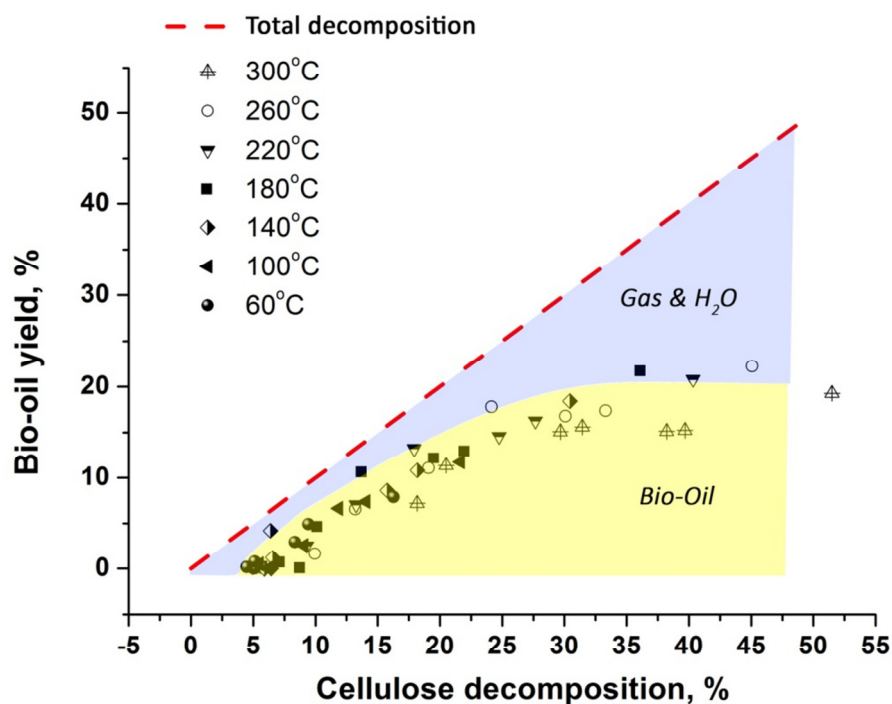
Figure 4-34   Relationship between cellulose decomposition, bio-oil and gas/water yields

Nevertheless, when we examine the extent of decomposition in relation to the weights of bio-oil and gas/water produced (see Figure 4-34) we find that a maximum bio-oil yield is reached by 35wt.% cellulose decomposition. Beyond this no further production is observed with decomposition yielding increased weights of gas. This would appear to further suggest that the for a given bio-oil yield a maximum temperature must be achieved, beyond which the oil undergoes further decomposition to lighter volatile compounds and the decomposition of the remaining solid most likely consists of the elimination of smaller molecular fragments and hetero atoms.

The rate of decomposition and production of bio-oil and gas for samples pre-heated to 260 and 300°C do show an exceptional difference to that of all prior pre-heating temperatures. This is most likely linked to the temperature attained during pre-heating being within the range that microcrystalline cellulose undergoes thermal decomposition and the reduction in molecular weight. During this phase the opening of the cellulose structure, reduction in

molecular weight and increase in amorphous structure will increase the number of microwave receptive sites, hence it is logical to expect the degree of pyrolysis to increase with greater pre-heating temperature as a greater proportion of cellulose is converted to an amorphous state.

As discussed by Roig *et al.* (2011), water within a hydrogen bonded network involving –CH_2OH and –OH groups can act as an antiplasticiser, specifically in bio-polymers involving glycosidic rings. Hence, it is also possible that at significantly elevated temperatures moisture is eliminated from the crystalline cellulose structure to the greatest degree, allowing the freedom of movement for -CH_2OH and -OH groups to respond to the microwave field, enabling greater transfer of energy from the microwave field to the cellulose polymer. This in turn will result in a greater degree of fragmentation of the cellulose polymer.

4.4.2.2   *Product Analysis*

Bio-oils obtained from pre-heating experiments were analysed by FT-IR and GC-MS to determine their composition and potential changes in this. The FT-IR spectra of pyrolysis oils shown in Figure 4-35 to Figure 4-37 show signature peaks precisely the same as those found in microwave only pyrolysis experiments; as shown in Figure 4-18 and Figure 4-19. Small differences arise in the intensity of peaks at $1402cm^{-1}$ and $2860-2970cm^{-1}$. These are observed to the greatest extent on microwave exposure of 40 and 60 seconds whereby the intensity is notably greater, accompanied by sharp increases in peaks at $1621cm^{-1}$ and $1706cm^{-1}$, indicating the increase in aromatic nature of the oil produced. This is further supported by the substantial increase in signal at $635cm^{-1}$, indicating the increased presence of C-H bonding of aromatic hydrogen.
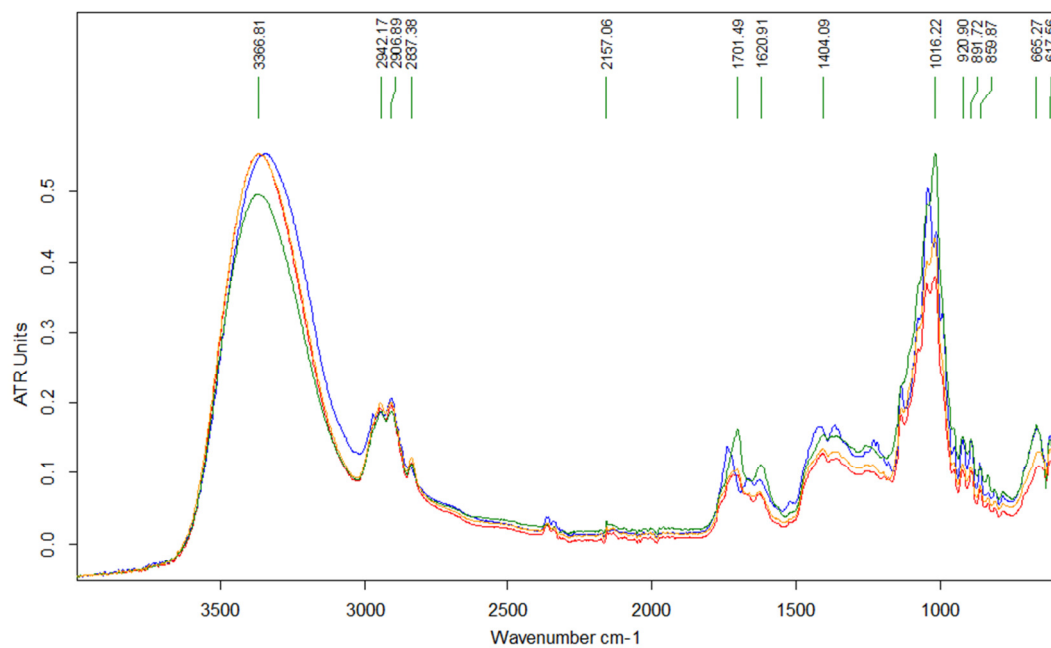
Figure 4-35   FT-IR spectrum from pyrolysis oils of pre-heated cellulose samples to 100 (dark blue), 180 (red), 220 (purple) and 300ºC (green) for a duration of 20 seconds at 300W
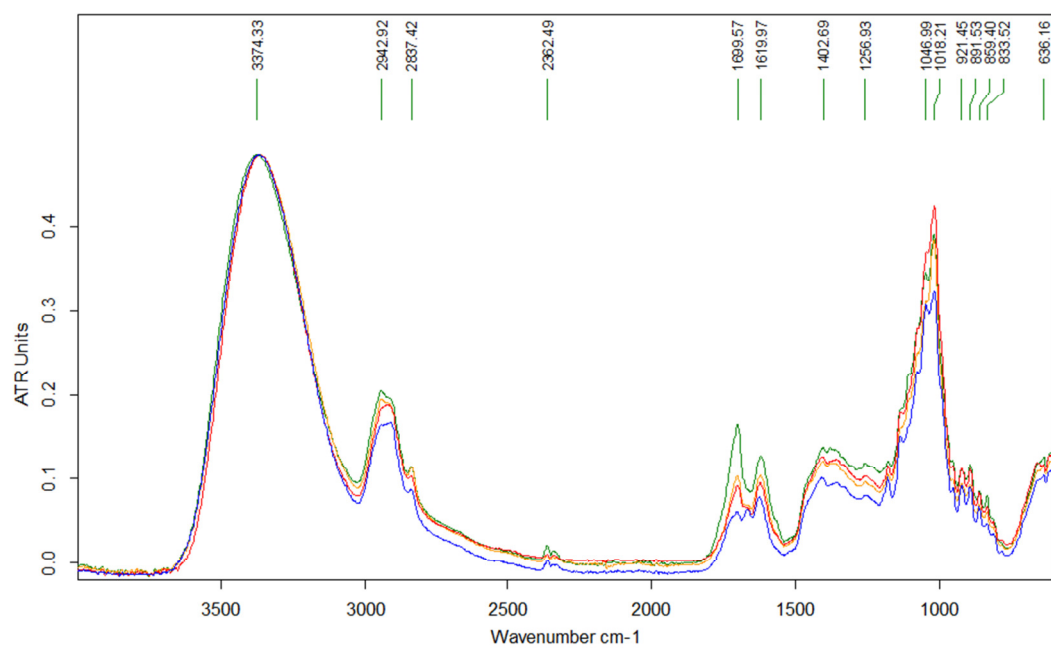
Figure 4-36   FT-IR spectrum from pyrolysis oils of pre-heated cellulose samples to 100 (dark blue), 180 (red), 220 (orange) and 300ºC (green) for a duration of 40 seconds at 300W
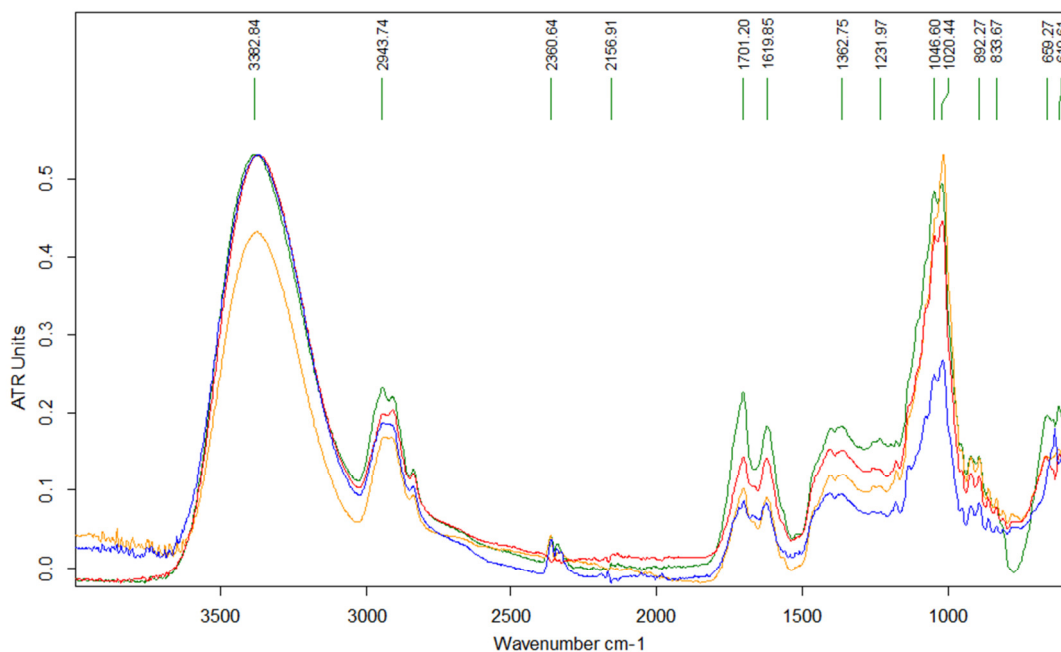
Figure 4-37 **FT-IR spectrum from pyrolysis oils of pre-heated cellulose samples to 100 (dark blue), 180 (red), 220 (purple) and 300°C (green) for a duration of 60 seconds at 300W**

The greatest of these increases are seen for the pre-heating temperature of 300°C at both 40 and 60 seconds microwave duration, which coincides with the reduction of bio-oil fraction; as shown in Figure 4-31 and Figure 4-32. This supports the suggestion that the oil is undergoing carbonisation at these points resulting in the greater yield of aromatic species. Nevertheless, no reduction in the intensity of groups at 1047cm^{-1} and 3000-3600cm^{-1} show little in the loss of hydroxyl and C-O bonding within the bio-oil.

Table 4-5 **Typical composition of bio-oils produced during pre-heating microwave pyrolysis runs**

Retention Time	Compound Name	Empirical Formula
8.40	Levoglucosenone	$C_6H_6O_3$
10.13	1,4:3,6-Dianhydro-α-D- glucopyranose	$C_6H_8O_4$
11.75	3-Butenyl Pentyl Ether	$C_9H_{18}O$
14.70	Levoglucosan	$C_6H_{10}O_5$
16.18	1,6-Anhydro-β-D-glucofuranose	$C_6H_{10}O_5$
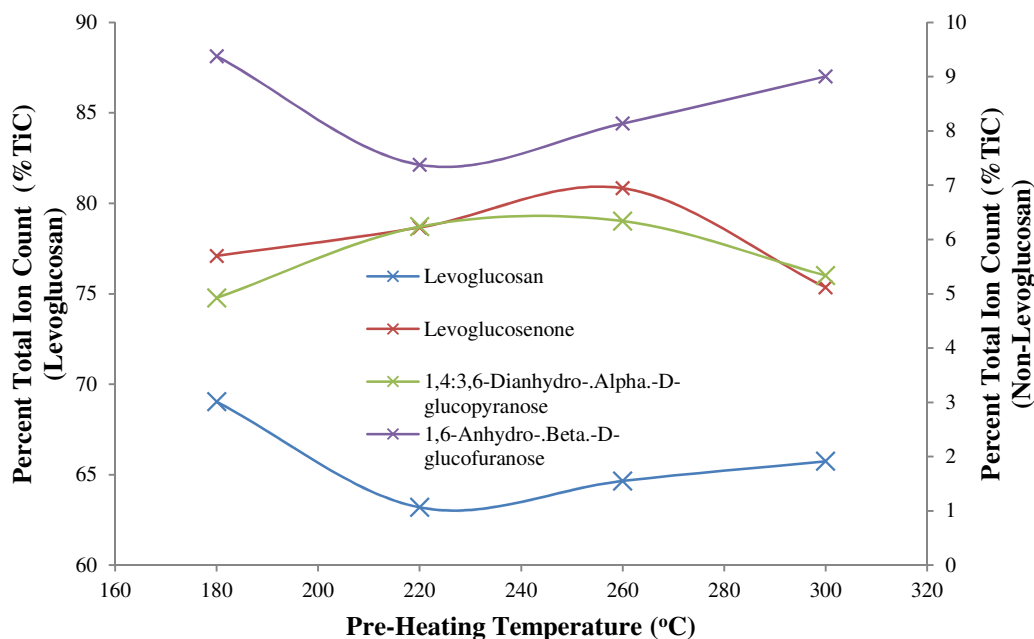
Figure 4-38 Changes in TiC signal for the four major bio-oil components of Levoglucosan (left axis), Levoglucosenone, 1,4:3,6-Dianhydro-α-D-glucopyranose and 1,6-Anhydro-β-D-glucofuranose (right axis) for 300W, 60second experiments for pre-heating temperatures of 180, 220, 260 and 300°C

GC-MS results (see Table 4-5 and Figure 4-38) of bio-oils produced at 180-300°C pre-heating are consistent with the indications in compositional change as derived from FT-IR analysis. The composition of the bio-oil is largely similar to that shown in microwave only experiments (see Table 4-2 and Table 4-3) with the presence on the five major components of Levoglucosenone, 1,4:3,6-Dianhydro-.A.-D- glucopyranose, 3-Butenyl Pentyl Ether, Levoglucosan and 1,6-Anhydro-.B.-D-glucofuranose. Little difference in the relative %TiC of each individual component arises, displaying a similar relative composition to those oils experiencing maximum temperatures of approximately 300°C. This would indicate that pre-heating has little effect on the composition of cellulose microwave pyrolysis oils.

4.5 Conclusions

The low temperature microwave induced decomposition of cellulose displayed a number of significant findings over that of a conventional thermal decomposition.

From microwave only processing of cellulose it was possible to achieve 65wt.% decomposition, resulting in formation of 44wt.% or 26wt.% bio-oil and gas, respectively

when optimum conditions for each components were used. Of this loss 5wt.% was as a result of free water which is held between polymer chains.

As an overall trend greater power input resulted in an increase in extent of decomposition, however this was largely resulting from these experiments being able to attain higher overall temperatures. However, when temperatures exceeded 220°C the gains in oil produced were minimal, with the main decomposition of cellulose occurring between the temperatures of ~180 and 220°C. This was found to correlate to the phase transition temperature of the cellulose used. This in itself was also of significance as it showed the decomposition of cellulose occurred a full 120°C less than that seen in a conventional thermal decomposition process.

The moisture content of cellulose was also found to be a critical component of the microwave decomposition process, with it assisting in the initial heating of cellulose by conduction due to its high dielectric response and subsequent absorption of microwaves at the temperatures between ambient and 100°C.

Under microwave conditions of 300W it was found that a differing mechanism of heating may be present, with greatly accelerated heating rates than that of other microwave powers. This was theorised to be as a result of power density being such that the simultaneous microwave dielectric heating of water and cellulose structure could occur. This was also reflected in peak heating rates of 420°C/min.

The rapid heating of cellulose was also thought to result in a change in a degree of crystallinity, with opening of new areas to produce an amorphous structure which would more readily undergo microwave heating. These accelerated heating rates were also postulated as being a result of chemical dehydration and the resultant interaction of microwaves with the moisture released as it migrated through the sample.

At the other end of the spectrum, when low microwave powers were used it was found that upon the sample reaching 100°C no further heating would occur, resulting form the dielectric response of cellulose being insufficient to absorb enough microwave energy so that the thermal losses from the reactor could be overcome.

From pre-heating experiments it was evident that conventional thermal heating resulted in changes in the phase transition temperature of cellulose and subsequent microwave decompositions demonstrating an increase in decomposition temperatures to attain the same degree of decomposition as a non-pre-heated process.

Nevertheless, when pre-heating temperatures of 220°C or greater were used the phase transition temperature was exceeded and partial decomposition of the cellulosic structure occurred. Due to the loss of crystallinity the freer movement of $-CH_2OH$ and $-OH$ groups resulted and a greater proportion of cellulosic structure was able to convert microwave energy to heat.

However, when pre-heating temperatures reached 300°C thermal decomposition of cellulose was extensive and the microwave process was seen to produce some oil, but to a much larger degree gas, with oils retained within the reactor undergoing cracking to gaseous components or secondary reactions to form bio-char.

The composition of oils produced from both the microwave only and pre-heating methods were similar in nature with the four major component of levoglucosenone, 1,4:3,6-dianhydro-α-D- glucopyranose, levoglucosan and 1,6-anhydro-β-D-glucofuranose being present in all. The changes in the oil composition that were observed, appeared to be as a result of the chemical dehydration of levoglucosan following the same chemical decomposition pathway as those recognised in the thermal decomposition of cellulose.

Chapter 5:

Effects of Increased Scale and Sample Density

Under Preparation

5 Increased Scale and Sample Density

5.1 Introduction

As previously mentioned in Section 1.3.2.3.3, the products of a conventional thermal pyrolysis process are dependent upon a number of key process conditions; these include heat transfer from an energy source, the sample heating rate, the maximum reaction temperature and the operating pressure (Mohan *et al.*, 2006). By varying these factors independently or in combination, it is possible to influence the final product distribution of the pyrolysis process to favour bio-char, bio-oil or bio-gas. When applied to a conventional thermal pyrolysis bio-refinery, problems arise with the inability to achieve and maintain a number of these factors due to limitations in current technology. This often results in decreased bio-oil yields, higher operating costs (Gray *et al.*, 2006, Huber *et al.*, 2006) and increased cost of refining infrastructure (Matson *et al.*, 2011). The use of microwave technology provides potential to overcome these limitations and deliver uniform heating at the greatest rate to possible biomass samples, reducing capital expenditure and cost of bio-oil (Domínguez *et al.*, 2005, Bu *et al.*, 2012).

In microwave heating, the sample density (ρ) is a significant parameter in determining dielectric properties of the material, specifically dielectric constant (ε') and loss factor (ε''). These were found to be a quadratic function of bulk density (Nelson, 2004), where a, b, c and d are constants for a given material:

$$\varepsilon' = a\rho^2 + b\rho + 1$$

$$\varepsilon'' = c\rho^2 + d\rho$$

Equation 5-1   Relationship of dielectric constant and loss factor to density (Nelson, 2004)

It is also possible to determine the theoretical heating rate of a sample as a function of the microwave field frequency (f), dielectric constant in a vacuum (ε_o), dielectric loss factor (ε''), the electric field strength (E), the bulk sample density (ρ) and the specific heat capacity (C_p) according to Equation 5-2.

$$\frac{\Delta T}{\Delta t} = \frac{2\pi f \varepsilon_o \varepsilon'' E^2}{\rho C_p}$$

Equation 5-2   Determination of sample heating rate as a function of density under microwave irradiation (Yixin and Chunpeng, 1996)

From Equation 5-2, if all parameters are kept constant apart from those of sample density it is possible to predict the heating rate of cellulose when differing densities are used. Nevertheless, with increasing temperature changes in the dielectric loss factor will inevitably take place alongside changes in specific heat capacity as the sample decomposes. As such, it is not possible to use this equation for a sample undergoing microwave pyrolysis.

As previously determined in Section 4.3, the rate of heating was not seen to be the most significant factor determining the extent of decomposition of microcrystalline cellulose, but rather the maximum temperature achieved.

Nevertheless, due to the dependency of the maximum temperature on the microwave properties of the material, it could be said that the maximum temperature is dependent on the heating rate. Differing sample density could potentially have a significant effect on the microwave pyrolysis process enabling heating rates and maximum temperatures to be more efficiently achieved without the need to alter power input. This may have the further benefit of eliminating possible increases in interaction of the microwave field with evolved pyrolysis products (bio-oils). Hence, regulating the sample heating through changes in density may also maintain the mechanism of oil formation during the pyrolysis process; as increased microwave power input is not required and microwave interactions with oils will be reduced.

However, a distinct lack of knowledge surrounding the effect of sample density exists within the microwave pyrolysis, with Equation 5-2 unlikely to apply as the decomposition process progresses, with changes in both the dielectric permittivity and the specific heat capacity of the microcrystalline cellulose occurring with increased temperature. With this, the conduction of heat (or lack thereof) throughout the material will likely have a significant effect on the bulk sample temperature and heating rates, resulting in the formation of hotspots. This may affect localised heating rates or result in thermal runaway (Fernández *et al.*, 2011).

Due to limitations in scale it was not possible to use the CEM Discover microwave to investigate the effects of density on the cellulose microwave pyrolysis process. As such, scaled up experiments were carried out using the "SRL Milestone RotoSYNTH" multimode

batch microwave at 1200W, as per the method described in Section 9.2.4. For this process it was necessary to prepare microcrystalline cellulose samples of differing sample density. For this samples were prepared using a hydraulic press, with densities produced ranging from $0.67 - 1.24 \text{g/cm}^3$. The corresponding applied pressures and resulting densities are shown in Table 5-1. For each experiment 100g ±1.5g of these samples were used.

Table 5-1   Influence of applied pressure on the resultant density of cellulose samples

Pressure kN	Resulted Density g/cm^3
6.30	0.67
12.5	0.83
25.0	1.04
37.5	1.17
50.0	1.24

From preliminary tests it was found that pyrolysis was complete in 10 minutes with irradiation at 1200W, therefore microwave experiments for each density were performed from 2.5 to 10 minutes in 2.5 minute increments. After each run, bio-oil and bio-char yield was measured, with gas yield estimated by difference. Temperature was measured using an IR sensor from the external temperature of the reactor.

5.2   Results

As seen from Figure 5-1, the product distribution of char and oil after 10 minutes demonstrated a non-linear relationship with density. The maximum bio-oil achieved was observed for a cellulose density of 1.04g/cm^3. When examined further Figure 5-1 also reveals an inverse relationship between solid and bio-oil formation; with gas yield essentially being constant throughout the experiment, demonstrating a net shift between solid and liquid as the density changed.
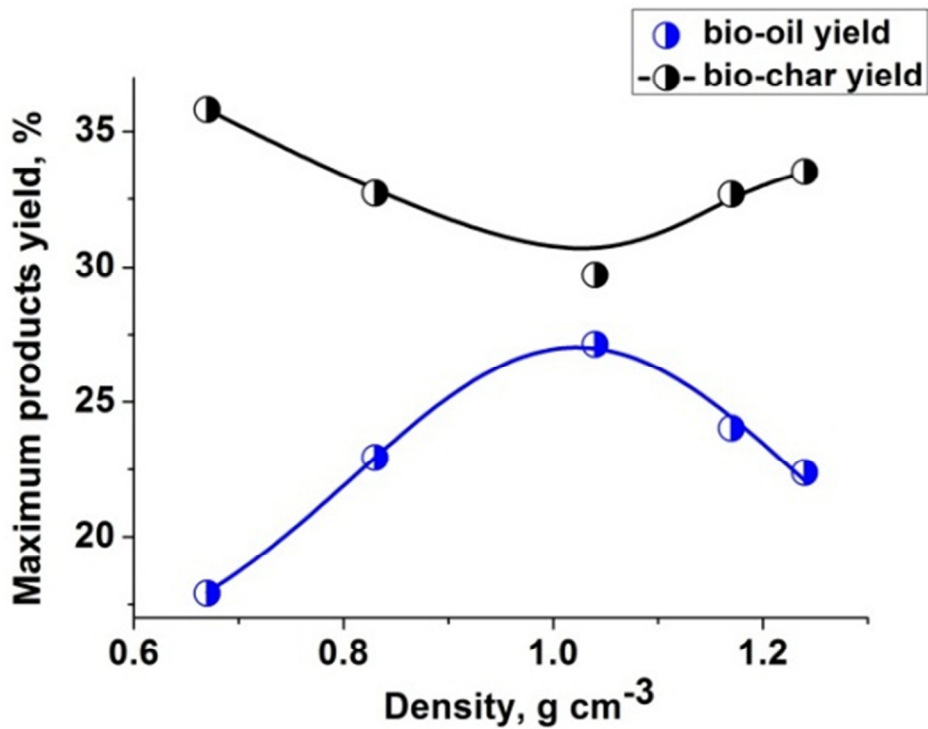
Figure 5-1   Influence of cellulose density on final product yields. (Gas varied between 42-46wt.%)
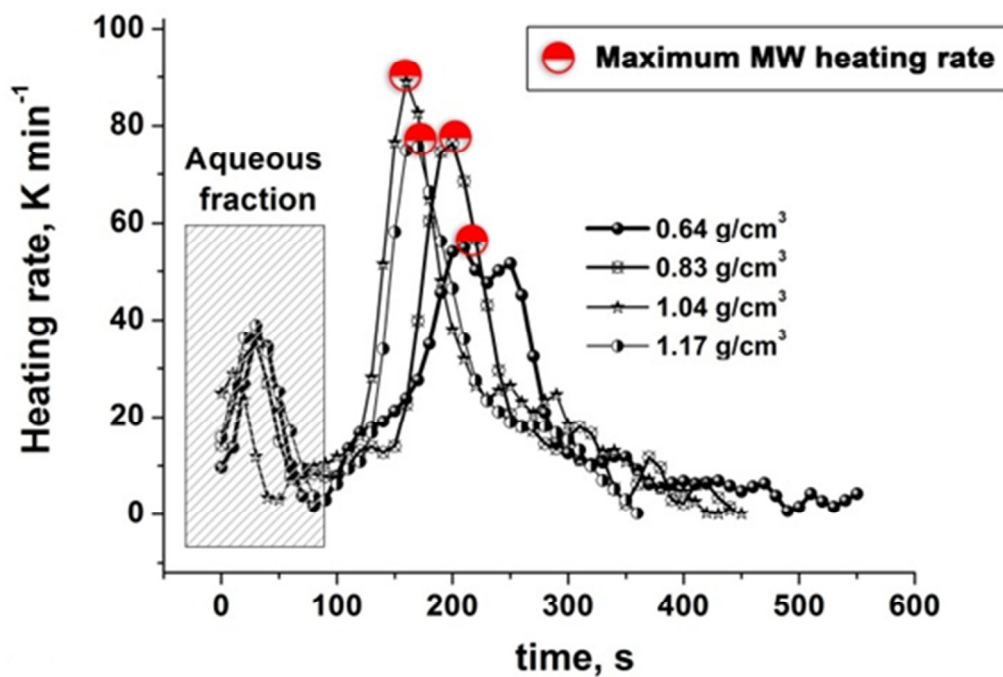
Figure 5-2   Sample heating rates for differing density cellulose samples when exposed to 1200W microwave radiation

It is shown in Figure 5-2, from heating rate profiles derived from temperature with time, that two maxima arise at approximately 40 and 150 seconds. This is in good agreement with previous heating rates derived from CEM experiments; as shown in Figure 4-7.

From this it is possible to determine that the first peak in heating rate is derived from moisture content acting as a "molecular radiator" (Kaiser *et al.*, 2000); as previously described in Section 4.3.1.1. The reduction in heating rate after this peak correlates to evaporation of water resulting in a plateau in the thermal profile. The reproducibility of this first peak verifies the accuracy of temperature measurement and that no significant differences in the mechanism of heating arise due the use of differing microwave system or sample load. The intensity of the second peak is largely dependent upon the cellulose density, corresponding to the interaction of cellulose with the microwave field.

Upon reaching higher temperatures and peak heating rates between ~150-200°C with respect to differening desities (see Figure 5-2), the dependency of the heating rate fits that of a Gaussian approximation (see Figure 5-3) with a maximum heating rate observed for 1.04g/cm^3. Although,when examined in conjuction with Figure 5-2, a more complex realtionship with density occurs; whereby denisty affects the heating rates of the cellulose in a non linear fashion over the whole temperature range. This is reflected most obviously in the sample density 0.64g/cm^3 where heating rate between ~95 and 140°C exceed those of all other densities, see Figure 5-2. However, the peak heating rate of the sample is lowest but the length of time the deompositon takes place over is longest.
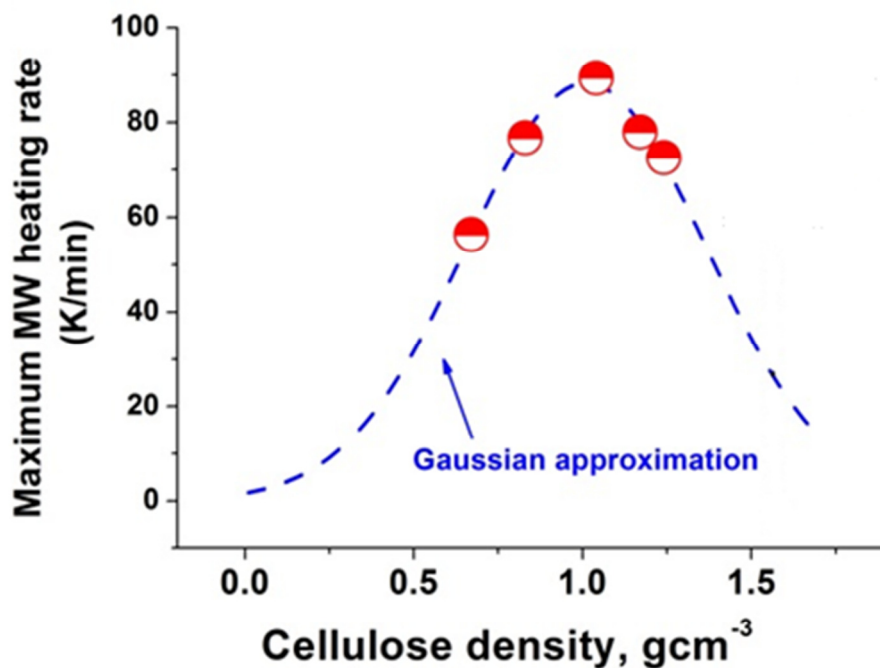
Figure 5-3 **Peak sample heating rates of differing cellulose density samples when exposed to 1200W microwave irradiation with Gaussian approximation trend line**

The rate and extent of decomposition would appear to demonstrate the complex nature of the decomposition taking place. It is likely that the rate of volatile product evolution and the proportion of condensed bio-oil within the reactor help to control the maximum heating rate achieved. This is most probably as a result of the production of dielectrically responsive decompostion prodcuts or through exothermic reactions taking place during the decomposition process, this theory is supported by McLaughlin *et al.* (1996) and Bilali *et al.* (2005). It is also possible that void volume and the reduction of evolution pathways plays a crtitical role, trapping oil within the cellulose structure and undergoing secondary reactions to form char (Miura *et al.*, 2004), a substatially more responsive microwave receptor. A further possibilty is the change in proportions of crystalline and amorphous regions with the cellulose arises with increasing sample desnity (Mazeau and Heux, 2003), resulting in decreased biopolymer fluctuations. When we examine the rate of bio-oil production, we also find a non-linear dependency of maximum oil production rate and sample desnity; see Figure 5-4.
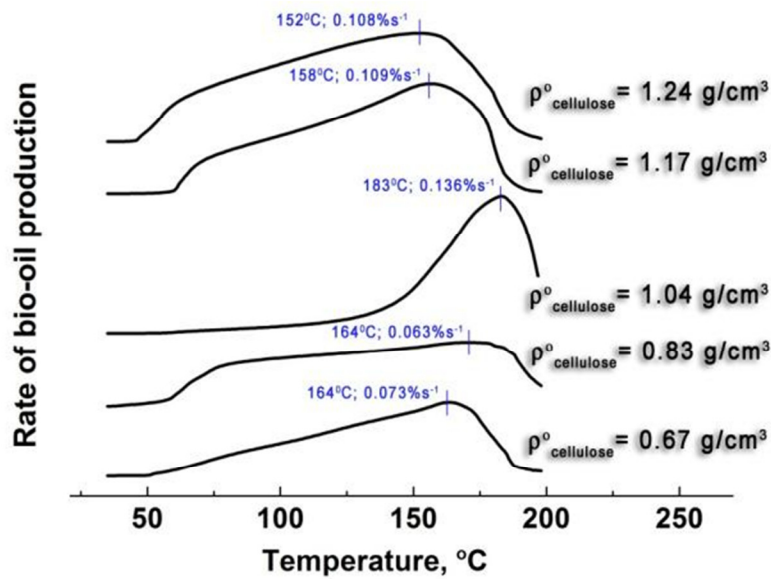
Figure 5-4   Stacked kinetic profile traces showing the influence of initial density of cellulose sample on the rate of bio-oil production (all traces use the same y axis scale)

From Figure 5-4 we find that the maximum rate of bio-oil production also varies with sample temperature, increasing from 164-183°C with growing density from 0.67-1.04g/cm^3 and above 1.04g/cm^3 a reduction in the temperature occurs from 183-152°C for 1.04-1.24g/cm^3, respectively. When examined further the overall bio-oil yield and heating rate are found to have a linear relationship; see Figure 5-5
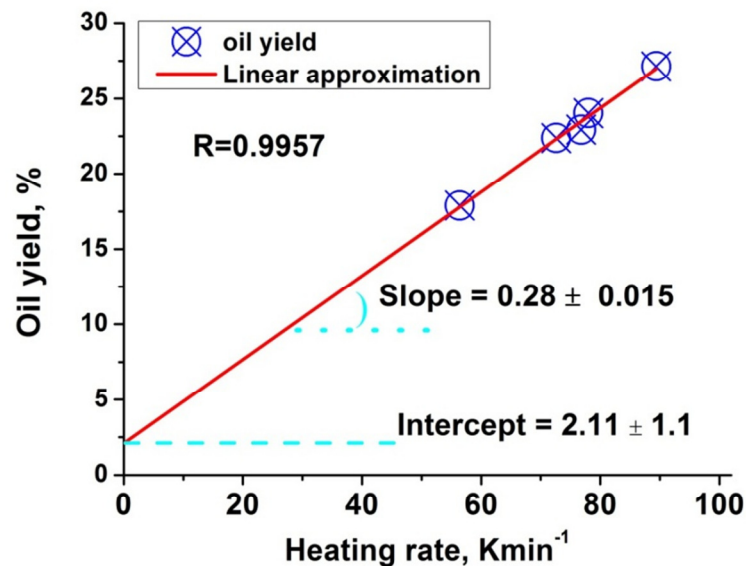
Figure 5-5   Correlation between maximum heating rate and oil yield

When we examine the rate of bio-oil production with sample density and temperature as a 2D and 3D plot (see Figure 5-6) a clearer picture is formed. The rate of bio-oil production gradually increasing with temperature, alongside the sample density increases, to a peak rate of 0.136wt.%/s at 1.04g/cm^3. This is consistently followed by a sharp decline in oil production after the peak rate. This occurs between 152-183°C. The overall rate of oil production follows a similar profile for all sample densities, suggesting no change in the mechanism of degradation with increasing density.
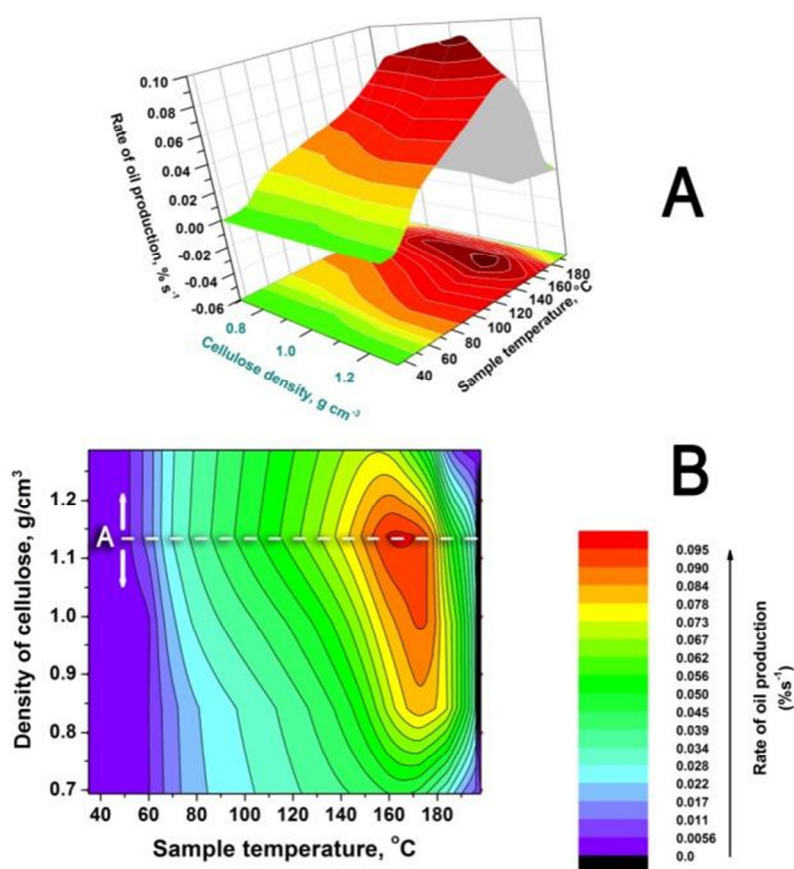
Figure 5-6   The rate of bio-oil production as a function of temperature and the initial density of cellulose sample represented as A) three and B) two dimensional graphs

When examined further we find that bio-oil yield is independent of heating rate during the first four minutes of the microwave pyrolysis process; see Figure 5-7. This would suggest that for the first four minutes of the pyrolysis process, irrespective of sample density that the aqueous fraction produced (up-to 7.8wt.%) is as a result of the steam distillation of the cellulosic structure. During second phase of rapid sample heating, oil yield increases quickly to a maximum of ~24.0wt.%.
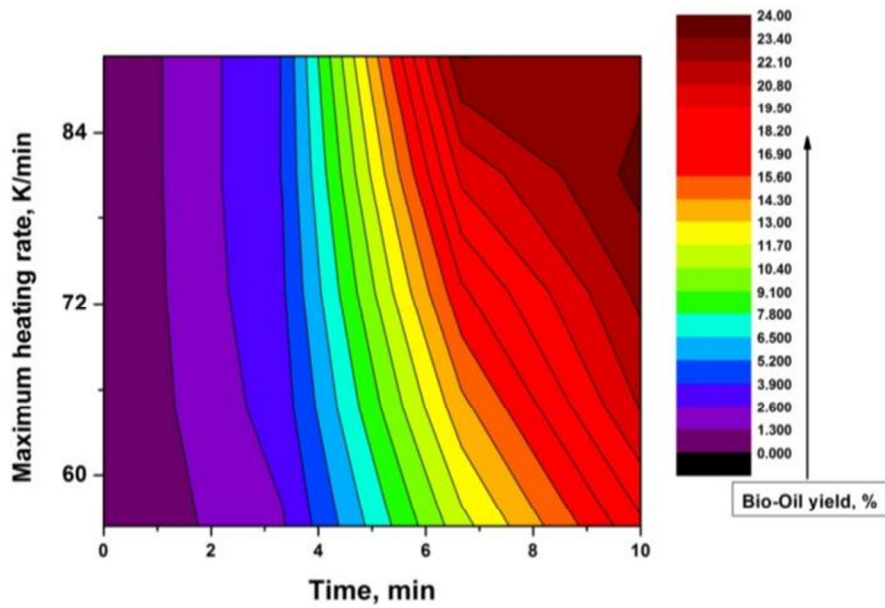
Figure 5-7   Bio-oil yield as a function of pyrolysis time and maximum heating rate achieved during the pyrolysis process
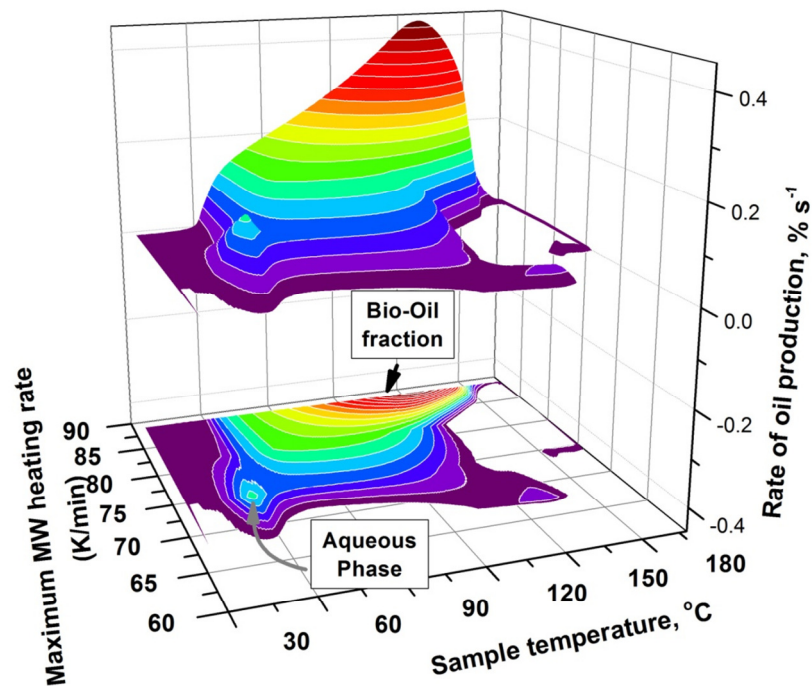
Figure 5-8   The rate of bio-oil produced as a function of temperature and microwave heating rate of cellulose

Figure 5-8 shows the relationship between the two critical factors of sample temperature plus maximum heating rate and the resultant rate of oil production. The data supports the

theory that heating rate could be the major variable responsible for the maximum generation of bio-oil, proving that heating rate is a fundamental parameter in the mechanism of the microwave pyrolysis of cellulose. However, due to the interdependencies of cellulose density, the resultant dielectric properties, subsequent heating rate, maximum temperature and rate of oil production, it is not possible to conclude that heating rate is the only factor determining the production of bio-oil. This is an overriding theme of microwave pyrolysis research, whereby the interdependency of all properties mean that it is almost impossible to determine which has the greatest effect on yields and the mechanism of degradation, but rather it is a combination of all factors that determine the overall extent of decomposition and products formed.

The liquids produced during experimentation were examined for their composition by GC-MS, the results of which are found in Table 5-2. From this, it is possible to determine that the mechanism of degradation is essentially the same for the decomposition of cellulose throughout the microwave pyrolysis investigation, with no change in the products formed as a result of changes in density.

Table 5-2   Major products of bio-oils produced during the microwave pyrolysis of cellulose samples of differing density

Retention Time	Compound Name	Empirical Formula
7.68	2-Ethoxyethyl acetate	$C_6H_{12}O_3$
8.40	Levoglucosenone	$C_6H_6O_3$
10.13	1,4:3,6-Dianhydro-α-d-glucopyranose	$C_6H_8O_4$
11.65	4,5-Dimethyl-3-heptanol	$C_9H_{18}O$
12.40	4-Oxotetrahydropyran-2-carboxylic acid	$C_6H_8O_4$
13.90	D-Allose	$C_6H_{12}O_6$
14.70	Levoglucosan	$C_6H_{10}O_5$
16.18	1,6-Anhydro-β-D-glucofuranose	$C_6H_{10}O_5$

Calorific values of oils and chars were also determined by bomb calorimetry and displayed in Table 5-3. It is evident that little variation in both calorific values (CV) are observed in any one experiment. However, a maximum CV of bio-oil is observed for cellulose pellet density of $1.17g/cm^3$ (22.2 MJ/Kg). This supports the GC-MS data that the composition of bio-oils is similar regardless of the experimental conditions examined.

Table 5-3   Calorific values of solid and bio oils produced at 10 minutes microwave exposure

Sample density g/cm^3	Bio-Oil CV MJ/Kg	Solid CV MJ/Kg
0.67	21.7	25.3
0.83	21.9	23.6
1.04	20.0	23.4
1.17	22.2	26.7
1.24	21.2	27.2

Solid residue CV also showed little variation with density or the extent of pyrolysis, indicating that the composition of both solid and bio-oil were similar throughout all experimentation.

5.3   Conclusion

From the work performed it is possible to conclude that the formation of bio-oil was significantly impacted by the density of microcrystalline cellulose samples. The yields of oil formed a Gaussian distribution with microcrystalline cellulose density of an optimum yield of bio-oil at 1.04g/cm^3. From this, it was possible to determine the potential process controlling the pyrolysis process and deduce that heating rate had the greatest overall effect. However, a greater understanding of the variation in the dielectrics of cellulose during the decomposition is required to understand the process further. This is due to the density changing the dielectric properties of cellulose, which in turn change the heating rate which subsequently change the temperature, that again change the dielectric properties and so the process continues.

Nevertheless, the implications are that there is an optimum density of microcrystalline cellulose at which maximum oil yield can be attained, a critical heating rate below which steam distillation is the dominant process and above this, pyrolysis occurs and optimum pellet density corresponds to the greatest heating rate combined with the rapid removal of bio-oils from the reactor which in turn reduces the number of secondary reactions that occur.

Chapter 6:

Microcrystalline Cellulose Hydrolysis

Published Work

Fan, J., De , M., Budarin, V., Gronnow, M., Shuttleworth, P., Breeden, S., Macquarrie, D., & Clark, J. (2013)Direct Microwave-Assisted Hydrothermal Depolymerization of Cellulose, Journal of the American Chemical Society 135 (32), 11728-11731

Fan, J., De , M., Zhu, Z., Budarin, V., Gronnow, M., Gomez, L. D., Macquarrie, D. & Clark, J. (2013) Microwave-enhanced formation of glucose from cellulosic waste. Chemical Engineering and Processing: Process Intensification.

6 Microcrystalline Cellulose Hydrolysis

6.1 Introduction

As ascertained in Chapter 6, low temperature microwave pyrolysis process has significant advantages over a conventional thermal process, with degradation taking place at significantly lower temperatures. The oils produced largely comprise of C6 anhydro sugars, these being levoglucosan, 1,4:3,6-dianhydro-α-D- glucopyranose, levoglucosenone and 1,6-anhydro-β-D-glucofuranose, demonstrating significantly less complexity to those produced by conventional thermal means. However, these bio-oils have significant limitations if they are to be directly used as liquid bio-fuel in transportation, with the extremely high oxygen content making them hydrophilic to the extent, that without the use of emulsifying agents they do not easily blend with conventional fuels (Dilcio Rocha *et al.*, 1999). They also require de-oxygenation to increase their calorific value and their long term stability (Mortensen *et al.*, 2011). Subsequently, extensive reforming (upgrading) of the bio-oils is required which is often energy intensive and expensive (Butler *et al.*, 2011), likely rendering the use of these bio-oils economically unviable.

It is possible to convert the anhydrous sugars contained within pyrolysis bio-oil to glucose, by hydrolysis; as demonstrated by Shafizadeh (1982) and Bennett *et al.* (2009). The process often requires the use of additives such as acid (Bennett *et al.*, 2009). This has further complications as the acid used requires neutralisation or removal (Shafizadeh *et al.*, 1979) before the glucose can be used within a fermentation process.

Cellulose can also be directly decomposed to glucose by conventional hydrolysis, however, the yields are significantly limited due to accessibility of cellulose chains. Furthermore, the high temperatures required for these processes lead to limited glucose selectivity, with the main products being anhydrous sugars (e.g. levoglucosan), secondary breakdown products (e.g. HMF) and phenols (Lin *et al.*, 2009). This can be enhanced significantly by the pre-treatments such as acid (Bjerre *et al.*, 1996), carbon dioxide explosion (Zheng *et al.*, 1998) or addition of lime (Wyman *et al.*, 2005). However, the interaction of amorphous regions within cellulose by microwaves and the opening of the polymer structure (as discussed in

Section 4.3.1.2), pose an interesting new path for the hydrolysis of cellulose without the need for pre-treatment or addition of additives.

6.2 Conventional Thermal Hydrolysis: Applied to Biomass Decomposition

The conventional hydrolysis process is normally used to decompose organic molecules through their treatment with water at elevated temperatures and pressures: typically 280-370°C and 1450-3650 psi (Behrendt *et al.*, 2008), respectively. Under these conditions water is still in its liquid state but behaves very differently, exhibiting the exotic properties of acting as both reactant and catalyst (Toor *et al.*, 2011). By utilising this behaviour it is possible to directly convert biomass to its decomposition products, without the need for energy intensive drying step often required before a thermal pyrolysis process (Bridgwater *et al.*, 1999).

6.2.1 Subcritical and Supercritical Water

Water can exists in four states, solid, liquid, gas and supercritical fluid (see Figure 6-1), dependent upon the temperature and pressure it is subjected to.
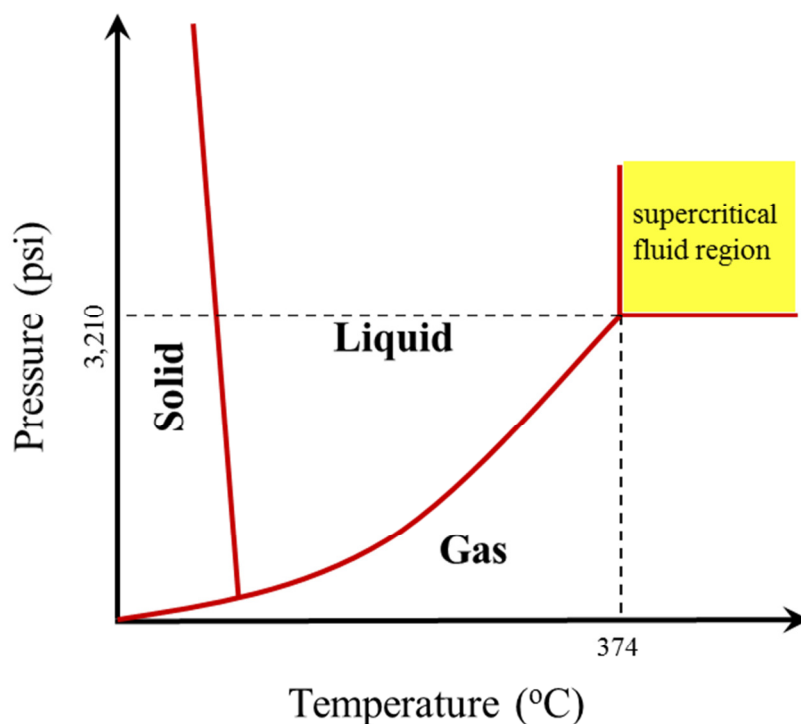
Figure 6-1   The phase diagram of water

When water undergoes heating with increased pressures, the changes in state become blurred, with regions in which water remains a liquid past its atmospheric boiling point, these being subcritical and supercritical conditions. Subcritical conditions exist between waters atmospheric boiling point and 374°C (Zhang *et al.*, 2010b). Within this region it exhibits interesting properties, whereby the water has low viscosity and high solubility for organic substances (Toor *et al.*, 2011). These enable fast, homogenous reactions to take place, making it a perfect medium for the conversion of biomass to its constituent components (Franck, 1983, Krammer and Vogel, 2000). When in its subcritical condition, water demonstrates significant changes in its, density (Toor *et al.*, 2011), dielectric constant (Uematsu and Frank, 1980) and hydrocarbon solubility (W. King *et al.*, 1999) (see Figure 6-2) but also to a significant degree, its ionic product (K_w) (Hunter and Savage, 2004).
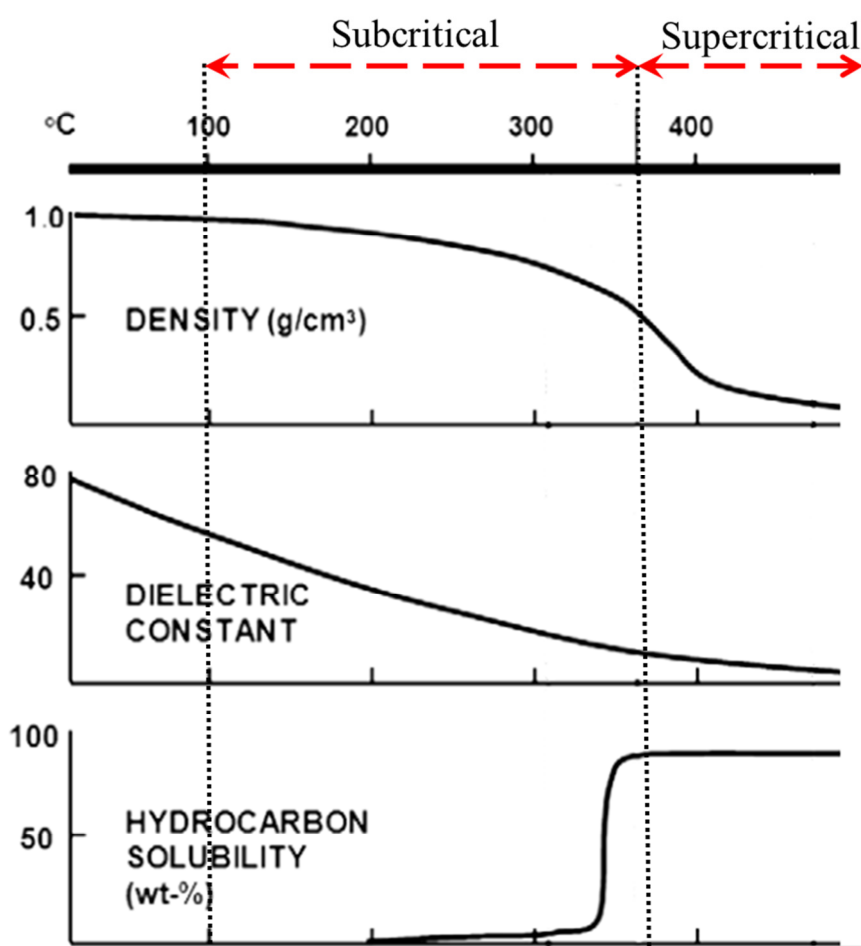
Figure 6-2   Changes in density, dielectric constant and hydrocarbon solubility with increasing temperature of water through subcritical and supercritical conditions (adapted from Zhang *et al.* (2010b))

The dissociation of water into its ionic products, H^+ and OH^-, are relatively high within the subcritical range (Hunter and Savage, 2004). When this is combined with little change in its density, the concentration of waters ionic products become accentuated further, enabling the catalysis of many acid/base reactions (Akiya and Savage, 2002). Alongside this, the reduction in waters dielectric constant allows for hydrophobic components to experience increased solubility allowing for their extraction from a substrate without the need of organic solvents (Holliday *et al.*, 1997).

Within the supercritical region of water, significant changes arise, with it displaying similar properties to that of a gas, nevertheless its density is similar to that of water in its liquid state (Zhang *et al.*, 2010b). Within this region the viscosity of water is the same as a gas and diffusion rates in excess of one order of magnitude greater than that of its liquid state (Brunner, 2009). With this, atmospheric gases and organic compounds become completely soluble with the supercritical water (Shaw *et al.*, 1991). However, inorganic (salts) compounds become less miscible (Kritzer and Dinjus, 2001).

Nevertheless, of interest is the significant reduction in dielectric properties of water in the supercritical region (>374°C and 3210psi) (Hawthorne *et al.*, 1994). This is as a result of the slight decrease in waters density and the disruption/breakage of hydrogen bonds (Zhang *et al.*, 2010b). The subsequent reduction in the dielectric properties indicates a decrease in waters polarity and hence an increase in its ability to dissolve organic compounds (Hong and Spritzer, 2002). However, this does render supercritical water almost impossible to heat by a microwave radiation. This has important implications for a microwave hydrolysis process as the energy efficiency of achieving supercritical conditions will decrease dramatically rendering the process unachievable. As such, sub-critical conditions were only investigated in the following chapter.

6.2.1.1   The Effect of Process Variables

To ascertain the potential of a hydrolysis process on the decomposition of cellulose it is necessary to understand the effect of conventional hydrothermal process conditions. Similar to that of pyrolysis, process conditions play a critical role in the hydrolysis of any material, such as:

- particle size
- feedstock

- heating rate
- solvent density
- pressure
- residence time

These affect the product compositions and yields to varying degrees. As supercritical conditions will not be achieved during the hydrolysis process, the following parameters have only been discussed for a subcritical state.

6.2.1.1.1   Particle Size

Particle size reduction is used to increase the accessibility of the substrate structure to hydrothermal treatment, increasing the degree of hydrolysis and fragmentation (Akhtar and Amin, 2011). During subcritical hydrolysis the effect of particle size is minimal as water acts as a heat transfer medium and extractant. It is found that particle size reduction of materials to between 4 and 10mm is suitable to overcome heat and mass transfer limitations (Mani *et al.*, 2004).

6.2.1.1.2   Feedstock

As per pyrolysis, the biomass feedstock plays an important role in the hydrothermal decomposition, with the proportions of its constituents to a large extent dictating yields and composition of hydrolysate (Zhong and Wei, 2004). As a general rule, if the feedstock largely consists of cellulose and hemicellulose it will produce hydrolysate, but if the major component is lignin the process will favour the production of char (Demirbaş, 2000).

6.2.1.1.3   Heating Rate

Heating rate plays a critical role in hydrolysis, similar to that of pyrolysis, enabling the bulk fragmentation of the substrate, inhibiting char formation (Kamio *et al.*, 2008, Akhtar and Amin, 2011). However, heating rate has little effect on the product distribution of oils formed with the dissolution and stabilisation of organic fragments by the subcritical water acting as a solvent. Nevertheless, if high heating rates are used, significant fragmentation of the substrate occurs and yield of gas increases in comparison to oil (Kamio *et al.*, 2008).

6.2.1.1.4   Solvent Density

The effect of water density within a hydrolysis reaction is considered to be a key parameter. High water to substrate ratio often results in the production of high oil and gas yields due to the increased salvation of organic components (Sato *et al.*, 2003) and the enhanced stability of fragmented components. As substrate ratio increases, the effects of water stabilisation decreases and the interaction of fragments increases undergoing secondary reactions, resulting in greater solid yields (Boocock and Sherman, 1985).

6.2.1.1.5   Operating Pressure

Pressure plays a critical role in the hydrolysis process, enabling a single phase medium to be maintained as long as a critical pressure is achieved. Increasing the boiling point of water by increasing pressure removes the change in enthalpy required for the phase variation (liquid to gas), which decreases the amount of energy required for the process to operate (Akhtar and Amin, 2011). Further to this, pressure of the medium can be used to control the rate of hydrolysis and dissolution of the substrate. This can enable preferential reaction pathways to enhanced so that the production of liquid or gas can be optimised (Aida *et al.*, 2007). Alongside this, pressure increases the solvent density, penetrating the substrate further enhancing decomposition and extraction (Maynard *et al.*, 1998).

6.2.1.1.6   Residence Time

Of the processing parameters, residence time has one of the greatest effects on the final composition and overall conversion of biomass. This has been reported by a number of authors, finding that hydrolysate yield is a function of residence time (Yan *et al.*, 1999, Xu and Lancaster, 2008). As a rule it was found that with increased residence times, hydrolysate yield either increased, if the hydrolysis temperature was low (~150°C) or decreased when higher temperatures were used (250-280°C) (Karagöz *et al.*, 2003, Sugano *et al.*, 2008). This is considered to be as a result of secondary and tertiary reactions taking place, reducing heavier intermediate species to liquids, gases or solid residues (Su *et al.*, 2004).

6.2.1.2   Acid and Alkali Hydrolysis

Acid hydrolysis of biomass has been investigated extensively and is used regularly to treat biomass for production of hydrolysate in a hydrolysis process (von Sivers and Zacchi, 1995). Dilute acid hydrolysis has been proven to achieve higher reaction rates, whilst significantly

improving conversion of cellulose to sugars (Lee *et al.*, 1999). In lignocellulosic materials, with the use of high temperatures and dilute acid concentrations, it is possible to achieve conversion of xylan and xylose in lignin to sugars and oligosaccharides (Carroll and Somerville, 2009). Nevertheless the process often involves the use of H_2SO_4 and HCl, which pose a significant problem in themselves, as they are toxic, corrosive, and hazardous to handle. Furthermore they add additional costs to the infrastructure required, with the need for corrosion resistant reactors and recovery of the acid; as without these, the process would not be economically viable (von Sivers and Zacchi, 1995).

The use of bases has also been beneficial in the pre-treatment of lignocellulosic materials, with the saponification of ester bonds cross linking xylans and cellulose (McMillan James, 1994). This improves the porosity of the substrate making the structure more accessible to hydrolysis (Tarkow and Feist, 1969). The use of NaOH has been proven to cause the swelling of lignocellulosic materials increasing their internal surface area, decreasing the degree of polymerisation/crystallinity and disruption of lignin's structure. This also makes it more accessible to hydrolysis enabling the greater conversion of its structural components to basic sugars (Sun and Cheng, 2002).

6.2.1.3   Mechanism of Cellulose Hydrolysis

It is important to understand the products formed from the thermal hydrolysis process as it provides a comparative basis on which the microwave hydrolysis process of cellulose can be compared.

From the thermal hydrolysis of cellulose performed by Kabyemela *et al.* (1997), Kabyemela *et al.* (1999), Sasaki *et al.* (1998) and Sasaki *et al.* (2004) it is understood that cellulose undergoes several stages of decomposition dependent upon reaction temperature. The main products of decomposition are cellohexaose, cellopentaose, celletraose, cellotriose, cellobiose and glucose, forming from the cleavage of the polymer chain; resulting in oligomers and monomers of cellulose. Upon increased temperature or residence times glucose is observed to undergo epermization to fructose or decompose to erythrose plus glycolaldehyde or glyceraldehyde and dihydroxyacetone which can undergo dehydration to form pyruvaldehyde. The compounds pyruvaldehyde, erythrose and glycolaldehyde further undergo decomposition to acids, aldehydes and alcohols. The formation of 5-hydroxymethyl-2-furfural (HMF) is thought to arise through the direct decomposition of

glucose; of which the concentrations increase with longer residence time and higher temperatures. The mechanisms of cellulose degradation are represented further in Figure 6-3.
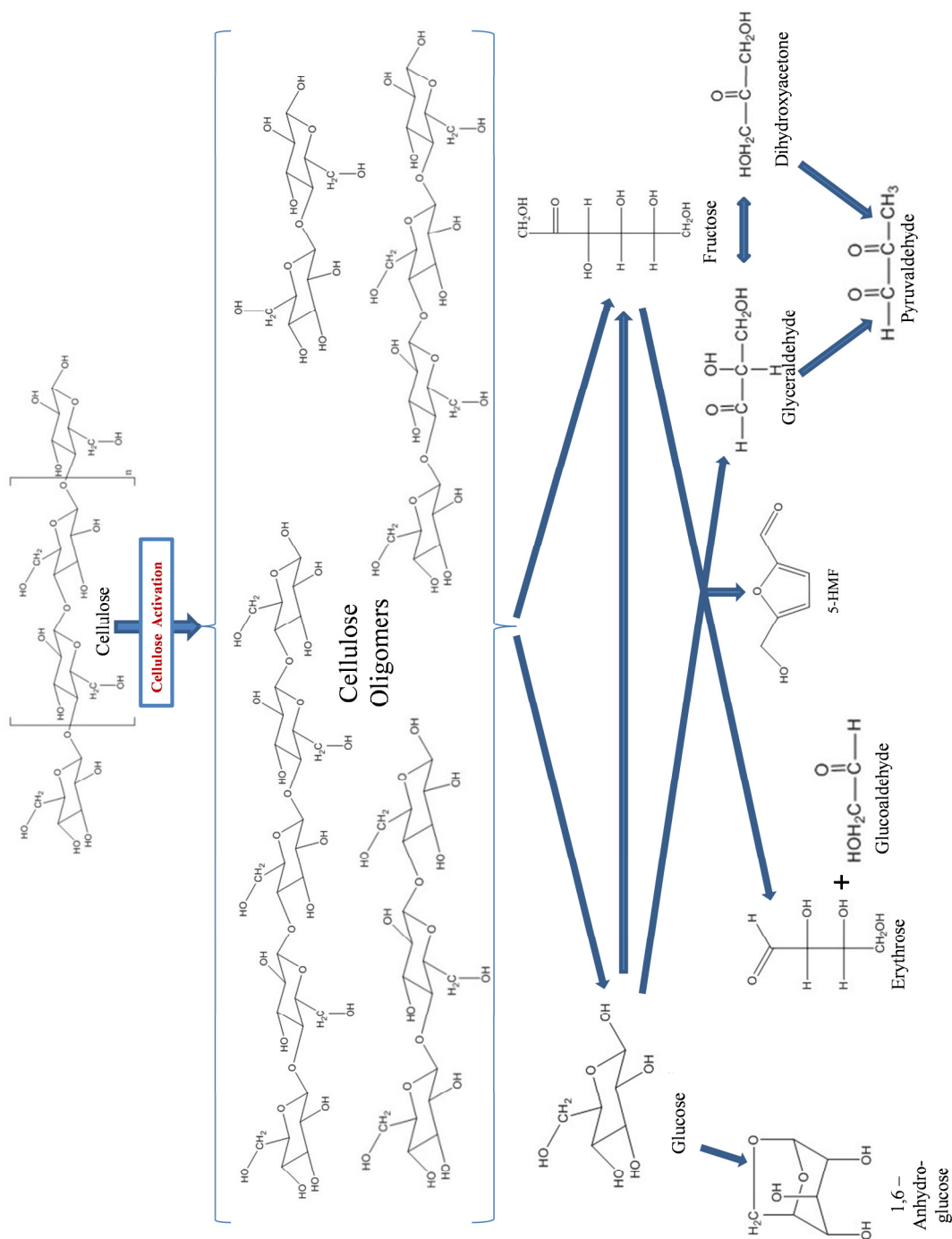
Figure 6-3 **The main reaction pathways in cellulose hydrolysis**

6.3   The Microwave Hydrolysis of Cellulose

As previously discussed in Section 6.2, hydrothermal processing offers a potentially beneficial route to hydrolyse lignocellulosic biomass into simple sugars by using elevated temperatures and pressures (Orozco *et al.*, 2007, Ross *et al.*, 2010). When this is combined with microwave heating, a potentially faster, more efficient, selective method of treatment is possible in the conversion of biomass components to sugars (Zhao *et al.*, 2010, Luque *et al.*, 2012b)

6.3.1   Results: Comparison of Conventional Thermal and Microwave Hydrolysis of Cellulose

6.3.1.1   Temperature Measurement

The conventional thermal and microwave hydrolysis of cellulose were investigated as per the methods outlined in Section 9.4, investigating the effect of temperature on the conversion of microcrystalline cellulose. However, for conventional hydrolysis it was not possible to measure the temperature of the reactor. Nevertheless, the microwave and conventional hydrolysis process used the same pressure measurement head (as seen in Figure 9-4: A and B). As such, from determining the temperature and pressure readings (see Figure 6-4) from the microwave process it was possible to derive an indication of the temperature in the conventional hydrolysis process.
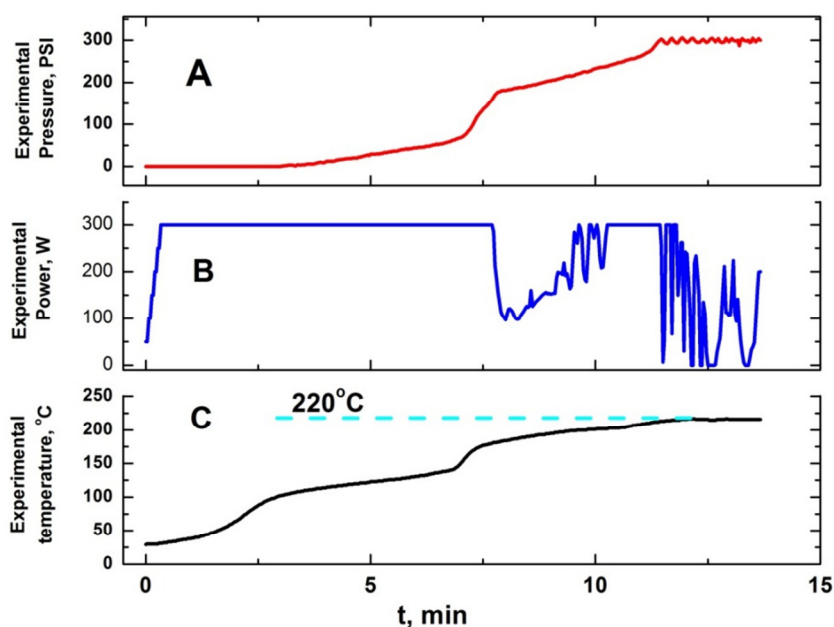
Figure 6-4   Profiles of microwave assisted cellulose hydrolysis: a) pressure recording, b) power recording, and c) temperature recording

The pressure/temperature readings were then used from the microwave process to confirm the relationship in conjunction with the Antoine equation for water (see Equation 6-1) (Thomson, 1946): results shown in Figure 6-5. This was then applied to the conventional thermal reactor to determine the temperature.

————

Equation 6-1   The Antoine Equation for Water

Where:

P = vapour pressure of a liquid

A, B and C = component specific constants

T = absolute temperature
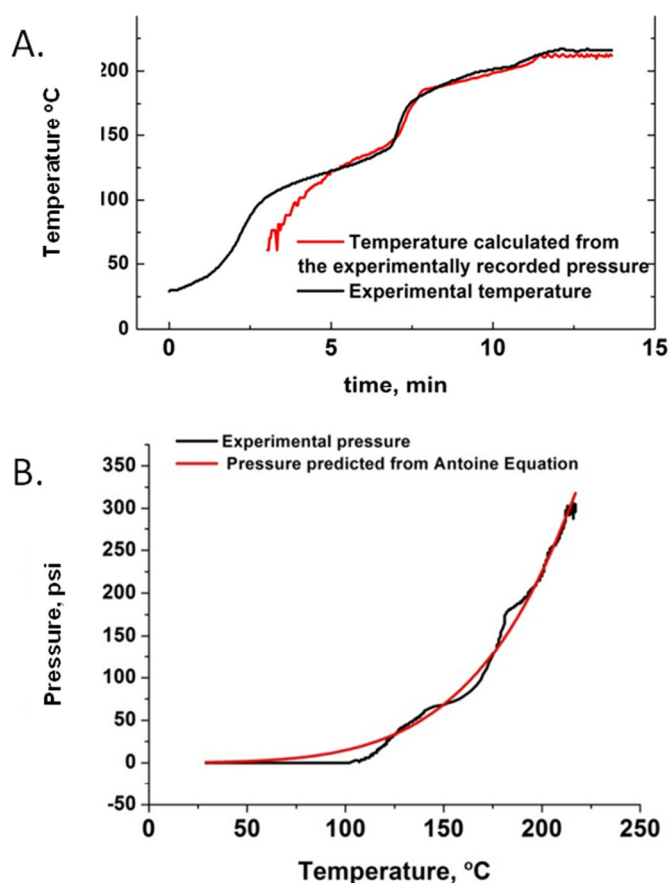
Figure 6-5   Comparison of the microwave experimentally obtained A.) temperature profile with the theoretical temperature profile as calculated from the measured experimental pressure, and B.) observed pressure with calculated temperature readings, from the Antonie equation for water

From the results shown in Figure 6-5, it was possible to determine that the Antonie equation for water held true (see Figure 6-5:B). Hence, the maximum temperatures achieved during conventional thermal hydrolysis experiments could confidently be determined.

6.3.1.2   Cellulose Decomposition and Product Yields

The mixture of microcrystalline cellulose and water was exposed to conventional or microwave heating to the temperatures of 100-230°C at 10°C intervals. From this it was possible to determine the extent of decomposition and the subsequent yield of major bio-oil components.

From Figure 6-6, it appears that the degradation of cellulose under hydrothermal conditions is almost constant between the temperatures of 100-180°C with between 4 and 5wt.% lost. This most likely corresponds to the ~5wt.% water contained within the original cellulose sample, hence no degradation has occurred. This is in agreement with mass loss observed in Section 3.
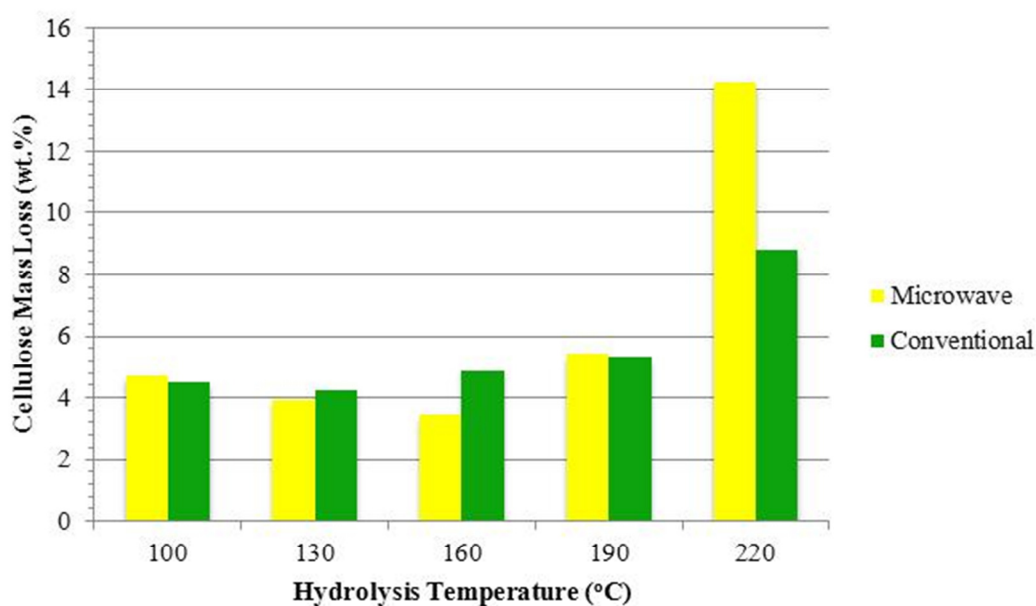
Figure 6-6   Cellulose mass loss for microwave and conventional hydrolysis experiments between 100-220°C

When 180°C is exceeded it was found that the cellulose decomposed to a much greater extent, with up to 14.3wt.% mass lost by 220°C under microwave conditions. However,

conventional thermal hydrolysis resulted in significantly less decomposition with a maximum of 8.8wt.% lost by the same temperature. This is of considerable value as it signifies that the temperature of 180°C is important in the microwave decomposition of cellulose. This is in good agreement with Budarin *et al.* (2010) plus results in section 4.3.1 and 4.4.2, in which the microwave pyrolysis of cellulose demonstrate significant decompositions initiated at 180°C, the phase transition temperature of cellulose (see section 4.4.2) . However, the hydrolysis process adds increased weight to this finding, as the likelihood of thermal gradients decreases due to the presence of water acting as a conduction medium. This is further supported by Horikawa and Sugiyama (2008) and Wada (2002) in which elevated temperatures were demonstrated to transform microcrystalline cellulose to its amorphous form.

From this result the crystallinity of cellulose was estimated, by stirring 1g of microcrystalline cellulose with10mL of deuterated water for 24 hrs and then drying for 6 hours at 110°C under vacuum. ATR-FTIR samples of this cellulose were taken and peaks corresponding to R-OH (3400cm^{-1}) and R-OD (2500cm^{-1}) in the respective regions were integrated and compared (see Figure 6-7).
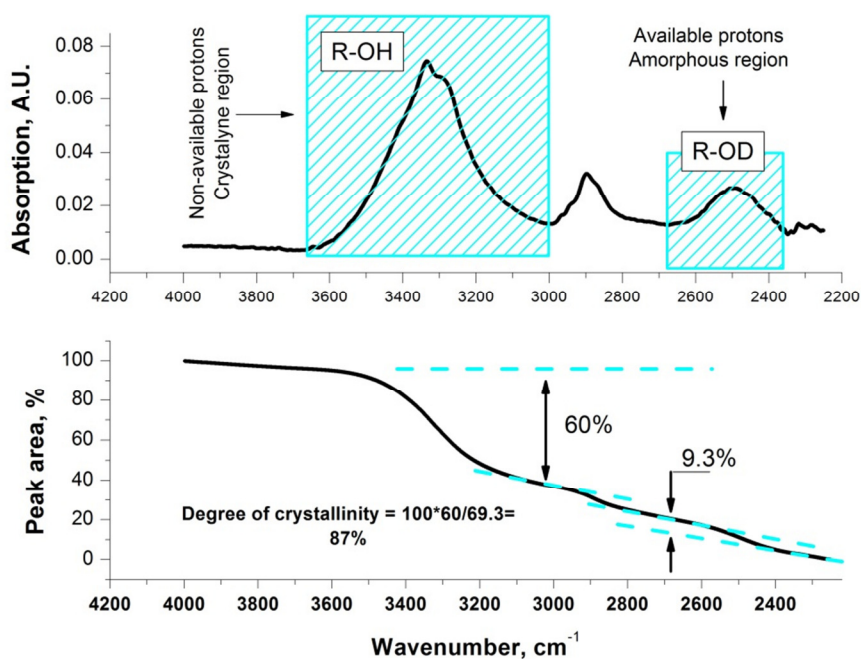
Figure 6-7   Estimation of the degree of crystallinity of the original microcrystalline cellulose

From Figure 6-7, due to crystallinity being 87wt.%, it was estimated that 13wt.% of microcrystalline cellulose was amorphous. This value is in good agreement with the extent of decomposition seen in the microwave hydrolysis process at 220°C (see Figure 6-6), indicating that the amorphous region of cellulose is able to be decomposed in the microwave hydrolysis process under the temperatures examined.

6.3.1.3   Product Composition

The composition of hydrolysate was examined through the use of HPLC, ^{13}C NMR and ESI (as described in Section 9.4). It was found from the HPLC performed on hydrolysates (see Figure 6-8) that they largely composed of mono- and di- saccharides, being glucose, fructose, xylose, levoglucosan and cellobiose, with a single unidentified compound.
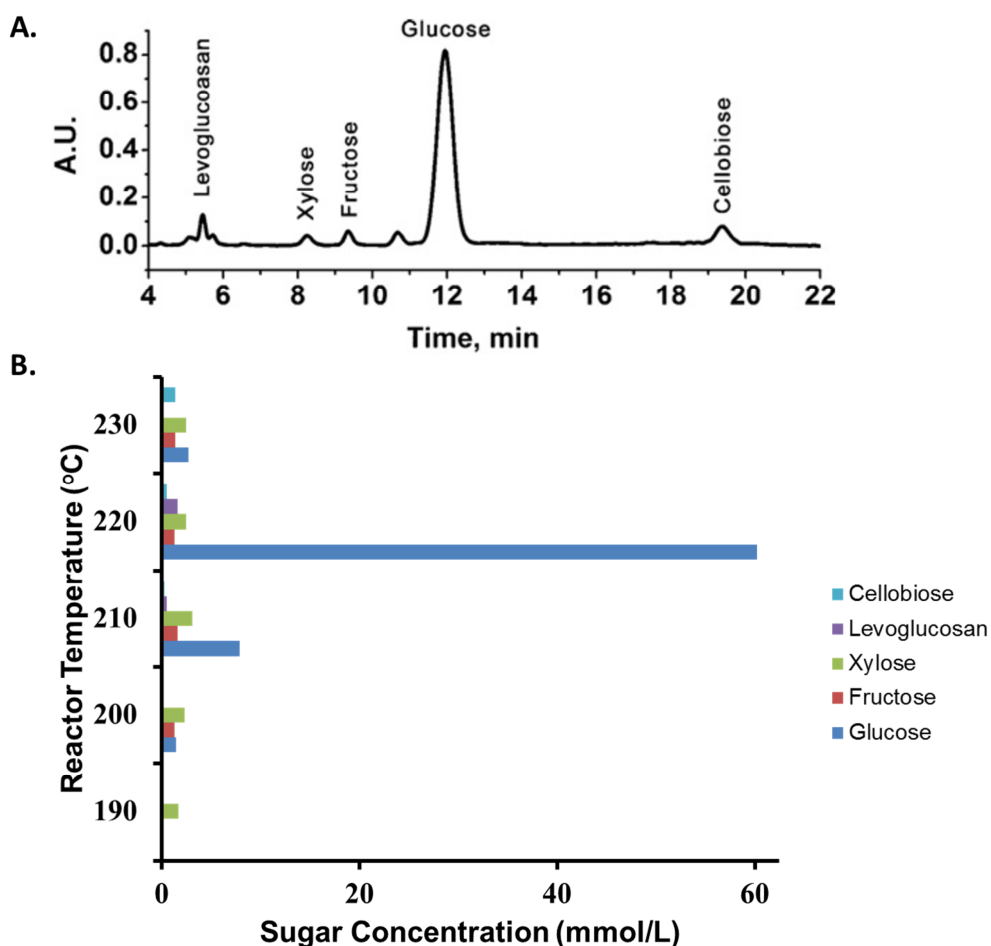
Figure 6-8   A) Typical HPLC trace and B)temperature influence on the composition of sugars formed in the microwave hydrolysis of cellulose

Nevertheless, the hydrolysis process demonstrated remarkable selectivity in the compounds formed. In particular the preferential formation of glucose at the temperatures of 210 and 220°C was observed, with a maximum yield of 60.2mmol/L at 220°C (see Figure 6-8:B).

When we compare the composition of hydrolysis products formed under both conventional thermal and microwave hydrolysis for the temperature of 220°C, we find that significant differences arise in the quantities of glucose formed, with greatly increased percentages of ~10.8wt.% compared to 0.2wt.% (see Figure 6-9) under microwave and conventional thermal process respectively. This equates to just over a 50 fold increase in glucose yield in the microwave process, showing a clear intensification in cellulose depolymerisation to glucose using microwave irradiation. It is also important to note that at this temperature the quantities of fructose and xylose are similar for both modes of heating but cellobiose demonstrated a 3-4 fold increase for microwave treatment. Further to this, the formation of levoglucosan only appeared in the microwave process.
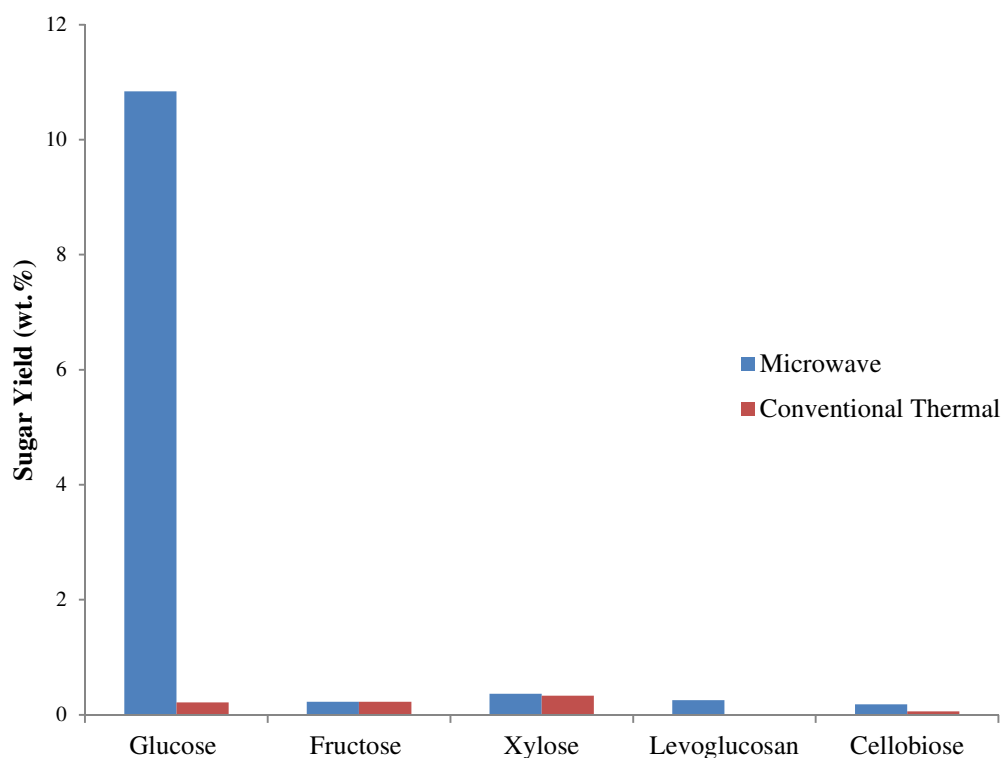
Figure 6-9   Comparison of microwave and conventional thermal sugar distributions for a hydrolysis temperature of 220°C

After further increases in temperature above that of 220°C a significant reduction in the proportions of glucose occurred, accompanied by decreasing amounts of all other components (see Figure 6-8). This most likely corresponds to the dehydration of the sugars or polymerisation to larger molecular weight components (Wu *et al.*, 2012). This is supported by data gained from ^{13}C NMR (conducted by Dr M. De) in which the spectrum confirms the presence of HMF, which is otherwise undetectable by ELSD. Interpretation of these peaks was performed in accordance with the methods set out by Bubb (2003). From the comparative analysis of the anomeric CH glucose carbons (97.04 and 92.39ppm) and the CH2 HMF peak at 110ppm, the approximation of the relative glucose to HMF content was calculated to be 3:1 at 220°C microwave treatment (Fan *et al.*); see Figure 6-10.
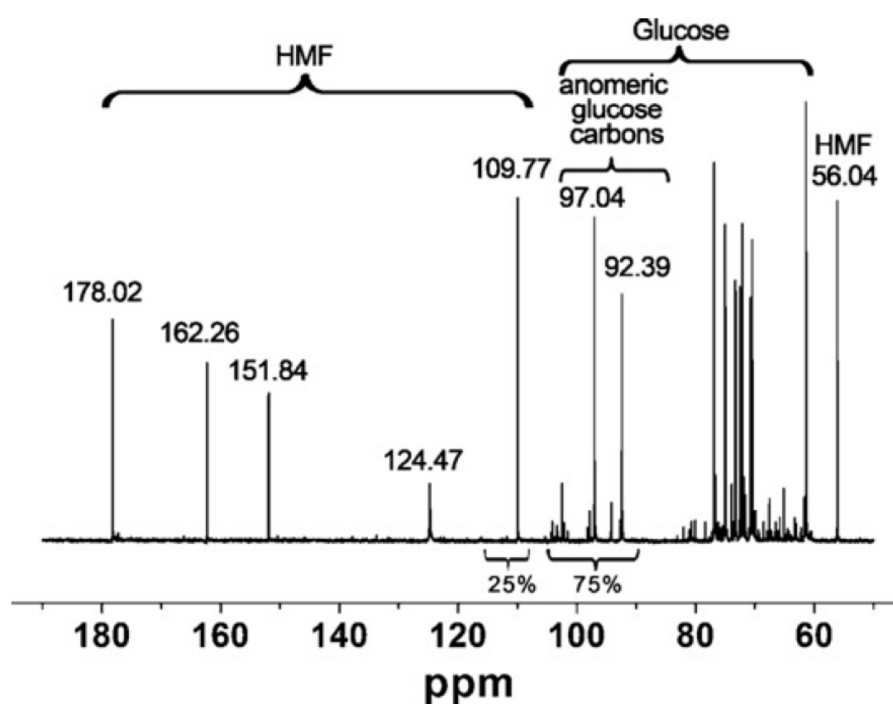
Figure 6-10 ^{13}**C NMR of microwave hydrolysis products of cellulose at 220°C (from Fan *et al.* (2013))**

The presence of HMF within the hydrolysis mixture was also confirmed by GC-FID (as per Fan *et al.* (2013)) (see Figure 6-11), when hydrolysis products were compared against retention times of standards.
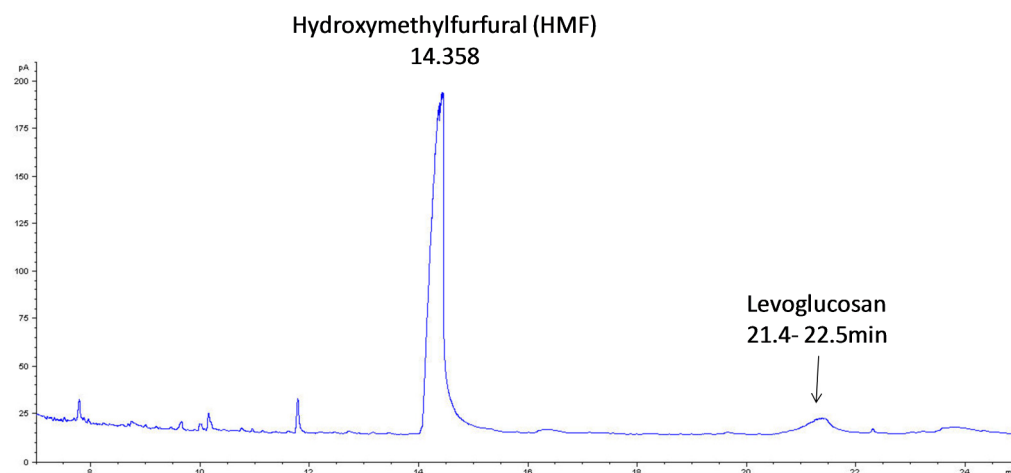
Figure 6-11 **Confirmation of the presence of HMF within microwave hydrolysis products attained at 220°C (from Fan *et al.* (2013))**

Due to limitation in the CD microwave system, the efficiency of microwave conversion of cellulose was assessed up to 270°C utilising the CEM MARS6 (CM6) microwave reactor. The experimental procedure of CM6 was performed in accordance with CD microwave experiments, with the quantities of microcrystalline cellulose and water being replicated as to maintain these parameters as a constant; see section 9.4. The results of these experiments demonstrated a substantial increase in glucose yield to 21wt.% under microwave hydrolysis conditions at 250°C (see Figure 6-12:A).
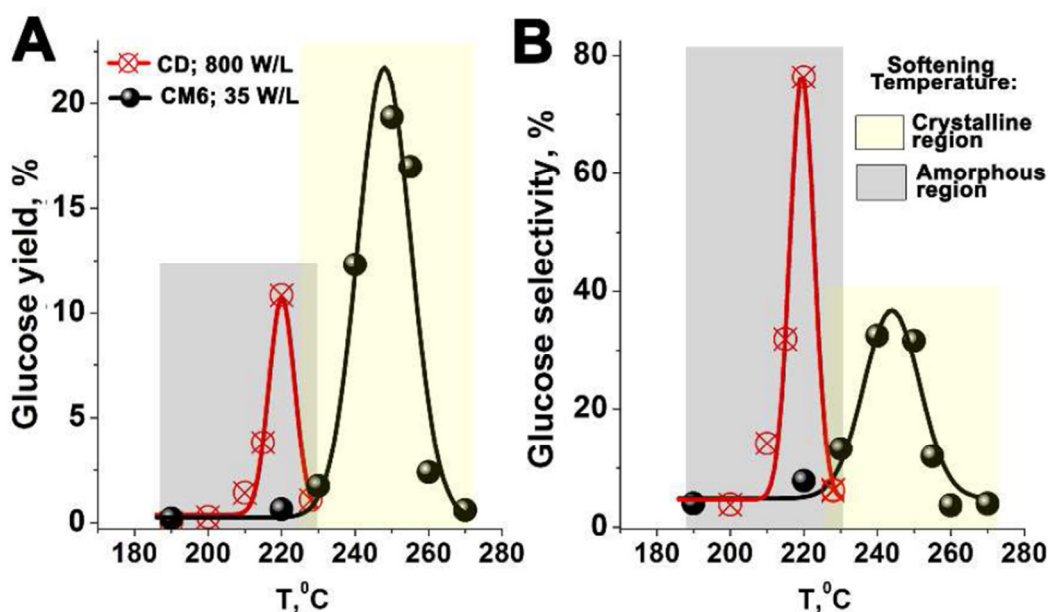
Figure 6-12 **Comparison of CEM Discover (CD) and CEM MARS6 (CM6) experiments: A)glucose yield; B)glucose selectivity. Contributions from amorphous and crystalline regions are indicated**

It was also observed during this process that the selectivity of glucose formation decreased substantially from 75wt.% to 36wt.% for CD and CM6 microwave systems respectively (see Figure 6-12:B). Alongside this, it was also observed that the temperature range at which the maximum decomposition occurred in CM6 experiments moved to 250°C, rather than for the CD experiments in which peak decomposition occurred at 220°C. This indicated that a substantial change in the mechanism of interaction of microcrystalline cellulose and the microwave field had occurred.

As discussed in Section 4.4.2.1, the microwave heating of cellulose and decomposition of its structure is most likely accounted for as a result of the freedom of movement of $-CH_2OH$ groups within the amorphous regions. Hence, lower decomposition temperatures than a conventional thermal process (see Figure 6-13). Nevertheless, when exposed to microwaves in the CM6 the interaction of these groups and the point of decomposition initiating at 180°C did not occur. This can only be explained as insufficient power density within the microwave cavity to promote these reactions, with 800 and 35W/L for the CD and CM6 microwave systems, respectively.
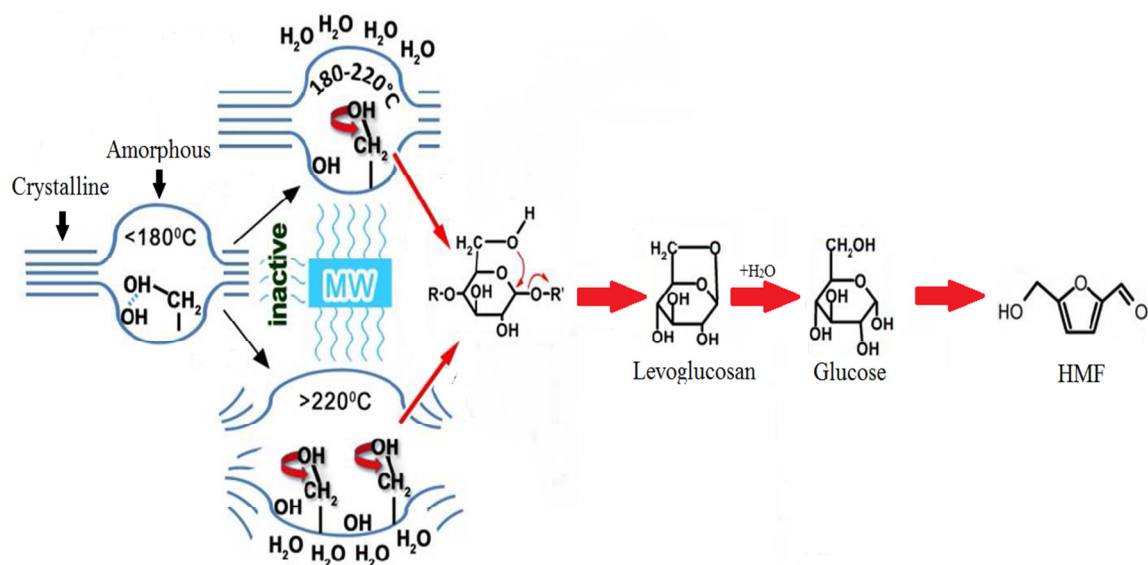
Figure 6-13   Proposed interaction of cellulose and microwave radiation and resulting decomposition products

The dependence of glucose yield with power density further suggests that two competing mechanisms are occurring within the cellulose structure, with the speed of $-CH_2OH$ group rotation playing a significant role (see Figure 6-13). These mechanisms are explained as:

1. Acceleration of the –CH$_2$OH group by microwave photons
2. Deceleration through interaction with neighbouring groups

The relative dominance of either process is dependent upon the degree of freedom of the –CH$_2$OH to react in phase with the microwave field and the potential of the group to undergo possible reactions with surrounding groups as a result of molecular collisions and subsequent nucleophilic substitution reactions (S$_N$2) (see Figure 6-13). For this to occur, sufficient activation energy is required. When a high microwave power density is used, sufficient kinetic energy is transferred into the –CH$_2$OH group so that the sum total of kinetic energy and thermal energy only require lower temperatures for the activation energy to be reached. At lower microwave power densities, the reverse is true. Hence, decomposition occurring at 180-220°C at 800W/L and 240-260°C at 35W/L.

6.3.1.4 *Glucose Generation through Cellulose Recycling*

To determine the maximum potential recovery of sugars, specifically glucose from the hydrolysis of microcrystalline cellulose, an experiment was performed in which cellulose was recycled. To achieve this, the same experimental procedure was used as in Section 9.4, where the CD microwave system was utilised. The sample was exposed to microwaves under a dynamic mode until the temperature of 220°C (the optimal temperature for the production of glucose under CD microwave system; see Figure 6-8) was achieved, and then cooled to room temperature by the built in compressed air. The solid residue was recovered by filtering (as described in Section 9.4) after which it was mixed with 20ml of distilled water and subjected to microwave irradiation again. The composition of solutions resulting from each run were determined by HPLC.

It can be observed from Figure 6-14, that the concentration of sugars contained with hydrolysate decreases rapidly after each hydrolysis run quickly diminishing from ~68mmol/L total sugars with the first hydrolysis run, to ~10mmol/L by the eighth, followed by a slow decline in the concentration of sugars attainable after this occurred thereafter.
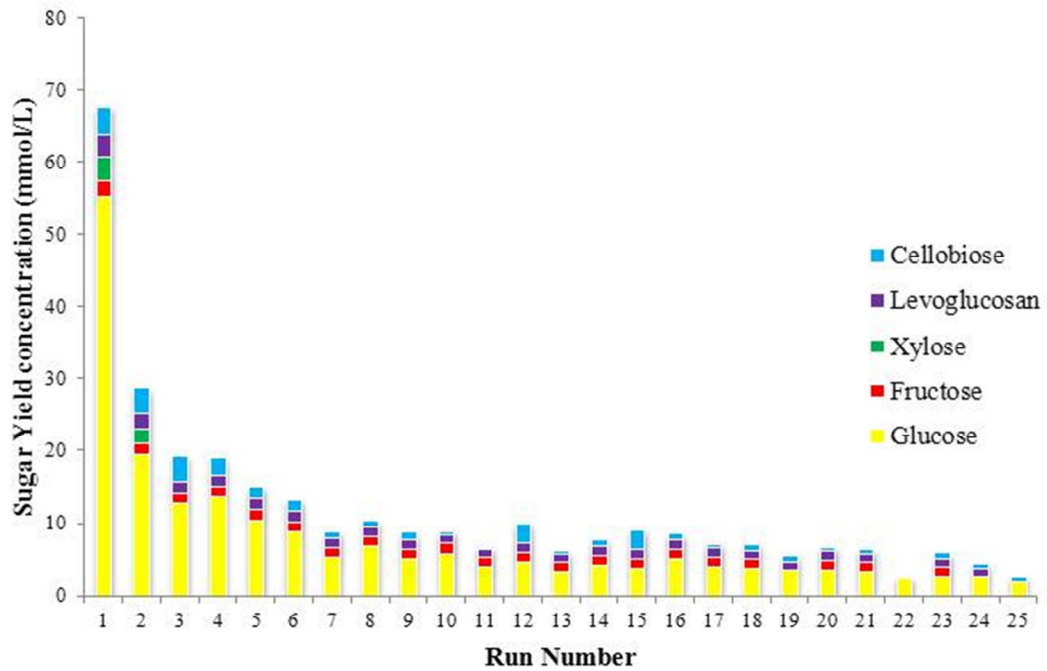
Figure 6-14   Influence of number of microwave runs on the composition of sugars within hydrolysate

The total sugar yields after 25 runs were found to be ~30wt.% glucose and ~40% total sugars of the original microcrystalline cellulose mass, with a total mass loss of 80wt.%. Of this ~8wt.% sugar was attained in the first hydrolysis run, with ~1wt.% attained for each run thereafter (see Figure 6-15).
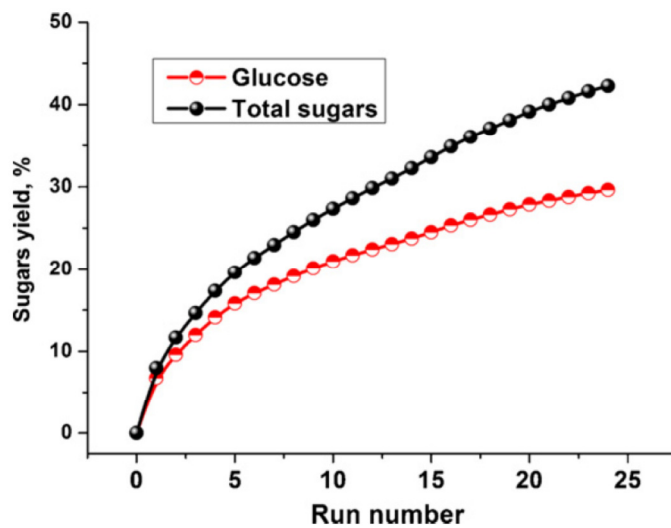
Figure 6-15   Cumulative sugar yield for repeated microwave hydrolysis treatments of cellulose

Cellulose from the hydrolysis process was tested by ATR-FTIR to determine if cellulose structure had changed after each run. It was found that after the first hydrolysis run, no change in the cellulose structure had occurred with spectra showing an exact match (see Figure 6-16).
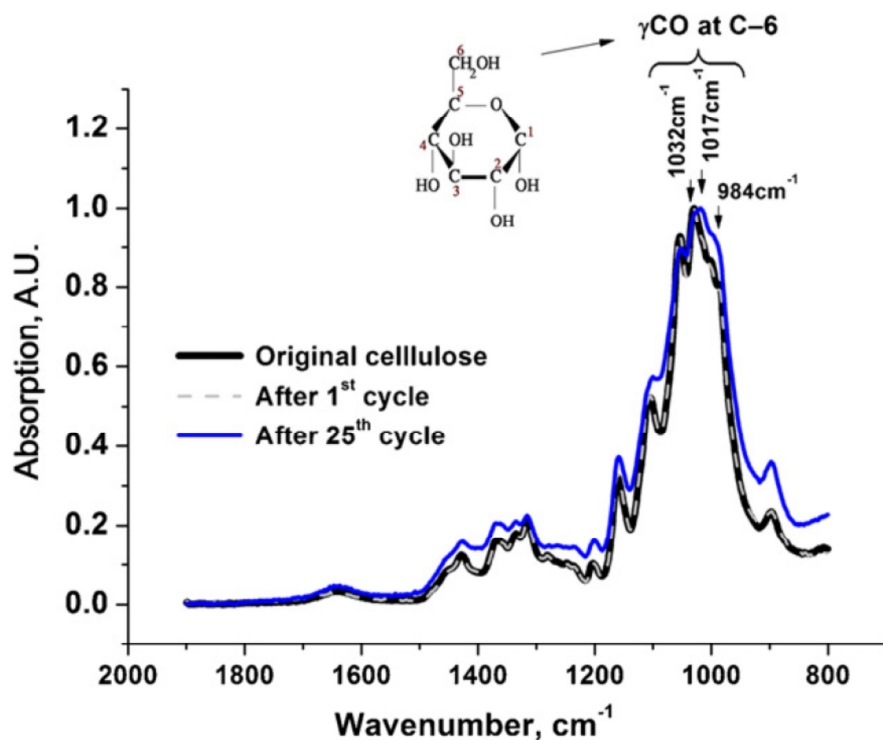
Figure 6-16   **Comparison of ATR-FTIR spectra of cellulose before and after microwave induced hydrolysis**

By the 25th run differences in the infrared spectra were seen, with changes occurring at 1020cm^{-1} region. This relates to differences in intermolecular hydrogen bonding, supporting the hypothesis that cellulose undergoes gradual conversion from its microcrystalline structure to amorphous; with the resultant generation of glucose units as chain scissions occur from the mechanism proposed in Figure 6-13.

6.4 Conclusions

The microwave hydrolysis process demonstrated significant advantages over a pyrolysis process, with the milder process conditions favouring the production of fermentable sugars. During this investigation it was found for both conventional thermal and microwave hydrolysis that the conversion of microcrystalline cellulose did not occur, however for a

microwave process when 180°C was exceeded extensive decomposition occurred within the amorphous regions of the cellulose structure reaching a maximum at 220°C, with 14.3wt.% vs 8.8wt.% decomposition for a microwave and conventional thermal process respectively.

The microwave hydrolysis process also offers a route for the highly selective conversion of cellulose to glucose with 50 fold increase over that of the conventional thermal process at the same temperature with up to ~10wt.% glucose yield. However, evidence suggested that the formation of glucose was not only a function of the microwave heating process but also the microwave field strength, with the interaction of the CH$_2$OH groups on the cellulose chain interacting with the microwave field in the amorphous regions of cellulose. With sufficient total energy from the microwave interaction of these groups and thermal energy of the system it was possible to induce a nucleophilic substitution with this group and the C4 carbon on the glycosidic ring, resulting in the production of glucose monomers.

It was further found that upon recycling of the cellulose the opening of the structure occurred and amorphous regions formed, which subsequently underwent further decomposition. From this procedure it was possible to attain 80wt.% decomposition of cellulose with ~30-40wt.% fermentable sugars formed.

Chapter 7:

Short Investigations

Published Work

Fan, J., De , M., Zhu, Z., Budarin, V., Gronnow, M., Gomez, L. D., Macquarrie, D. & Clark, J. (2013) Microwave-enhanced formation of glucose from cellulosic waste. Chemical Engineering and Processing: Process Intensification.

7 Short Investigations

7.1 Pea Waste Bio-Refinery

7.1.1 Introduction

Within the UK the production of peas constitutes 80,500 tonnes per annum. From this approximately 54,000 tonnes of by-products are produced as of 2010(Living Countryside, 2013). Currently the waste generated is used as fertilisers on arable land or disposed of as food waste. However, pea waste comprises of a number of valuable chemicals contained within the pod. Within pea pods a large quantity is dietary fibre, being approximately 58.6wt.% (see Table 7-1) (Mateos-Aparicio *et al.*, 2010).

Table 7-1   Proximate composition and low molecular weight carbohydrates of pea pods based on dry weight (Mateos-Aparicio *et al.*, 2010)

Component	Weight Percent (wt.%)
Protein	10.8 ± 0.3
Fat	1.3 ± 0.2
Sucrose	7.9 ± 0.3
Glucose	11.9 ± 0.6
Galactose	0.8 ± 0.1
Arabinose	0.9 ± 0.2
Fructose	1.2 ± 0.1
Starch	3.7 ± 0.1
Dietary fibre (DF)	58.6 ± 1.2
Ash	6.6 ± 0.5

With pea farming being widespread throughout Europe, North and South America, the Middle East and Asia, the development of a pea waste biorefinery would be of economic and environmental importance, with the potential export of both technology and processes. If successful, the process may provide a route of utilising agricultural residue for the production of chemicals and energy or even the basis to manufacture useful materials.

The results herein present the findings of initial testing via the Green extraction technologies of Supercritical CO_2 extraction and Microwave Pyrolysis along with the conventional solvent extractions of ethanol and hexane.

7.1.2   Results

7.1.2.1   Drying and Pre-Processing

Oven drying of pea pods at 110°C was attempted but found to have adverse effects on with significant changes in their physical and chemical characteristics, most likely arising from the presence of sugars and their subsequent caramelisation. Hence, air drying of pea waste was performed to remove excess water. This was performed over a 72 hour period at room temperature, after which 84wt.% was lost as moisture. The dried pea waste were subsequently used in further experimentation.

Samples were initially milled to uniform size to improve extractability. However, it was found that this was not beneficial, as brittle wax-like materials fractured from the surface and were lost as a dust which reduced overall extraction yield. Furthermore, during milling friction caused excessive heating of the pea waste causing further losses possible extractants (e.g. waxes)

7.1.2.2   Solvent Extraction

A soxhlet extraction method was employed for ethanol and hexane extraction of pea waste in which ~16g of dried pea waste was refluxed with 170 mL of solvent over a 5 hour period. The resulting solid residue was collected for further microwave pyrolysis experimentation.

Table 7-2 shows the relative percentage extraction yields using differing polarity solvents. From previous work in this area, it is known that ethanol can extract a wide variety of compounds, specifically sugar compounds from biomass which are not soluble in the significantly less polar, hexane. This most likely accounts for the large differences in extraction yield, with sugars making up a significant proportion of pea pod waste, as indicated in Table 7-1. The similarity in yields observed between hexane and $scCO_2$ support this, as $scCO_2$ displays similar extraction properties as hexane with low solvent polarity (Friedrich and Pryde, 1984).

Table 7-2   Percentage weight extracted from pea waste by the solvents Ethanol and Hexane

Extraction Solvent	Percentage Weight extracted (wt.%)
Ethanol	23.10
Hexane	0.78
scCO$_2$	0.79

Extracted content was analysed by GC/MS, data and possible MS identification of compounds is shown below (Figure 7-1and Table 7-3).

From Table 7-3 it was possible to determine that hexane and scCO$_2$ were able to extract the same compounds with no significant differences observed in the composition. However, ethanol demonstrated less variety in the compounds able to be extracted. This was attributed to the preparation of samples for GC-MS analysis requiring dissolution in dichloromethane, a non-polar solvent. This would have resulted in those extracts which were non polar being dissolved and highly polar compounds not. This was a significant limitation of the GC-MS analytical methodology.
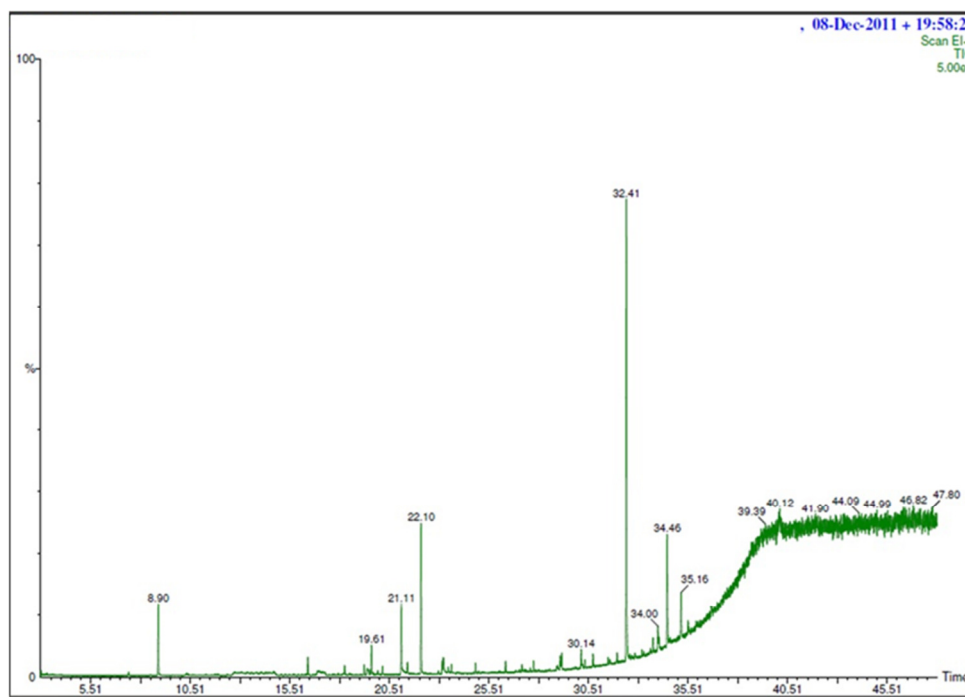
Figure 7-1   GC-MS spectrum of hexane extract from pea waste.

Table 7-3   GC/MS Analysis of Extracts

Solvent Extraction	Compound	Empirical Formula	Retention Time (min)
Ethanol	N-Hexadecanoic Acid	$C_{16}H_{32}O_2$	21.11
	β-Sitosterol	$C_{28}H_{58}O$	34.46
Hexane	N-Hexadecanoic Acid	$C_{16}H_{32}O_2$	21.11
	Octacosanol	$C_{28}H_{58}O$	32.41
	β -Sitosterol	$C_{29}H_{50}O$	34.46
	Triterpenoids: e.g. Lupeol	$C_{30}H_{50}O$	35.16
scCO₂	N-Hexadecanoic Acid	$C_{16}H_{32}O_2$	21.11
	Octacosanol	$C_{28}H_{58}O$	32.41
	β -Sitosterol	$C_{29}H_{50}O$	34.46
	Triterpenoids: e.g. Lupeol	$C_{30}H_{50}O$	35.16

These compounds are attributable to membrane structure in plants and are necessary for respiration and development of aromas (Aharoni *et al.*, 2005).

7.1.2.3   Thermal Analysis

Analysis was performed on air dried samples. Approximately 15 – 20 mg of sample was accurately weighed into aluminium crucibles and was placed in the STA for analysis. All experiments were performed under a nitrogen atmosphere with samples heated from 25-625°C at heating rates of 2, 10 and 50°C/min, weight (mg) and heat flow (mW) being recorded at a rate of 1 sample point per 1°C. It was found that decomposition of pea waste is a highly exothermic process (Figure 7-2) and considerable energy is released during the pyrolysis. This is unusual for pyrolysis of biomasses which are largely endothermic, which in majority of cases (pine wood, wheat straw, Canary grasses) decompose in an endothermic manner, adsorbing energy during pyrolysis, and therefore pyrolysis is uneconomic for many types of biomasses. Figure 7-2:C shows that exothermicity of pea waste pyrolysis became considerably higher after ethanol extraction, which could be associated with sugars extraction.
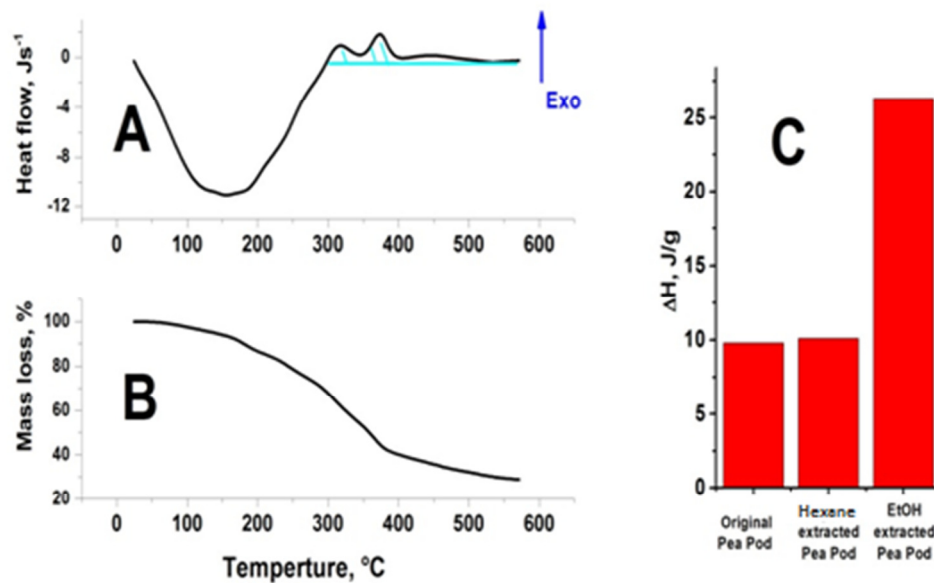
Figure 7-2   Results of STA analysis of pea waste. A) Heat flow trace for original pea waste; B)Mass loss trace for original pea waste; C) Comparison of heat of exothermic process for different samples.

Exothermicity of pea waste decomposition makes thermal treatment very attractive as a way of biorefining and adding value to this biomass waste. To investigate further the potential of thermal treatment for biorefining pea processing waste, the microwave pyrolysis of pea waste was carried out.

7.1.2.4   Microwave Pyrolysis

Microwave pyrolysis has been performed on ethanol and hexane extracted pea waste in a laboratory scale CEM Discover microwave.   Initial tests were performed on ethanol extracted samples in an closed vessel reactor at a fixed power (FP) of 300W on sample masses of 0.50, 0.75, 1.00 and 2.00 g ± 0.05g, respectively. A closed vessel system was used rather than an optimal open vessel, as this work was performed as part of a short project in conjunction with a local company which required a closed vessel to be used. In sample masses below 1 g, rapid evolution of heat and associated gas was observed. Above 1g experiments were also stopped early due to rapid increase in pressure being observed, see Figure 7-3.

This data indicates that the decomposition of ethanol extracted pea waste is exothermic (releases energy), allowing continuation of the decomposition of the sample even after external energy input has ceased (e.g. microwave turned off).
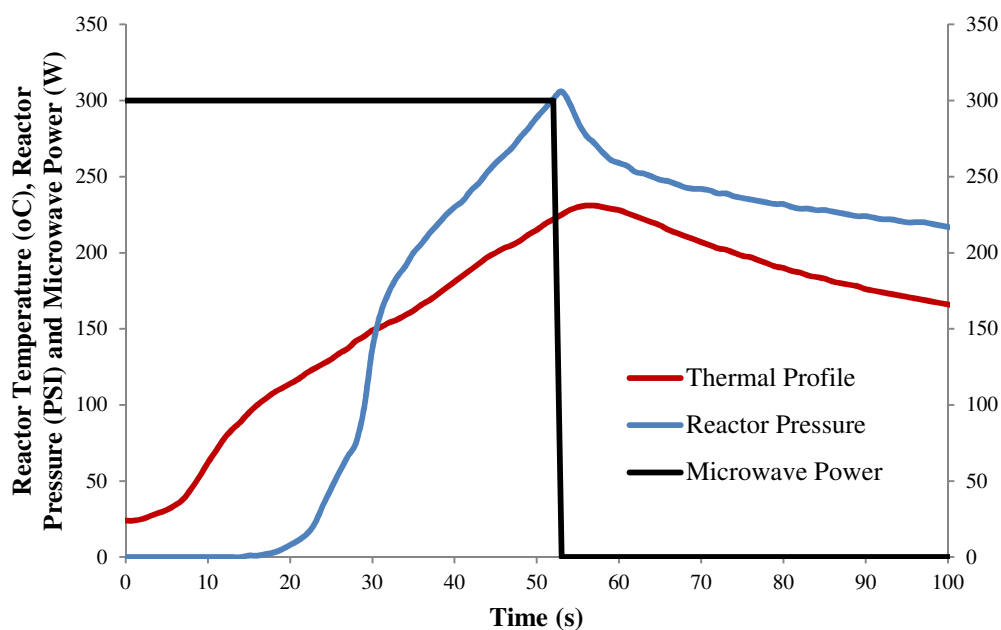
Figure 7-3   Thermal Profile, Reactor Pressure and Microwave Power for 1.00 g fixed power 300 W.

Following these initial difficulties a new procedure was developed to systematically investigate the behavior of the material during microwave heating. This method was designed to avoid rapid pressure/heat buildup. Two heating programs (Dy1 and Dy2) were developed (see Table 7-4). The heating program Dy1 was used to achieve sample temperature below 220°C. Experimentally, it was found that the maximum achievable temperature was 255°C and therefore to achieve maximum temperature program Dy2 was developed.

Table 7-4   Microwave Heating Programs: Method 1 (Dy1) and Method 2 (Dy2)

Dynamic Microwave Pyrolysis Method 1		Dynamic Microwave Pyrolysis Method 2	
Temperature (°C)	Hold (s)	Temperature (°C)	Hold (s)
20 - 100	*15*	*20 - 140*	*10*
100 - 130	*15*	*140 - 180*	*10*
130 - 160	*15*	*180 - 220*	*10*
160 - 190	*15*	*220 – 255*	*20*
190 - 220	*15*		

The resultant solid yields are shown in Figure 7-4, liquid and gas yields account for the difference to 100%. From the results, it becomes apparent that fixed power microwave experiments yield higher conversion rates to oil and gas with low char yields of 23wt.% (77wt.% oil and gas) and 34wt.% (66wt.% oil and gas) for 1.0 and 2.0 g experiments respectively. Dynamic (Dy) experiments yielded significantly higher yields of char of between 55 and 61wt.%, with no discernible difference observed between the ethanol and hexane extracted samples. This is likely to be due to low heating rates, which is known from previous microwave pyrolysis work to lead to high char, low oil yields (Budarin *et al.*, 2011b). The results also show there is minimal difference in product distribution caused by solvent used in extraction pre-processing.
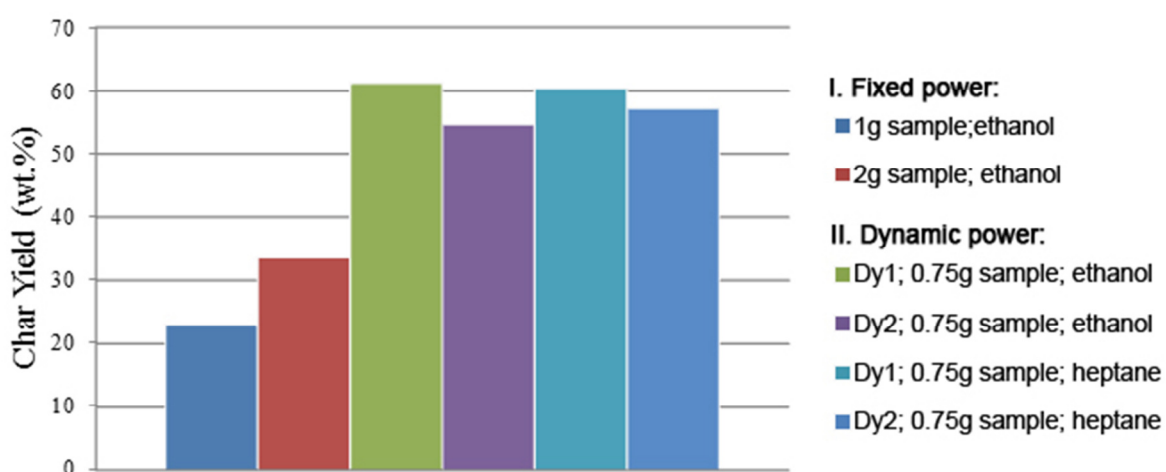
Figure 7-4   Char Yields for Fixed Power (FP) and Dynamic (Dy) Microwave Experiments
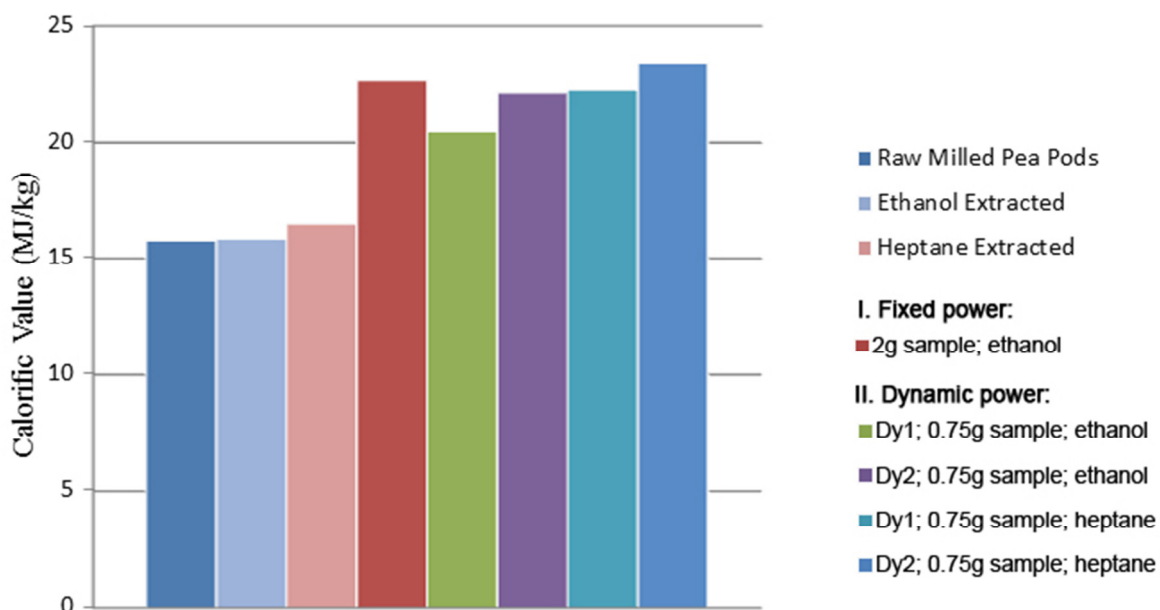
Figure 7-5   Calorific values of raw and extracted pea waste, Fixed Power (FP) and Dynamic (Dy) microwave experiments char

Calorific values of pea waste samples obtained at different stages of treatment are shown in Figure 7-5. From this they show that the extraction process does not significantly change the calorific value of pea waste. Calorific values of all samples after pyrolysis were found to be between 20 and 25 MJ/kg (calorific value of mid-range coal is c.a. 30 MJ/kg) (see Figure 7-5). For samples prepared under fixed power conditions a full mass balance has been done (See Table 7-5). It was found that under these conditions the major product of microwave pyrolysis is bio-gas. Bio-oil yield was found to be above 10% and their composition by GC/MS analysis is shown in Figure 7-6 and Table 7-6.

Table 7-5   Mass balance for fixed power microwave pyrolysis of Pea waste.

Sample	Bio-Char Yield (wt.%)	Bio-Oil Yield (wt.%)	Bio-Gas Yield (wt.%)
1g sample ethanol; fixed power	23.05	11.18	65.77
2g sample ethanol; fixed power	33.61	13.47	52.92

It was found from the analysis that the bio-oils produced comprised of the same chemical composition and relative proportion, with 8 major components seen in both chromatograms. The results of these analyses are presented in Table 7-6.
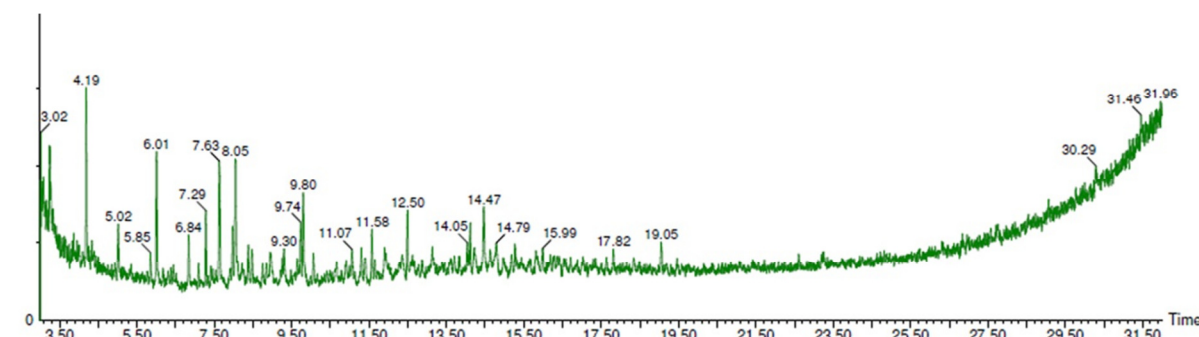
Figure 7-6 **GC-MS trace of microwave obtained bio-oil from a 1g sample at a fixed power of 300W**

Table 7-6 **Chemical breakdown of sample prepared at fixed power**

Ethanol Extracted		
Compound	**Empirical Formula**	**Retention Time (min)**
2-Furanmethanol	$C_5H_6O_2$	4.19
2-Methyl-Phenol	C_7H_8O	7.29
3-Methyl-Phenol	C_7H_8O	7.63
4(1H)-Pyridone	C_5H_5ON	8.05
Naphthalene	$C_{10}H_8$	9.74
1,2-Benzenediol	$C_6H_6O_2$	9.80
2,6-Dimethoxy-Phenol	$C_8H_{10}O_3$	12.50
Levoglucosan	$C_6H_{12}O_6$	14.47

From the compounds observed in the GC/MS spectrum the presence of levoglucosan indicated the decomposition of cellulose. Nevertheless, the absence of levoglucosenone and HMF further indicated that the decomposition process was not sufficiently aggressive to cause the dehydration of levoglucosan.

Table 7-7   Carbon, Hydrogen and Nitrogen Ratios of Samples

Sample Name	% C	% H	% N
Original milled pea waste	40.1	6.0	2.4
Ethanol extracted pea waste	40.6	5.8	2.6
Heptane extracted pea waste	41.7	5.8	2.5
Fixed power, 1g sample, bio-char	63.0	2.3	3.0
Fixed power, 2g sample, bio-char	61.9	3.2	3.2

7.1.2.5   Conclusion and Discussion

Results demonstrate that the combination of extraction of high value chemicals and microwave pyrolysis of pea waste has potential to form the basis of a biorefinery process. However, due to limited sample stock, each extraction was only performed once and thermo-chemical processing has been limited.

Although, the microwave pyrolysis was found to be an exothermic process, which has potential to improve energy balance and economics of thermo-chemical processing.

- o   Chars obtained have high calorific values.
- o   Bio-oils contains phenolic compounds which are suitable as anti- oxidants or platform molecules.

After closed vessel work had been completed insufficient material was available for open vessel experiments to be performed. As such, future work is required to establish the products formed under an open vessel microwave pyrolysis process.

7.2   Waste Paper Hydrolysis

7.2.1   Introduction

As previously found in section 6.3 the hydrolysis of cellulose proved the conversion of cellulose to the fermentable sugar glucose was possible with high yields able to be achieved. As such, a number of biomass types were screened to ascertain their potential for hydrothermal conversion. From this it was found the waste office paper posed a significant source of cellulose, with up to 80wt.% cellulose and also being almost free of hemi cellulose/ lignin but containing up to 15wt.% $CaCO_3$ (Spence *et al.*, 2000). Hence, the

microwave hydrolysis process presents an interesting route for the valorisation of waste office paper.

7.2.2 Method

Waste office paper was prepared via milling to reduce the particle size. This was then prepared as a ratio of 1:10, paper to distilled water (2.00 ± 0.05g to 20.00 ± 0.05g, respectively). This was prepared into a standard CD microwave reaction tube and irradiated under dynamic mode to 220°C (300psi) and held to maintain a total of 20 minutes microwave exposure; temperature and pressure were recorded during this process using the microwave pressure head and the inbuilt IR sensor, as per section 9.4.

7.2.3 Results

From the initial analysis of results by HPLC, the presence of sugars could not be established. However, it was found that the presence of calcium ions from the paper interfered with the detection of the potential sugars present. This was confirmed by running sugar analytical standards through the HPLC with and without calcium ions present. As such quantitative analysis of sugars was not performed. To determine the change in glucose concentration with each consecutive hydrolysis run a blood glucose monitor was used to identify the trend in glucose generation.

After repeated runs the colour of aqueous solutions were observed to change dramatically (See Figure 7-7). During the first five runs of the experiment the paper was observed to change from a fibrous solid into a clay like solid. Nevertheless, the solution was consistently a dark brown colour over the first 12 runs, indicating the presence of secondary decomposition products. A step change was then observed after the 12th run reflected by a change in solution colour to light yellow.

Figure 7-7 **Hydrolysate recovered from 1st to 17th recycle run (left to right, respectively)**

When the colour change was compared with the glucose generated, it was observed that there was an initial high yield, that subsequently steadily declined with increasing number of runs. However, at the 13th run an increase in glucose yield was observed with the change in solution colour, indicating increased sugar selectivity. This may be attributable to the reduction in inorganic ions in the aqueous solution.
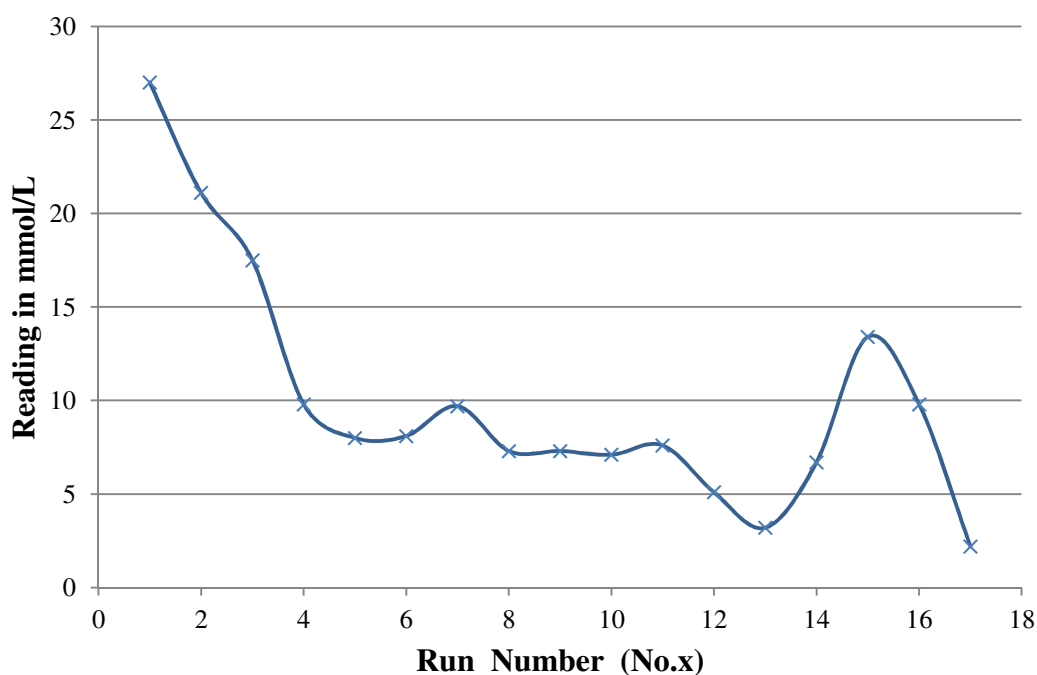
Figure 7-8 **The glucose generated from repeated microwave hydrolysis of waste office paper**

After the 17th run the remaining solid was found to be 16.8wt.% of the original mass. This is similar to that of the inorganic content of waste office paper of approximately 15wt.%, indicating almost complete decomposition of the organic component.

7.2.4 Conclusion

The work demonstrated the feasible process of microwave hydrolysis on cellulosic materials to produce glucose in a more intense manner than a conventional thermal hydrolysis process.

Chapter 8:

Conclusions and Future Work

8   Conclusions and Future Work

The microwave hydrolysis and pyrolysis of microcrystalline cellulose has proved successful both to identify key parameters and reveal the fundamental differences between a conventional thermal and microwave process.

From the microwave pyrolysis of cellulose a number of key findings were identified, relating to the crucial effects of moisture content, microwave power, pre-heating and final temperature.

Firstly, it was possible to identify that the extensive decomposition of cellulose was attainable through microwave irradiation with a decomposition of 65.5wt.% through the microwave only processing of cellulose under the experimental conditions investigated. From this it was found that the formation of 44.8wt.% or 26.5wt.% bio-oil and gas, respectively, could be attained under optimum conditions for each component were used.

When microwaves alone were used during the pyrolysis process, it was also found that the greater power input resulted in the increase in state of decomposition, nevertheless this was attributed to the experiments being able to attain higher overall temperatures as increased power input was able to overcome the thermal losses from the reactor.

It was identified that when temperatures exceeded 220°C for all microwave experiments, minimal further gains in oil yield could be achieved, with the main decomposition of cellulose occurring at the temperatures of ~180°C. This was found to correlate to the phase transition temperature of the cellulose used. This in itself was also of significance as it demonstrated the decomposition of cellulose occurred almost 120°C less than that seen in a conventional thermal decomposition process.

It was further determined that the moisture content of cellulose was also a critical component of the microwave decomposition process, with it assisting in the initial heating of cellulose by the method of conduction due to its high dielectric response and subsequent absorption of microwaves at the temperatures between ambient and 100°C. It is also possible

that water retained between polymer chains to higher temperatures aided in the heating of the cellulosic structure to much higher temperatures.

Evidence also arose to suggest that over a critical field density, 800W/L a differing mechanism of heating may have been present, with greatly accelerated heating rates than that of other microwave powers. This was theorised to be as a result of power density being such that the simultaneous microwave dielectric heating of water and cellulose structure could occur. This was also reflected in peak heating rates of $420^{o}C/min$. However, upon further examination of the results during pre-heating experiments the mechanism of interaction became clearer.

From pre-heating experiments it was evident that conventional thermal heating process resulted in changes in the phase transition temperature of cellulose and the resulting microwave decompositions demonstrated an increase in the required decomposition temperatures to attain the same degree of decomposition as a non-pre-heated process. Nevertheless, when pre-heating temperature of $220^{o}C$ or greater were used the phase transition temperature was exceeded and the partial decomposition of the cellulosic structure occurred. Due to the loss of crystallinity, the freer movement of $-CH_2OH$ and $-OH$ groups resulted and a greater proportion of cellulosic structure was able to convert microwave energy to heat. However, when pre-heating temperatures reached $300^{o}C$ the thermal decomposition of cellulose was extensive and the microwave process was seen to produce bio-oil, but to a much larger degree gas, with bio-oils retained within the reactor undergoing cracking to gaseous components or secondary reactions to form char.

The composition of oils produced from both the microwave only and pre-heating methods were similar in nature with the four major components of levoglucosenone, 1,4:3,6-dianhydro-.α.-D- glucopyranose, levoglucosan and 1,6-anhydro-.β.-D-glucofuranose being present in all. The changes in the oil composition that were observed, appeared to be as a result of the chemical dehydration of levoglucosan following the same chemical decomposition pathway as those recognised in the thermal decomposition of cellulose.

Upon examination of cellulose density and its interaction with the microwave field during the pyrolysis process, it was also possible to conclude that the formation of bio-oil was significantly affected. The yields of oil formed a Gaussian distribution with microcrystalline

cellulose density of an optimum yield at 1.04g/cm^3. From this, it was possible to determine the potential mechanisms controlling the pyrolysis process and decide that heating rate had the greatest overall effect. However, a greater understanding of the variation in the dielectrics of cellulose during the decomposition is required to comprehend the process further. This is due to the density changing the dielectric properties of cellulose, which in turn change the heating rate which subsequently change the temperature, that again change the dielectric properties and so the process continues.

Nevertheless, the implications are that there is an optimum density of microcrystalline cellulose at which maximum bio-oil yield can be attained, a critical heating rate below which steam distillation is the dominant process and above this, pyrolysis occurs and optimum pellet density corresponds to the greatest heating rate combined with the rapid removal of oils from the reactor which in turn reduces the number of secondary reactions that occur.

Throughout all microwave experiments, the rapid heating of cellulose was seen to be a result of the change in the degree of crystallinity, with the opening of new areas to produce amorphous structure which would more readily undergo microwave heating as a result of the free movement of the -CH$_2$OH groups on the glucose chain. It is also possible that these were aided by the chemical dehydration of decomposition products and the resultant interaction of microwaves with the moisture released as it migrated through the sample. At the other end of the spectrum, when low microwave powers were used it was found that upon the sample reaching 100°C no further heating would occur, resulting from the dielectric response of cellulose being insufficient to absorb enough microwave energy so that the thermal losses from the reactor could be overcome.

The microwave hydrolysis process demonstrated significant advantages over a pyrolysis process, with the milder process conditions favouring the production of fermentable sugars. During this investigation, it was found for both conventional thermal and microwave hydrolysis that the conversion of crystalline regions within the cellulose did not occur below 220°C. However for a microwave process when 180°C was exceeded extensive decomposition occurred within the amorphous regions of the cellulose structure reaching a maximum at 220°C, with 14.3wt.% vs 8.8wt.% decomposition for a microwave and conventional thermal process respectively.

The microwave hydrolysis process also offers a route for the highly selective conversion of cellulose to glucose with 50 fold increase over that of the conventional thermal process at the same temperature with up to ~11wt.% glucose yield. However, evidence suggested that the formation of glucose was not only a function of the microwave heating process but also the microwave field strength, with the interaction of the -CH$_2$OH groups on the cellulose chain interacting with the microwave field in the amorphous regions of cellulose. With sufficient total energy from the microwave interaction of these groups and thermal energy of the system, it was possible to induce a nucleophilic substitution with this group and the C4 carbon on the glycosidic ring, resulting in the production of glucose monomers.

It was further found that upon recycling of the cellulose the opening of the structure occurred and amorphous regions formed, which subsequently underwent further decomposition. From this procedure, it was possible to attain 80wt.% decomposition of cellulose with ~30-40wt.% fermentable sugars formed.

In the hydrolysis process it appeared that the microwave field strength played a critical role in the decomposition process, the extent of decomposition and the products formed. If too low a microwave field strength was used the effect nueclophilic substitution reaction of glucose formation could not arise and the fragmentation of the cellulose chain was based on a purely thermal decomposition pathway. This resulted in the reduction of product selectivity as the chemical dehydration and fragmentation of products was promoted through increased energy of the system. However, when high microwave field strengths were used the promotion of the nucleophilic substitution pathway occurred and the resulting selectivity of product to glucose occurred during hydrolysis. Hence the microwave decomposition process has proved an interesting new pathway for the production of specific chemical compounds, warranting further investigation to determine its application in the processing of biomass feedstocks.

From the research performed it has been possible to establish major differences between a conventional thermal and microwave decomposition process using both pyrolysis and hydrolysis. However, significant advances in the understanding of the decomposition processes could be established if new methods were adopted and research performed on the following:

Microwave Pyrolysis

- Determine a method of measuring simultaneous weight loss with microwave heating, whilst also measuring the absorption of microwaves by a sample; microwave gravimetric analysis
- Test the dielectric properties of cellulose up to 400°C
- Perform experiments to set temperatures between 100 and 300°C at differing microwave powers to fully determine the effect of heating rate and maximum temperature on the extent of decomposition
- Confirm that for differing mode microwaves the same power density results in the same decomposition effects.
- Investigate the effect of increased moisture content of cellulose on the microwave decomposition process
- Quantitatively determine bio-oil composition
- Investigate fully changes in di-electric properties of cellulose with increased sample density

Microwave Hydrolysis

- Determine if a microwave hydrolysis process can enter the supercritical phase and the decomposition products formed during this
- Use cellulose samples of differing crystallinity to confirm the hypothesis of microwave interaction with the amorphous structure of cellulose
- Study the gases produced after the microwave hydrolysis process is complete so that the decomposition process can be further understood
- Identify and quantify all sugars and non-sugar species found within hydrolysis liquids through HPLC-MS.
- Investigate the effect of microwave hydrolysis heating rate

For both microwave pyrolysis and hydrolysis it is also important to determine the scalability of the process for industrial use and hence it would be desirable to examine the potential of larger batch and continuous feed microwave decomposition processes.

Chapter 9:

Materials and Methods

9 Materials and Methods

9.1 Materials and Reagents

The analytical standard reagents of arabinose, cellobiose, fucose, fructose, galactose, glucose, levoglucosan, mannose, sucrose and xylose, of a purity of >99% were purchased from Sigma-Aldrich Co. LLC and subsequently used in chromatographic work.

During experimentation, microcrystalline cellulose was used from Sigma-Aldrich Co. LLC. Pea waste was attained from private gardens in York, United Kingdom. Waste office paper was from waste paper recycling bins in the Green Chemistry Centre of Excellence, the University of York.

During experimentation, the solvents acetonitrile, methanol and ethanol were used as analytical grade purities of >99%, from Fischer Scientific UK Ltd.

Oxygen free Nitrogen gas of >99.99% purity from BOC was used during pyrolysis experimentation.

9.2 Experimental Methods

9.2.1 Conventional Pyrolysis Preparation

Conventional chars were prepared in a Netzsch STA 409. Approximately 80mg of sample were weighed into an alumina crucible. This was subsequently placed on the Netzsch sample holder. The samples were consequently heated to a target temperature at a heating rate of $10^{o}C/min$ whilst applying a nitrogen purge of 100mL/min. During the process weight (mg) and heat flow (mW) were recorded at a rate of 1 data point per $1^{o}C$ rise in temperature. The resulting data was used to model the thermal decomposition behaviour of material under investigation.

9.2.2 Small Scale Single Mode Microwave Pyrolysis Experiments with Pre- Heating

A sample of microcrystalline cellulose of 1g ± 0.05g for CEM Discover microwave experiments, was weighted out into a custom design microwave tube (borosilicate glass). A Dreschel head was subsequently fitted and nitrogen purge of 600mL/min applied for 2 minutes.
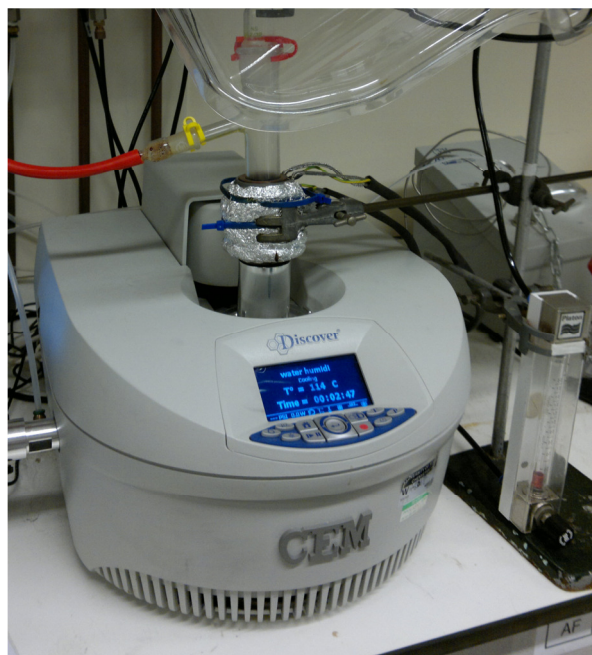
Figure 9-1   CEM microwave reactor experimental setup

The microwave tube was then inserted into a custom design pre-heating block at a pre-designated temperature (40- 300°C) and allowed to equilibrate for a period of 5 minutes (calibration results shown in Figure 4-2). The microwave tube was then quickly placed into the CEM microwave chamber and the outlet of the dreschel head connected to a methanol wash condensing system (see Figure 9-1). The tube and contents were subsequently irradiated (whilst maintaining a nitrogen purge of 600mL/min) for a designated microwave period (0-120 seconds) and a set power (300W) at appropriate intervals dependent upon parameters being tested.

At the end of each experiment, the contents of the microwave tube were cooled to room temperature using compressed air, whilst maintaining a nitrogen atmosphere. The contents were then rinsed from the tube using methanol and filtered to separate oils and solids. The solid was subsequently dried at 105°C for 12 hours and then weighed. Methanol and

pyrolysis oils were rotary evaporated at 40°C under vacuum and the remaining oil collected and weighed. Oils produced were viscous and dark brown in colour (see Figure 9-2).

Figure 9-2   Photograph of typical oil sample

Mass balances were subsequently performed and the relative proportions of solid and bio-oil with gas being calculated by difference. It was found that oil results showed a reproducibility of less than 3wt.% for all CEM Discover pyrolysis experiments.

9.2.3   Small Scale Single Mode Microwave Pyrolysis Experiments

This same method was utilised as in section 9.2.2, however, pre-heating was not performed prior to microwave irradiation. During this experimentation microwave powers were utilised between 50 and 300W at 50W intervals.

9.2.4   Microwave treatment of cellulose – 100g Scale

A Milestone Rototsynth Rotative Solid Phase Microwave Reactor (Milestone Srl. , Italy) fitted with a VAC2000 vacuum module, was used to investigate the influence of microwave and material parameters on a scaled up microwave process (see Figure 9-3).
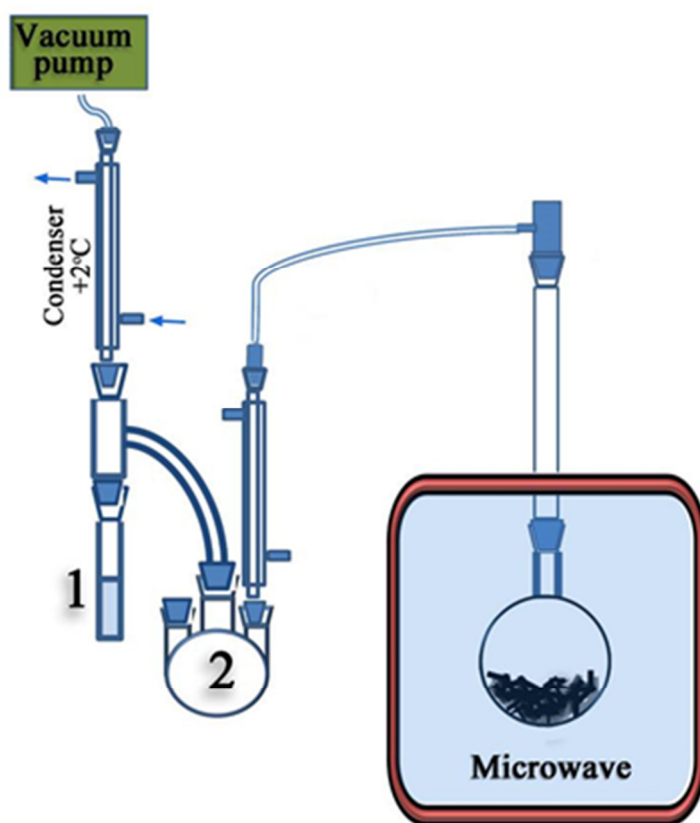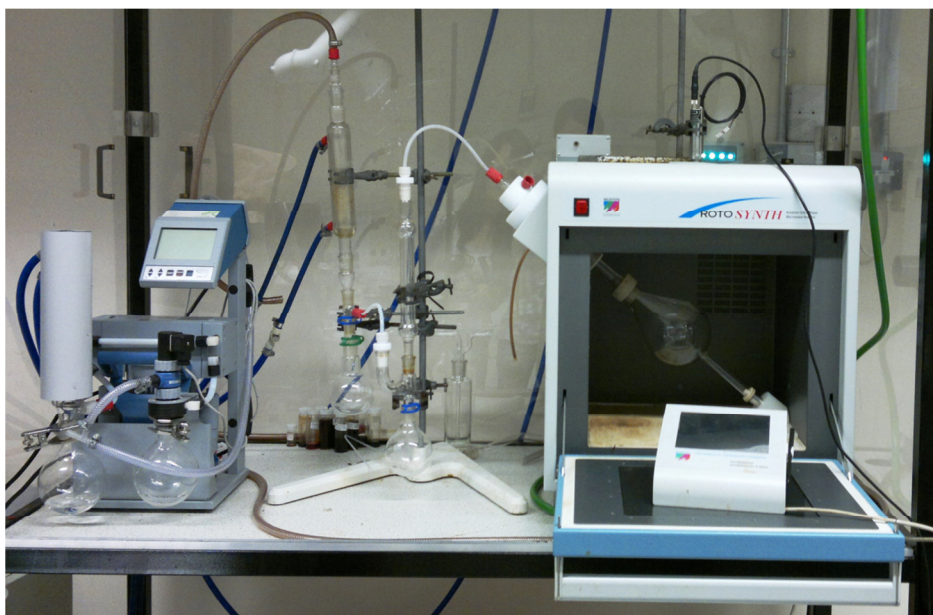
Figure 9-3   Milestone microwave reactor setup photograph (top) and schematic: 1. Secondary condensate pot, 2. Primary condensate flask (bottom)

For each experiment, 100g ± 0.5g of material was loaded into a custom design pear shaped borosilicate reactor flask. The design of the flask was such that the removal of pyrolysis volatiles was facilitated, as well as, the rotation of the flask to enable sample mixing. The reactor was loaded into the microwave cavity and connected to the fixings inside so that a gas tight seal was made. The reactor flask was allowed to evacuate for a period until a vacuum of ~20mbar was established.

The sample was subsequently subjected to microwave irradiation for a given period and power, during which the pyrolysis volatiles evolved were condensed and collected using two Liebig condensers. The typical operating conditions of microwave experiments were: 400W, 800W and 1200W for periods of 5 – 20 minutes at 5 minute intervals.

During the experiment the temperature of the reactor was monitored externally (at 1 second intervals) using an infrared pyrometer (Calex, Pyro USB CF), which had been calibrated against a thermocouple during process development. The subsequent information gathered was used to determine thermal profiles and heating rates.

At the end of each experiment, the contents of the microwave reactor were cooled to room temperature, whilst maintaining the experimental atmosphere. The contents were then rinsed from the reactor and connecting pipes using methanol. This mixture was filtered to separate oils and solids. The solid was subsequently dried at 105°C for 12hrs and then weighed. Methanol and pyrolysis bio-oils were rotary evaporated at 40°C under vacuum and the remaining bio-oil collected and weighed. Mass balances were subsequently performed and the relative proportions of solid, bio-oil and gas were calculated. As it was not possible to collect the gas during pyrolysis runs, the yield of gas was calculated by percentage difference.

9.3 Analytical Methods

9.3.1 Moisture Content

Moisture content was determined using ASTM D4442-07, whereby samples were dried at $105^{\circ}C$ for a minimum period of 24 hours or until constant weight was achieved. Before weighing, samples were allowed to cool to ambient temperatures whilst contained within a desiccator, so than atmospheric moisture could not be absorbed onto the sample. The moisture content was then calculated using Equation 9-1.

$$Moisture\ content\ (\%) = \frac{(A - B)}{A}.\,100$$

Equation 9-1   Determination of moisture content

Where:

A = Original Weight

B = Weight of dried sample

This method was also used to dry solid samples prior to analysis.

9.3.2 Calorific Value

Calorific values of both solids and oils were determined using a Parr 6200 Calorimeter with 1108 Oxygen Bomb. Approximately $0.5g \pm 0.01g$ of sample was weighed into a sample cup. This was loaded into the head of the oxygen bomb along with $10cm \pm 0.1cm$ of fuse wire attached to the ignition relay. The head of the bomb was loaded into the main body of the bomb and sealed. The bomb was subsequently filled with oxygen. The calorimeter sample bucket was filled with 2 liters ($2000 \pm 0.5g$) of distilled water and placed inside the calorimeter. The bomb was subsequently immersed in the bucket and the ignition wires attached. The calorimeter was initiated and the test run.

9.3.3 Carbon, Hydrogen and Nitrogen (CHN) Content

Elemental analysis of carbon, hydrogen and nitrogen ratios were performed on selected solid and bio-oil samples, using the departmental service utilising Exeter Analytical (Warwick, UK) CE440 Elemental Analyser (calibrated against acetanilide with S-benzyl-thioronium chloride internal standard.

9.3.4　Water Content by Karl Fischer Analysis

Karl Fisher Coulometer (Mettler Toledo DL32) was used to determine the water content in microwave oils. The method relies upon the injection of a sample into titration mixture of coulometric reagents containing iodide and a sulphur dioxide/imidazole. During the titration the current passed through the solution is measured and water content determined.

For this an oil sample which had been diluted 10 fold in methanol was injected in to the reagent cell of the Karl Fischer, this was subsequently titrated and water content calculated. After rotary evaporation of all pyrolysis oil sample it was found that less than 1wt.% moisture was contained within the oils produced.

9.3.5　Gas Chromatography/Mass Spectrometry (GC/MS)

GC/MS was used to examine the oils produced from pyrolysis experiments to tentatively determine their composition.

Samples were prepared at a concentration of 20mg/mL of pyrolysis oil in methanol. A sample of 0.5µL was injected on to a Perkin ElmerClarus 500 Gas chromatography and Clarus 560S Mass spectrometer at an injector temperature of 350°C and a column flow rate of 1.0ml/min with a 1:10split ratio applied. The oils were passed onto a Phenomenex Zebron DB5-HT column (30m × 0.25m × 0.25µm) at a temperature of 60°C. The column was held for 1 miute at this temperature and then ramped to 360°C at 8°C/min. It was then held for further 10 minutes. An example GC/MS trace is given in Figure 4-20.

During the GC run the mass spectrometer with Ei+ source of 70eV was scanning between 40 to 1200 Da at a scan duration of 0.39s and cycle time of 0.400s, with an inter scan delay of 0.050s. The subsequent m/z spectra recorded were compared against the NIST 2005 spectral database and possible chemical matches identified.

9.3.6　Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FT-IR) was used to collect infrared spectra of the pyrolysis oils. A Bruker VERTEX 70 infrared spectroscopy and ATR probe with Golden gate attachment were used to perform this analysis. Samples spectra were collected between

400 and 4000cm^{-1} at a resolution of 4cm^{-1} and a scan rate of 64. The spectra were subsequently analysed to determine possible bond types and functional group.

9.4   Microwave Hydrolysis

Samples were prepared by mixing microcrystalline cellulose (Sigma-Aldrich) with distilled water in a ratio of 1:10, with 2.00 ± 0.05g to 20.00 ± 0.05g, respectively. This slurry was prepared into the standard CEM Discover (CD) microwave reaction tube. The sample was subsequently inserted into the microwave and irradiated under dynamic mode to enable the system to achieve the desired temperature by varying the power input (with a maximum 300W input) (see Figure 9-4: A), temperature and pressure were recorded during this process using the microwave pressure head and the inbuilt IR sensor. Examples of which are shown in Figure 6-5. Experiments were completed for the set temperatures of 100-220°C at 10°C intervals. The total microwave exposure for each experiment was 20 minutes.
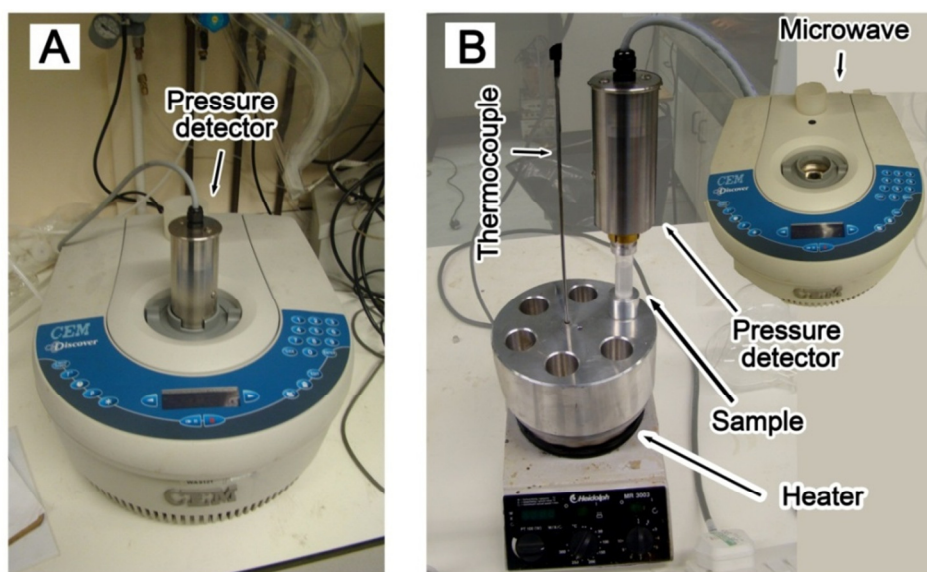
Figure 9-4   The A) microwave and B) conventional thermal heating apparatus

To determine the influence of heat source, a simultaneous experiment was designed allowing microwave and conventional thermal heating reactions to be performed under the same conditions, 1:10 microcrystalline cellulose to distilled water ratio. To achieve this, the pressure head of the CD microwave reactor was used in conjunction with the standard

microwave reaction tube (see Figure 9-4: B). The reactor was placed in a heating block and similar heating rates and exact final temperature to that of the microwave process were simulated.

For both experimental setups, upon completion the sample was cooled using compressed air. When room temperature was achieved, the contents of the reaction tube were filtered through a S4 synthesis filter.

The solid portion was oven dried at 105°C for 12 hours and the mass determined. The liquid solution was weighed and samples taken for high performance liquid chromatography (HPLC) with evaporative light scattering detector (ELSD) plus a Luna HN$_2$ 5μm column (Hewlett Packard Series 1100 HPLC with Alltech 3300 ELSD detector) and electron spray ionisation – mass spectrometry (ESI-MS). The remaining solution was freeze dried and used for ^{13}C nuclear magnetic resonance (NMR) analysis, results of which are displayed in Figure 6-10.

Both ESI-MS and ^{13}C NMR were performed by the Dr M. De Green Chemistry Centre of Excellence, University of York using a Bruker microOTOF mass spectrometer with ESI source and Jeol ECX-400, respectively (Fan *et al.*, 2013).

The conversion of cellulose was calculated by Equation 9-2, where W_o, is the initial weight of cellulose and W_R, is the remaining weight after hydrolysis.

$$Percentage\ Conversion(\%)\ = \frac{(W_o - W_R)}{W_o}.100$$

Equation 9-2   Determination of converted cellulose mass after hydrolysis

HPLC chromatogram facilitated the identification and quantification of glucose, fructose xylose, cellobiose, and levoglucosan hydrolysates after calibrations were performed for each component using standard materials purchased from Sigma Aldrich. The quantity of components as identified by HPLC, were calculated in mmol/L after standard calibrations had been performed on the HPLC.

List of Abbreviations

ATR	Attenuated Total Reflectance
CD	CEM Discover
CHN	Carbon, Hydrogen and Nitrogen
CM6	CEM Mars 6
CV	Calorific Values
DF	Dietary Fibre
DSC	Differential Scanning Calorimetry
DTG	Differential Thermal Gravimetric
Dy	Dynamic
Dy1	Dynamic Microwave Pyrolysis Method 1
Dy2	Dynamic Microwave Pyrolysis Method 2
ELSD	Evaporative Light Scattering Detector
ESI-MS	Electron Spray Ionisation - Mass Spectrometry
FFA	Free Fatty Acid
FP	Fixed Power
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GC-FID	Gas Chromatography - Flame Ionisation Detector
HMF	Hydroxymethylfurfural
HPLC	High Performance Liquid Chromatography
IR	Infra-Red
ISM	Industrial, Scientific and Medical
MDSC	Modulated Differential Scanning Calorimetry
NMR	Nuclear Magnetic Resonance
scCO$_2$	Supercritical Carbon Dioxide
STA	Simultaneous Thermal Analysis
TGA	Thermal Gravimetric Analysis
TiC	Total Ion Count
TWh/yr	Tera Watt Hour / Year
wt.%	Weight Percentage

References

ABBASI, T. & ABBASI, S. A. 2011. 'Renewable' hydrogen: Prospects and challenges. *Renewable and Sustainable Energy Reviews,* 15**,** 3034-3040.

AGARWAL, A. K. 2007. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progress in Energy and Combustion Science,* 33**,** 233-271.

AHARONI, A., JONGSMA, M. A. & BOUWMEESTER, H. J. 2005. Volatile science? Metabolic engineering of terpenoids in plants. *Trends in Plant Science,* 10**,** 594-602.

AIDA, T. M., SATO, Y., WATANABE, M., TAJIMA, K., NONAKA, T., HATTORI, H. & ARAI, K. 2007. Dehydration of d-glucose in high temperature water at pressures up to 80 MPa. *The Journal of Supercritical Fluids,* 40**,** 381-388.

AJANOVIC, A. 2011. Biofuels versus food production: Does biofuels production increase food prices? *Energy,* 36**,** 2070-2076.

AKHTAR, J. & AMIN, N. A. S. 2011. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews,* 15**,** 1615-1624.

AKIYA, N. & SAVAGE, P. E. 2002. Roles of Water for Chemical Reactions in High-Temperature Water. *Chemical Reviews,* 102**,** 2725-2750.

ALLAN, G. G., KRIEGER, B. B. & WORK, D. W. 1980. Dielectric loss microwave degradation of polymers: cellulose. *Journal of Applied Polymer Science,* 25**,** 1839-1859.

ALVIRA, P., TOMÁS-PEJÓ, E., BALLESTEROS, M. & NEGRO, M. J. 2010. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresource Technology,* 101**,** 4851-4861.

ANASTAS, P. T. A. & WARNER, J. C. A. 2000. *Green Chemistry: Theory and Practice*, OXFORD University Press (NC).

ANTAL, M. J., JR. & VARHEGYI, G. 1995. Cellulose Pyrolysis Kinetics: The Current State of Knowledge. *Industrial & Engineering Chemistry Research,* 34**,** 703-717.

BABU, B. V. 2008. Biomass pyrolysis: a state-of-the-art review. *Biofuels, Bioproducts and Biorefining,* 2**,** 393-414.

BARTON, J. P. & INFIELD, D. G. 2004. Energy storage and its use with intermittent renewable energy. *Energy Conversion, IEEE Transactions on,* 19**,** 441-448.

BAUGH, K. D. & MCCARTY, P. L. 1988. Thermochemical pretreatment of lignocellulose to enhance methane fermentation: I. Monosaccharide and furfurals hydrothermal decomposition and product formation rates. *Biotechnology and Bioengineering,* 31**,** 50-61.

BEHRENDT, F., NEUBAUER, Y., OEVERMANN, M., WILMES, B. & ZOBEL, N. 2008. Direct Liquefaction of Biomass. *Chemical Engineering & Technology,* 31**,** 667-677.

BENDER, M. H. 2000. Potential conservation of biomass in the production of synthetic organics. *Resources, Conservation and Recycling,* 30**,** 49-58.

BENNETT, N. M., HELLE, S. S. & DUFF, S. J. B. 2009. Extraction and hydrolysis of levoglucosan from pyrolysis oil. *Bioresource Technology,* 100**,** 6059-6063.

BERNDES, G., HOOGWIJK, M. & VAN DEN BROEK, R. 2003. The contribution of biomass in the future global energy supply: a review of 17 studies. *Biomass and Bioenergy,* 25**,** 1-28.

BILALI, L., BENCHANAA, M., EL HARFI, K., MOKHLISSE, A. & OUTZOURHIT, A. 2005. A detailed study of the microwave pyrolysis of the Moroccan (Youssoufia) rock phosphate. *Journal of Analytical and Applied Pyrolysis,* 73**,** 1-15.

BIOMASS ENERGY CENTRE. 2013. *Poutlry Litter* [Online]. Surrey UK: Biomass Energy Centre. Available: http://www.biomassenergycentre.org.uk/portal/page?_pageid=75,17976&_dad=portal&_schema=PORTAL [Accessed 25.11.09 2009].

BJERRE, A. B., OLESEN, A. B., FERNQVIST, T., PLÖGER, A. & SCHMIDT, A. S. 1996. Pretreatment of wheat straw using combined wet oxidation and alkaline hydrolysis resulting in convertible cellulose and hemicellulose. *Biotechnology and Bioengineering,* 49**,** 568-577.

BOLLER, A., SCHICK, C. & WUNDERLICH, B. 1995. Modulated differential scanning calorimetry in the glass transition region. *Thermochimica Acta,* 266**,** 97-111.

BOLTON, W. 1992. *Electrical and magnetic properties of materials,* Harlow, Essex, Longman Scientific & Technical.

BONAWITZ, N. D. & CHAPPLE, C. 2010. The Genetics of Lignin Biosynthesis: Connecting Genotype to Phenotype. *Annual Review of Genetics,* 44**,** 337-363.

BOOCOCK, D. G. B. & SHERMAN, K. M. 1985. Further aspects of powdered poplar wood liquefaction by aqueous pyrolysis. *The Canadian Journal of Chemical Engineering,* 63**,** 627-633.

BOZELL, J. J. & PETERSEN, G. R. 2010. Technology development for the production of biobased products from biorefinery carbohydrates-the US Department of Energy's "Top 10" revisited. *Green Chemistry,* 12**,** 539-554.

BRIDGWATER, A. V. & COTTAM, M. L. 1992. Opportunities for biomass pyrolysis liquids production and upgrading. *Energy & Fuels,* 6**,** 113-120.

BRIDGWATER, A. V., MEIER, D. & RADLEIN, D. 1999. An overview of fast pyrolysis of biomass. *Organic Geochemistry,* 30**,** 1479-1493.

BRIDGWATER, T. 2006. Biomass for energy. *Journal of the Science of Food and Agriculture,* 86**,** 1755-1768.

BROIDO, A. & NELSON, M. A. 1975. Char yield on pyrolysis of cellulose. *Combustion and Flame,* 24**,** 263-268.

BRUNNER, G. 2009. Near critical and supercritical water. Part I. Hydrolytic and hydrothermal processes. *The Journal of Supercritical Fluids,* 47**,** 373-381.

BU, Q., LEI, H., REN, S., WANG, L., ZHANG, Q., TANG, J. & RUAN, R. 2012. Production of phenols and biofuels by catalytic microwave pyrolysis of lignocellulosic biomass. *Bioresource Technology,* 108**,** 274-279.

BUBB, W. A. 2003. NMR spectroscopy in the study of carbohydrates: Characterizing the structural complexity. *Concepts in Magnetic Resonance Part A,* 19A**,** 1-19.

BUDARIN, V. L., CLARK, J. H., LANIGAN, B. A., SHUTTLEWORTH, P., BREEDEN, S. W., WILSON, A. J., MACQUARRIE, D. J., MILKOWSKI, K., JONES, J. & BRIDGEMAN, T. 2009. The preparation of high-grade bio-oils through the controlled, low temperature microwave activation of wheat straw. *Bioresource Technology,* 100**,** 6064-6068.

BUDARIN, V. L., CLARK, J. H., LANIGAN, B. A., SHUTTLEWORTH, P. & MACQUARRIE, D. J. 2010. Microwave assisted decomposition of cellulose: A new thermochemical route for biomass exploitation. *Bioresource Technology,* 101**,** 3776-3779.

BUDARIN, V. L., SHUTTLEWORTH, P. S., DODSON, J. R., HUNT, A. J., LANIGAN, B., MARRIOTT, R., MILKOWSKI, K. J., WILSON, A. J., BREEDEN, S. W., FAN, J., SIN, E. H. K. & CLARK, J. H. 2011a. Use of green chemical technologies in an integrated biorefinery. *Energy & Environmental Science,* 4**,** 471-479.

BUDARIN, V. L., ZHAO, Y. Z., GRONNOW, M. J., SHUTTLEWORTH, P. S., BREEDEN, S. W., MACQUARRIE, D. J. & CLARK, J. H. 2011b. Microwave-mediated pyrolysis of macro-algae. *Green Chemistry,* 13**,** 2330-2333.

BUTLER, E., DEVLIN, G., MEIER, D. & MCDONNELL, K. 2011. A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading. *Renewable and Sustainable Energy Reviews,* 15**,** 4171-4186.

CARROLL, A. & SOMERVILLE, C. 2009. Cellulosic biofuels. *Annual Review of Plant Biology,* 60**,** 165-182.

CASTELLO, D., KRUSE, A. & FIORI, L. 2013. Biomass gasification in supercritical and subcritical water: The effect of the reactor material. *Chemical Engineering Journal,* 228**,** 535-544.

CEM CORPORATION 2013. Microwave Chemistry: How it all Works.

CHANDRA, R. P., BURA, R., MABEE, W. E., BERLIN, A., PAN, X. & SADDLER, J. N. 2007. Substrate Pretreatment: The Key to Effective Enzymatic Hydrolysis of Lignocellulosics? *In:* OLSSON, L. (ed.) *Biofuels.* Springer Berlin Heidelberg.

CHANG, V. & HOLTZAPPLE, M. 2000. Fundamental Factors Affecting Biomass Enzymatic Reactivity. *In:* FINKELSTEIN, M. & DAVISON, B. (eds.) *Twenty-First Symposium on Biotechnology for Fuels and Chemicals.* Humana Press.

CHEN, M., SIOCHI, E. J., WARD, T. C. & MCGRATH, J. E. 1993. Basic ideas of microwave processing of polymers. *Polymer Engineering & Science,* 33**,** 1092-1109.

CHENG, Y.-S., ZHENG, Y., YU, C. W., DOOLEY, T. M., JENKINS, B. M. & VANDERGHEYNST, J. S. 2010. Evaluation of high solids alkaline pretreatment of rice straw. *Applied biochemistry and biotechnology,* 162**,** 1768-1784.

CLARK, D. E. & SUTTON, W. H. 1996. Microwave processing of materials. *Annual Review of Materials Science,* 26**,** 299-331.

CZERNIK, S. & BRIDGWATER, A. V. 2004. Overview of Applications of Biomass Fast Pyrolysis Oil. *Energy & Fuels,* 18**,** 590-598.

DAMARTZIS, T. & ZABANIOTOU, A. 2011. Thermochemical conversion of biomass to second generation biofuels through integrated process design—A review. *Renewable and Sustainable Energy Reviews,* 15**,** 366-378.

DEMIRBAS, A. 2007. Progress and recent trends in biofuels. *Progress in Energy and Combustion Science,* 33**,** 1-18.

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

DEMIRBAŞ, A. 1997. Calculation of higher heating values of biomass fuels. *Fuel,* 76**,** 431-434.

DEMIRBAŞ, A. 2000. Effect of lignin content on aqueous liquefaction products of biomass. *Energy Conversion and Management,* 41**,** 1601-1607.

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

DEMIRBAŞ, A. & ŞAHIN, A. 1998. Evaluation of biomass residue: 1. Briquetting waste paper and wheat straw mixtures. *Fuel Processing Technology,* 55**,** 175-183.

DEPARTMENT OF ENERGY & CLIMATE CHANGE 2012. Energy consumption in the UK. *In:* CHANGE, D. O. E. C. (ed.). London: GOV.UK.

DESWARTE, F. E. I., CLARK, J. H., WILSON, A. J., HARDY, J. J. E., MARRIOTT, R., CHAHAL, S. P., JACKSON, C., HESLOP, G., BIRKETT, M., BRUCE, T. J. & WHITELEY, G. 2007. Toward an integrated straw-based biorefinery. *Biofuels, Bioproducts and Biorefining,* 1**,** 245-254.

DILCIO ROCHA, J., LUENGO, C. A. & SNAPE, C. E. 1999. The scope for generating bio-oils with relatively low oxygen contents via hydropyrolysis. *Organic Geochemistry,* 30**,** 1527-1534.

DINCER, I. 2000. Renewable energy and sustainable development: a crucial review. *Renewable and Sustainable Energy Reviews,* 4**,** 157-175.

DOMÍNGUEZ, A., MENÉNDEZ, J. A., FERNÁNDEZ, Y., PIS, J. J., NABAIS, J. M. V., CARROTT, P. J. M. & CARROTT, M. M. L. R. 2007. Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas. *Journal of Analytical and Applied Pyrolysis,* 79**,** 128-135.

DOMÍNGUEZ, A., MENÉNDEZ, J. A., INGUANZO, M. & PIS, J. J. 2005. Investigations into the characteristics of oils produced from microwave pyrolysis of sewage sludge. *Fuel Processing Technology,* 86**,** 1007-1020.

DOWNING, M. & GRAHAM, R. L. 1996. The potential supply and cost of biomass from energy crops in the Tennessee valley authority region. *Biomass and Bioenergy,* 11**,** 283-303.

DURKA, T., STEFANIDIS, G., GERVEN, T. & STANKIEWICZ, A. 2010. On the accuracy and reproducibility of fiber optic (FO) and infrared (IR) temperature measurements of solid materials in microwave applications. *Measurement Science Technology,* 21.

ESCOBAR, J. C., LORA, E. S., VENTURINI, O. J., YÁÑEZ, E. E., CASTILLO, E. F. & ALMAZAN, O. 2009. Biofuels: Environment, technology and food security. *Renewable and Sustainable Energy Reviews,* 13**,** 1275-1287.

FADEEV, A. G. & MEAGHER, M. M. 2001. Opportunities for ionic liquids in recovery of biofuels. *Chemical Communications***,** 295-296.

FAN, J., DE BRUYN, M., BUDARIN, V. L., GRONNOW, M. J., SHUTTLEWORTH, P. S., BREEDEN, S., MACQUARRIE, D. J. & CLARK, J. H. 2013. Direct Microwave-Assisted Hydrothermal Depolymerization of Cellulose. *Journal of the American Chemical Society,* 135**,** 11728-11731.

FAN, J., DE BRUYN, M., ZHU, Z., BUDARIN, V., GRONNOW, M., GOMEZ, L. D., MACQUARRIE, D. & CLARK, J. Microwave-enhanced formation of glucose from cellulosic waste. *Chemical Engineering and Processing: Process Intensification.*

FATIH DEMIRBAS, M. 2009. Biorefineries for biofuel upgrading: A critical review. *Applied Energy,* 86, Supplement 1**,** S151-S161.

FERNÁNDEZ, Y., ARENILLAS, A. & MENÉNDEZ, J. Á. 2011. Microwave heating applied to pyrolysis.

FIELD, C. B., CAMPBELL, J. E. & LOBELL, D. B. 2008. Biomass energy: the scale of the potential resource. *Trends in Ecology & Evolution,* 23**,** 65-72.

FRANCK, E. U. 1983. Thermophysical properties of supercritical fluids with special consideration of aqueous systems. *Fluid Phase Equilibria,* 10**,** 211-222.

FRIEDRICH, J. P. & PRYDE, E. H. 1984. Supercritical CO2 extraction of lipid-bearing materials and characterization of the products. *Journal of the American Oil Chemists' Society,* 61**,** 223-228.

FUKUDA, H., KONDO, A. & NODA, H. 2001. Biodiesel fuel production by transesterification of oils. *Journal of bioscience and bioengineering,* 92**,** 405-416.

GABRIEL, C., GABRIEL, S., H. GRANT, E., H. GRANT, E., S. J. HALSTEAD, B. & MICHAEL P. MINGOS, D. 1998. Dielectric parameters relevant to microwave dielectric heating. *Chemical Society Reviews,* 27**,** 213-224.

GALBE, M. & ZACCHI, G. 2007. Pretreatment of Lignocellulosic Materials for Efficient Bioethanol Production. *In:* OLSSON, L. (ed.) *Biofuels.* Springer Berlin Heidelberg.

GILL, P., SAUERBRUNN, S. & READING, M. 1993. Modulated differential scanning calorimetry. *Journal of Thermal Analysis and Calorimetry,* 40**,** 931-939.

GOLDEMBERG, J. 2006. The promise of clean energy. *Energy Policy,* 34**,** 2185-2190.

GRAY, K. A., ZHAO, L. & EMPTAGE, M. 2006. Bioethanol. *Current Opinion in Chemical Biology,* 10**,** 141-146.

GROOM, M. J., GRAY, E. M. & TOWNSEND, P. A. 2008. Biofuels and Biodiversity: Principles for Creating Better Policies for Biofuel Production

Biocombustibles y Biodiversidad: Principios para la Creación de Mejores Políticas para la Producción de Biocombustible. *Conservation Biology,* 22**,** 602-609.

GROVER, P. & MISHRA, S. 1996. *Biomass briquetting: technology and practices*, Food and Agriculture Organization of the United Nations.

HAGUE, J. Biomass as feed-stocks for the forest products industry. Biomass and energy crops. Meeting of the Association of Applied Biologists, 7-8 April 1997, Royal Agricultural College, Cirencester, UK., 1997. 455-464.

HAJALIGOL, M., WAYMACK, B. & KELLOGG, D. 2001. Low temperature formation of aromatic hydrocarbon from pyrolysis of cellulosic materials. *Fuel,* 80**,** 1799-1807.

HANAOKA, T., HIASA, S. & EDASHIGE, Y. 2013. Syngas production by CO2/O2 gasification of aquatic biomass. *Fuel Processing Technology,* 116**,** 9-15.

HANCOCK, B. & ZOGRAFI, G. 1994. The Relationship Between the Glass Transition Temperature and the Water Content of Amorphous Pharmaceutical Solids. *Pharmaceutical Research,* 11**,** 471-477.

HAWTHORNE, S. B., YANG, Y. & MILLER, D. J. 1994. Extraction of organic pollutants from environmental solids with sub-and supercritical water. *Analytical Chemistry,* 66**,** 2912-2920.

HERRERO, M. A., KREMSNER, J. M. & KAPPE, C. O. 2007. Nonthermal Microwave Effects Revisited: On the Importance of Internal Temperature Monitoring and Agitation in Microwave Chemistry. *The Journal of Organic Chemistry,* 73**,** 36-47.

HESS, J. R., WRIGHT, C. T. & KENNEY, K. L. 2007. Cellulosic biomass feedstocks and logistics for ethanol production. *Biofuels, Bioproducts and Biorefining,* 1**,** 181-190.

HILL, J. M. & MARCHANT, T. R. 1996. Modelling microwave heating. *Applied Mathematical Modelling,* 20**,** 3-15.

HIMMEL, M. E., DING, S.-Y., JOHNSON, D. K., ADNEY, W. S., NIMLOS, M. R., BRADY, J. W. & FOUST, T. D. 2007. Biomass Recalcitrance: Engineering Plants and Enzymes for Biofuels Production. *Science,* 315**,** 804-807.

HOEKMAN, S. K. 2009. Biofuels in the U.S. – Challenges and Opportunities. *Renewable Energy,* 34**,** 14-22.

HOLLIDAY, R. L., KING, J. W. & LIST, G. R. 1997. Hydrolysis of Vegetable Oils in Sub- and Supercritical Water. *Industrial & Engineering Chemistry Research,* 36**,** 932- 935.

HOLM-NIELSEN, J. B., AL SEADI, T. & OLESKOWICZ-POPIEL, P. 2009. The future of anaerobic digestion and biogas utilization. *Bioresource Technology,* 100**,** 5478- 5484.

HONG, G. & SPRITZER, M. Supercritical water partial oxidation. Proceedings of the 2002 US DOE Hydrogen Program Review NREL/CP-610-32405, 2002. 18.

HORIKAWA, Y. & SUGIYAMA, J. 2008. Accessibility and size of Valonia cellulose microfibril studied by combined deuteration/rehydrogenation and FTIR technique. *Cellulose,* 15**,** 419-424.

HOSOYA, T., KAWAMOTO, H. & SAKA, S. 2007. Cellulose–hemicellulose and cellulose–lignin interactions in wood pyrolysis at gasification temperature. *Journal of Analytical and Applied Pyrolysis,* 80**,** 118-125.

HUANG, Y. F., KUAN, W. H., LO, S. L. & LIN, C. F. 2008. Total recovery of resources and energy from rice straw using microwave-induced pyrolysis. *Bioresource Technology,* 99**,** 8252-8258.

HUBER, G. W., IBORRA, S. & CORMA, A. 2006. Synthesis of Transportation Fuels from Biomass:☐ Chemistry, Catalysts, and Engineering. *Chemical Reviews,* 106**,** 4044- 4098.

HUNTER, S. E. & SAVAGE, P. E. 2004. Recent advances in acid- and base-catalyzed organic synthesis in high-temperature liquid water. *Chemical Engineering Science,* 59**,** 4903-4909.

INTERNATIONAL ENERGY FORUM 2010. Assessment of Biofuels Potential and Limitations. *A report commissioned by the International Energy Forum.*

ISHIDA, Y., YŌSHINO, M., TAKAYANAGI, M. & IRIE, F. 1959. Dielectric studies on cellulose fibers. *Journal of Applied Polymer Science,* 1**,** 227-235.

JANSEN, R. A. 2012. First-and Second-Generation Biofuels. *Second Generation Biofuels and Biomass: Essential Guide for Investors, Scientists and Decision Makers***,** 21-29.

JANULIS, P. 2004. Reduction of energy consumption in biodiesel fuel life cycle. *Renewable Energy,* 29**,** 861-871.

JONES, D. A., LELYVELD, T. P., MAVROFIDIS, S. D., KINGMAN, S. W. & MILES, N. J. 2002. Microwave heating applications in environmental engineering—a review. *Resources, Conservation and Recycling,* 34**,** 75-90.

KABYEMELA, B. M., ADSCHIRI, T., MALALUAN, R. M. & ARAI, K. 1997. Kinetics of Glucose Epimerization and Decomposition in Subcritical and Supercritical Water. *Industrial & Engineering Chemistry Research,* 36**,** 1552-1558.

KABYEMELA, B. M., ADSCHIRI, T., MALALUAN, R. M. & ARAI, K. 1999. Glucose and Fructose Decomposition in Subcritical and Supercritical Water:□ Detailed Reaction Pathway, Mechanisms, and Kinetics. *Industrial & Engineering Chemistry Research,* 38**,** 2888-2895.

KAISER, N. F. K., BREMBERG, U., LARHED, M., MOBERG, C. & HALLBERG, A. 2000. Fast, convenient, and efficient molybdenum-catalyzed asymmetric allylic alkylation under noninert conditions: An example of microwave-promoted fast chemistry. *Angewandte Chemie-International Edition,* 39**,** 3596-3598.

KALASHNIK, A. T., PAPKOV, S. P., RUDINSKAYA, G. V. & MILKOVA, L. P. 1991. Liquid crystal state of cellulose. *Polymer Science U.S.S.R.,* 33**,** 107-112.

KAMIO, E., TAKAHASHI, S., NODA, H., FUKUHARA, C. & OKAMURA, T. 2008. Effect of heating rate on liquefaction of cellulose by hot compressed water. *Chemical Engineering Journal,* 137**,** 328-338.

KAPARAJU, P., SERRANO, M., THOMSEN, A. B., KONGJAN, P. & ANGELIDAKI, I. 2009. Bioethanol, biohydrogen and biogas production from wheat straw in a biorefinery concept. *Bioresource Technology,* 100**,** 2562-2568.

KAPPE, C. O. 2004. Controlled microwave heating in modern organic synthesis. *Angewandte Chemie-International Edition,* 43**,** 6250-6284.

KAPPE, C. O. 2013. How to measure reaction temperature in microwave-heated transformations. *Chemical Society Reviews,* 42**,** 4977-4990.

KAPPE, C. O., PIEBER, B. & DALLINGER, D. 2013. Microwave Effects in Organic Synthesis: Myth or Reality? *Angewandte Chemie-International Edition,* 52**,** 1088-1094.

KARAGÖZ, S., BHASKAR, T., MUTO, A., SAKATA, Y. & UDDIN, M. A. 2003. Low-Temperature Hydrothermal Treatment of Biomass:□ Effect of Reaction Parameters on Products and Boiling Point Distributions. *Energy & Fuels,* 18**,** 234-241.

KATZ, J. D. 1992. Microwave sintering of ceramics. *Annual Review of Materials Science,* 22**,** 153-170.

KAWAMOTO, H., MORISAKI, H. & SAKA, S. 2009. Secondary decomposition of levoglucosan in pyrolytic production from cellulosic biomass. *Journal of Analytical and Applied Pyrolysis,* 85**,** 247-251.

KHAN, F. & PILPEL, N. 1987. An investigation of moisture sorption in microcrystalline cellulose using sorption isotherms and dielectric response. *Powder Technology,* 50**,** 237-241.

KIMREY, H. D. & JANNEY, M. A. 1988. *Design principles for high-frequency microwave cavities.*

KLASS, D. L. 1998. *Biomass for renewable energy, fuels, and chemicals*, Access Online via Elsevier.

KLASS, D. L. 2004. Biomass for renewable energy and fuels. *Encyclopedia of energy,* 1**,** 193-212.

KRAMMER, P. & VOGEL, H. 2000. Hydrolysis of esters in subcritical and supercritical water. *The Journal of Supercritical Fluids,* 16**,** 189-206.

KRIEGERBROCKETT, B. 1994. MICROWAVE PYROLYSIS OF BIOMASS. *Research on Chemical Intermediates,* 20**,** 39-49.

KRIEGSMANN, G. A. 1992. Thermal runaway in microwave heated ceramics: A one dimensional model. *Journal of Applied Physics,* 71**,** 1960-1966.

KRIEGSMANN, G. A. 1997. Hot spot formation in microwave heated ceramic fibres. *IMA Journal of Applied Mathematics,* 59**,** 123-148.

KRITZER, P. & DINJUS, E. 2001. An assessment of supercritical water oxidation (SCWO): Existing problems, possible solutions and new reactor concepts. *Chemical Engineering Journal,* 83**,** 207-214.

KUHNERT, N. 2002. Microwave-Assisted Reactions in Organic Synthesis—Are There Any Nonthermal Microwave Effects? *Angewandte Chemie International Edition,* 41**,** 1863-1866.

KULKARNI, M. G., GOPINATH, R., MEHER, L. C. & DALAI, A. K. 2006. Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification. *Green Chemistry,* 8**,** 1056-1062.

LAM, S. S. & CHASE, H. A. 2012. A review on waste to energy processes using microwave pyrolysis. *Energies,* 5**,** 4209-4232.

LAVOIE, J.-M., MARIE-ROSE, S. & LYNCH, D. 2013. Non-homogeneous residual feedstocks to biofuels and chemicals via the methanol route. *Biomass Conversion and Biorefinery,* 3**,** 39-44.

LEE, Y., IYER, P. & TORGET, R. W. 1999. Dilute-acid hydrolysis of lignocellulosic biomass. *Recent Progress in Bioconversion of Lignocellulosics.* Springer.

LIDSTRÖM, P., TIERNEY, J., WATHEY, B. & WESTMAN, J. 2001. Microwave assisted organic synthesis—a review. *Tetrahedron,* 57**,** 9225-9283.

LIN, Y. & TANAKA, S. 2006. Ethanol fermentation from biomass resources: current state and prospects. *Applied Microbiology and Biotechnology,* 69**,** 627-642.

LIN, Y. C., CHO, J., TOMPSETT, G. A., WESTMORELAND, P. R. & HUBER, G. W. 2009. Kinetics and Mechanism of Cellulose Pyrolysis. *Journal of Physical Chemistry C,* 113**,** 20097-20107.

LIVING COUNTRYSIDE. 2013. *Spring Peas Production Cycle* [Online]. http://www.ukagriculture.com/. Available: http://www.ukagriculture.com/production_cycles/spring_peas_production_cycle.cfm/ [Accessed 12.09.13 2013].

LONDO, M. & DEURWAARDER, E. 2007. Developments in EU biofuels policy related to sustainability issues: overview and outlook. *Biofuels, Bioproducts and Biorefining,* 1**,** 292-302.

LUDLOW-PALAFOX, C. & CHASE, H. A. 2001. Microwave-Induced Pyrolysis of Plastic Wastes. *Industrial & Engineering Chemistry Research,* 40**,** 4749-4756.

LUQUE, R., DE LA OSA, A. R., CAMPELO, J. M., ROMERO, A. A., VALVERDE, J. L. & SANCHEZ, P. 2012a. Design and development of catalysts for biomass-to-liquid-Fischer–Tropsch (BTL-FT) processes for biofuels production. *Energy & Environmental Science,* 5**,** 5186-5202.

LUQUE, R., MENENDEZ, J. A., ARENILLAS, A. & COT, J. 2012b. Microwave-assisted pyrolysis of biomass feedstocks: the way forward? *Energy & Environmental Science,* 5.

LYND, L. R. 1996. OVERVIEW AND EVALUATION OF FUEL ETHANOL FROM CELLULOSIC BIOMASS: Technology, Economics, the Environment, and Policy. *Annual Review of Energy and the Environment,* 21**,** 403-465.

MALÇA, J. & FREIRE, F. 2006. Renewability and life-cycle energy efficiency of bioethanol and bio-ethyl tertiary butyl ether (bioETBE): Assessing the implications of allocation. *Energy,* 31**,** 3362-3380.

MANI, S., TABIL, L. G. & SOKHANSANJ, S. 2004. Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass. *Biomass and Bioenergy,* 27**,** 339-352.

MANSFIELD, S. D., MOONEY, C. & SADDLER, J. N. 1999. Substrate and Enzyme Characteristics that Limit Cellulose Hydrolysis. *Biotechnology Progress,* 15**,** 804-816.

MASCHIO, G., KOUFOPANOS, C. & LUCCHESI, A. 1992. Pyrolysis, a promising route for biomass utilization. *Bioresource Technology,* 42**,** 219-231.

MATEOS-APARICIO, I., REDONDO-CUENCA, A., VILLANUEVA-SUÁREZ, M.-J., ZAPATA-REVILLA, M.-A. & TENORIO-SANZ, M.-D. 2010. Pea pod, broad bean pod and okara, potential sources of functional compounds. *LWT - Food Science and Technology,* 43**,** 1467-1470.

MATSON, T. D., BARTA, K., IRETSKII, A. V. & FORD, P. C. 2011. One-Pot Catalytic Conversion of Cellulose and of Woody Biomass Solids to Liquid Fuels. *Journal of the American Chemical Society,* 133**,** 14090-14097.

MAYNARD, F., WEINGAND, A., HAU, J. & JOST, R. 1998. Effect of High-pressure Treatment on the Tryptic Hydrolysis of Bovine β-Lactoglobulin AB. *International Dairy Journal,* 8**,** 125-133.

MAZEAU, K. & HEUX, L. 2003. Molecular dynamics simulations of bulk native crystalline and amorphous structures of cellulose. *The Journal of Physical Chemistry B,* 107**,** 2394-2403.

MCKENDRY, P. 2002. Energy production from biomass (part 1): overview of biomass. *Bioresource Technology,* 83**,** 37-46.

MCLAUGHLIN, S., SAMSON, R., BRANSBY, D. & WISELOGEL, A. Evaluating physical, chemical, and energetic properties of perennial grasses as biofuels. Proc. Bioenergy, 1996. 1-8.

MCMILLAN JAMES, D. 1994. Pretreatment of Lignocellulosic Biomass. *Enzymatic Conversion of Biomass for Fuels Production.* American Chemical Society.

MEHER, L. C., VIDYA SAGAR, D. & NAIK, S. N. 2006. Technical aspects of biodiesel production by transesterification—a review. *Renewable and Sustainable Energy Reviews,* 10**,** 248-268.

MENÉNDEZ, J. A., DOMÍNGUEZ, A., FERNÁNDEZ, Y. & PIS, J. J. 2006. Evidence of Self-Gasification during the Microwave-Induced Pyrolysis of Coffee Hulls. *Energy & Fuels,* 21**,** 373-378.

MENÉNDEZ, J. A., INGUANZO, M. & PIS, J. J. 2002. Microwave-induced pyrolysis of sewage sludge. *Water Research,* 36**,** 3261-3264.

METAXAS, A. & DRISCOLL, J. 1974. Comparison of the Dielectric Properties of Paper and Board at Microwave and Radio Frequencies. *Journal of Microwave Power*.

METTLER, M. S., VLACHOS, D. G. & DAUENHAUER, P. J. 2012. Top ten fundamental challenges of biomass pyrolysis for biofuels. *Energy & Environmental Science,* 5**,** 7797-7809.

MINGOS, D. M. P. & BAGHURST, D. R. 1991. Tilden Lecture. Applications of microwave dielectric heating effects to synthetic problems in chemistry. *Chemical Society Reviews,* 20**,** 1-47.

MIURA, M., KAGA, H., SAKURAI, A., KAKUCHI, T. & TAKAHASHI, K. 2004. Rapid pyrolysis of wood block by microwave heating. *Journal of Analytical and Applied Pyrolysis,* 71**,** 187-199.

MIURA, M., KAGA, H., YOSHIDA, T. & ANDO, K. 2001. Microwave pyrolysis of cellulosic materials for the production of anhydrosugars. *Journal of wood science,* 47**,** 502-506.

MOHAN, D., PITTMAN, C. U. & STEELE, P. H. 2006. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy & Fuels,* 20**,** 848-889.

MOK, W. S. L., ANTAL JR, M. J., SZABO, P., VARHEGYI, G. & ZELEI, B. 1992. Formation of charcoal from biomass in a sealed reactor. *Industrial & Engineering Chemistry Research,* 31**,** 1162-1166.

MOLINA, M. J. & MOLINA, L. T. 2004. Megacities and Atmospheric Pollution. *Journal of the Air & Waste Management Association,* 54**,** 644-680.

MONTÈS, H. & CAVAILLÉ, J. Y. 1999. Secondary dielectric relaxations in dried amorphous cellulose and dextran. *Polymer,* 40**,** 2649-2657.

MORIWAKI, S., MACHIDA, M., TATSUMOTO, H., KUGA, M. & OGURA, T. 2006. A study on thermal runaway of poly(vinyl chloride) by microwave irradiation. *Journal of Analytical and Applied Pyrolysis,* 76**,** 238-242.

MORTENSEN, P. M., GRUNWALDT, J. D., JENSEN, P. A., KNUDSEN, K. G. & JENSEN, A. D. 2011. A review of catalytic upgrading of bio-oil to engine fuels. *Applied Catalysis A: General,* 407**,** 1-19.

MOSIER, N., WYMAN, C., DALE, B., ELANDER, R., LEE, Y., HOLTZAPPLE, M. & LADISCH, M. 2005. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology,* 96**,** 673-686.

MULLEN, C. A., STRAHAN, G. D. & BOATENG, A. A. 2009. Characterization of Various Fast-Pyrolysis Bio-Oils by NMR Spectroscopy†. *Energy & Fuels,* 23**,** 2707-2718.

NAIK, S. N., GOUD, V. V., ROUT, P. K. & DALAI, A. K. 2010. Production of first and second generation biofuels: A comprehensive review. *Renewable and Sustainable Energy Reviews,* 14**,** 578-597.

NELSON, S. O. Permittivity and density relationships for granular and powdered materials. Antennas and Propagation Society International Symposium, 2004. IEEE, 20-25 June 2004 2004. 229-232 Vol.1.

NIGAM, P. S. & SINGH, A. 2011. Production of liquid biofuels from renewable resources. *Progress in Energy and Combustion Science,* 37**,** 52-68.

O'SULLIVAN, A. 1997. Cellulose: the structure slowly unravels. *Cellulose,* 4**,** 173-207.

OBERMAYER, D., GUTMANN, B. & KAPPE, C. O. 2009. Microwave Chemistry in Silicon Carbide Reaction Vials: Separating Thermal from Nonthermal Effects. *Angewandte Chemie,* 121**,** 8471-8474.

OLLIVON, M., QUINQUENET, S., SERAS, M., DELMOTTE, M. & MORE, C. 1988. Microwave dielectric measurements during thermal analysis. *Thermochimica Acta,* 125**,** 141-153.

OLSON, E., SHARMA, R. & AULICH, T. 2004. Higher-Alcohols Biorefinery. *In:* FINKELSTEIN, M., MCMILLAN, J., DAVISON, B. & EVANS, B. (eds.) *Proceedings of the Twenty-Fifth Symposium on Biotechnology for Fuels and Chemicals Held May 4–7, 2003, in Breckenridge, CO.* Humana Press.

OROZCO, A., AHMAD, M., ROONEY, D. & WALKER, G. 2007. Dilute acid hydrolysis of cellulose and cellulosic bio-waste using a microwave reactor system. *Process Safety and Environmental Protection,* 85**,** 446-449.

PANWAR, N. L., KAUSHIK, S. C. & KOTHARI, S. 2011. Role of renewable energy sources in environmental protection: A review. *Renewable and Sustainable Energy Reviews,* 15**,** 1513-1524.

PERT, E., CARMEL, Y., BIRNBOIM, A., OLORUNYOLEMI, T., GERSHON, D., CALAME, J., LLOYD, I. K. & WILSON, O. C. 2001. Temperature Measurements during Microwave Processing: The Significance of Thermocouple Effects. *Journal of the American Ceramic Society,* 84**,** 1981-1986.

PULS, J. 1997. Chemistry and biochemistry of hemicelluloses: Relationship between hemicellulose structure and enzymes required for hydrolysis. *Macromolecular Symposia,* 120**,** 183-196.

PURI, V. P. 1984. Effect of crystallinity and degree of polymerization of cellulose on enzymatic saccharification. *Biotechnology and Bioengineering,* 26**,** 1219-1222.

PUSCHNER MICROWAVE POWER SYSTEMS. 2013. *Microwave heating - Physical basis in the molecule* [Online]. Germany: Puschner. [Accessed 04/07/13 2013].

RACHOCKI, A., MARKIEWICZ, E. & TRITT-GOC, J. 2005. Dielectric relaxation in cellulose and its derivatives. *Acta Physica Polonica-Series A General Physics,* 108**,** 137-146.

RAMIREZ, R. S., HOLTZAPPLE, M. & PIAMONTE, N. 2013. Fundamentals of Biomass Pretreatment at High pH. *Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals.* John Wiley & Sons, Ltd.

RANZI, E., CUOCI, A., FARAVELLI, T., FRASSOLDATI, A., MIGLIAVACCA, G., PIERUCCI, S. & SOMMARIVA, S. 2008. Chemical Kinetics of Biomass Pyrolysis. *Energy & Fuels,* 22**,** 4292-4300.

READING, M., LUGET, A. & WILSON, R. 1994. Modulated differential scanning calorimetry. *Thermochimica Acta,* 238**,** 295-307.

ROBINSON, J., KINGMAN, S., IRVINE, D., LICENCE, P., SMITH, A., DIMITRAKIS, G., OBERMAYER, D. & KAPPE, C. O. 2010. Understanding microwave heating effects in single mode type cavities-theory and experiment. *Physical Chemistry Chemical Physics,* 12**,** 4750-4758.

ROIG, F., DANTRAS, E., DANDURAND, J. & LACABANNE, C. 2011. Influence of hydrogen bonds on glass transition and dielectric relaxations of cellulose. *Journal of Physics D: Applied Physics,* 44**,** 045403.

ROSS, A. B., BILLER, P., KUBACKI, M. L., LI, H., LEA-LANGTON, A. & JONES, J. M. 2010. Hydrothermal processing of microalgae using alkali and organic acids. *Fuel,* 89**,** 2234-2243.

SÁNCHEZ, C. 2009. Lignocellulosic residues: Biodegradation and bioconversion by fungi. *Biotechnology Advances,* 27**,** 185-194.

SANNIGRAHI, P., RAGAUSKAS, A. J. & TUSKAN, G. A. 2010. Poplar as a feedstock for biofuels: A review of compositional characteristics. *Biofuels, Bioproducts and Biorefining,* 4**,** 209-226.

SANTOS, T., COSTA, L., VALENTE, M., MONTEIRO, J. & SOUSA, J. 2010. 3D electromagnetic field simulation in microwave ovens: a tool to control thermal runaway. *COMSOL.* Paris.

SASAKI, M., ADSCHIRI, T. & ARAI, K. 2004. Kinetics of cellulose conversion at 25 MPa in sub- and supercritical water. *AIChE Journal,* 50**,** 192-202.

SASAKI, M., KABYEMELA, B., MALALUAN, R., HIROSE, S., TAKEDA, N., ADSCHIRI, T. & ARAI, K. 1998. Cellulose hydrolysis in subcritical and supercritical water. *Journal of Supercritical Fluids,* 13**,** 261-268.

SATO, T., OSADA, M., WATANABE, M., SHIRAI, M. & ARAI, K. 2003. Gasification of Alkylphenols with Supported Noble Metal Catalysts in Supercritical Water. *Industrial & Engineering Chemistry Research,* 42**,** 4277-4282.

SCHANCHE, J.-S. 2003. Microwave synthesis solutions from personal chemistry. *Molecular Diversity,* 7**,** 291-298.

SCOTT, D. S., PISKORZ, J. & RADLEIN, D. 1985. Liquid products from the continuous flash pyrolysis of biomass. *Industrial & Engineering Chemistry Process Design and Development,* 24**,** 581-588.

SHAFIEE, S. & TOPAL, E. 2009. When will fossil fuel reserves be diminished? *Energy Policy,* 37**,** 181-189.

SHAFIZADEH, F. 1982. Introduction to pyrolysis of biomass. *Journal of Analytical and Applied Pyrolysis,* 3**,** 283-305.

SHAFIZADEH, F. & FU, Y. L. 1973. Pyrolysis of cellulose. *Carbohydrate Research,* 29**,** 113-122.

SHAFIZADEH, F., FURNEAUX, R. H., COCHRAN, T. G., SCHOLL, J. P. & SAKAI, Y. 1979. Production of levoglucosan and glucose from pyrolysis of cellulosic materials. *Journal of Applied Polymer Science,* 23**,** 3525-3539.

SHAW, R. W., BRILL, T. B., CLIFFORD, A. A., ECKERT, C. A. & FRANCK, E. U. 1991. Supercritical water: A medium for chemistry. *Chem. Eng. News,* 69**,** 26-39.

SHEN, D. K. & GU, S. 2009. The mechanism for thermal decomposition of cellulose and its main products. *Bioresource Technology,* 100**,** 6496-6504.

SIMMONS, B. A., LOQUE, D. & BLANCH, H. W. 2008. Next-generation biomass feedstocks for biofuel production. *Genome biology,* 9**,** 242-242.

SIMON, S. L. 2001. Temperature-modulated differential scanning calorimetry: theory and application. *Thermochimica Acta,* 374**,** 55-71.

SIMS, R. E., MABEE, W., SADDLER, J. N. & TAYLOR, M. 2010. An overview of second generation biofuel technologies. *Bioresource Technology,* 101**,** 1570.

SPENCE, L. D., BAKER, A. T. & BYRNE, J. P. 2000. Characterization of document paper using elemental compositions determined by inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry,* 15**,** 813-819.

STÖCKER, M. 2008a. Biofuels and Biomass-To-Liquid Fuels in the Biorefinery: Catalytic Conversion of Lignocellulosic Biomass using Porous Materials. *Angewandte Chemie International Edition,* 47**,** 9200-9211.

STÖCKER, M. 2008b. Biofuels and biomass-to-liquid fuels in the biorefinery: Catalytic conversion of lignocellulosic biomass using porous materials. *Angewandte Chemie International Edition,* 47**,** 9200-9211.

STOOPS, W. 1934. The dielectric properties of cellulose. *Journal of the American Chemical Society,* 56**,** 1480-1483.

STURM, G. S. J., VERWEIJ, M. D., VAN GERVEN, T., STANKIEWICZ, A. I. & STEFANIDIS, G. D. 2012. On the effect of resonant microwave fields on temperature distribution in time and space. *International Journal of Heat and Mass Transfer,* 55**,** 3800-3811.

SU, X., ZHAO, Y., ZHANG, R. & BI, J. 2004. Investigation on degradation of polyethylene to oils in supercritical water. *Fuel Processing Technology,* 85**,** 1249-1258.

SUGANO, M., TAKAGI, H., HIRANO, K. & MASHIMO, K. 2008. Hydrothermal liquefaction of plantation biomass with two kinds of wastewater from paper industry. *Journal of Materials Science,* 43**,** 2476-2486.

SUN, Y. & CHENG, J. 2002. Hydrolysis of lignocellulosic materials for ethanol production: A review. *Bioresource Technology,* 83**,** 1-11.

SUTTON, W. H., BROOKS, M. H. & CHABINSKY, I. I. 1988. *Microwave processing of materials.*

SZCZEŚNIAK, L., RACHOCKI, A. & TRITT-GOC, J. 2008. Glass transition temperature and thermal decomposition of cellulose powder. *Cellulose,* 15**,** 445-451.

TAHERZADEH, M. & KARIMI, K. 2008. Pretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: A Review. *International Journal of Molecular Sciences,* 9**,** 1621-1651.

TAO, L. & ADEN, A. 2009. The economics of current and future biofuels. *In Vitro Cellular & Developmental Biology - Plant,* 45**,** 199-217.

TARKOW, H. & FEIST, W. C. 1969. A mechanism for improving the digestibility of lignocellulosic materials with dilute alkali and liquid ammonia. *Adv. Chem. Ser,* 95**,** 197-218.

TAYLOR, G. 2008. Biofuels and the biorefinery concept. *Energy Policy,* 36**,** 4406-4409.

THOMSON, G. W. 1946. The Antoine Equation for Vapor-pressure Data. *Chemical Reviews,* 38**,** 1-39.

THOSTENSON, E. T. & CHOU, T. W. 1999. Microwave processing: fundamentals and applications. *Composites Part A: Applied Science and Manufacturing,* 30**,** 1055-1071.

TIMILSINA, G. R., DU, X. & CARRIQUIRY, M. A. 2010. Second-Generation Biofuels.

TOOR, S. S., ROSENDAHL, L. & RUDOLF, A. 2011. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy,* 36**,** 2328-2342.

TYNER, W. E. & TAHERIPOUR, F. Future biofuels policy alternatives. Biofuels, Food, & Feed Tradeoffs Conference Organized by the Farm Foundation and USDA, St. Louis, Missouri, 2007.

UEMATSU, M. & FRANK, E. U. 1980. Static Dielectric Constant of Water and Steam. *Journal of Physical and Chemical Reference Data,* 9**,** 1291-1306.

UNITED NATIONS – ENERGY 2007. Sustainable Bio energy: A framework for decision makers. *United Nations – Energy, April 2007.*

VÁRHEGYI, G., ANTAL JR, M. J., JAKAB, E. & SZABÓ, P. 1997. Kinetic modeling of biomass pyrolysis. *Journal of Analytical and Applied Pyrolysis,* 42**,** 73-87.

VON SIVERS, M. & ZACCHI, G. 1995. A techno-economical comparison of three processes for the production of ethanol from pine. *Bioresource Technology,* 51**,** 43-52.

W. KING, J., L. HOLLIDAY, R. & R. LIST, G. 1999. Hydrolysis of soybean oil . in a subcritical water flow reactor. *Green Chemistry,* 1**,** 261-264.

WADA, M. 2002. Lateral thermal expansion of cellulose I-beta and IIII polymorphs. *Journal of Polymer Science Part B-Polymer Physics,* 40**,** 1095-1102.

WALLACE, M., ATTWOOD, D., DAY, R. & HEATLEY, F. 2006. Investigation of the microwave curing of the PR500 epoxy resin system. *Journal of Materials Science,* 41**,** 5862-5869.

WAN, C. & LI, Y. 2012. Fungal pretreatment of lignocellulosic biomass. *Biotechnology Advances,* 30**,** 1447-1457.

WANG, S., GUO, X., WANG, K. & LUO, Z. 2011. Influence of the interaction of components on the pyrolysis behavior of biomass. *Journal of Analytical and Applied Pyrolysis,* 91**,** 183-189.

WILL, H., SCHOLZ, P. & ONDRUSCHKA, B. 2004. Microwave-Assisted Heterogeneous Gas-Phase Catalysis. *Chemical Engineering & Technology,* 27**,** 113-122.

WOOTEN, J. B., SEEMAN, J. I. & HAJALIGOL, M. R. 2003. Observation and Characterization of Cellulose Pyrolysis Intermediates by 13C CPMAS NMR. A New Mechanistic Model. *Energy & Fuels,* 18**,** 1-15.

WORLD ENERGY COUNCIL 2007. Survey of Energy Resources. *World Energy Council, London.*

WRIGHT, M. M., BROWN, R. C. & BOATENG, A. A. 2008. Distributed processing of biomass to bio-oil for subsequent production of Fischer-Tropsch liquids. *Biofuels, Bioproducts and Biorefining,* 2**,** 229-238.

WU, X., FU, J. & LU, X. 2012. Hydrothermal decomposition of glucose and fructose with inorganic and organic potassium salts. *Bioresource Technology,* 119**,** 48-54.

WYMAN, C. E. 1999. BIOMASS ETHANOL: Technical Progress, Opportunities, and Commercial Challenges. *Annual Review of Energy and the Environment,* 24**,** 189-226.

WYMAN, C. E., DALE, B. E., ELANDER, R. T., HOLTZAPPLE, M., LADISCH, M. R. & LEE, Y. Y. 2005. Coordinated development of leading biomass pretreatment technologies. *Bioresource Technology,* 96**,** 1959-1966.

XIA, D. K. & PICKLESI, C. A. 2000. Microwave caustic leaching of electric arc furnace dust. *Minerals Engineering,* 13**,** 79-94.

XU, C. & LANCASTER, J. 2008. Conversion of secondary pulp/paper sludge powder to liquid oil products for energy recovery by direct liquefaction in hot-compressed water. *Water Research,* 42**,** 1571-1582.

YAGMUR, E., OZMAK, M. & AKTAS, Z. 2008. A novel method for production of activated carbon from waste tea by chemical activation with microwave energy. *Fuel,* 87**,** 3278-3285.

YAN, Y., XU, J., LI, T. & REN, Z. 1999. Liquefaction of sawdust for liquid fuel. *Fuel Processing Technology,* 60**,** 135-143.

YANG, H., YAN, R., CHEN, H., ZHENG, C., LEE, D. H. & LIANG, D. T. 2005. In-Depth Investigation of Biomass Pyrolysis Based on Three Major Components:□ Hemicellulose, Cellulose and Lignin. *Energy & Fuels,* 20**,** 388-393.

YAZDANI, S. S. & GONZALEZ, R. 2007. Anaerobic fermentation of glycerol: a path to economic viability for the biofuels industry. *Current Opinion in Biotechnology,* 18**,** 213-219.

YIXIN, H. & CHUNPENG, L. 1996. HEATING RATE OF MINERALS AND COMPOUNDS IN MICROWAVE FIELD■ jj.

YU, F., DENG, S., CHEN, P., LIU, Y., WAN, Y., OLSON, A., KITTELSON, D. & RUAN, R. 2007. Physical and chemical properties of bio-oils from microwave pyrolysis of corn stover. *Applied Biochemistry and Biotecnology.* Springer.

ZHANG, J., LUO, J., TONG, D., ZHU, L., DONG, L. & HU, C. 2010a. The dependence of pyrolysis behavior on the crystal state of cellulose. *Carbohydrate Polymers,* 79**,** 164-169.

ZHANG, L., XU, C. & CHAMPAGNE, P. 2010b. Overview of recent advances in thermo-chemical conversion of biomass. *Energy Conversion and Management,* 51**,** 969-982.

ZHANG, S., ASADULLAH, M., DONG, L., TAY, H.-L. & LI, C.-Z. 2013. An advanced biomass gasification technology with integrated catalytic hot gas cleaning. Part II: Tar reforming using char as a catalyst or as a catalyst support. *Fuel*.

ZHAO, X., SONG, Z., LIU, H., LI, Z., LI, L. & MA, C. 2010. Microwave pyrolysis of corn stalk bale: A promising method for direct utilization of large-sized biomass and syngas production. *Journal of Analytical and Applied Pyrolysis,* 89**,** 87-94.

ZHENG, Y. 2009. Overview of biomass pretreatment for cellulosic ethanol production. *International journal of agricultural and biological engineering,* 2**,** 51.

ZHENG, Y., LIN, H. M. & TSAO, G. T. 1998. Pretreatment for cellulose hydrolysis by carbon dioxide explosion. *Biotechnology Progress,* 14**,** 890-896.

ZHONG, C. & WEI, X. 2004. A comparative experimental study on the liquefaction of wood. *Energy,* 29**,** 1731-1741.

ZONG, L., ZHOU, S., SGRICCIA, N., HAWLEY, M. C. & KEMPEL, L. C. 2003. A review of microwave-assisted polymer chemistry (MAPC). *J Microw Power Electromagn Energy,* 38**,** 49-74.