Microwave processing of lignocellulosic biomass for production of fuels

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Abstract

Current environmental issues and resource demands are driving the global development of renewable energy. The work described in this thesis applies green and energy efficient microwave technology to transform lignocellulosic biomass into solid and liquid fuels suitable for application in coal burning power plants or upgrading into transportation fuels.

Current thermochemical biofuel production (e.g. pyrolysis and gasification) suffer many drawbacks such as high energy consumption and poor flexibility. Herein, it is shown that by applying novel low temperature microwave processing, fuels can be produced at temperatures up to 190 °C lower than required in equivalent conventional thermal treatments.

Studies on the microwave activation of the major components of biomass give insight into the mode of action. 180 °C was identified as the key temperature in the degradation of cellulose. Softening of the amorphous region of cellulose at this temperature enables microwave induced rearrangement increasing the efficiency of microwave interaction resulting in acid catalysed decomposition. It was shown possible to produce high calorific value chars at 150 °C lower than previously expected. A reduction of 100 °C was observed in the degradation temperature of hemicellulose.

The technology is versatile, effective on a variety of biomass species, and has a favourable energy balance. In studies on whole biomass, the processing conditions and energy usage were found to be favourable when compared with conventional methods. Chars were produced at low temperatures with increased calorific values and material properties in parallel with high quality bio-oils. Pilot scale trials were also carried out proving the technology to be scalable and open to industrial application.

This thesis shows for the first time the possibility to produce biofuels via microwave processing, while operating at temperatures below 300 °C. The impact of these findings is being further investigated at the dedicated microwave facility at the University of York.

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“...the stone age didn’t end because we ran out of stones. The oil age won’t end because we run out of oil.”

Sheik Ahmed Zaki Yamani Saudi Arabian Minister of petroleum and mineral resources (1962-1986)

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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.

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Work	Collaborator (based in Green Chemistry Centre of Excellence, University of York unless otherwise stated)
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2.4.1: Direct microwave effect	Dr. V. Budarin, Dr. P. Shuttleworth
2.4.2: Preparation of conventional char	Dr. V. Budarin
2.4.2: Measurement of calorific value (process development)	Dr. V. Budarin, Dr. P. Shuttleworth
2.4.2: Microwave IR experiment	Dr. V. Budarin, Dr. P. Shuttleworth
2.4.5: MDSC	Dr. P. Shuttleworth
2.4.6: Crystallinity of cellulose	Dr. V. Budarin
2.4.7: Isotope exchange studies	Dr. V. Budarin
Chapter 3	
3.4.1: XRF	Jennie Dodson
Chapter 4	
4.2.1 Process development	Dr. V. Budarin
4.2.2 & 4.2.5 Preparation of microwave bio-oil	Dr. V. Budarin
4.2.4: Preparation of pyrolysis bio-oil	Dr. T. Bridgeman, University of Leeds
4.2.4: Acid number measurement	Dr. P. Shuttleworth
4.2.4 Water content	Dr. V. Budarin

Chapter 5

5.3: Pilot scale trials	Rotawave Ltd., Sandycroft, Deeside, Clwyd Dr. V. Budarin, Dr. P. Shuttleworth, Dr. D. Macquarrie

Solid state ^{13}C MAS NMR was carried out by external services at the University of Durham. Elemental analysis and GC-MS were carried out through University of York chemistry department services.

1.1 Project Background

Climate change has been defined by the United Nations Framework Convention on Climate Change (UNFCCC) as: "a change of climate which is attributed directly or indirectly to human activity that alters the composition of the global atmosphere and which is in addition to natural climate variability over comparable time periods".[1] There are several theories as to the causes of climate change, but it is widely accepted that the major driving force is the increased levels of green house gases, such as CO_2 and methane, being released into the atmosphere. In an attempt to reduce CO_2 emissions, the European Commission published a white paper in 1997 on the use of renewable energy within the European Union. Targets were set requiring EU member states to increase the role of renewable resources in total energy production to 12 % by 2010 and ultimately to 20 % by 2020, with 33 % of electricity production needing to come from renewable resources.[2] As shown in Figure 1.1, it is estimated that the role of biomass in energy production will need to increase by more than six-fold from the year 2000 level.[2] As a result of the envisaged increased role of biomass in energy production, there is increased interest in methods of improving the efficiency of the conversion of biomass for energy production.

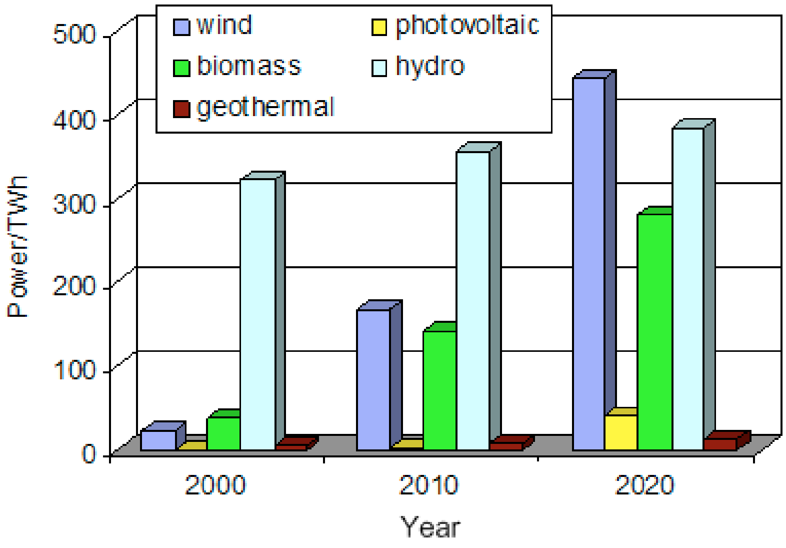

Fig. 1.1: EU renewable energy production targets[2]

By writing the Climate Change Bill into law in November 2008, the UK became the first country to set a legally binding framework for significant carbon reductions over a significant timeline. The Act sets targets to reduce the UK carbon emissions by 80 % in 2050 compared to 1990 levels, with an interim target of between 26 – 32 % by 2020.[3] In April 2009 the Committee on Climate Change, along with the Department on Energy and Climate Change, published carbon budgets which were subsequently passed into legislation. These set out legally binding targets of a 34 % reduction of carbon emissions by 2022 (relative to 1990), requiring an annual average emissions reduction of 1.7 %.[4] If these targets are to be reached, biomass will play a major role in the immediate future and long term as second generation biofuels become more widely available.

1.2 Project Aims

The core aim and focus of this project is to find novel methods of producing value added products from biomass, in particular those that can be used for energy production, using alternative green processing methods.

Summary of objectives:

- Study **effects of microwave processing on biomass components** in temperature ranges associated with torrefaction and pyrolysis.
- Produce **biomass-derived solid fuel** through microwave processing for use in energy production.
- Produce **biomass-derived liquid chemical mixtures** through green processing methods for use in energy production.
- Examine methods of **controlling properties** of solid and liquid products through process understanding.

1.3 Climate Change[5]

There are four main gases released by human activity: carbon dioxide, methane, nitrous oxide and the halocarbons, all of which accumulate in the earth's atmosphere and contribute to global warming and climate change. Marked increases in the concentration of all of these gases have been seen since the start of the industrial revolution when an economy based on manual labour became dominated by industry and machines. Human activity contributes in many ways to global climate change, but it is our increase in CO_2 emissions which has had the biggest anthropogenic influence on the climate.

The level of CO_2 in the atmosphere has increased mainly due to combustion of fossil fuels, cement production, gas flaring, deforestation and changes in land usage. When CO_2 is released it enters the global atmospheric carbon cycle, being absorbed by reservoirs such as the ocean and the terrestrial biosphere. In the past this process was in balance, with the natural reservoirs capable of absorbing most of the CO_2 released into the atmosphere. Between 1990 and 1999 the emissions of CO_2 as a result of fossil fuel burning and cement production increased by 0.7 % per annum, however the rate of increase has jumped from this level to about 3 % per annum between 1999 and 2005, a much higher level of emissions than had previously been expected.[5]

Fossil fuel combustion is responsible for the majority of CO_2 emissions caused by mankind. Electricity generation is the largest emitter of CO_2, accounting for approximately 41 % of all CO_2 emissions in the US in 2006, followed by the transport sector at 33 %.[6, 7] Similarly, in the UK, energy and transport are the sectors responsible for the largest portions of CO_2 emissions (Figure 1.2). Overall, emissions have fallen by 19.25 % since 1990 due to significant savings in waste management, industrial processing and energy sectors. Transport emissions have in fact increased over this period. Regardless of the reduction, energy production is still the largest contributor (35 % of total) and therefore a top priority along with transport when looking to cut emissions.[8] As a result, there is a significant drive in research and initiatives for the use of renewable and sustainable fuels to facilitate the development of society while minimising the impact on the environment.

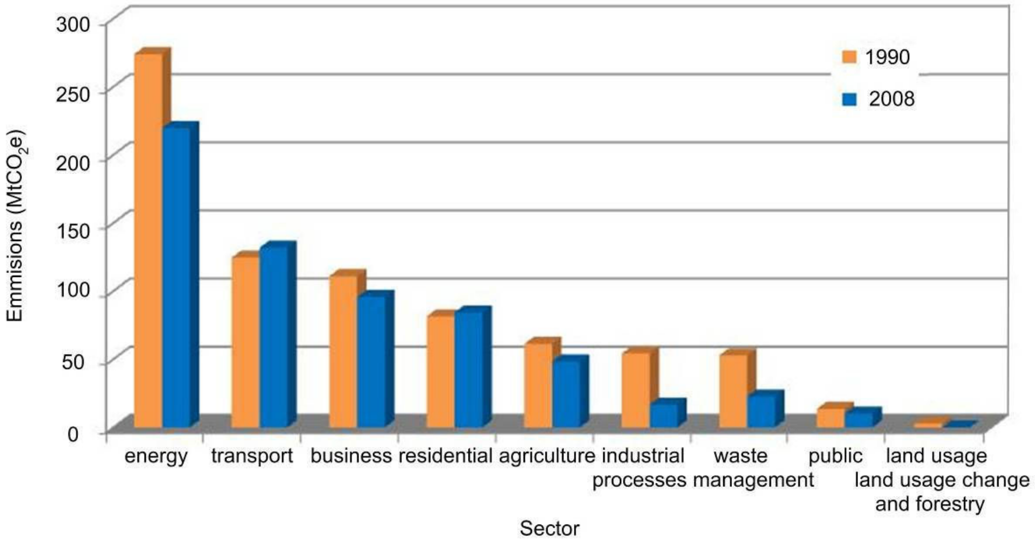

Figure 1.2: UK greenhouse gas emissions by sector 1990 % 2008 (MtCO$_2$e)[8]

1.4 Sustainable Development and Green Chemistry

The concept of sustainable development is something which goes hand in hand with Green Chemistry. In 1987 sustainable development was defined by a United Nations Commission on Environment as "...meeting the needs of the present without compromising the ability of future generations to meet their own needs".[9]

In order to achieve sustainable development mankind needs to move away from petrochemical feedstocks to renewable alternatives. One potential pathway to the production of alternative renewable products is the use of agricultural, forestry and municipal waste materials.[10]

The move away from our reliance on petrochemical feedstocks to a more sustainable society will result in a significant reduction in our impact on the environment. The change to renewable feedstocks and materials will come with a number of challenges, requiring a change, not only in the production methods, but also in the mindset of industry and the public alike, however the potential associated benefits should speed the transition (Table 1.1).

Table 1.1: Potential benefits and challenges associated with renewable feedstocks[11]

Benefits	Challenges
Low environmental impact	Natural variability
New opportunities	Cost
New functionalities	Complexity
Geographically diffuse	Competition for food production
Renewable	Unknown technology

The aims of this project are closely tied in with the concepts of renewable materials and sustainability, but the key issue is to ensure that the production of these materials is carried out using “green” methods and technology.

In 1996, IUPAC defined Green Chemistry as “the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances”.[12] By assessing and taking into account the entire lifecycle of products their environmental impact from “cradle to grave” can be minimised. The aims of green chemistry are summarised by the “Twelve Principles of Green Chemistry” as set out by Anastas and Warner (Table 1.2).[13]

Table 1.2: The Twelve Principles of Green Chemistry[13]

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances should be made unnecessary wherever possible, and innocuous when used.

6. Energy requirements should be recognised for their environmental and economic impacts, and should be minimised. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivatisation should be avoided whenever possible.
9. Catalytic reagents are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimise the potential for chemical accidents.

The production of fuel from renewable feedstocks relieves pressure being put on depleting fossil fuel reserves. Using agricultural and forestry waste opens a new stream of income for rural economies and enables avoidance of green house gas emissions associated with their decay, making them ideal alternatives to current feedstocks.

1.5 Biorefinery Concept

In recent years, concerns have been rising in relation to our reliance on foreign fuel supplies and the impact they are having on the environment. The concept of the biorefinery has been put forward as a method of removing this dependency by not only producing our own fuels from renewable feedstocks, but also chemicals and materials through various conversion processes.

A biorefinery can be defined as "a facility that integrates conversion processes and equipment to produce fuels, power, and chemicals from biomass"[14] (Figure 1.3). It can be seen as being analogous to the current day petroleum refinery in that it produces a number of different fuels, commodity chemicals and platform molecules from the raw material. In the case of a biorefinery, this starting material is some form of biomass, which consists of carbohydrates, lignin, fats, proteins and various other chemicals present at low levels.

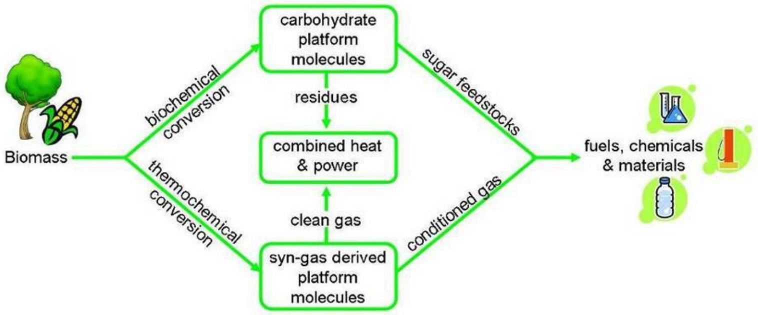

Fig. 1.3 : Illustration of biorefinery concept[14]

The output of a biorefinery can be placed in two categories; high-volume products, such as fuels, and low-volume chemicals, such as succinic acid, sorbitol and glycerol which can be used as platform molecules in the polymer and pharmaceutical industries.[15, 16]

1.6 Biomass composition

The potential products which can be derived from biomass depend on its chemical composition. Edible biomass contains starch as an energy store; the majority of first generation biofuels have focussed on the conversion of the starch into liquid, e.g. bioethanol. Second generation biofuels use non-food lignocellulosic biomass. It is made up of polysaccharides (cellulose and hemicelluloses) and lignin which compose the cell walls. Cell wall components are distinguished from extraneous (low molecular weight) components such as extractives and inorganic components which are not seen as an essential structural part of material (Figure 1.4).[17]

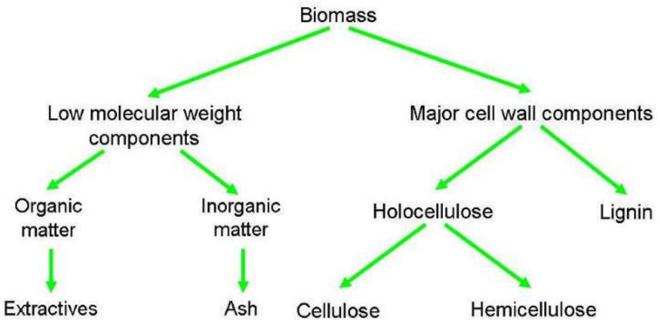

Fig. 1.4: Outline of components of lignocellulosic biomass[17, 18]

The role of each cell wall component can be represented by the simple analogy of reinforced concrete. Cellulose is like the iron, giving the structure strength, lignin is the concrete itself giving rigidity to the secondary cell wall structure, and the hemicellulose is the binding agent, promoting interaction between the other two.[19]

Cellulose is a polymer containing long linear chains of 1,4-D-glucopyranose units, connected by ß 1-4 linkages. Hemicelluloses are complex branched polysaccharides containing a mixture of xylose, glucose, mannose, arbinose, methylglucuronic and galacturonic acids as structural units (reviewed in [20, 21]). The relative abundance of the structural units varies depending on the biomass species. For example hemicellulose found in hardwood trees is predominately xylan with some glucomannan based while in softwoods it contain a small amount of xylan, being mainly rich in galactoglucomannan.[18] The average molecular weight is lower than that of cellulose at <30,000 as opposed to 100,000 average molecular weight reported for cellulose.[21] Lignin is defined as "an amorphous, polyphenolic material arising from an enzyme-mediated polymerisation of three phenylpropanoid monomers".[22] The resulting polymer is highly resistant to degradation[23] and is often cited as nature's most abundant source of aromatics. The three monomeric precursors of lignin are usually defined as (a) *p*-coumaryl alcohol, (b) coniferyl alcohol, and (c) sinapyl alcohol which are linked by carbon–carbon and ether bonds. The ratio of these units is also different depending on the tree species, even varying in different parts of the same tree. In softwood lignin, coniferyl alcohol is the major precursor (up to 95 % abundant) while *p*-coumaryl alcohol is a minor constituent, with sinapyl alcohol present only in trace amounts.[24] Hardwood lignins are composed of coniferyl alcohol and sinapyl alcohol in different ratios.[22] The structures of cellulose, hemicellulose and lignin are shown in Figure 1.5.

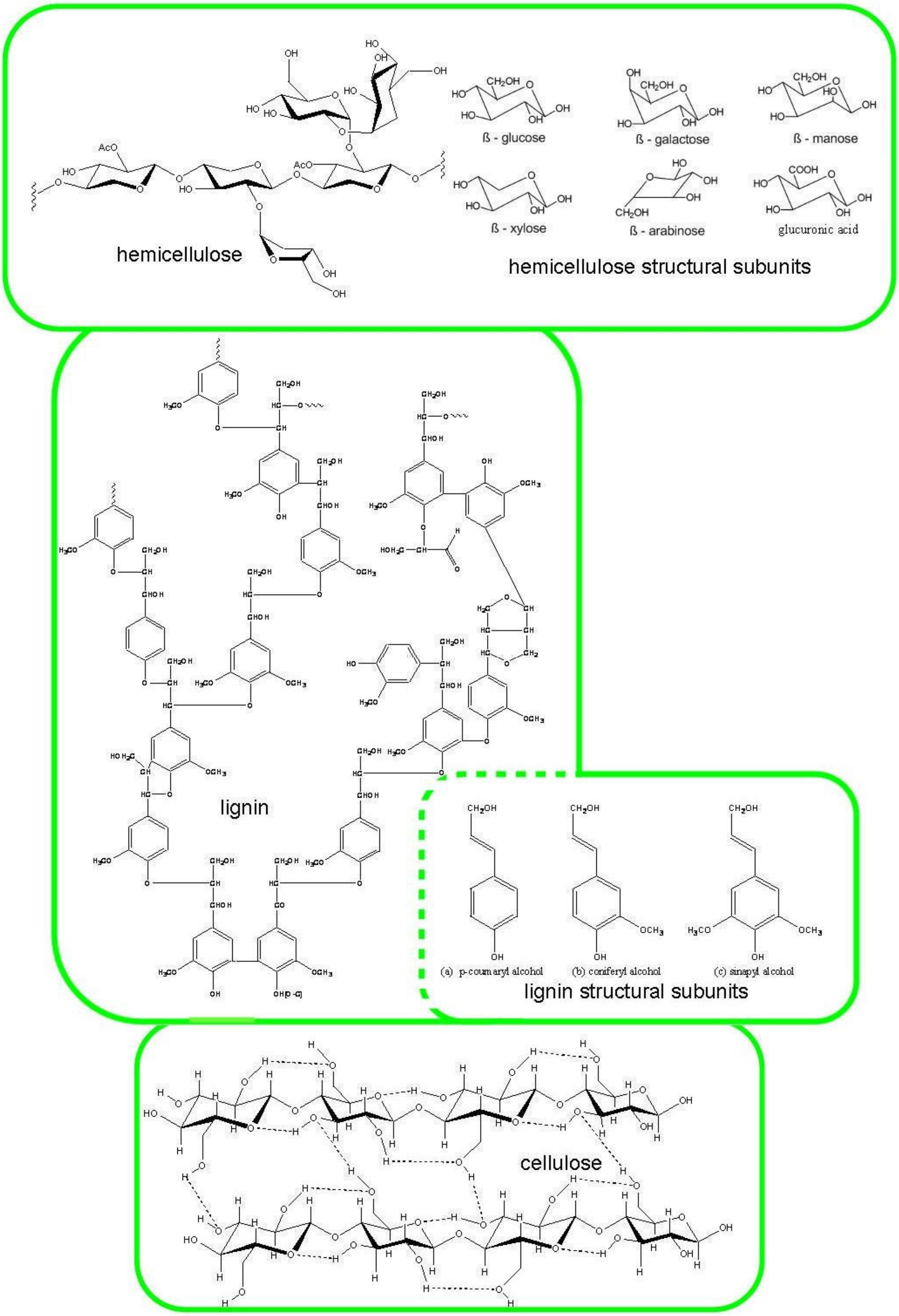

Fig 1.5: Proposed structure of hemicellulose, cellulose and lignin[18, 22]

Table 1.3 shows the relative abundance of each of these components in a selection of lignocellulosic materials.

Table 1.3: Typical Chemical Composition of Selected Lignocellulosic Species [24-26]

Species Common Name	Cell wall components			Extraneous components
	Cellulose	Hemicellulose	Lignin	
Chestnut Oak	41	30	22	7
White Ash	49	22	23	5
Sycamore	43	27	25	4
White Spruce	40	31	28	2
Scots Pine	40	29	28	4
Corncob	51	31	15	4

Note: all values shown as percent oven dry mass.

1.7 Biomass for Energy Production

Conventional energy production relies on the combustion of fossil fuels, resulting in the release of carbon which has been stored in the earth for several millennia. The release of CO_2 from energy production processes is contributing to the heating of the planet's atmosphere and hence climate change. The replacement of fossil fuels with biomass results in a reduction of the net CO_2 released during energy production. Indeed the CO_2 released during combustion of biomass is equivalent to that captured through photosynthesis during growth, as illustrated in Figure 1.6. As a result, the use of biomass for energy production is generally accepted as being carbon neutral under these terms. The energy used in growing, harvesting and transporting biomass and the associated emissions must be acknowledged when assigning the carbon neutral status. This must be done using renewable fuels in order minimise the related emissions.

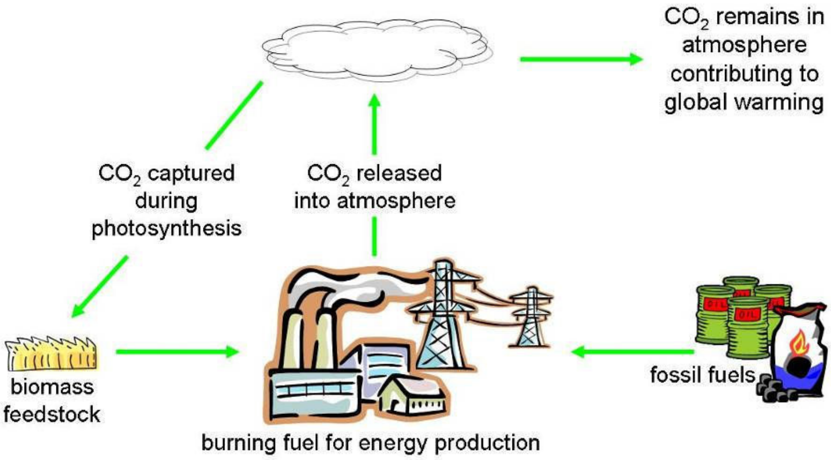

Fig. 1.6: Carbon cycle

While biomass has been used as a solid fuel for millennia, the potential for further use in energy production is significant. Biofuels can be defined as solid, liquid, or gaseous fuels derived from organic matter. They are already used to produce electricity, heat homes, as transport fuels and to heat industrial processes. Ethanol derived from biomass is an established fuel in Brazil where it is produced on a large scale from sugar cane. In the US and some European countries, industrial scale production of bioethanol has been established using starch starting materials.[27]

The implementation of bioenergy has been found to have a positive socio-economic impact. In developing countries, bioenergy is already the major energy source for people at the subsistence level, bringing important income to vulnerable economies, although poor practices may make this environmentally unsustainable. Amongst developed countries, especially in the European Union, the image of bioenergy is swiftly changing away from what used to be a 'poor man's fuel'. Studies have found modern biomass-use systems can result in a better quality of life, through increased rural employment and development, improved health through better wood stove design and lower sulfur dioxide emissions due to reduced coal burning in power plants. On a national scale, the increased employment leads to economic growth along with the energy independence offered by bioenergy production.[28]The rapid development of large scale bioenergy production has become a victim of its own success as the "fuel versus food" debate has grown. Brazilian ethanol is not seen as impacting on food supplies or prices as sugar cane production has risen to meet demands, although the associated changes in land usage impact negatively on the fuel's "green credentials". In the US concerns have been growing as the lucrative corn for ethanol prices resulted in much of the corn supply being diverted away from food and feed uses. In the EU biodiesel (the major liquid bio-fuel) is often produced from rapeseed oil, again raising issues with regard to diverting oils and fats from food production.[29] Concerns have also been raised with regard to the use of fertile agricultural land for the growth of fuels rather than food. These resource intensive crops have been selected for fuel production as a result of the ease of conversion of the starch and sugars into fuels. The global transition to biofuels cannot succeed without capitalising on the potential of lignocellulosic biomass.[20] The US Department of Energy has reported the potential to produce 1.3 billion tonnes of lignocellulosic biomass each year without interfering with current agriculture; this would be equivalent to 270 billion litres of ethanol, 30 % of their transport fuel requirements.[30] In addition, the move to lignocellulosic biomass will result in production of energy from agricultural, forestry and municipal waste, which may otherwise be sent to landfill, and increased activity in the agricultural and forestry sectors which have been in decline in recent years.

1.7.1 Biomass for liquid fuel

Transport systems throughout the developed world rely on the internal combustion engine driven by volatile liquid fuels, 98 % of which are currently derived from fossil fuels. In industrialised countries, transportation accounts for approximately 30 % of CO_2 emissions. As a result, there is renewed interest in the field of liquid biofuel production (Figure 1.7).[31]

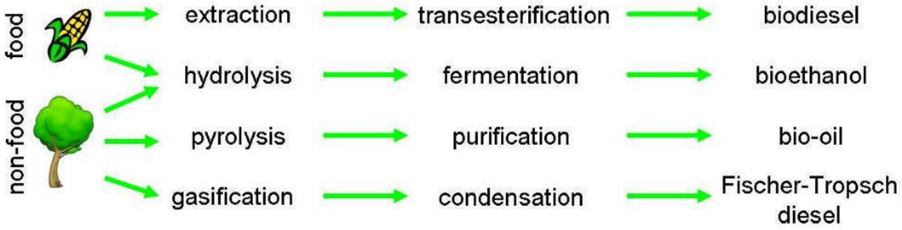

Figure 1.7: Production of liquid fuels from biomass

Biodiesel and bioethanol are leading the way in terms of alternative transport fuels. Use of biofuels in the EU has increased exponentially over the last ten years. Bioethanol use has increased 18 fold, while biodiesel use has increased by 13 times to over 3,500 ktoe (kilo tonnes of oil equivalent) in 2006.[32]

Bio-oil from thermal treatment of biomass is one of the lower profile liquid biofuels. It can be used for the production of chemicals as well as being a possible fuel. So far bio-oils have successfully been tested in stationary engines and boilers, and have been shown to be suitable for upgrading into high-quality hydrocarbon fuels.[33] Until now the energy and financial demands associated with pyrolysis and purification of bio-oil have prevented bio-oils from becoming a competitive fuel source. Throughout this project alternative thermal processing techniques have been studied in order to overcome this obstacle to progress.

1.7.2 Biomass for solid fuel

Biomass is used without thermochemical pre-processing in 97 % of current bio-energy production worldwide.[34] It can be used directly in dedicated boilers or co-fired with coal in existing power plants. Mixing biomass with coal reduces fossil-based carbon emissions as the amount of coal burnt per unit energy is reduced, and also avoids the methane or carbon dioxide produced during biomass decay. In terms of fuel properties, biomass contains highly volatile components resulting in a highly reactive fuel. Nonetheless, issues arise due to the high oxygen and moisture content which result in a lower heating value. This, along with often high chlorine and inorganic content, has led to problems with uptake of this technology.[35] However, the suitability of biomass as a fuel can be increased through pre-treatments such as torrefaction and slow pyrolysis to produce a fuel or char with lower water content than the untreated material. All in all, the production of a high quality fuel requires a high energy input. As a result this project has attempted to couple the production of a quality char with oil production in a low energy process, the aim being to maximise the benefit of the energy use by generating two fuel products.

1.8 Biomass upgrading for energy production

In 2007 only 1.5 % of UK energy was produced from biomass and waste residues (Figure 1.8A).[36] Direct use accounted for a small proportion of this (Figure 1.8B).

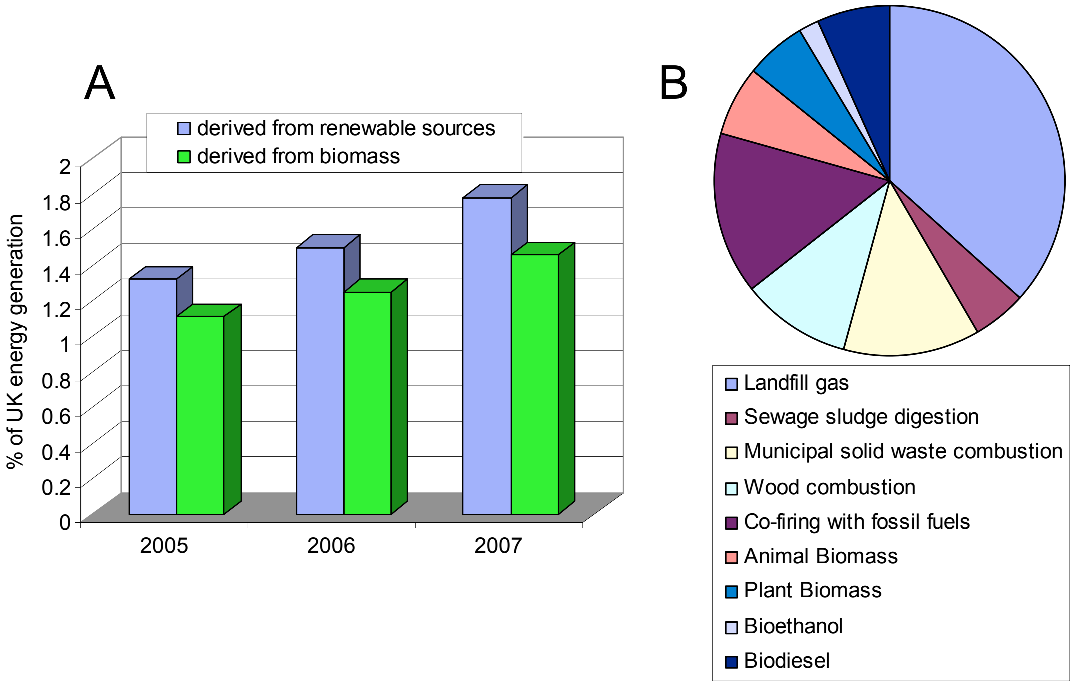

Fig. 1.8: A) Energy generation from renewable sources (2005-2007) B) Contribution of various types of biomass to production of energy (electricity, heat and transport).

(Note: "Animal biomass" includes farm waste, poultry litter, and meat and bone combustion. "Plant biomass" includes straw and energy crops)[36]

With the increasing demand for biomass use in energy production, research is being invested in pre-combustion biomass treatment methods to produce fuels to be burnt in engines and power generation facilities. The current main biomass conversion technologies are: [34, 35]

- Destructive carbonisation of woody biomass to charcoal
- Thermal conversion of biomass and waste (e.g., gasification, pyrolysis, torrefaction)

- Generation of electricity by direct combustion or gasification and pyrolysis (including co-firing with coal)
- Biological treatment of biomass and waste (e.g., fermentation, anaerobic digestion)
- Biomass densification (e.g., peletisation, production of briquettes, torrefaction)
- Conversion of biomass to a pyrolytic oil for transport fuel
- Chemical conversion of biomass (e.g., biodiesel)

Chemical pre-treatment methods for biomass are generally divided into two categories biochemical and thermochemical processes.

Biochemical processing involves the conversion of biomass to fermentable sugars for the production of specific alcohols, such as ethanol and butanol. The process can be carried out on small scales allowing localised processing and energy production. On the other hand, the conversion tends to be slow, requiring a batch-wise manufacturing process, and can only be used to convert polysaccharide components of biomass.

Thermochemical processing produces a range of products through the thermal decay and chemical reformation of biomass. Transformations are carried out under differing concentrations of oxygen, varying from the extremes of direct combustion in air through gasification in low air levels, to pyrolysis in the absence of oxygen. This route suffers from high capital and operational costs due to the high temperatures involved. In order to benefit from economies of scale, these processes must operate on a large regional basis requiring transport of feedstocks over long distances. Nonetheless, thermochemical processing holds a clear benefit over biochemical as it can essentially convert all the organic components of the biomass, fully capitalizing on its fuel and chemical potential.[31, 37, 38] It is therefore clear that what is needed in order to best use biomass for energy production is a low temperature continuous process which can maximise the conversion of the fuel and chemical potential of biomass into useful products.

1.8.1 Thermochemical upgrading of biomass for energy production

Each of the three main thermal processes (gasification, pyrolysis and torrefaction) converts the biomass to a preferred form which may then be used for energy production. Figure 1.9 gives an overview of the applications of the products of thermal treatment and decomposition of biomass.

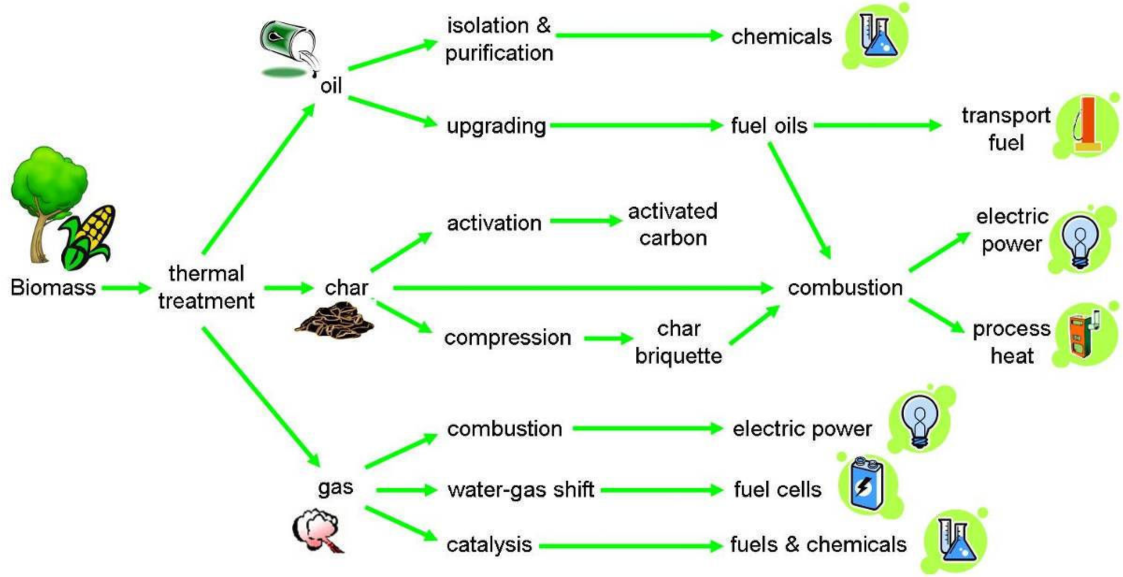

Fig. 1.9: Products of thermochemical treatment of biomass.[39]

The use of biomass as a feedstock for energy conversion depends greatly on physical properties and the nature of its chemical constituents. It is therefore important to understand the thermal behaviour of the major components of biomass when considering thermal upgrading treatments.

1. Hemicellulose is the first component to degrade. The first hemicellulose decomposition step usually occurs below 250 ^{o}C, when a series of depolymerisation reactions results in rearrangement of the glycosidic ring structure.. These oligosaccharides and monosaccharides then decompose around 300 ^{o}C to produce a char, CO, CO_2 and water as the main products.
2. Thermal degradation of lignin occurs over a wide temperature range with some softening occurring below 200 ^{o}C, while char formation and volatilisation of

components can begin at 240 ^{o}C, temperatures as high as 600 ^{o}C are necessary for complete thermal decomposition.[40]

3. The thermal degradation of cellulose requires the highest initiation temperature, close to 300 ^{o}C, and is complete by 500 ^{o}C. Several different pathways have been suggested for the decomposition process, as cellulose undergoes several different dehydration, elimination, condensation and fragmentation reactions resulting in the formation of a mixture of gases, a complex liquid portion and a solid char residue.[41,42]

1.8.2 Gasification of biomass

Gasification is the conversion of solid biomass fuels into flammable gas mixtures, so-called syngas, rich in CO, CO_2, CH_4 and H_2 which can then be transformed into chemicals and fuels (Equations 1-3) or used to heat industrial processes.

Equation 1: Fischer Tropsch transformation $(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$
Equation 2: Water gas shit reaction $H_2O + CO \rightarrow H_2 + CO_2$
Equation 3: Steam reforming $H_2O + CH_4 \rightarrow CO + 3H_2$

Under conventional heating conditions gasification is carried out between 750 – 1800 ^{o}C. The process is carried out by partial oxidation in air or by steam gasification. Using oxygen as the oxidation medium results in gases of a medium heating value (~10 – 12 MJ m^{-3}) which are significantly better than the results associated with oxidation in air (~5 MJ m^{-3}). Steam gasification is a two step process with similar products but an improved medium heating value of ~15 – 20 MJ m^{-3}. After production of the primary gas, char residues are burnt in a second reactor to provide heat for the next gasification, maximising the overall energy efficiency of the system. Steam gasification results in higher levels of CH_4 and hydrocarbons within the gas stream which increase the heating value. The use of the gas, and the potential production of value-added products depends on the levels of the various components within the stream which in turn determines the heating value of the gas.[38] Figure 1.10 shows the various potential applications of medium and lower heating value gases.

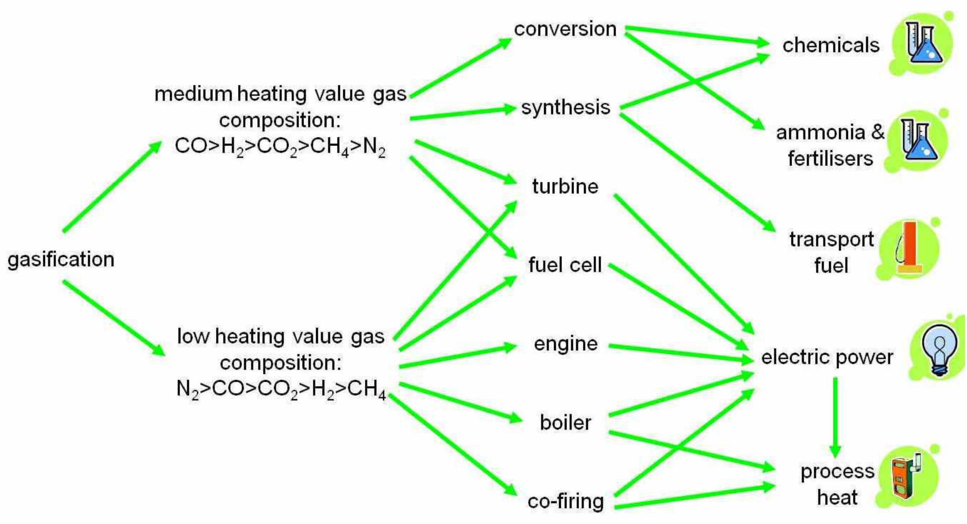

Fig. 1.10: Application of products of biomass gasification[38]

One of the most successful biomass gasifiers currently in operation is located in Güssing, Austria. The facility outputs 2 MW of electrical power along with 4.5 MW of heat, providing sufficient energy for its municipal region, supplying electricity and heat for the district heating grid. All of the biomass used (generally woodchips) is sourced within five kilometres of the facility reducing the environmental impact of any feedstock transport.[43]

1.8.3 Pyrolysis of biomass for liquid biofuel production

Pyrolysis results in the production of oil (up to 70 %), solid char and gas, by the thermal decomposition of organic compounds in the absence of oxygen above 400 ^{o}C.[44] The pyrolysis of biomass is a versatile process; the relative yields of the products can be controlled through variation of system parameters such as heating rate, maximum temperature and residence time.[45] Fast pyrolysis usually heats the biomass to the relatively moderate temperature of 500 ^{o}C at rates in the order of 10^3 ^{o}Cs^{-1}. The short residence time (~1 s) favours the production of a liquid portion (~75 %) over gas (~13 %) and char (~12 %). Increasing the residence time to 10 – 20 s results in a significant change in the product distribution, (~50 % liquid, ~30 % gas and ~20 % char).[38]

In this case, the charcoal and gas are treated as by-products, with the major focus on use of the liquid fraction as outlined in Figure 1.11.

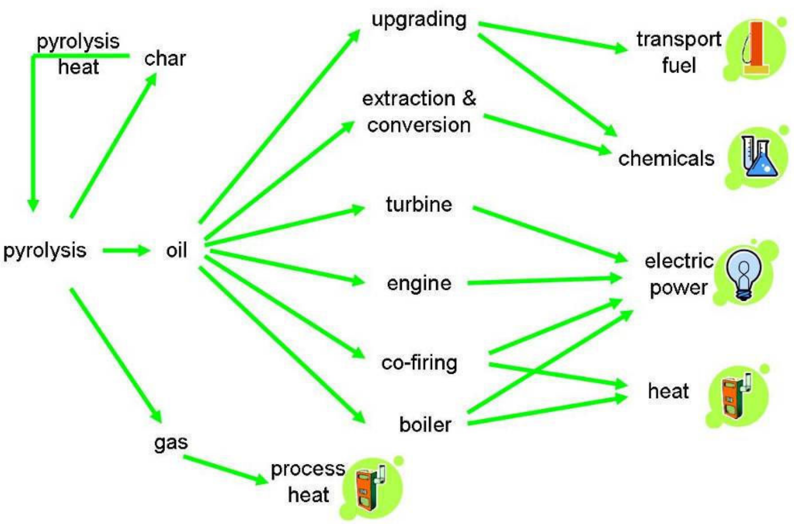

Fig. 1.11: Application of products of biomass pyrolysis[38]

Fig. 1.12: Bio-oil

The liquid fraction, known as bio-oil, is a dark brown liquid the composition of which varies greatly depending on the biomass feedstock (Figure 1.12). Bio-oil contains a complex mixture of oxygenated organic components, formed as a result of degradation of holocellulose and lignin within the biomass, along with a significant amount of water. The oil forms a type of aqueous microemulsion containing many reactive species, present due to the rapid quenching of the system during fast pyrolysis. Fast pyrolysis bio-oil has a higher heating value of 16 – 17 kJ g^{-1}, based on a water content of ~25 % wt. The liquid contains several hundred chemicals in varying proportions including formaldehyde, acetic acid, high molecular weight phenols, oligosaccharides and anhydrosugars. The quantity of water present varies depending on the feedstock and preparation conditions from ~ 15 – 50 % wt.[38] Over 300 chemical compounds have been identified as bio-oil components derived from the breakdown of hemicellulose, cellulose and lignin. In spite of extensive effort, it is thought that only 40 – 50 % of bio-oil has been fully structurally characterised. The structures present vary greatly depending on factors such as the heating rate, rate of heat transfer through the sample and the nature of the biomass itself.[18]

Bio-oils are not miscible with standard hydrocarbon fuels. As a result they require special systems for utilisation. The simplest application for bio-oil is in stationary fuel burners such as boilers, furnaces and turbines for electricity production but its high viscosity, poor storage stability and corrosiveness stand in the way of the large scale uptake.[38] As a result much research has been carried out into processes which will make it more suitable for the desired application. The main upgrading routes include hydrogenation, esterification, hydrodeoxygenation, catalytic cracking of the pyrolysis vapours, steam reforming and the physical emulsification of bio-oil with diesel, the majority of which require complicated expensive procedures and rely on the use of catalysts which are subject to fouling during processing.[46-48] The only current commercial use of bio-oil is as a liquid smoke for the flavouring of meat and fish products. Fast pyrolysis is still a relatively new technology with few commercial examples although much research worldwide is focused on getting the technology to the stage when this will be possible.[18]

1.8.4 Torrefaction of biomass

Of all sources of CO_2, the burning of fossil fuels for electricity production is responsible for the greatest proportion of emissions; therefore the replacement of fossil fuels in power production facilities is vital for the reduction of our impact on global warming. Potential biomass fuels include short rotation woody crops (such as willow and miscanthus), wood, agricultural waste, industrial residues, forestry waste, waste paper and municipal waste (Figure 1.13).

Fig 1.13: Diverse range of biomass available

The use of biomass in energy production faces challenges due its low calorific value when compared to oil or coal. While biomass is a cleaner fuel than coal, generally with lower sulfur content, the corrosive properties of biomass ash and the formation of tar during combustion can result in damage of burners and fouling of downstream systems.[49] The tar is produced as a by-product during the gasification of biomass; it condenses as the vapour temperature reduces on leaving the gasification chamber. The condensed tar can lead to blocking, fouling in duct, valve, and engine.[50] The inherent high moisture content and highly oxygenated nature of biomass means that the efficiency of energy production is not optimised when used for direct combustion. Biomass also raises material handling issues and is energy inefficient to transport in its raw state due to the low energy density, and high water content.[34, 49]

Torrefaction is carried out at lower temperatures than other thermochemical processes, usually between 200 – 300 ^{o}C under atmospheric conditions or in the absence of air. It essentially corresponds to high temperature drying which results in a higher energy density product due to the removal of low calorific value volatile components. The resulting solid is then easier to handle and store due to the reduced water content and the reduced risk of self heating due to the volatile content.[40] The term torrefaction comes from the process of roasting coffee beans to make them easier to grind. The main product of torrefaction is a solid char residue. Volatile products are also evolved during the thermal treatment process including carbon dioxide, carbon monoxide, water, acetic acid and methanol, some of which condense to produce a yellowish liquid. The liquid and gas phase contain relatively more oxygen compared to the original biomass, while the char is typically characterised by lowered oxygen to carbon ratios resulting in the increased calorific value. The product can be used as a direct combustion fuel in power production or as a feed for gasification or pyrolysis.[51]

1.9 Microwave Chemistry

Since the late 1980s interest has been growing in the field of microwave-assisted chemistry. Microwave irradiation lies between radio and infrared in the electromagnetic spectrum in the frequency range of 0.3 to 300 GHz (Figure 1.14). Similar to domestic microwaves, specialised chemistry microwave reactors operate at 2.45 GHz. The advantage microwave chemistry offers is in the increased efficiency of heating the material by "microwave dielectric heating effects", which are dependent on the ability of a material (solvent or reagent) to absorb the microwave energy and convert it into heat.[52,53]

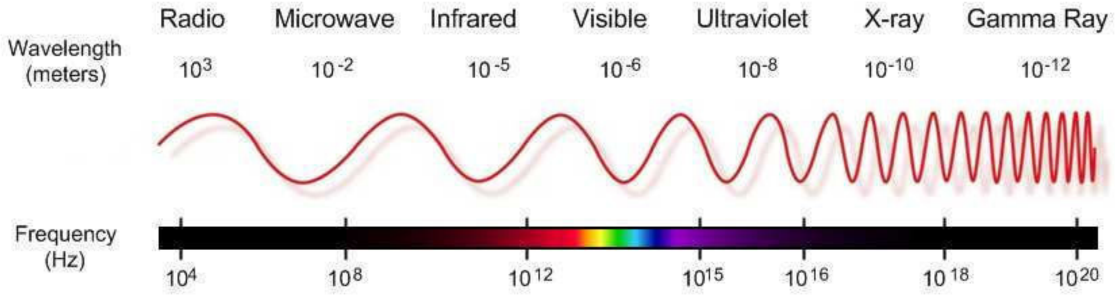

Fig. 1.14: Electromagnetic spectrum

There are two main mechanisms through which interaction occurs: dipolar polarisation and ionic conduction. When polar molecules are exposed to a strong electric field, the displaced positive and negative charges will orientate opposite to the direction of the electric field. Heat is then dissipated as the distortions within the molecule relax to their original orientation. The ability to convert electromagnetic energy into heat under given microwave conditions is strongly dependent on the "loss factor", expressed as tan δ. This value is calculated as $\tan \delta = \varepsilon'' / \varepsilon'$, where ε'' is the dielectric loss, a measure of the efficiency of conversion of electromagnetic energy to heat, and ε' the dielectric constant, which represents the molecule's ability to be "polarized by the electric field". Table 1.4 shows the tan δ values of a variety of solvents, a high tan δ value is therefore required for efficient absorption of the microwave energy and hence a greater rate of heating. Microwave energy can also cause a heating effect through ionic conduction.

This process can occur when free ions are present in the substance; the electric field caused by the microwave energy generates ionic motion causing rapid heating.[52]

Table 1.4: tan δ values of selected solvents at 25 °C

Solvent	tan δ value
Ethanol	0.941
Methanol	0.659
Water	0.123
Hexane	0.02

A microwave photon at this frequency is of too low energy to break chemical bonds therefore microwaves should not be able to induce the chemical reactions that occur. Increased rates and altered reaction pathways under microwave conditions have led to theories of an additional microwave influence. Much discussion has surrounded these so called “non-thermal” and “specific” microwave effects. Specific microwave effects (such as selective heating of microwave absorbing reagents, formation of hotspots and uniform heating of the sample) are generally agreed to be due to the accelerated rate of heating which causes results that cannot be duplicated or achieved under conventional conditions. Non-thermal effects are classed as accelerations which cannot be accounted for by kinetics or specific microwave effects and are subject to widespread discussion and controversy. Much more research is required to understand these phenomena.[52, 54]

Microwave chemistry offers many advantages over conventional methods of heating. Overall the process is more energy efficient as microwave irradiation heats the whole volume of a sample while conventional heating heats the sample in contact with the reaction vessel before the bulk. Unlike conventional heating methods, the heating effect is almost instantaneous, there is no time spent waiting for the source to heat up or cool down. Microwave reactor operating systems allow easy control of pressure and temperature to exact and steady values. The speed of microwave systems also allows for quick screening of parameters and testing of new methods.[52] The application of microwave technology in high throughput reactions such as flow reactors[55, 56] adds further to the advantages of microwave irradiation.

Figure 1.15 compares the heating of biomass by microwave and conventional methods. Conventional heating conducts the heat from the walls of the chamber through to the centre of the sample, resulting in the core of the sample being cooler than the walls and the surrounding gas above the sample. Microwave energy heats the entire sample, with head space above remaining much cooler. As a result of the heating of the entire sample, liquid fractions which are evolved during the process escape the bulk and condense in the cool walls and space above, preventing secondary reactions and alterations to the volatile components which could occur in a heated environment.

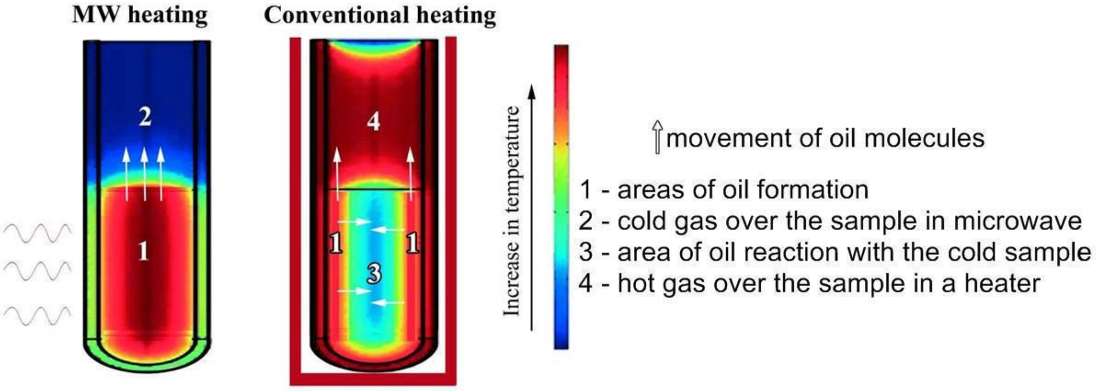

Fig. 1.15: Comparison of microwave irradiation (left) and conventional heating (right)[52]

1.9.1 Microwave treatment of biomass

The use of microwaves for treatment of biomass dates back to the early 1970s. Examples of substrates employed in this type of slow pyrolysis are numerous and include plant biomass such as wood or agricultural residues, plastics and municipal waste.[45, 57] The microwave treatment of cellulose and wood has been optimised for the production of chemicals such as levoglucosan and levoglucosenone, both important chiral precursors in the synthesis of natural products.[58] Factors such as starting material particle size, microwave power, irradiation time and source of biomass are all considered to have an effect on the efficiency of microwave interactions.[58-60]

The specific effect of microwave energy on biomass has also been studied. The microwave heating of materials is dependent on polarisability and dielectric loss factor. For macromolecules, such as biomass components, the polarisation is considered to occur in only small portions of the molecule as segments of the structure are not responsive to microwave radiation. For high polymers, the areas which are polarisable are further restricted by the rigidity of structures in the crystalline regions. As a result, only amorphous regions can align to the applied electric field. Polymers, such as those present in biomass, generally have a wide distribution of relaxation times (time taken to revert to original orientation after polarisation), resulting in a smaller dielectric loss but over a wide range of frequencies. In the case of cellulose the dielectric constant within the microwave range gives an intermediate microwave heating value ($\tan \delta \sim 0.2$ depending on source). The susceptibility of a material to uniform microwave heating may be completely independent of the thermal conductivity of the material, and is more strongly influenced by the depth of penetration of the microwave into the material. For cellulose at 2450 MHz, the depth is 2.4 m, therefore there is potential for fast processing of cellulose in bulky samples.[61]

By comparison with cellulose, there is less literature to date relating to the behaviour of lignin and hemicellulose under microwave conditions. It is known that the behaviour of lignin is quite different to that of cellulose, as lignin possesses fewer groups which are easily polarised, and a wider distribution of bond strengths.[62]

1.9.1.1 Microwave gasification of biomass

The calorific value of microwave gasification products of biomass have been investigated for processes above 500 °C.[45, 57, 63] Microwave energy was used to gasify sewage sludge up to a final reaction temperature of 1040 °C, with the aim to optimise the fuel properties of the gas produced. The sludge was heated to 135 °C to remove moisture, then rapidly heated to 1040 °C, at 5 $°Cs^{-1}$, where it was held for a residence time of 10 min. It was found that microwave gasification produces more gas and less oil than conventional thermal processes carried out under similar temperature conditions. Additionally, the amount of hydrogen in the gas mixture was much higher adding to the value of the gas produced. The calorific values of the collected fractions were up to 7, 37 and 10 kJ/g for char, oil and gas, respectively, while the typical heating values of commercial fossil fuels are 32, 42 and 40 kJ/g for coal, oil and gas. While the heating values for the oil do not compare favourably with that for coal, the yield was relatively small, meaning that the greatest percentage of energy was accumulated in the char and gas fractions optimising the energetic yield of the products.

1.9.1.2 Microwave pyrolysis of biomass for liquefaction

Microwave biomass pyrolysis for the production of a liquid fuel has been investigated between temperatures of 260-600°C, with most results reporting the need for temperatures above 350 ^{o}C. Using a maximum heating rate of 3.33 $^{o}Cs^{-1}$ under microwave conditions and 6.67 $^{o}Cs^{-1}$ in a furnace, the samples were held for 15 minutes at the reaction temperature. Under these optimised conditions it was found that 50 % of the biomass energy can be condensed into liquid products, 20 % in the char and the remaining 30 % in the gas phase. Analysis of the pyrolysis oil in terms of water content, density, pH, viscosity, elemental analysis and calorific value (CV) were reported to be similar to bio-oils produced by traditional fast pyrolysis.[64-66]

1.9.1.3 Microwave pyrolysis of biomass for char production

Microwave-induced pyrolysis has also been investigated previously, focussing on the production of char at lower temperatures than above. Slow pyrolysis of rice straw was investigated using temperatures between 266 and 563 ^{o}C. While the calorific value of the rice straw solid residue was no more than 20 kJ/g, and no better than those achievable by thermal methods in this temperature range, the principle of char production through low temperature microwave treatment was shown to be possible. As a result of the poor calorific value of the chars, Huang et al. investigated alternative applications for the solid, e.g. as absorbent, reporting surface areas of up to 270 m^2g^{-1}.[67]

1.9.2 Industrial application of microwave processes

Microwave treatment of biomass can be used before and/or during extraction processes to improve yields of secondary metabolites and aroma chemicals. The microwave acts by heating water in the core of the material, and the resulting steam can then act to induce opening of outer layers of the material.[68] Microwave heating has found industrial scale applications in a number of diverse areas. It is used to remove low levels of moisture from soybeans before further processing, forcing unwanted hulls to be released from the beans in a much more uniform product than conventional processing methods. Other food processing applications include meat thawing and tempering, dough treatment and pasta drying. The use of microwaves is also growing in the processing of materials. Microwave treatment is used by the Goodyear tyre company for rubber devulcanisation. The devulcanised rubber produced can then substitute up to 25 % new rubber, as opposed to only 5 % for rubber devulcanised by other methods.[69] Microwave processing is also used for "the production of advanced ceramics, the deposition of thermal barrier coatings, and the remediation of hazardous wastes" with new applications constantly being researched.[70]

1.10 Introduction to work in this thesis

There is reasonable literature outlining both the thermal treatment of biomass and microwave technology. However the potential application of microwaves in the thermal upgrading of biomass has yet to be fully explored. In particular, low temperature (100 – 300 °C) microwave processing has received little attention. Therefore, there is extensive scope to investigate and optimise this process, and to investigate the mechanisms of the action. The work in this thesis is split into four areas:

Chapter 2 looks into the effect of microwave irradiation on the individual components of biomass. The study focussed on cellulose, the most abundant biomass component on earth. Thermal and spectroscopic investigations were used to study the mechanism of degradation and product formation. Hemicellulose and lignin were also studied in terms of char formation to gain a better understanding of the mechanism of char production.

In Chapter 3, the knowledge gained in the investigation of the components of biomass was applied to whole biomass for the production of char. Three biomass types were selected, namely miscanthus (energy crop), wheat straw (agricultural residue) and cocoa husk (food industry waste).

Pyrolysis oils generated through microwave irradiation of wheat straw under various conditions are discussed in Chapter 4. The oils produced were characterised and compared to conventional fast pyrolysis oils, and microwave pyrolysis oils reported in literature.

Finally, the industrial applicability of this technology is discussed in chapter 5. Results from pilot-scale trials and energy calculations are used to access its suitability for use in large scale applications.

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Chapter 2: Microwave treatment of biomass components

Publications:

Budarin, V. L.; Clark, J. H.; Lanigan, B. A.; Shuttleworth, P.; Macquarrie, D. J., Microwave assisted decomposition of cellulose: A new thermochemical route for biomass exploitation. *Bioresource Technology* 2010, *101* (10), 3776-3779.

2.1 Introduction

It is widely accepted that the thermal behaviour of biomass is strongly dependent on its chemical composition and structure. The stages of primary pyrolysis, which take place between 200-400 ^{o}C, can be correlated to the initial fast decomposition of cellulosic components and the slower decomposition of lignin over a wide temperature range.[1] The decomposition pattern of biomass can be closely linked to cellulose, hemicellulose and lignin content. Indeed, biomass rich in cellulose behaves more similarly to pure cellulose, with high-lignin biomass demonstrating behaviour closer to lignin itself.[2, 3] A better understanding of the decompositional behaviour of these major components will be vital for progress towards optimisation of their conversion into useful products. Therefore, a better understanding of the behaviour of these major biomass components under microwave irradiation, the subject of this chapter, is crucial for progress towards efficient processing of biomass. The properties of these products will viewed in comparison to those of conventional slow pyrolysis under similar thermal conditions.

2.2 Composition of biomass

Lignocellulosic biomass consists of three structural polymers, typically about 35 to 50% cellulose, 20 to 35% hemicellulose, and 10 to 25% lignin depending on the plant species, each of which are naturally resistant to processing.[4] Lignocellulose is a composite material, with high tensile strength and high rigidity provided by a framework of cellulose microfibrils. This cellulose framework is in turn coated with hemicellulose which binds to the surface of the microfibrils and acts as a plasticiser preventing neighbouring fibrils from coming into contact with each other, and hence maintaining a certain level of flexibility.[5] This polysaccharide network is protected by the final cell wall component, lignin, which forms a type of waterproof, chemically resistant seal.[5]

2.2.1 Cellulose

Alpha cellulose is a polysaccharide having the general formula $(C_6H_{10}O_5)_n$ and an average molecular weight range of 300,000–500,000.[6] Cellulose is formed by β-1,4 links between glucose rings resulting in its insolubility in water and most common solvents, which poses challenges for processing.[7] Conversion of cellulose to fuel and lower molecular weight chemicals is strongly influenced by physical factors such as the degree of polymerization, level of crystallinity and number of reducing ends associated with the substrate. As a result of forming microfibril bundles of linearly linked glucose units in the cell wall, an extensive inter-strand hydrogen-bonding network occurs, giving rise to the crystallinity of the structure. The degree of crystallinity in cellulose has a major influence on the susceptibility to transformation, the more crystalline, the more difficult it is to access for conversion. The overall rigidity of cellulose as a macromolecule makes it all the more resistant to breakdown (summarized by [8]).

As can be seen in Figure 2.1, the D-anhydroglucopyranose units of cellulose are joined by β-type glycosidic linkages forming the long polymer chain. The linkages cause alternate glucose rings to be rotated by 180°; consequently the arrangement is very ordered, resulting in an extensive network of inter and intra molecular hydrogen bonds, holding large numbers of chains together (Figure 2.1B)(summarized by [9]). Faults in the order within chains lead to formation of amorphous regions. These regions are believed to be more susceptible to chemical conversions and are thought to be the points of association with hemicellulose.[5, 9]

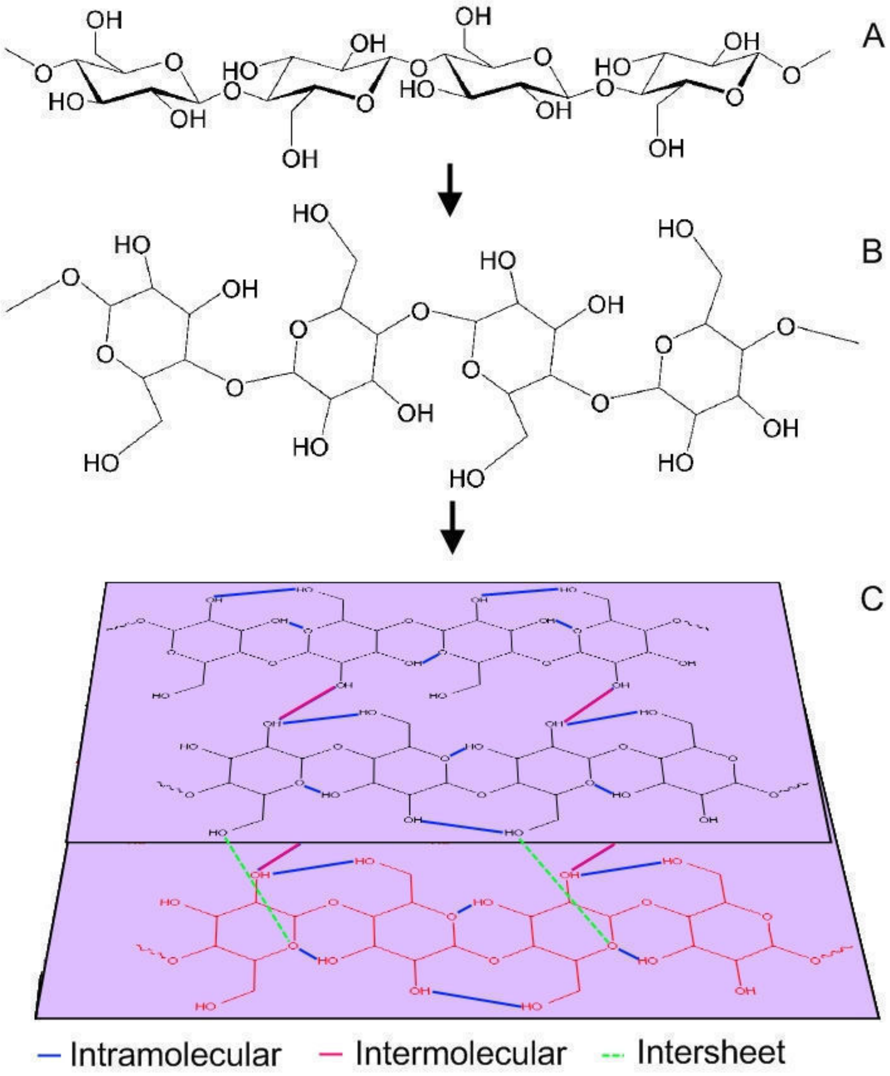

Fig. 2.1: Structure of cellulose A: stereochemistry within chain B:planar view C: extensive hydrogen bond network in cellulose (adapted from reference[9])

Cellulose typically accounts for 35-50 % of lignocellulosic biomass making it the most abundant biomolecule on earth and hence a key focus in the production of fuels from biomass.[4]

2.2.2 Hemicellulose

Hemicellulose is a collection of complex polysaccharides in the cell wall, typically accounting for up to 35 % of cell wall components. It is a branched polymer, the structure of which varies greatly depending on the biomass type. Hemicellulose, with an average molecular weight of 30,000, is built up of pentoses (xlyose, arabinose) hexoses (mannose, glucose, galactose) and uronic acids. Hemicelluloses formed of xylose and glucose dominate in the primary cell wall, while the secondary cell wall is mostly arabinoxylose and xylose (Figure 2.2) (summarised in [8-10])

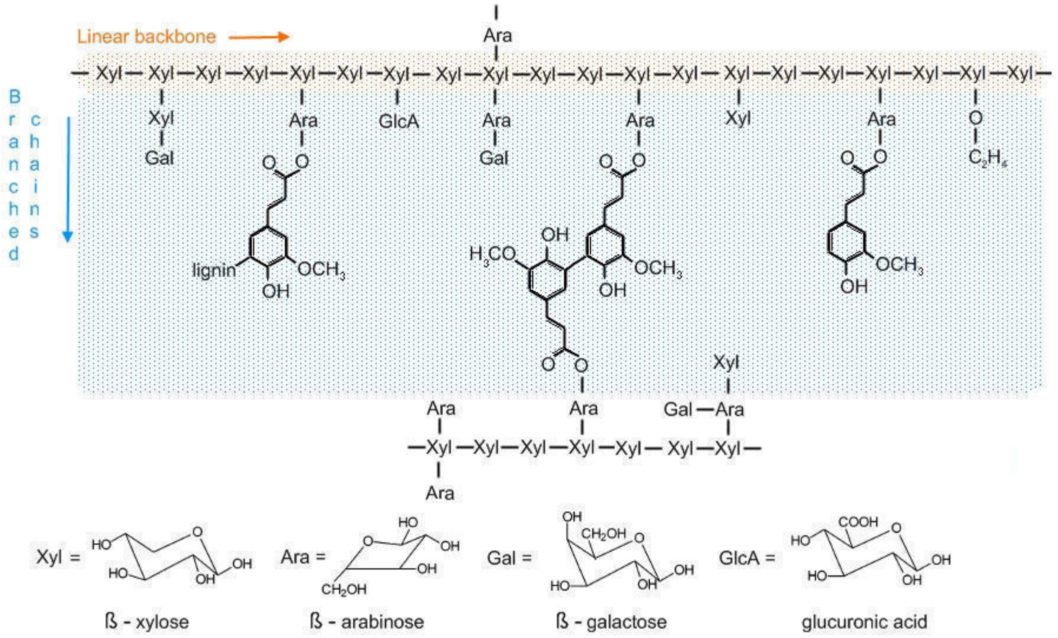

Fig. 2.2: Structure of arabino-xylan showing complex branched nature of polymer (adapted from reference [5])

Hemicellulose interacts with cellulose through further hydrogen bonding to the glucan chain. The presence of side chains prevents formation of a crystalline structure resulting in a higher solubility than cellulose.[5]

2.2.3 Lignin

Lignin is the most resistant component of the cell wall, essentially protecting cellulose and hemicellulose from degradation. It is made up of three phenylpropanoid monomers which form an amorphous polymer through enzyme mediated conversion resulting in a variety of chemical bonds (Figure 2.3). Similarly to hemicellulose, the structure of lignin is dependent on the biomass source. For example, coniferyl alcohol is the major precursor in softwood lignin (up to 95 %

abundant), while hardwood lignins contain various ratios of coniferyl alcohol and sinapyl alcohol.[11, 12]

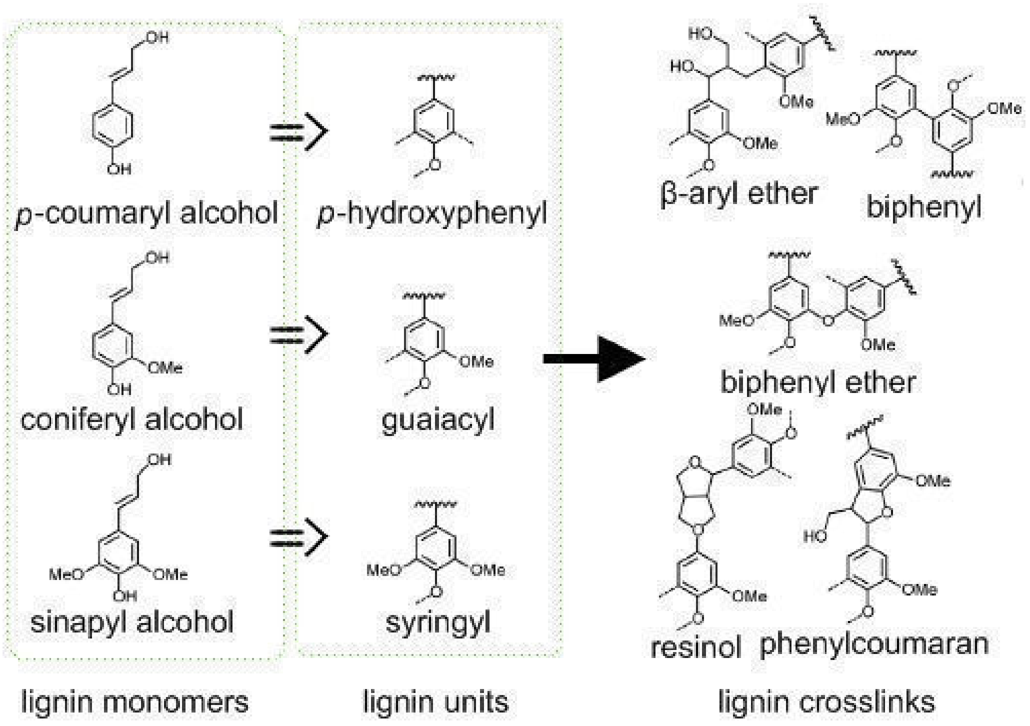

Fig. 2.3: Lignin building blocks (adapted from reference [8])

Lignin is subject to much research interest as it offers a major potential source of aromatic molecules if an efficient method can be found to break it down selectively. It is currently used as a stabiliser in drilling muds and emulsions, and as a dispersant in paints and dyes. The majority of lignin is seen as waste and burnt for energy production leaving this tremendous renewable source of aromatic compounds unexploited and ready for conversion to a useful product if a conversion process can be developed.[12]

2.3 Microwave treatment of biomass

As discussed in Section 1.9.2, limited investigations have been carried out into the specific effect of microwave energy on biomass. During microwave treatment the initial interaction is due to the presence of hydrogen bonding between cellulose layers as shown in Figure 2.4. As the microwave process continues the temperature within the sample increases as a result of this interaction. The increased temperature reduces the crystallinity within cellulose, increasing the freedom of movement and polarisability of groups within the molecule.

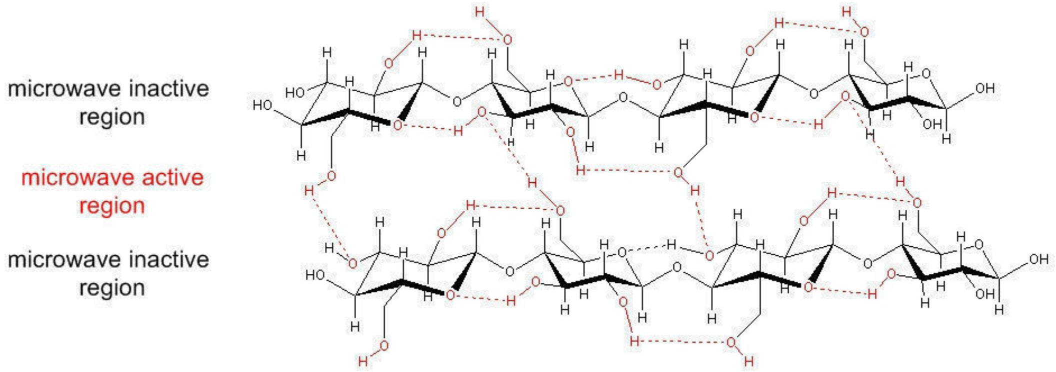

Fig. 2.4: Initial microwave interaction with cellulose due to the presence of H-bonding[13]

It is thought, that as the loss factor increases, i.e. the ability of cellulose to convert microwave energy to heat, significant amounts of water are released through chemical dehydration. The loss factor of water is about 60 times higher than that of cellulose in the microwave region; as a result, the water molecules generated lead to a significant increase in the microwave energy absorbed by the sample and subsequently an increase in the rate of heating within the material.[13]

Cellulose, as the major component of biomass, was chosen as the case study for investigation of the effect of microwave irradiation. As previously mentioned, conversion of cellulose to fuel and chemicals is strongly influenced by a number of physical factors such as degree of polymerization, level of crystallinity and number of reducing ends associated with the substrate. Of these, degree of the crystallinity in cellulose has the most significant influence on its susceptibility to transformation, the greater the degree, the more difficult it is to access for conversion.[8] Consequently, conversion of cellulose to other useful products could potentially be improved if microwave irradiation can be used to reduce the level of crystallinity.

2.4 Microwave treatment of cellulose

The majority of reported microwave treatments of biomass have been carried out at temperatures above 350 °C (typical for conventional pyrolysis), resulting in gasification or liquefaction of the starting material to produce fuels.[14-17] However there is much debate in the field of microwave technology; while it is agreed that they offer a more efficient method of heating, they also promote novel reaction pathways or greatly accelerate reaction rates, as a result of a so-called non-thermal effect.[18] These novel pathways result in milder operating conditions such as reduced temperature. Consequently, it is possible that the high temperatures and heating rates in previous microwave pyrolysis studies may have masked important lower temperature processes. Therefore, decomposition of cellulose at lower temperatures (below 300 °C) was investigated.

2.4.1 The "microwave-effect"

In order to differentiate thermal and non-thermal events during microwave treatment an experimental set-up was designed (Experimental section 7.2.1). As is shown in Figure 2.5, a narrow packed column of cellulose (allowing homogeneous exposure to microwave irradiation) was placed in a well stirred thermostated oil bath within the microwave chamber (to ensure uniform heating throughout the sample). The top portion of the cellulose was wrapped in aluminium foil to shield it from microwave irradiation (Figure 2.5A). Visual examination of the sample after the experiment showed the area which had been exposed to microwave irradiation had begun to decompose, while the area above shows little colour change (Figure 2.5B). The experiment was repeated using conventional heating. Little change was visible in the cellulose after heating to similar temperatures. Further microwave experiments were carried out over a range of oil bath temperatures between 150-220 °C (Figure 2.5C). While some decomposition of cellulose can be seen under microwave irradiation at 150 °C, there is a marked change in the level of decomposition above 180 °C.

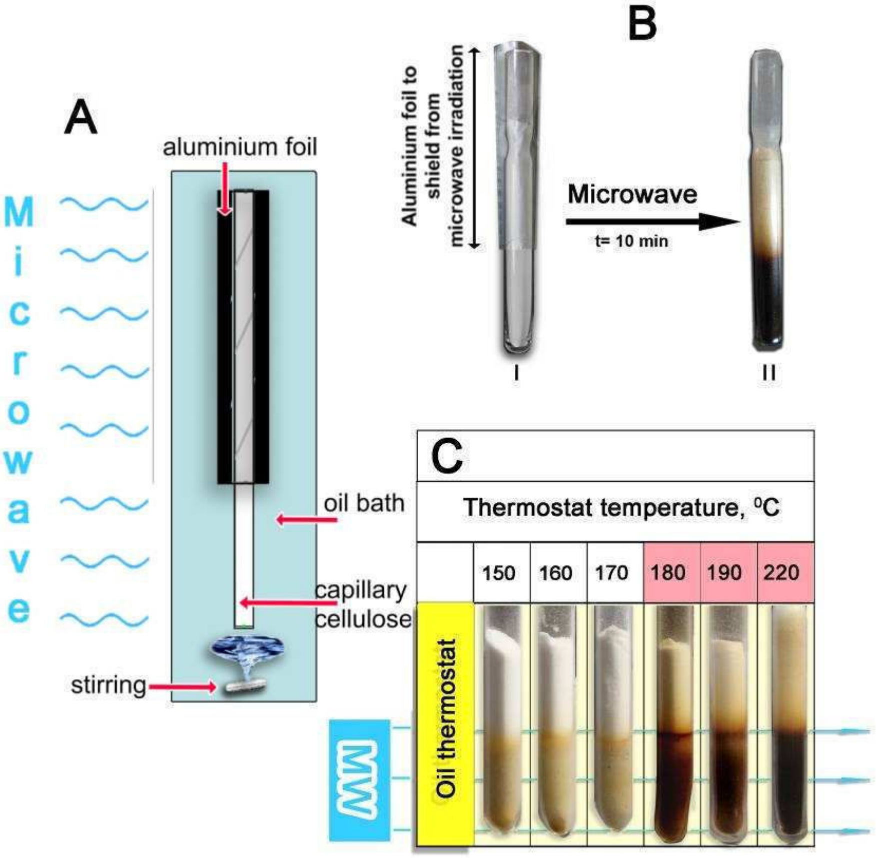

Fig. 2.5: Scheme of experimental set-up for estimation of direct microwave effect on the cellulose. A) Construction of the cell. B) Image of cellulose in capillary before (I) and after (II) microwave treatment. C) Cellulose samples treated in the microwave from 150 – 220 °C under the sample processing condition as those in B.

2.4.2 Effect of power and temperature on char formation

To gain a better understanding of the mechanism of the microwave effect on cellulose, the influence of microwave processing temperature on the production of char was investigated in parallel with conventional pyrolysis experiments.

Following the procedure described in experimental section 7.2.2, cellulose was irradiated at temperatures between 120 – 300 °C. In parallel, cellulose was also pyrolysed under conventional thermal conditions (between 150 – 450 °C). Figure

2.6 shows the comparison of the resulting chars based on their calorific values measured following the procedure described in Experimental section 7.3.1.

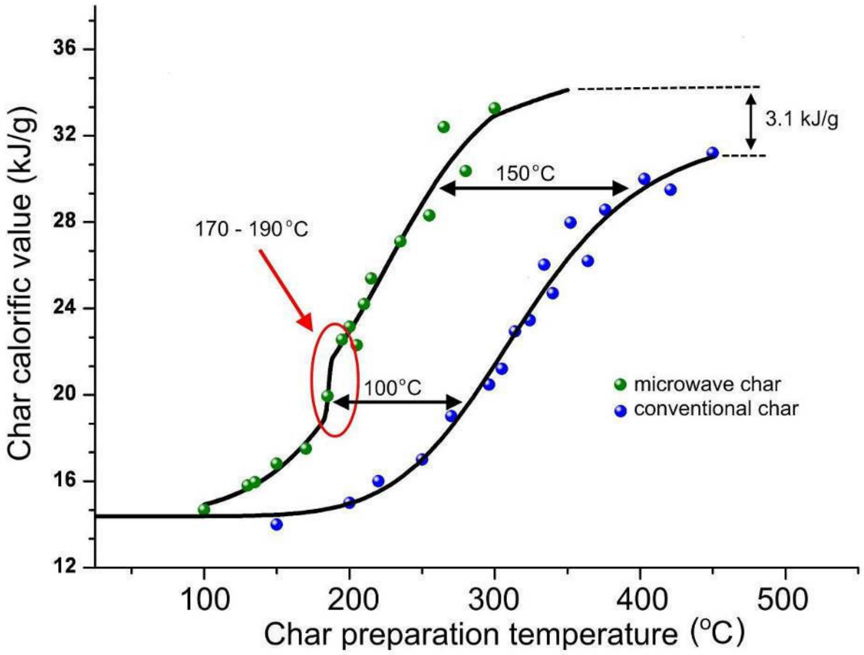

Fig. 2.6: Calorific value of char obtained from cellulose through thermal and microwave-assisted slow pyrolysis

It can be seen that through microwave irradiation, chars of similar calorific value could be produced at temperatures 100 ºC lower than those produced using conventional pyrolysis. While the increase in calorific value for conventional pyrolysis chars follows a smooth trend, the rate of increase for the microwave chars showed a jump at ~180 °C, in agreement with earlier qualitative observations (Figure 2.5). The maximum calorific value (34 kJg^{-1}) was achieved through microwave irradiation at 300 °C. This represents a significant process enhancement as microwave irradiation has facilitated production of a biomass char with a calorific value close to that of coal (32 – 42 kJg^{-1}).[19]

The char formation process simultaneously resulted in the release of volatile components which were subsequently condensed into a liquid. To investigate the kinetics of liquid formation under microwave conditions, the volatiles evolved were monitored by FTIR (Experimental section 7.3.4). The total absorption of IR radiation by the evolved gases is represented by the Gram-Schmidt trace (Figure 2.7 A).

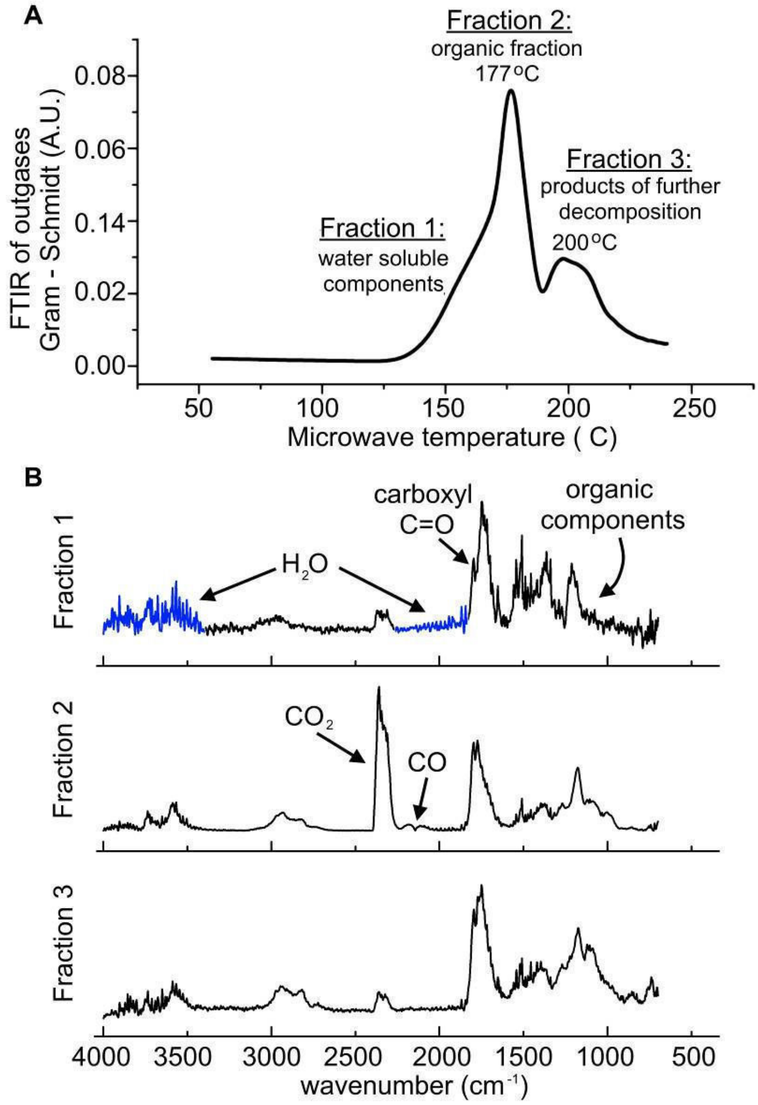

Fig. 2.7: A) Gram Schmidt FTIR trace of the volatiles produced during the microwave decomposition of cellulose B) IR spectra of evolved fractions

The first fraction was observed at temperatures as low as 155 °C, within 2-3 minutes of exposure to microwave irradiation. As can be seen in Figure 2.7 B, this fraction contains high levels of water, organic acids and aldehydes. Thereafter, a sharp peak is observed around 180 °C corresponding to an organic fraction with lower water content and the release of CO and CO_2. Finally, at 200 ºC, a third fraction of further decomposition products was seen. The composition of the fractions was confirmed by parallel studies on biomass (Chapter 4).

2.4.3 Cellulose char characterisation: Spectroscopic analysis

The chars produced by microwave irradiation were compared by FTIR and ^{13}C MAS (Magic Angle Spin) NMR on the basis of preparation temperature (Figure 2.8). Both showed a loss of signals corresponding to the glycosidic bonds of the cellulose ring structure as preparation temperature increased.

The change of structure between 1370 – 900 cm^{-1} and 60 - 110 ppm show the break down and re-arrangement of the glycosidic ring.[20-24] FTIR studies showed a clear increase in carboxyl groups and changes in the C-H region along with the disintegration of the ring structure. It also showed the early stages of decomposition at temperatures as low as 180 ^{o}C as the signals corresponding to non-glycosidic carboxyl groups at 1035 cm^{-1} and 1057 cm^{-1} increases, and a second peak at ca 1611 cm^{-1} appears, consistent with a conjugated C=C bond.

The ^{13}C MAS NMR also showed the breakdown of the glycosidic ring structure with increasing microwave preparation temperature. The final char shows predominately aromatic and carbonyl nature as shown by the signals above 110 ppm.

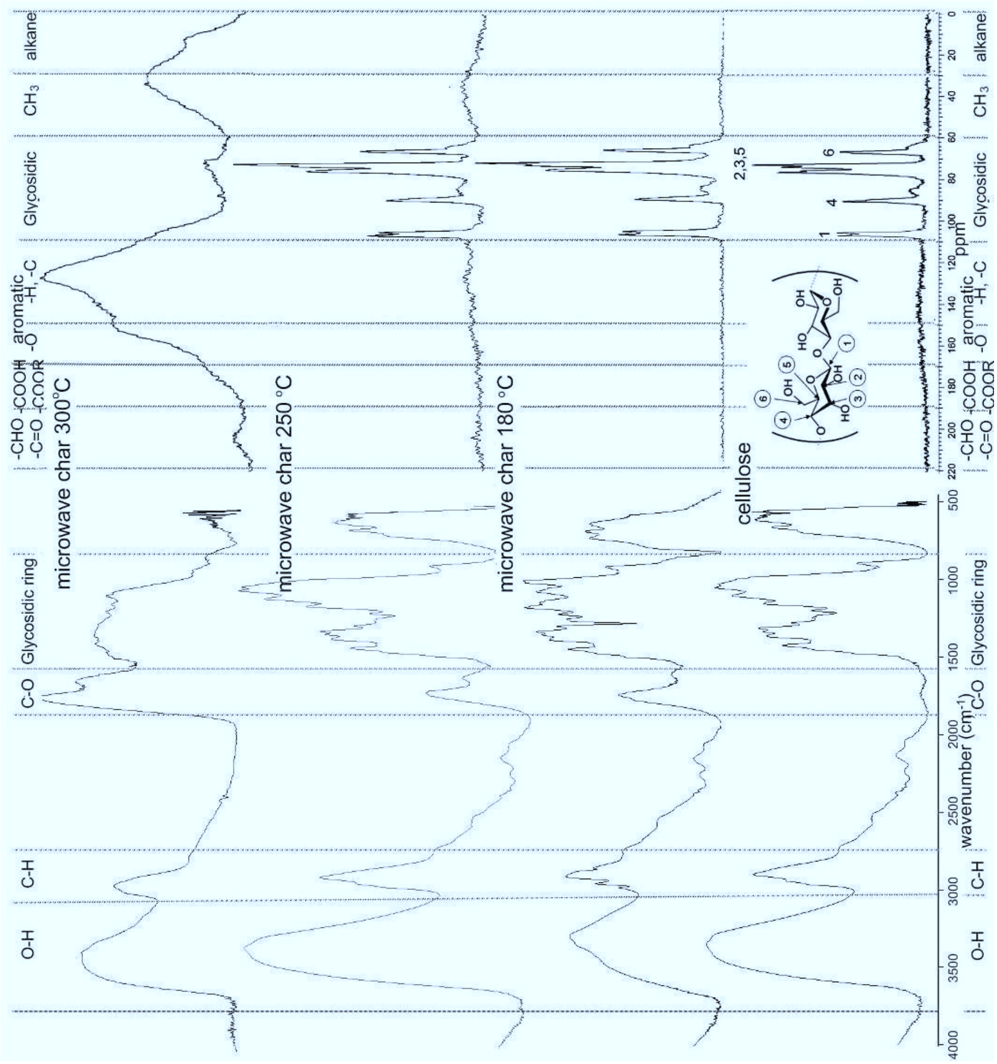

Fig. 2.8: FTIR and ^{13}C MAS NMR of cellulose with microwave chars prepared at 180 °C, 250 °C and 300 °C.

Changes to the glycosidic region, along with the formation of ethylenic (C=C) and carbonyl (C=O) bonds within the material is in agreement with reported data on the thermal cellulose pyrolysis, and is thought to be as a result of cleavage and dehydration reactions. These changess are thought to be formed as the oxygen bonds in pyranose rings break, resulting in a structural rearrangement and often release of volatile components.[13]

Comparison between chars prepared by microwave and thermal processes were carried out looking at those 1) prepared at the same temperature, 2) with the same calorific value and 3) those with the same elemental composition, corresponding to the three pairs of data shaded (Table 2.1). The comparison showed several interesting points, including an apparent disconnection between similar carbon content and calorific value, as microwave chars with lower carbon content than conventional chars have higher calorific values.

Table 2.1: Points of comparison between microwave (mw) and conventional (con) chars

Samples	Preparation Temperature (^oC)		Calorific Value (kJg^{-1})		Elemental Composition %C	
	mw	con	mw	con	mw	con
native	n/a		14.65±1.25		42.77±0.01	
a & b	300	305	35.34±1.04	26.49±3.42	68.41±0.005	44.19±0.02
a & c	300	450	35.34±1.04	31.2±0.1	68.41±0.005	75.33±0.085
a & d	300	364	35.34±1.04	27.97±0.54	68.41±0.005*	68.72±0.075*

*Hydrogen and oxygen content similar in both chars.

Further elemental composition data included in Appendix 1

Figure 2.9 shows the FTIR spectra of cellulose along with chars samples listed in Table 2.1 a) microwave 300 °C, b) conventional 305 °C, c) 450 °C and d) 364 °C. Microwave treatment of cellulose results in formation of char at 300 °C, while under conventional thermal treatment conditions, cellulose is hardly altered at 300 °C. It is necessary to use significantly higher temperatures (up to 180 °C greater than microwave preparation) in order to cause a change in the nature of the carbonyl and glycosidic bonds.

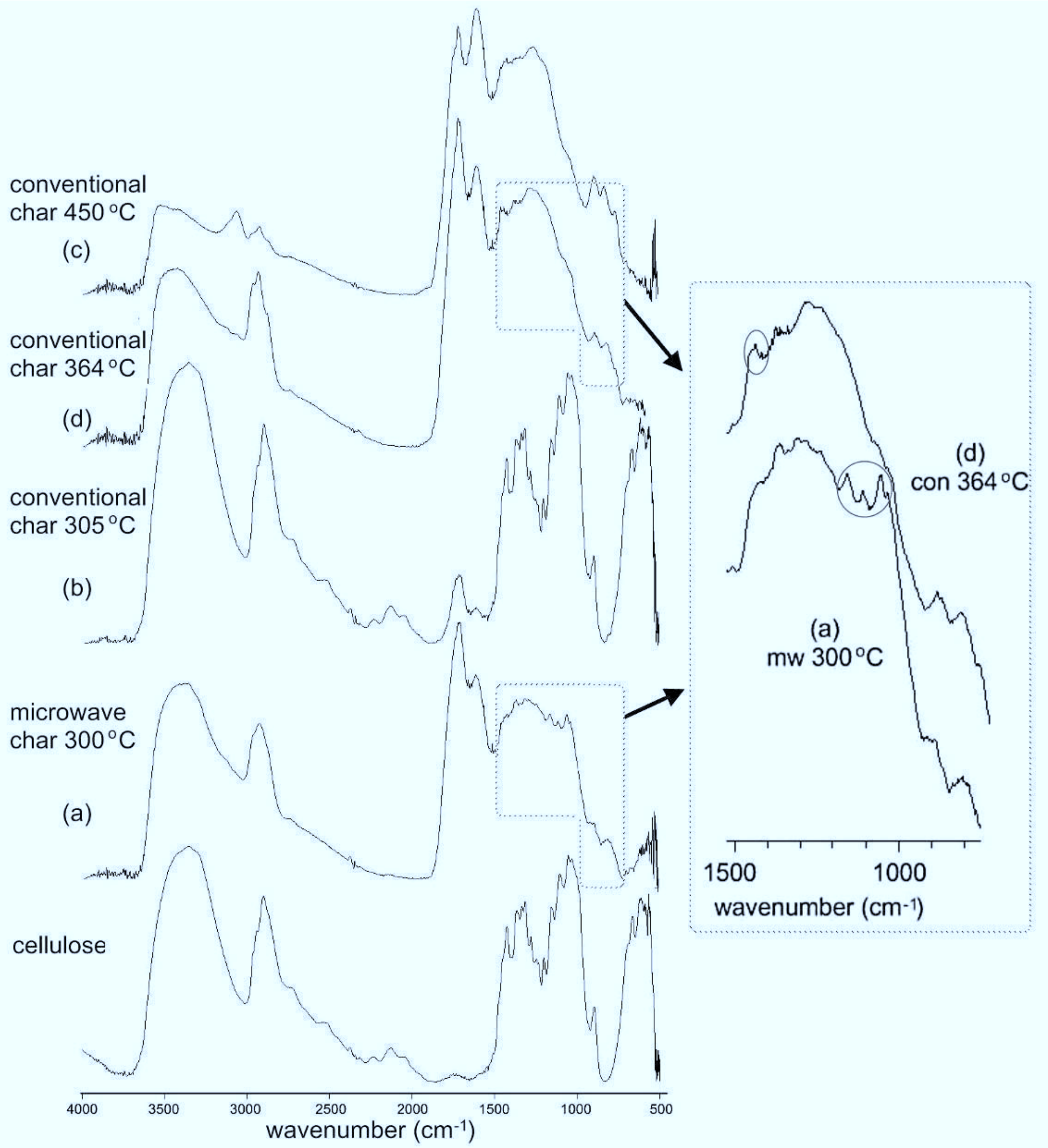

Fig. 2.9: FTIR spectra of cellulose and pyrolysis chars prepared under various conditions

While the microwave char prepared at 300 °C (a) shows clear signs of breakdown of the glycosidic structure of cellulose (1000 – 1500 cm^{-1}), the conventional char prepared at the same temperature (b) is almost unaltered from the native cellulose. Clear changes are visible in the conventional char prepared at 450 ^{o}C, (c) a new peak is visible at 3060 cm^{-1} corresponding to aromatic character or olefinic C-H. This peak is not seen in any of the other chars, although its prominence in this spectrum may be as a result of the weaker OH and aliphatic CH stretches. New peaks can be seen to be growing between 700 cm^{-1} and 800 cm^{-1}, in the microwave char (a) (300 ^{o}C) suggesting an increase in aromatic C-H groups present. These peaks can be seen to be appearing in the conventional char prepared at 364 ^{o}C becoming clearer again in the highest temperature char (c).

Perhaps the most interesting point of comparison is between the chars with the same elemental composition (a- microwave 300 ^{o}C and d- conventional 364 ^{o}C as shown in Figure 2.9 inset). Although both contain approximately the same level (± 0.2 %) of both carbon and hydrogen, there are differences in the spectral characteristics of each. The microwave char still shows peaks between 1050 – 1160 cm^{-1}, corresponding to OH vibrations of native cellulose,[25] although the intensity is weakened. These peaks have disappeared in the spectrum of the comparative conventional sample. Conversely, the CH bending stretch at 1428 cm^{-1} has shifted in the conventional char spectrum to 1437 cm^{-1}, while it has almost disappeared entirely from the microwave char spectrum.[25] Figure 2.10 shows the ^{13}C MAS NMR spectra of the samples. Although it is difficult to assign the differences between the two spectra, there is some variation in the aromatic and carboxylic regions. The differences between the two chars again suggest an alternative degradation pathway for the cellulose when treated with microwaves rather than by slow pyrolysis.

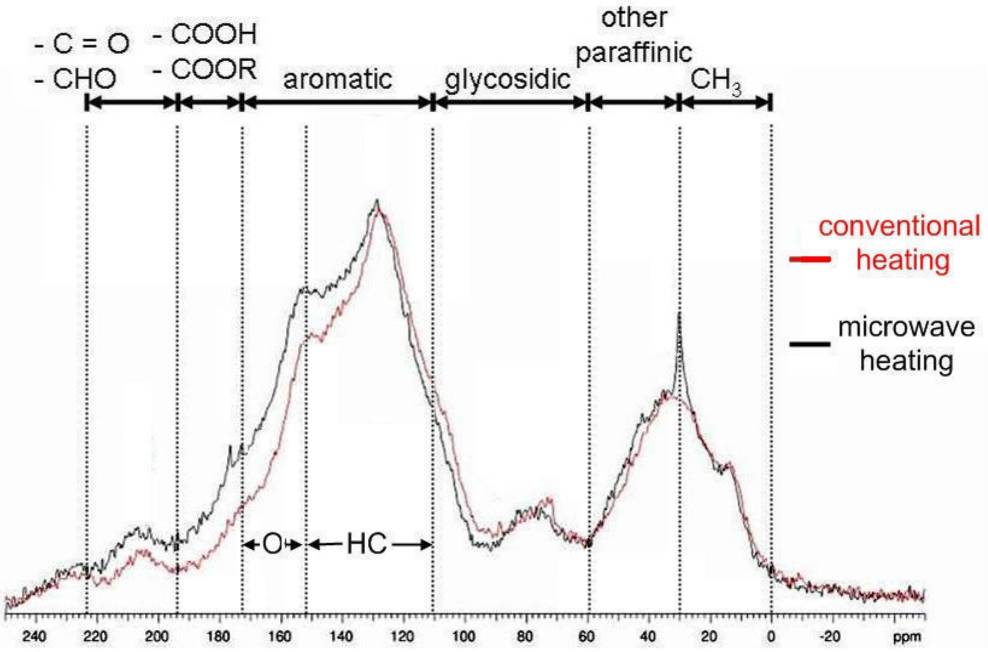

Fig. 2.10: ^{13}C MAS NMR spectra of microwave char at 300 °C and conventional char at 364 °C

2.4.4 Cellulose char characterisation: Elemental analysis

The properties of fuels are often compared in terms of their O/C and H/C ratios. A plot of these ratios, a so-called Van Krevelen diagram, indicates the suitability of the material for fuel use.[26] The lower the respective ratios the greater the energy content of the material. Along with information relating to fuel properties, information on reaction pathways can be obtained, as decarboxylation, dehydration, dehydrogenation, hydrogenation and oxidation should result in a straight line plot due to the related changes of ratios. As detailed in Table 2.2, the diagram can also be used to elucidate information about the carbon skeleton of polymers.[26]

Table 2.2: Relationship between H/C ratio and structure[26]

H/C ratio	Polymer skeleton
< 0.3	highly condensed aromatic ring structure
0.3 – 0.7	noncondensed aromatic structure
0.7 – 1.5	basic units consist of an aromatic nucleus with an aliphatic side chain
1.5 – 1.7	cyclic aliphatic compound
1.7 - 2	alkane system

Figure 2.11 shows the Van Krevelen diagram of cellulose chars. By plotting O/C and H/C ratios of the microwave and conventional chars it can be seen that elemental loss process is similar under both conditions. Chars produced via low temperature microwave processing result in a char with favourably low ratios. The straight line plot also shows that both microwave and conventional chars undergo at least one of the reactions listed above during degradation, although likely to be in a different combination thereby resulting in the different calorific values.

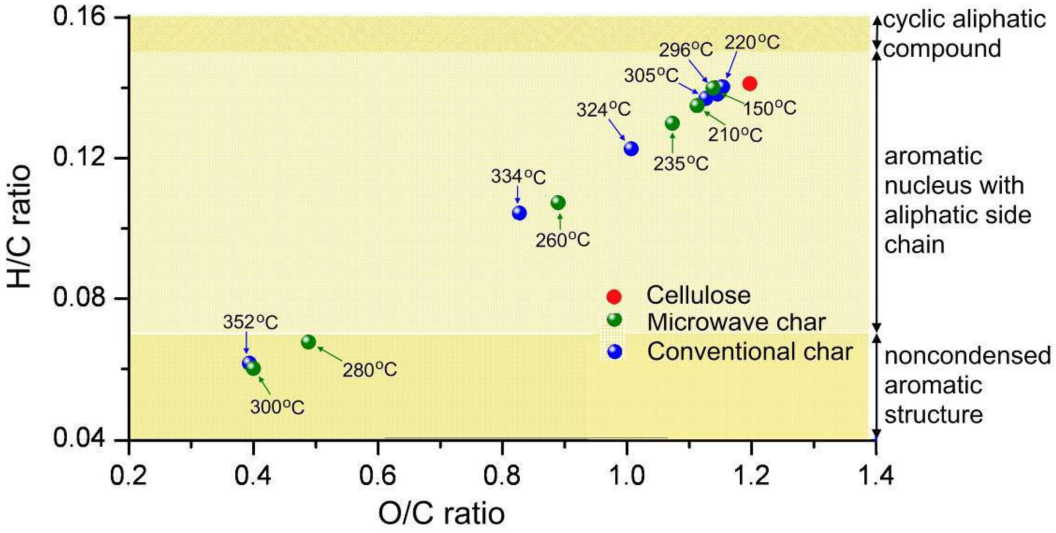

Fig. 2.11: Van Krevelen diagram showing the elemental ratios of cellulose chars [27]

(errors have not been displayed as they are negligible)

The ratios also show the transition of cellulose into an aromatic species at high char preparation temperatures in agreement with data from ^{13}C MAS NMR and FTIR (Figure 2.8).

2.4.5 Cellulose char characterisation: Thermal analysis

For any cellulose decomposition to occur, structural changes such as cold crystallisation or melting are necessary. These structural changes may occur within the crystalline or amorphous regions, with the possibility of a cooperative process affecting both regions. Furthermore, one or more thermal events can occur simultaneously, potentially masking what is truly occurring within the material. As a result, modulated differential scanning calorimetry (MDSC) was used to investigate the thermal behaviour of cellulose. As a technique, it offers increased sensitivity over conventional DSC, along with better resolution, due to a low average heating rate following a frequency dependent modulation.[28] In addition, previous studies have shown MDSC to be useful in the examination of microcrystalline cellulose.[29]

Similar to traditional DSC, MDSC detects changes and transitions within a sample by measuring the difference in the amount of heat required to increase the temperature of the sample and a reference as a function of temperature. When the sample undergoes a phase transition more or less heat is needed to flow to it rather than the reference to keep both at the same temperature. In the case of a melt or glass transition, more heat flows to the sample due to the absorption of heat in the endothermic process. Inversely less heat is needed to flow during crystallisation. The modulated heating of MDSC allows for the detection of simultaneous events in a material by exposing it to numerous heating rates. The total heat flow is mathematically deconvoluted to yield calorimetric response to the perturbation from the calorimetric response to the underlying temperature profile, none as the reversing and nonreversing heat flows.

Figure 2.12 shows an overall heat flow signal and both a reversing and non-reversing heat flow signal of the MDSC trace of cellulose. In the non-reversing heat flow signal, which accounts for the kinetic component of the total heat flow, an endothermic deviation in the base line starts around 100 ºC and peaks at 134 ºC. This process may be attributed to the evaporation of any residual moisture within the sample.

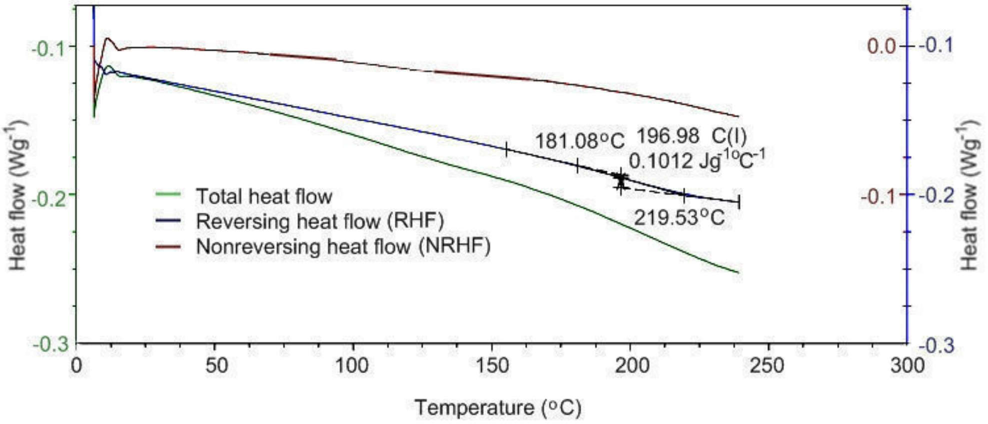

Fig. 2.12: MDSC trace of cellulose showing total heat flow signal and reversing and non-reversing heat flow signals.

From 170 ºC there is a continual decrease in the total heat flow signal which is believed to be due to depolymerisation of the material. This event coincides with what can be seen in the reversing heat flow signal with a glass transition (Tg) starting at approximately 185 ºC and returning to a steady state at 220 ºC, with the point of inflection at 197 ºC. This transition is more clearly visible in the derivative of the slope as shown in Figure 2.13. This transition is masked in the total heat flow from the continual depolymerisation in the non reversing signal and is not seen using conventional DSC analysis. Consequently, the depolymerisation of cellulose is linked with loss of crystallinity resulting from the glass transition.

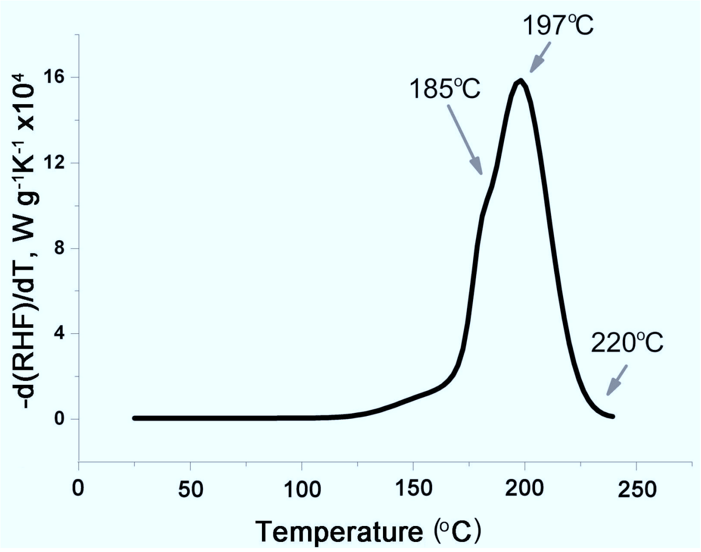

Fig. 2.13: Derivative of the reversing heat flow signal.

2.4.6 Cellulose char characterisation: Crystallinity

To verify the MDSC data, changes in the crystallinity of cellulose were monitored by FT-IR, using a temperature controlled diffuse reflectance infrared Fourier transform (DRIFT) apparatus. The crystalline structure of cellulose is usually determined through X-ray diffraction, FT Raman, IR absorption and scanning electron microscopy (SEM).[30-33] While X-ray diffraction is useful for quantitative analysis of the crystallinity index (CI), FTIR absorption is a very useful technique because it gives extra useful information regarding internal bonding and spatial conformations.[21] The fixed vibrations of the crystalline structure result in sharp bands which disappear on decrystallisation, while bands corresponding to the amorphous region do not appear in the spectrum of a pure crystalline polymer.[31] A ratio of the intensity of two such bands can be taken as the crystallinity index, which is a relative measure of how a sample varies between the extremes of completely amorphous and totally crystalline. In this case, the crystallinity index was calculated based on the ratio of the peaks at 1430 and 898 cm^{-1}. The bonds, which correspond to CH_2 bending at C6 (1430 cm^{-1}) and C-O-C stretching at the β-(1→ 4) glycosidic linkage, have been reported to shift as a result of transformations in the crystalline structure (Figure 2.14).[21]

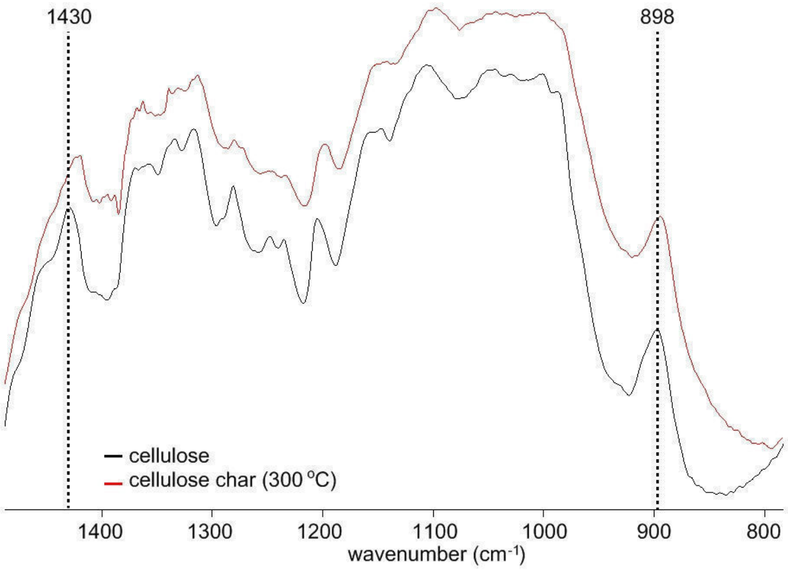

Fig. 2.14: FTIR spectrum of conventional cellulose chars

While this method (Experimental section 7.3.2) offers a useful way to compare the changes in crystallinity levels, the absolute values were found to be subject to variation. Infrared is a sensitive technique, therefore changes in intensity may occur due to experimental conditions such as particle size and varying levels of moisture within the system. As a result, the data obtained has been used to produce an indicative trend rather than an absolute measurement of crystallinity within the samples.

IR studies were carried out on cellulose samples prepared at a range of temperatures using microwave activation and conventional slow pyrolysis. Crystallinity rose in microwave chars with increased preparation temperature, suggesting the amorphous region is being decomposed preferentially and resulting in loss of the signal (at 898 cm^{-1}) from this region faster than from the crystalline region (Figure 2.15). This indicates that the amorphous region is more affected by microwave irradiation as the freedom of movement allows for better interaction.

In the case of chars produced under slow pyrolysis conditions, the change is much less significant and in the opposite direction. The decrease of the crystallinity correlates well with the MDSC information. With the increased molecular motion within the amorphous region, as illustrated by the glass transition, a stress is induced on the crystalline region resulting in a reduction in the level of crystallinity.

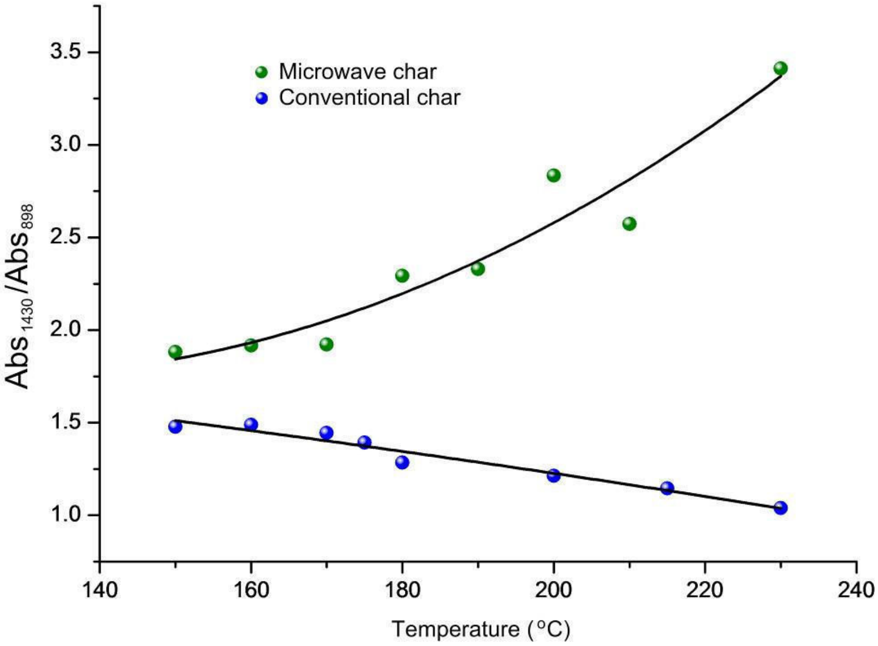

Fig. 2.15: Relative crystallinity of cellulose samples produced by conventional and microwave heating at different temperatures

2.4.7 Isotope exchange studies

In order to further investigate the mechanism of microwave interaction with cellulose, the biopolymer was partially deuterated. It is known that substitution of protons by deuterium significantly reduces the rate of processes involving the H-bonding network, therefore any changes in the behaviour of the cellulose may be correlated to this substitution. Following reported methodology, experimental section 7.3.3, cellulose was partially deuterated at 180 °C to restrict exchange mainly within the amorphous region.[34] Microwave chars were consequently prepared and analysed in terms of calorific value following the same procedure for standard cellulose. As can be seen in Figure 2.16, the deuterated cellulose activated by microwave, decomposes slower than the protonated form, most likely due to the slower molecular motion within the bonds. This decreased rate of decomposition reiterates the importance of the amorphous region for microwave processing.

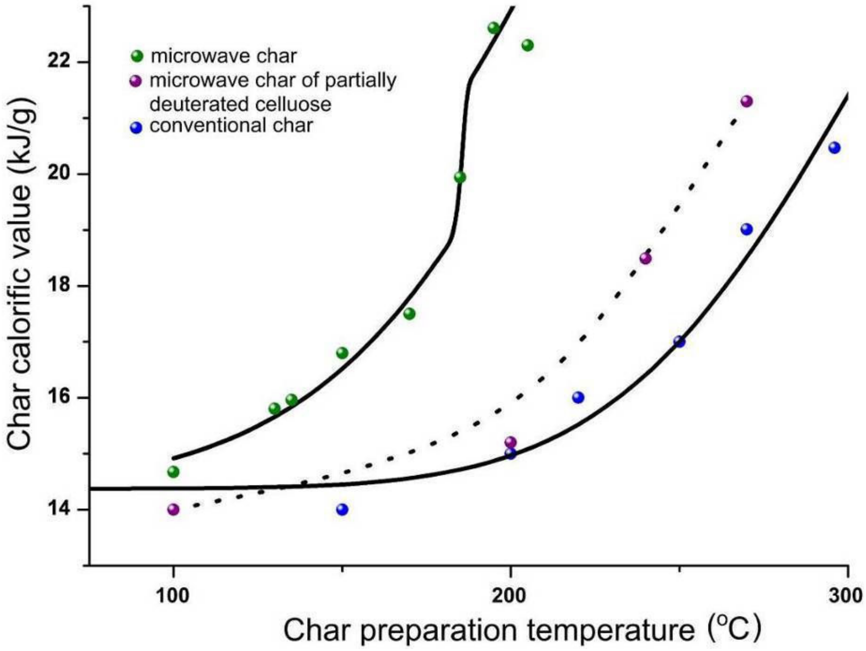

Fig. 2.16: Calorific value of microwave char of partially deuterated cellulose compared to non-deuterated chars prepared under microwave and conventional conditions

2.4.8 Discussion

Initial studies showed 180 ºC as a key turning point in the microwave degradation of cellulose (Section 2.4.1). Through thermal analysis (MDSC) and crystallinity studies, it was possible to associate this temperature with the onset of events occurring in the amorphous region of the polymer. This could suggest a simple melt decomposition occurring within the polymer, resulting in accelerated decomposition above this temperature, i.e. as the glass transition occurs within the polymer the softer material can decompose faster. This possibility has been ruled out as a similar trend is not seen under conventional heating conditions.

It can be said that above 180 °C the specific microwave effect becomes more prominent as the rate of cellulose degradation increases significantly. The glass transition which occurs, allows for increased molecular freedom within the amorphous region of the material resulting in improved interaction between the microwave energy and cellulose. As has been discussed (Section 1.9), there are two main mechanisms through which interaction occurs: dipolar polarisation and ionic conduction. Dipolar polarisation depends on polar groups within the material having the necessary freedom of movement to align with the waves of the microwave field.[18] We can therefore assume that before the glass transition, the polar groups in cellulose are more restrained by structural constraints and cannot rotate at the frequency of the microwave resulting in the poorer interaction. After the transition, as the number of groups capable of rotating increases, particularly in the amorphous region, the rate of decomposition significantly increases, as illustrated by the change around 180 °C.

It is known that cellulose exists as a microfibril network within the cell wall of plants, with amorphous and crystalline regions which alternate at a period of approximately 15 nm.[35] Crystalline cellulose contains a very ordered hydrogen bonded network within which a proton transport network is possible in the presence of an electromagnetic field. Above the glass transition temperature, the electrical conductivity of amorphous polymers increases greatly.[35] This phenomenon can be interpreted qualitatively in terms of the ionic current which is known to increase remarkably with temperature as a result of the simultaneous breaking of two hydrogen bonds, causing increased mobility within the hydrogen-bonding network. In the case of cellulose the activation barrier has been identified as 44.4 kJ/mol.[35, 36] Microwave energy has been reported to lower the activation energies in organic synthesis, therefore it can be taken that it could also allow for a lower activation energy for ionic conduction within cellulose.[18, 37] This, along with the increased mobility allowed by the glass transition, allows for increased motion of hydroxyls in the amorphous region and as result increased acidity.

Acidic conditions have been shown to promote char formation under conventional pyrolysis conditions.[38, 39] The acidity in the amorphous region is increased as the softening of the glass transition allows movement of protons within cellulose resulting in an acid catalysed decomposition process (Figure 2.17). As these components are produced the amorphous region will be further plasticised, intensifying the microwave effect. At higher temperatures the crystalline region is disrupted aiding further degradation and char formation.

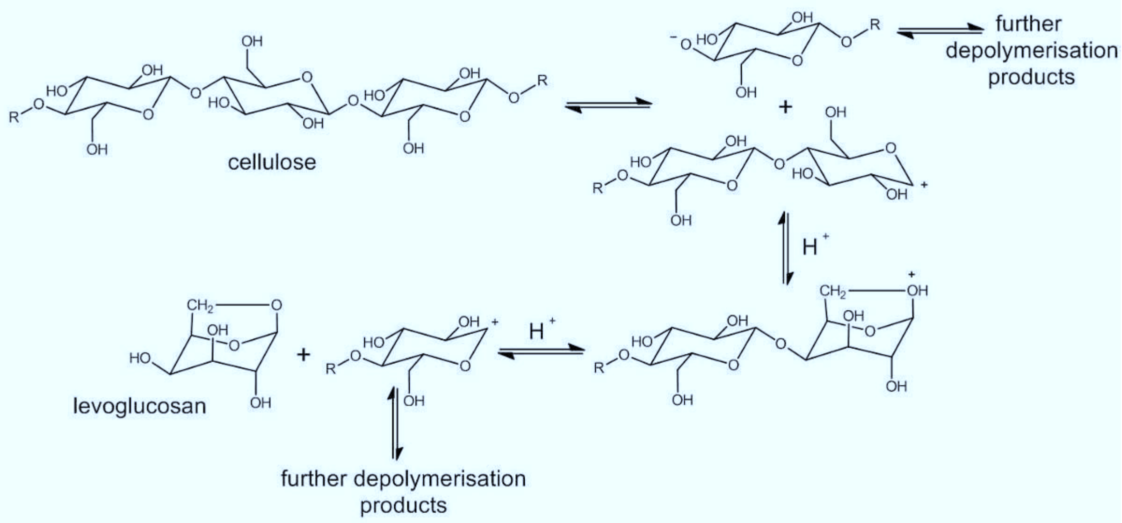

Fig. 2.17: Mechanism of acid catalysed cellulose degradation[40]

The proposed mechanism of the microwave interaction with cellulose consists of the following stages:

- a glass transition resulting in the softening of the amorphous region above 180 °C
- microwave-induced dipolar polarisation and ionic conduction within the amorphous region
- acid catalysed decomposition of the entire cellulose
- auto-catalytic microwave decomposition of cellulose

The proposed mechanism allows better understanding of the processes occurring within biomass during microwave treatment.

2.5 Microwave treatment of hemicellulose

A short investigation was made into the behaviour of hemicellulose under microwave conditions. Following the procedures used in the cellulose study (Experimental section 7.2.2) chars were prepared using xylan, a saccharide component of hemicellulose, as a model compound. Chars were prepared under microwave and conventional conditions, and characterised in terms of their calorific values and by MDSC, FTIR and elemental analysis.

2.5.1 Char formation

The influence of microwave temperature on the production of char was again investigated in parallel with conventional pyrolysis experiments.

Following the procedure described in experimental section 7.2.2, xylan was irradiated with microwave energy at temperatures between 120 – 300 °C, and under conventional thermal conditions in the range 250 – 450 °C. The resulting chars were compared based on calorific value as shown in Figure 2.18.

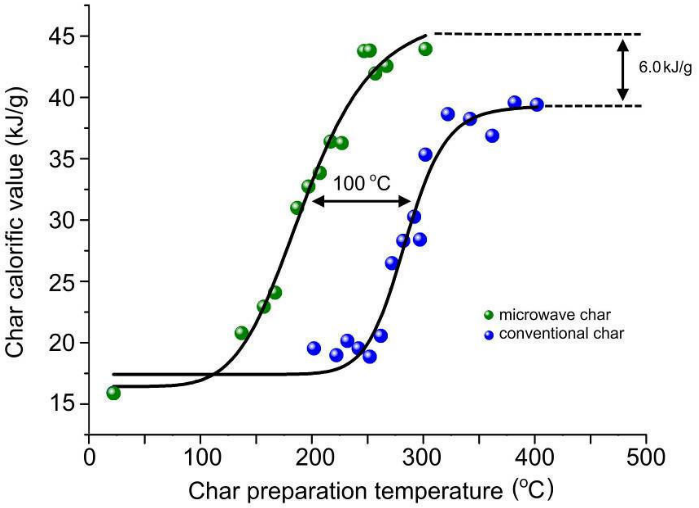

Fig. 2.18: Calorific value of char obtained from xylan processed conventionally and in the presence of microwaves. (Errors have not been displayed as they are negligible)

A greater increase in the energy density of xylan can be achieved through microwave treatment than through conventional thermal methods at the same temperature. For xylan, the increase in calorific value between starting material and the char with the highest calorific value is more than that achieved for cellulose, an increase of circa 30 kJg^{-1} as opposed to 24 kJg^{-1}. This is to be expected as the thermal degradation of hemicellulose is well known to occur at lower temperatures than cellulose.[1] The first hemicellulose decomposition step usually occurs below 250 °C, when a series of depolymerisation reactions results in rearrangement of the polysaccharide structure. These oligosaccharides and monosaccharides then decompose around 300 °C to produce a char, CO, CO_2 and water.[41, 42]

Also of interest is that the slope of both lines is parallel and do not diverge as they do with cellulose (Figure 2.6) where the calorific value of the microwave chars increases at a greater rate than those prepared under conventional conditions.

2.5.2 Hemicellulose char characterisation: Spectroscopic analysis

Again, following the analytical processes applied for cellulose, the microwave and conventional chars were compared under three headings: those i) prepared at the same temperature, ii) with the same calorific value and iii) those with the same elemental composition (Table 2.3).

Table 2.3: Points of comparison between microwave (mw) and conventional (con) chars

Preparation Temperature (°C)		Calorific Value (kJg^{-1})		Elemental Composition %C	
mw	con	mw	con	mw	con
xylan		15.9		39.5±0.04	
300	300	43.24±0.69	34.395±0.93	66.66±0.05	60.48±0.05
260	300	37.54±1.26	38.42±0.195	61.43±0.72	60.48±0.05

note: Further elemental composition data included in Appendix 1

As was seen with cellulose, the structural changes within the char are similar under microwave and conventional conditions although the changes occur at lower temperatures after microwave treatment. As can be seen in Figure 2.19, changes in the structure are apparent at 260 °C between 750-1900 cm^{-1}, indicating the break down or rearrangement of the ring structure as discussed by Bilba and Ouensanga.[43] In agreement with their data, the intensity of hydroxyl stretching (3000-3600 cm^{-1}) decreases with temperature while the CH signal increases suggesting dehydration and rearrangement of molecules leading to alkyl-carbonyl structure such as ketones and aldehydes.[43] Weak peaks can also be seen just above 3000 cm^{-1} in both the conventional char prepared at 400 °C and microwave char at 300 °C, corresponding to aromatic or olefinic C-H groups.

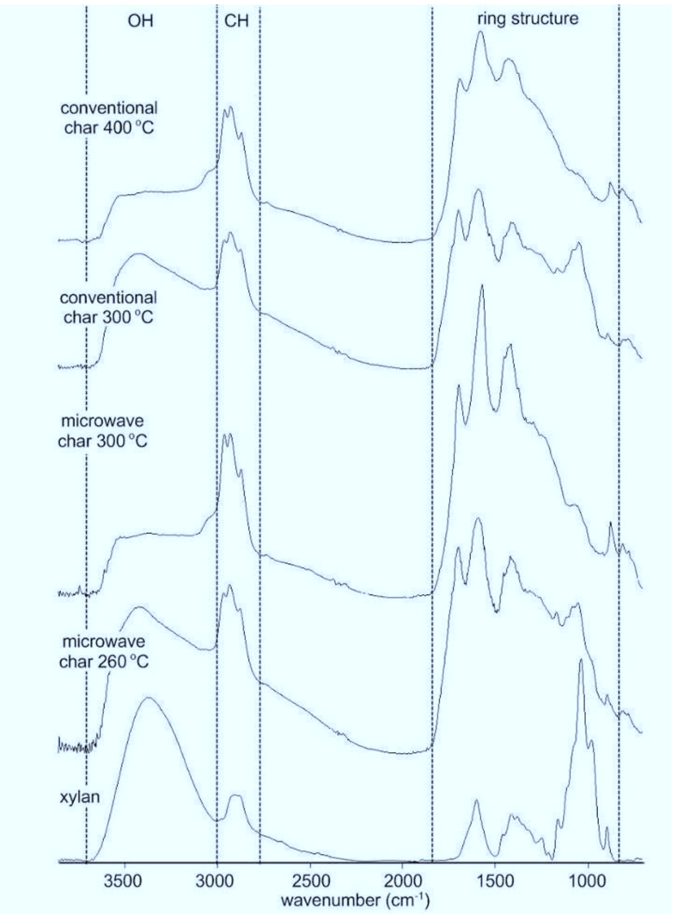

Fig. 2.19: FTIR spectrum of xylan chars prepared at various temperatures under microwave and conventional conditions

2.5.3 Structural analysis of hemicellulose: Elemental analysis

A Van Krevelen diagram was created for the chars from xylan (Figure 2.20). The plot of O/C vs. H/C ratio of chars produced via both microwave and conventional processing lead to straight lines. The trend shows that while both undergo a combination of decarboxylation, dehydration, dehydrogenation, hydrogenation or oxidation, the reaction path may be different under the altered conditions.[26] As discussed in Table 2.2, the H/C ratio of the chars shows the structure does not develop as much aromatic character as cellulose, in agreement with IR data.

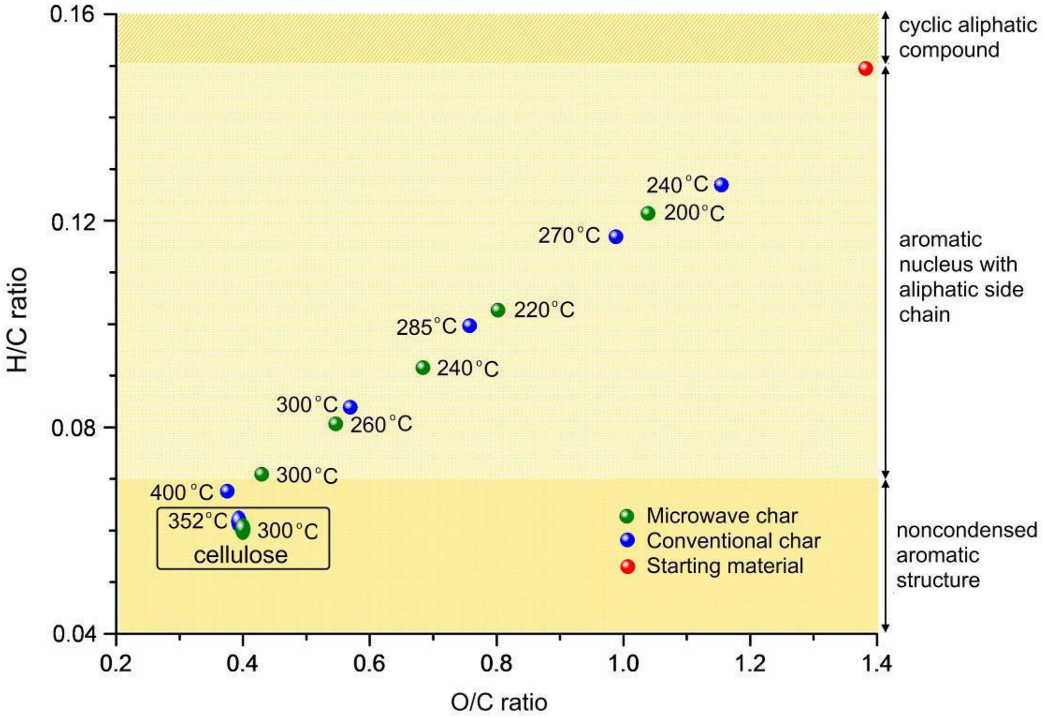

Fig. 2.20: Van Krevelen diagram showing the elemental ratios of hemicellulose chars [27] (Errors have not been displayed as they are negligible)

2.5.4 Hemicellulose char characterisation: Thermal analysis

MDSC was used to study thermal transitions in xylan. It was found that all phase changes were detectable in the total heat flow, with the reversing and nonreversing adding no extra information. Figure 2.21 shows the total heat flow for xylan. A single thermal transition peaking at 168 °C was identified by its characteristic appearance as a melt within the xylan. The low temperature of this melt is perhaps partly accountable for the consistently parallel degradation pattern between conventional and microwave degradation of hemicellulose, as there is little opportunity below this temperature for the microwave effect to gain advantage This is significantly different to the results found for cellulose and may contribute to the differing trends observed in the calorific value measurements and Van Krevelen diagram.

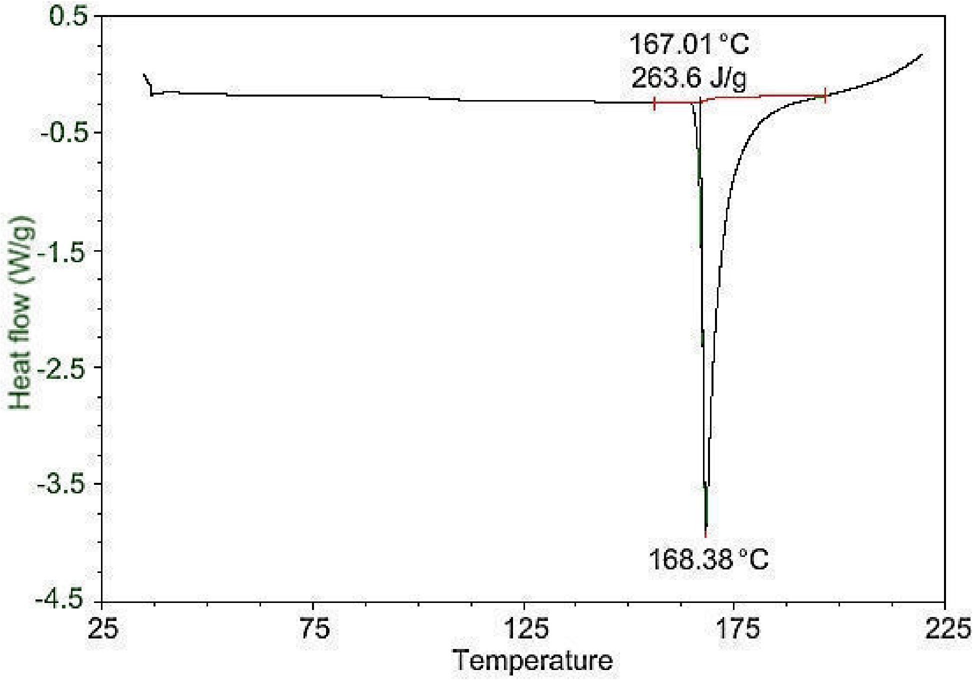

Fig. 2.21: MDSC trace of xylan showing total heat flow signal

Although cellulose and hemicellulose are both carbohydrates, the structures are significantly different resulting in substantial differences in their behaviour under both conventional and microwave treatment conditions, leading to chars with appreciably different properties.

2.5.5 Discussion

The amorphous structure of xylan means that the knowledge gained elucidating the mechanism of cellulose degradation cannot be directly applied to xylan, nor can the extra analytical methods (e.g. crystallinity studies). As a result, the mechanism of microwave degradation of hemicellulose (xylan) has not been identified. It may be assumed though that similar to cellulose, the melt within the polymer, along with the increased amorphous character of hemicellulose, enables increased molecular freedom of movement within the polymer. Polar groups within the xylan are then capable of dipolar polarisation, increasing ionic conduction, i.e. the interaction between xylan and the microwave energy increases. This results in an apparent lowering of the activation barrier for degradation and superior chars at lower temperatures.

2.6 Microwave treatment of lignin

Lignin was found to have much lower activity under microwave irradiation than the polysaccharides. As can be seen from Figure 2.22, the rate of heating of lignin under microwave irradiation was significantly less than that of cellulose. This was expected due the large sterically hindered complex structure, and lack of hydroxyl groups necessary for efficient microwave interaction. Alternative treatments of lignin were investigated and reported in Chapter 5.

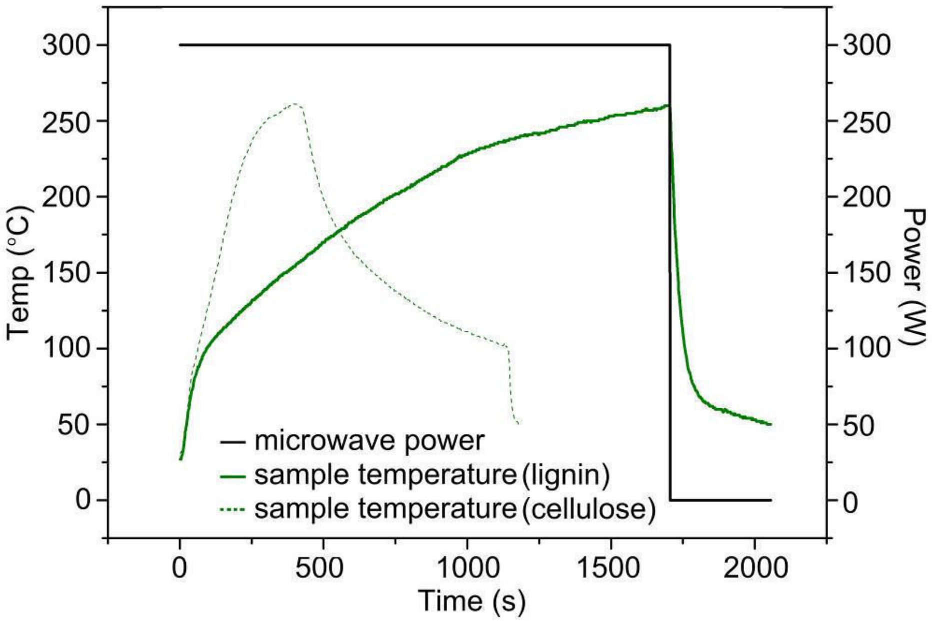

Figure 2.22: Heating profile of lignin under microwave conditions

2.7 Conclusion

These results show, for the first time, the specific temperatures at which microwave irradiation effects the rate of decomposition of cellulose and hemicellulose, yielding high calorific value chars which would require much higher temperatures (~100 ^{o}C higher) to produce under thermal conditions. This improvement is seen both in terms of the lower temperature at which carbonisation occurs, in the maximum calorific value of the final char, and in the properties of oils produced (Chapter 4). The understanding gained can now be applied to a variety of biomass (Chapter 3) in order to optimise the production of chars aimed at energy production as a renewable alternative to coal.

In order to achieve sustainable development, mankind needs to become less reliant on petrochemical feedstocks to renewable alternatives. Microwave processing of biomass may represent an energy efficient route to solid (and liquid) fuels for the development of a society which is no longer reliant on fossil fuels. Such a process could potentially offer many benefits over traditional methods. Unlike coal, biomass is renewable and readily available in the UK. Replacing coal with biomass could therefore reduce the UK's greenhouse gas emissions while improving energy security.

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Chapter 3: Production of char through microwave treatment of biomass

Publications:
Lanigan, B.; Budarin, V.; Clark, J.; Shuttleworth, P.; Deswarte, F.; Wilson A., Microwave processing as a green and energy efficient technology for the production of energy and chemicals from biomass and energy crops. *Aspects of Applied Biology* 2008, *90*, 277-282.

3.1 Introduction

The word “biomass” is used to refer to a diverse group of resources including various natural and processed materials such as wood, wood waste, agricultural and industrial residues, municipal waste, herbaceous species, food waste and aquatic plants. Biomass has been used for centuries to produce the energy needed to survive, as a source of heat, light and in more recent times as a raw material for electricity production; its direct combustion has played a vital role in the development of society.[1] There is now a move away from direct combustion of biomass due to issues relating to high water content, inefficient combustion and difficult material handling (Sections 1.7 & 1.8). As a result, methods to improve its fuel properties are subject to widespread research. This chapter will focus on applying the knowledge gained from the work described in Chapter 2 on individual biomass components (i.e. cellulose, hemicellulose and lignin) to whole biomass. The aim is to produce a high quality char suitable to replace coal in fossil fuel burning power plants and will be compared to traditional torrefaction processes. By focusing on non-food materials, the “food versus fuel” debate is avoided and the potential to produce fuels from biomass without affecting food supplies is demonstrated.

3.2 Process development

Biomass chars were prepared on two different scales. Firstly small scale experiments (< 1 g biomass) were carried out using a mono-mode CEM Discovery laboratory microwave as described in Experimental section 7.2.2. Temperature measurements in this apparatus were found to be unreliable when using larger masses due to poor mixing, although the small scale did allow for easy measurement of mass loss which was monitored in proportion to calorific value. Larger scale experiments (10 – 200 g) were carried out using a multi-mode Milestone SPMR (Solid Phase Microwave Reactor) fitted with a VAC2000 vacuum module in series

(Experimental section 7.2.5). This system rotates the sample within the microwave chamber during treatment resulting in an improved interaction between the microwave energy and the sample and, therefore more accurate overall temperature reading. These measurements were used to study the relationship between increases in calorific value, processing temperature and/or microwave residence time.

Conventional chars were produced through slow pyrolysis of biomass as outlined in Experimental section 7.2.3. Calorific value was measured following the method outlined in Experimental section 7.3.1, which was verified by analysis at external facilities. The method was found to work well for samples which could be ground to a small (< 250 µm) particle size. Some issues arose with regard to accuracy of the measurements due to error between repeat measurements, for samples of larger particle sizes. The use of larger sets of repeats did not improve the precision. Therefore the method was used to determine trends, and produce relative values rather than as an absolute measurement of calorific value of whole biomass.

3.3 Biomass for energy production

More than 10,000 times the current annual global energy consumption reaches the Earth's surface every year in the form of solar radiation. About 0.2 % of it (i.e. 20 times global energy consumption) is fixed by plant life, providing a potential source of energy.[2] As such, producing energy from biomass is generally seen as one of the important components in meeting EU targets for reducing CO_2 emissions and increasing the use of renewable energy. The opportunity exists for increased exploitation of biomass for energy but a process must be established which is economic, energetically efficient and environmentally sustainable.

This chapter describes the processing of biomass from three different sources, a dedicated energy crop, agricultural waste and industrial food waste. These three streams were chosen to investigate the versatility of microwave processing for the production of fuels from biomass.

3.3.1 Dedicated energy crop: Miscanthus x giganteus

An ideal dedicated biomass crop should provide high-energy output for little energy and agricultural input. It must be capable of producing large yields of biomass over relatively short periods of time, while, in order to be environmentally viable, grow on poor or difficult land with minimal labour and chemical inputs.[3] A wide variety of crops are under consideration for use in biofuel applications, the best known of which are probably miscanthus, willow and rape seed. The choice of crop depends on the growth conditions of the area and the expected requirements of the end user.

Miscanthus × *giganteus* (miscanthus) is a perennial rhizomatous grass, with a C4 photosynthetic pathway allowing for particularly efficient use of water, nutrients and solar energy.[4] Perennial rhizome crops also allow cycling of nutrients between the portions of the plant which are above and below ground, reducing the need for fertiliser. If harvested at the correct time, the material is low in inorganic mineral content making it ideal for fuel use. Environmental impact of the initial planting is also minimised as annual re-growth means it is spread over several years of fruitful harvest.[4]

Miscanthus grows as an erect stem, with little side branching. Under European growing conditions, the vigorous growth can amount to 2 m in the first year and up to 4 m in subsequent years (Figure 3.1).[5] It is suitable for cultivation in the UK, with yields of up to 18.7 t ha^{-1} reported under good conditions.[6]

Fig. 3.1: Harvesting of *Miscanthus* × *giganteus* which grows as a tall upright crop

Along with being used as an energy crop, it has been shown to be useful in terms of carbon sequestration ability along with soil quality improvement, and providing cover for wildlife. It is also a sterile hybrid species meaning it is incapable of spreading wildly, preventing its invasion into established ecosystems.[4] Miscanthus is already being adopted in the UK as a future energy crop; planting rose from 3,356 ha in 2006 to over 12,000 ha to be planted from 2007[7], therefore any process for treatment of biomass should be applicable to this feedstock.

3.3.2 Agricultural residue: Wheat straw

Agricultural plants such as cereals are grown worldwide for the grain, leaving the straw residues as a low value side product. UK straw yields were estimated at 11.9 million tonnes in 2007, 54 % coming from wheat, followed by oilseed rape (21 %), barley (20 %), oats (4 %), other cereals (1 %) and linseed (0.1 %). Straw is used in various agricultural roles and is already used for energy production, but approximately 2.5 million tonnes remains available for use (Figure 3.2).[8] While a portion of this is left in the field to maintain soil nutrient levels, there remains a potential source of income for the rural economy if value can be added to make it cost effective to process the straw for use.

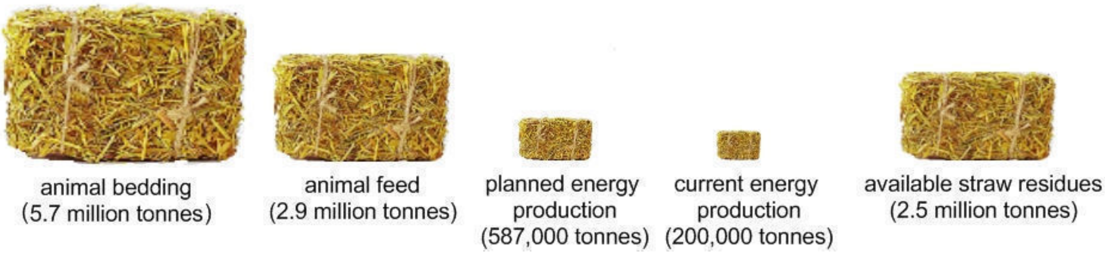

Figure 3.2: Uses of straw in the UK[8]

3.3.3 Industrial food waste: Cocoa husk

Research by the Waste & Resources Action Programme (WRAP) has revealed that 6.7 million tonnes of food is thrown away by UK consumers each year, contributing to environmental problems associated with the disposal of organic waste.[9] While it is vital that consumer attitudes change to reduce the level of fresh food being wasted, applications should be developed to find use for the unavoidable waste.

Cocoa husk (Figure 3.3) was chosen as the focus food waste in this study as it is available as waste from local chocolate processing facilities in high volumes.[10]

Fig 3.3: Cocoa husk sourced from Nestlé UK

Cocoa is a major agricultural product in parts of Africa and the neotropics, from where it is exported globally for chocolate production. Approximately 10 % by weight of this cocoa is made up of the commercially valuable beans, the rest finds use as low value animal feed or garden mulch. [11] Given that global production of cocoa beans in 2008 was 4.3 million tonnes, approximately 43 million tonnes of waste are available for potential transformation into higher value products.[12]

Research is currently being carried out into the industrial scale production of pectins from cocoa hulls.[11] This development would boost development in the countries of production but is not likely to be applied on site at the numerous chocolate processing plants around the globe who handle residual husk wastes transported with the beans. Direct use of the husks as a fuel faces problems due to the waxy surface of the material making it difficult to grind or mill. Thermal transformation of this product into an improved fuel, through a flexible and efficient process, may offer them a suitable alternative to current waste disposal.

3.4 Bio-char formation

3.4.1 Properties of unprocessed biomass

Following the procedures outlined in Chapter 7.3.8, the biomass was characterised in terms of cell wall components (total cellulose, hemicellulose and lignin), extractable fractions and inorganic composition (Figure 3.4). Three forms of wheat straw were studied to determine influence of further parameters on behaviour of biomass during biomass processing.

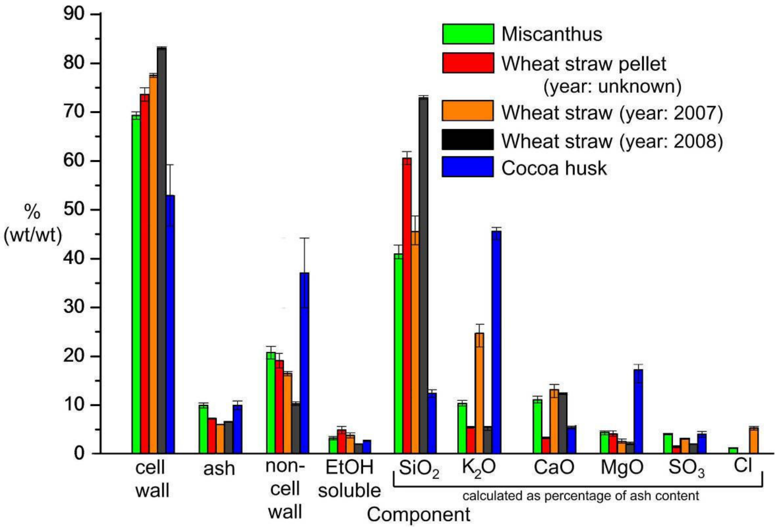

Fig 3.4: Composition of biomass samples (based on oven dried weight)

Cocoa husk showed a significantly different composition in comparison to the other biomass types studied. It has much higher levels of non cell wall components (likely to include fats from cocoa bean) and low amounts of silica, along with significant amounts of potassium and magnesium.

It can also been seen that composition varies within species. While the level of cell wall components is relatively similar, the three wheat straw samples have differing levels of inorganic components.

Inorganic species are known to play a catalytic role in the thermal decomposition of biomass therefore it is vital to know the ratios present in order to understand processes occurring during the pyrolysis of biomass.[13-18]

3.4.2 Bio-char from Miscanthus

Following the procedure detailed in Experimental section 7.2.5, miscanthus was exposed to microwave irradiation using a Milestone SPMR (Solid Phase Microwave Reactor) fitted with a VAC2000 vacuum module in series. For purpose of comparison, all chars were prepared by exposing the sample to a constant maximum power setting of 1200 W for a designated amount of time. The temperature was monitored but not controlled as the rate of heating is related to the dielectric properties of the processed material and therefore varies between biomass types.

Char prepared at 160 °C (Figure 3.5) after 30 minutes at 1200 W resulted in a 90 % increase in the calorific value of the material. As the temperature stabilised between 150 and 160 °C, the calorific value was also seen to stabilise suggesting the temperature may have a more significant effect on the increased calorific value than microwave residence time. This point was reinforced by comparison with a low power experiment. Char was prepared by using microwave power set at 800 W. This lower input of microwave energy resulted in a slower heating rate reaching a maximum temperature of 125 °C after 25 min, 27 °C less than that achieved using 1200 W. Temperature was seen to be the major influence on the final properties of the char, with the char produced at 125 °C being similar to that produced in the same temperature range in the presence of higher microwave energy (Figure 3.5A).

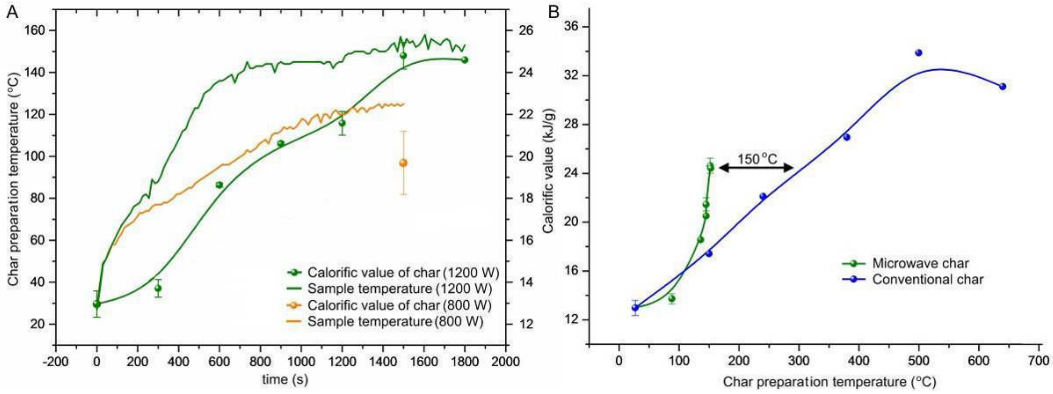

Fig. 3.5: Preparation of miscanthus chars A: under microwave conditions at 1200 W and 800W, B: comparison of chars prepared under microwave (1200 W) and conventional conditions

Following the method established for cellulose and hemicellulose (Chapter 2), the increased char calorific value was studied in comparison with chars prepared under conventional pyrolysis conditions (Figure 3.5B). At the maximum temperature achievable under microwave conditions, the calorific value of the miscanthus char is equivalent to that produced at temperatures 150 °C higher under conventional conditions, offering potential energy savings and better economics.

3.4.3 Bio-char from wheat straw

Wheat straw chars were prepared from wheat straw samples from 2007 and 2008, and wheat straw pellets. The effect of compositional variations within the same biomass type and also the influence of bulk density were investigated.

Firstly, chars were prepared from the two samples of loose wheat straw from 2007 (WS 07) and 2008 (WS 08). Figure 3.4 shows the compositional variations between the two samples. The most significant variation is in the potassium content, which is 20 % higher for WS 07 than WS 08. Chars were also prepared from commercially available wheat straw pellets to study the effect of sample density on the process.

Between the two loose straw samples, WS 07 heated marginally faster, reaching a final temperature of approximately 10 °C higher some 700 s sooner than WS 08 (Figure 3.6A). The heating profile for the pellets is further accelerated due to the dense structure of the material. As can be seen in Figure 3.6B, the pellets heated extremely quickly, 0.6 °C s^{-1}, until reaching the system maximum of 200 °C

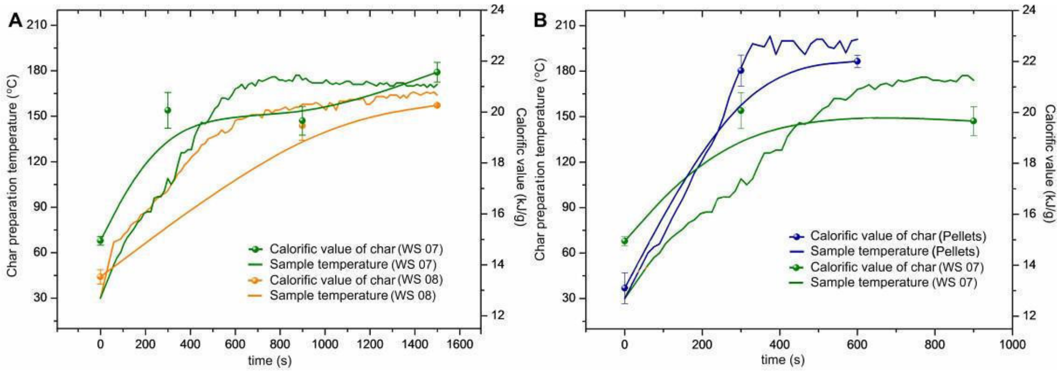

Fig. 3.6: Preparation of wheat straw chars under microwave conditions A) WS 07 and WS 08 B) WS 07 and pellets

Inorganic species in biomass have important influences on the thermal degradation of biomass. Potassium in particular has been cited as playing an important role in terms of rate and product yield during thermochemical breakdown of biomass, although the influence is not fully understood.[13, 15] As a result, the transformation and release of potassium during pyrolysis has been subject to study. There appears to be agreement in the literature as to the lowering of activation energies and increasing char yields due to the release of potassium during decomposition of the organic matrix. Under conventional conditions, a fraction of the potassium is released between 200 - 400 °C and thought to be re-deposited as discrete particles of KCl or dispersed in the char matrix. The effect of potassium can result in lowering the average activation energy for pyrolysis by up to 50 kJ/mol, and shift the temperature of peak conversion of lignin by 70 °C. The catalytic role of potassium in char formation and combustion experiments has been observed for wheat straw, therefore the above results for WS 07 and WS 08 are in agreement with reported behaviour. [13-15, 19]

By pelletising the biomass before microwave treatment the transfer of heat within the sample is maximised due to the increased surface contact within the sample. This results in a faster rate of heating and producing a higher calorific value char over a shorter period of time (Figure 3.6 B). Despite having low potassium content more similar to WS 08, the pellets yield a higher calorific value char than WS 07 for the same energy input. This suggests that peletisation might have a much greater influence than inorganic content in terms of maximising the output of the microwave process.

Figure 3.7 compares the microwave and thermal treatment of WS 07 and WS 08. WS 07 resulted in a char with a calorific value of 21.6 kJg^{-1} – at a temperature some 160 ^{o}C lower than under conventional conditions. In the case of WS 08, this margin is less but still significant with a difference close to 100 ^{o}C between the preparation temperatures of chars of similar calorific value.

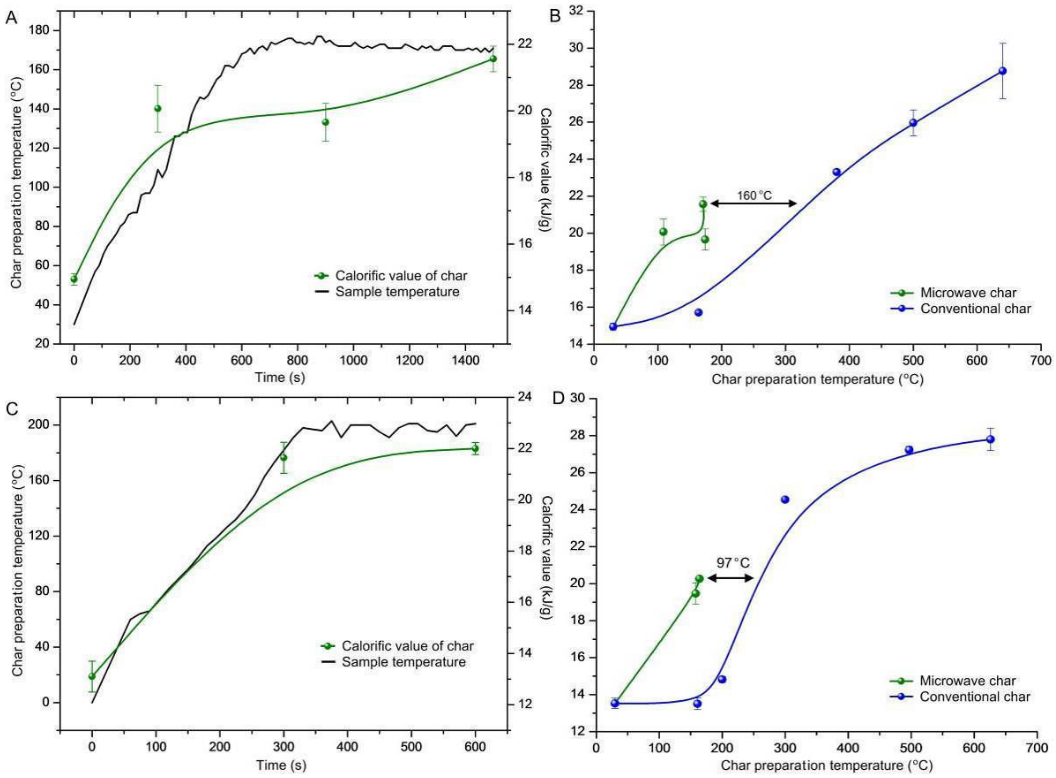

Fig. 3.7: Preparation of wheat straw chars under microwave conditions (A: WS 07, C: WS 08). Comparison of chars prepared under microwave and conventional thermal conditions (B: WS 07, D: WS 08)

3.4.4 Bio-char from cocoa husk

As cocoa husk acts as a protective outer coating for the cocoa bean, it is higher in lignin than wheat straw or miscanthus. As demonstrated in Chapter 2.6, the interaction of lignin with microwave irradiation is poorer than that of other cell wall components. As a result, the cocoa husk samples reached a maximum temperature of just over 140 °C under the standard microwave processing conditions (Figure 3.8 A).

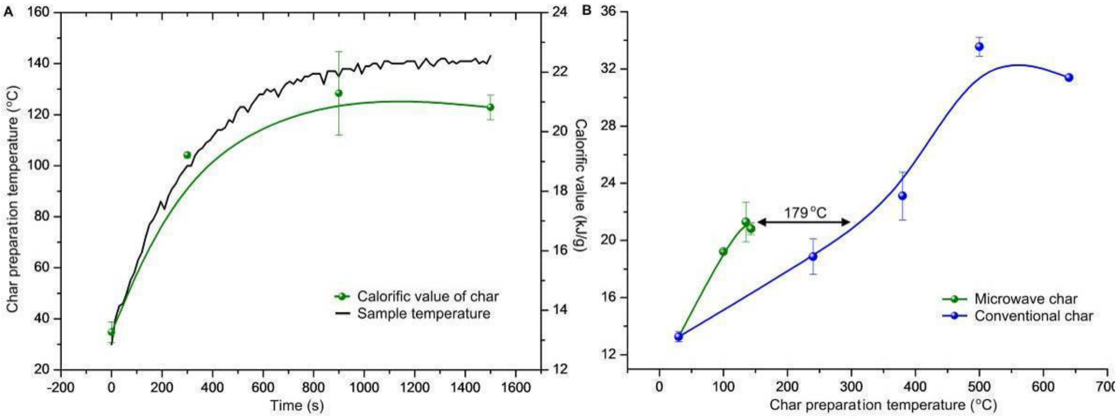

Fig. 3.8: A) Preparation of cocoa husk chars under microwave conditions. B) Comparison of chars prepared under microwave and conventional conditions

Nonetheless, microwave treatment resulted in a greater increase in the calorific value of the husk than conventional treatment at the same temperature. In fact, the difference between microwave and conventional char is greatest for cocoa husk of the three feedstocks. This shows that microwave treatment is an effective method of increasing the calorific value of a variety of feedstocks.

3.5 Characterisation of bio-char

The chars and starting materials were studied using FT-IR to identify structural changes occurring during the char formation. Table 3.1 shows the assignment of peaks present in biomass correlated to characteristic peaks of structural components.

Table 3.1: IR assignment of biomass [20, 21]

Wavenumber (cm^{-1})	Assignment	Corresponding structures	Carbo-hydrate	Lignin
3200–3700	O–H stretching	Hydroxyl	*	*
2800–3000	C–H stretching	Aliphatic structures	*	*
1650–1770	C=O stretching	Carbonyl	*	*
1610–1680	C=C stretching	Olefinic structures		*
1450–1600	C=C stretching	Aromatic structures		*
1420–1480	C–H bending	Aliphatic structures	*	*
1400–1430	O–H and C–H bending	Hydroxyl, acid, phenol, olefins and methyl	*	
1200–1300	C–O stretching	Unsaturated ethers	*	*
1000–1200	C–H out-of-plane bending	Aromatic structures	*	*
1000–1160	C–O stretching	Saturated ethers	*	*
1050–1160	C–O stretching	Tertiary hydroxyl	*	*
1070–1120	C–O stretching	Secondary hydroxyl	*	*
1000–1060	C–O stretching	Primary hydroxyl	*	*
625–1000	C–H out-of-plane bending	Olefinic and aromatic structures	*	*

3.5.1 Miscanthus char

Figure 3.9 shows infrared spectra for chars prepared from miscanthus under both conventional and microwave conditions. Conventional char prepared at 640 °C shows significant changes between 3500 cm^{-1} and 1600 cm^{-1} as a result of carbohydrate degradation. Remaining peaks between 1600 cm^{-1} and 1000 cm^{-1} are due to residual lignin and the rearranged carbon skeleton of the high calorific value char. The new peak at 1428 cm^{-1} corresponds to C=C skeletal stretches in a condensed aromatic system, indicating increased aromatisation of the sample. In addition, two new peaks are also found at 880 cm^{-1} and 821 cm^{-1} consistent with aromatic C-H out of plane bending vibrations.[22]

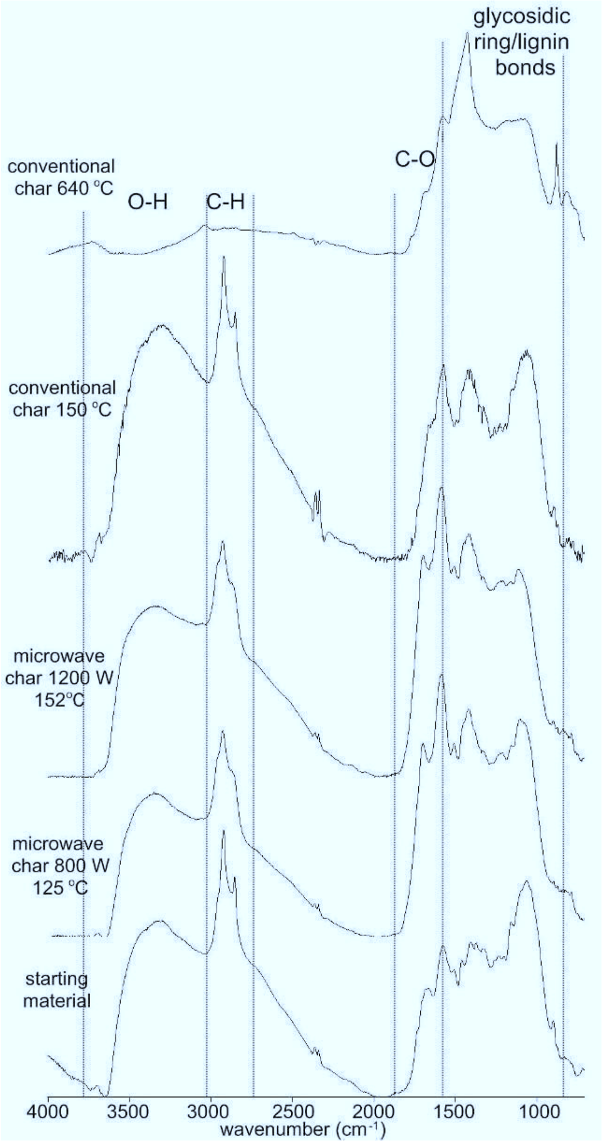

Fig. 3.9: FTIR spectra of miscanthus and chars prepared through microwave and conventional pyrolysis

The conventional char prepared at 150 °C shows little sign of degradation, in contrast to microwave char prepared at a similar temperature. It is clear from the infra-red spectra, that the microwave treatment resulted primarily in the breakdown of the carbohydrate components as peaks at 2928 cm^{-1} and 2855 cm^{-1} (C-H stretching) reduce along with O-H and C-H bending signals in the region of 1400 cm^{-1} and C-O at 1060 cm^{-1}. The lignin peaks at 1678 cm^{-1} and 1573 cm^{-1} appear relatively unaffected, rising in intensity as the neighbouring carbohydrate peaks decrease.

Under these conditions, microwave heating does not result in the total carbonisation of miscanthus but it does illustrate the increased capacity of microwave heating to produce a more charred product at lower temperatures.

3.5.2 Wheat straw char

The infra-red spectra of wheat straw and its chars show significant differences to miscanthus (Figure 3.10)

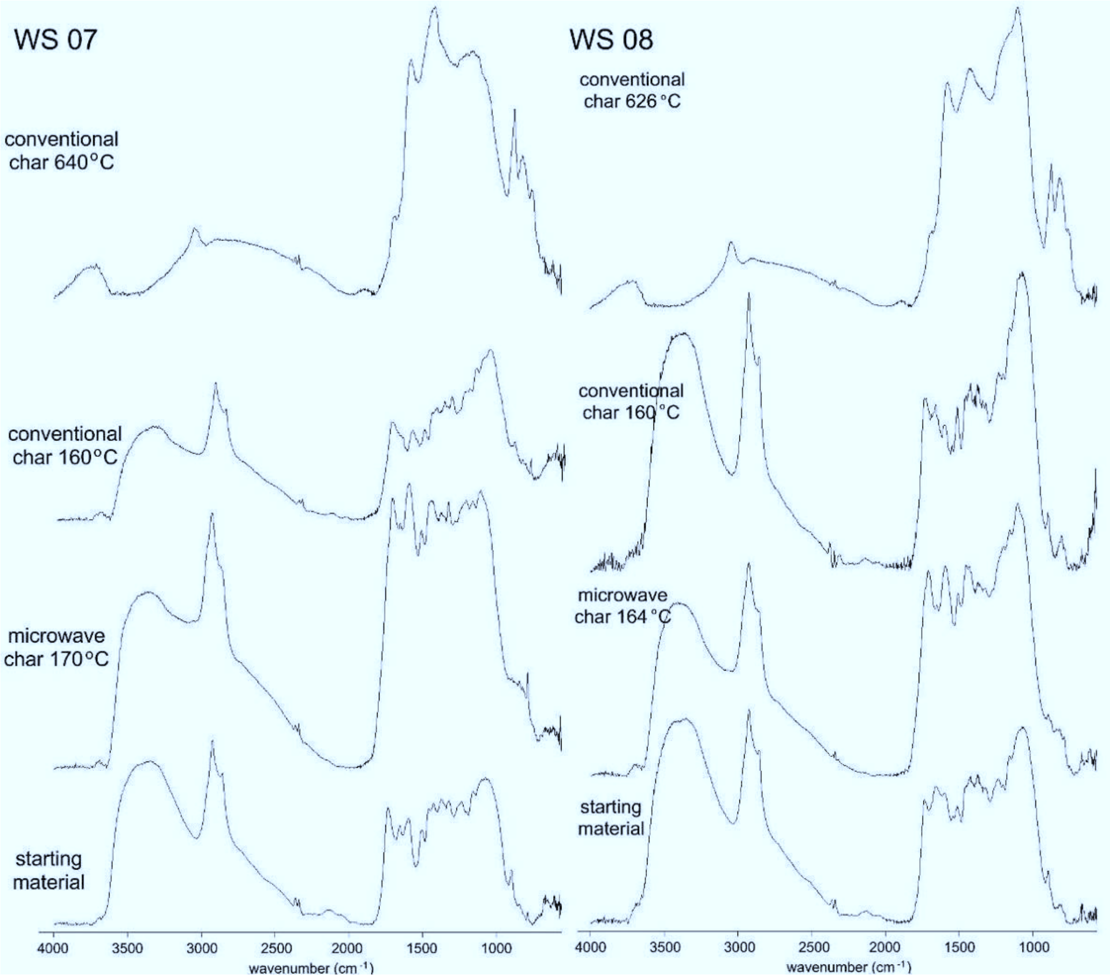

Fig. 3.10: FTIR spectra of wheat straw samples (WS 07 and WS 08) and chars prepared through microwave and conventional pyrolysis

Wheat straw is known to be slightly lower in lignin than miscanthus (on average 18 % as opposed to 23 % [23, 24]) therefore the signals in the infra-red spectrum associated with lignin are of lower relative intensity.

In WS 07, the conventional char prepared at 640 ^{o}C shows the same general properties as the high temperature miscanthus char. The broad peak between 1272 cm^{-1} and 1070 cm^{-1}, along with the peaks at 877 cm^{-1}, 824 cm^{-1} and 757 cm^{-1}, correlate to aromatic C-H stretching indicating a largely aromatic structure.

Both the microwave char (170 ^{o}C) and the conventional char prepared at 164 ^{o}C, show breakdown of carbohydrate structure as the hydroxyl stretching vibration at 3359 cm^{-1} diminishes with treatment. The reduction of the aliphatic C-H stretching peaks at 2926 cm^{-1} and 2863 cm^{-1} also indicate decreasing aliphaticity. While the carbonyl stretching signal at 1730 cm^{-1} shifts significantly in the microwave and conventional chars, it completely disappears from the high temperature char. This suggests that the microwave char is further decomposed than that prepared at a similar temperature under conventional conditions. The microwave char also shows more significant levels of aromaticity with the growing peak at 1160 cm^{-1}.

WS 08 is broadly similar but decomposition of the carbohydrate structure is less at low temperature. This can be assumed to be as a result of the lower potassium content, resulting in an uncatalysed degradation mechanism limiting the extent of degradation of the cell components in the biomass.

3.5.3 Cocoa husk char

While cocoa husk has higher lignin content than wheat straw the char formation mechanism is similar to that of WS 07 (Figure 3.4). It has been found that mineral content has a dominant effect on pyrolysis rather than lignin.[17] Therefore these similarities can be attributed to the high potassium content of cocoa husk (Figure 3.4). The microwave char (135 ^{o}C) shows greater signs of carbohydrate decomposition than the conventional char prepared at 150 °C (Figure 3.11). The hydroxyl stretching vibration at 3299 cm^{-1} remains in the conventional char, while it seen as a shoulder in the microwave char.

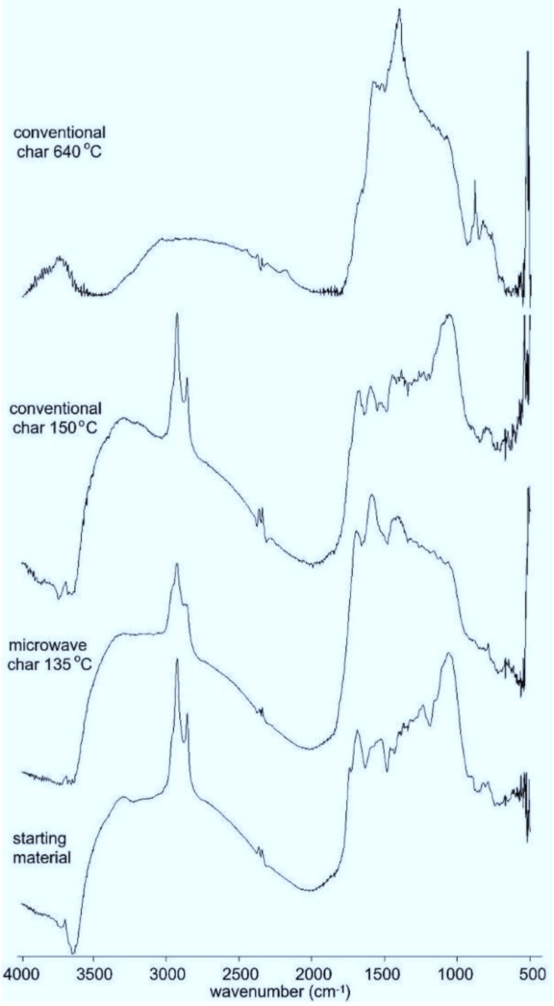

Fig. 3.11: FTIR spectra of cocoa husk and chars prepared through microwave and conventional pyrolysis

The microwave char also shows significantly greater reduction of the aliphatic C-H stretching peaks at 2926 cm^{-1} and 2855 cm^{-1}. The carbonyl stretch at 1689 cm^{-1} again shows greater reduction in the microwave char over the conventional char. Both chars show a relative increase in the level of olefinic C=C bonds as the signal at 1596 cm^{-1} develops. The most significant difference is at 1060 cm^{-1}; the C-O stretch has all but gone from the microwave char while it is largely unchanged in the conventional char. The conventional char prepared at 640 °C shows the same broad properties as the high temperature chars of the other biomass species. The peaks at 877 cm^{-1}, 828 cm^{-1} and 765 cm^{-1}, correlate to aromatic C-H stretching, while the peak at 1398 cm^{-1} indicates the presence of remaining O-H.

3.6 Fuel Properties

Elemental analysis was used to determine the suitability of the biomass chars as fuels. As discussed in Chapter 2 (section 2.4.4), the properties of fuels are often compared in terms of their O/C and H/C ratios in a Van Krevelen diagram. The lower the respective ratios the greater the energy content of the material.[25] Figure 3.12 shows the Van Krevelan diagram for the best chars produced via microwave and conventional thermal treatment.

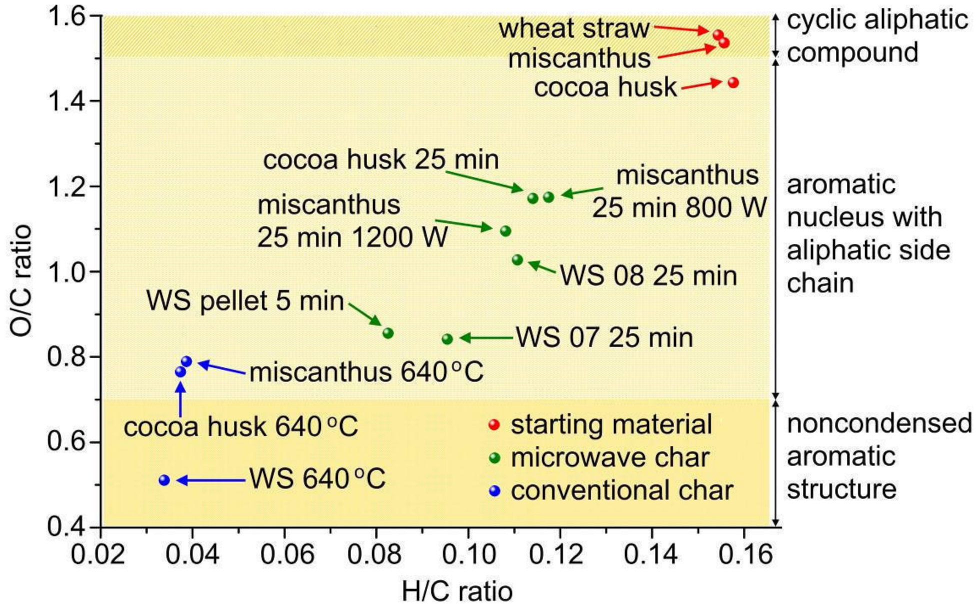

Fig 3.12: Van Krevelen diagram representing elemental composition of biomass chars (see Appendix 1 for complete elemental analysis)

It is clear from the diagram that the extreme heating conditions afforded by conventional treatment produce a char more suitable for fuel use, but it is vital that this data be viewed in context. While thermal treatment increases the calorific value of biomass, there is an inherent loss in mass as a result of the removal of moisture and volatile components. This loss must be balanced against the increasing calorific value of the product. Table 3.2 shows the correlation between increasing calorific value and decreasing char yields as represented by the energy yield.

Table 3.2: Calorific value of char relative to yield

Preparation Temp (°C)	Calorific value (kJ/g)	Char yield (%)	Energy yield (kJ/g)	Preparation Temp (°C)	Calorific value (kJ/g)	Char yield (%)	Energy yield(kJ/g)
Miscanthus:							
Starting material: 12.96 kJ/g							
Microwave char:				**Conventional char:**			
150	22.08	83.89	18.52	150	17.47	88.28	15.42
220	29.78	59.42	17.70	240	22.25	80.23	17.85
170	27.06	58.14	15.73	380	27.16	39.19	10.64
190	25.99	56.79	14.76	500	34.21	32.46	11.10
Wheat Straw:							
Starting material: 14.95 kJ/g							
Microwave char:				**Conventional char:**			
150	19.63	88.20	17.31	150	17.31	93.31	16.15
220	27.59	63.91	17.63	380	21.62	37.22	8.05
				640	29.45	28.39	8.36
Cocoa husk:							
Starting material: 13.24 kJ/g							
Microwave char:				**Conventional char:**			
170	20.115	73.04	14.69	150	15.67	89.67	14.05
190	31.7	72.66	23.03	240	20.10	73.26	14.73
150	28.44	68.87	19.58	500	34.21	35.6	12.21
220	28.82	67.30	19.40	640	31.39	32.49	10.20

It can be seen that high calorific value chars give a lower energy yield (per gram of starting material) than the original biomass due to significant mass losses. Assuming that the char is the sole product of this process (not utilising gaseous or liquid co-products), the final high calorific value of the product does not necessarily warrant the energy spent in producing it. Therefore, while conventional chars have better fuel properties than the microwave chars (Figure 3.12), the mass loss involved in further increasing the calorific value is greater, making the overall balance more favourable for microwave chars.

Along with increased energy density, char formation improves the material handling properties of biomass. Figure 3.13 shows unprocessed cocoa husk and char, both of which were stored in similar conditions for over a month. It is clear that the unprocessed cocoa husk has suffered as a result of the storage showing signs of growth of mould and as such may no longer be suitable for use, while the char remains in good condition and is of higher calorific value. The char is also easily ground into small particles (< 250 μm) making it ideal for burning in conventional firing systems.

Figure 3.13: Effect of storage on unprocessed cocoa husk and cocoa husk char

3.7 Conclusions & Future Work

In Chapter 2, it was shown that the microwave treatment of cell wall components can result in pyrolytic processes occurring at operating temperatures up to 150 ^{o}C lower than those required under conventional processing conditions. It has now been shown that microwave processing can be used to treat whole biomass to produce significant yields of increased calorific value chars at low temperatures. In agreement with the results reported for biomass components, temperature savings of up to 180 ^{o}C were possible when producing chars via microwave processing rather than conventional slow pyrolysis. The application of this technology has the potential to support transition to sustainable energy production with minimal alteration of current fuel burning systems. The success of these laboratory results led to scale up trials, which enabled further proof of the concept and its applicability (Chapter 5.2). Following on from this work, methods to further improve the fuel quality, such as reduction of ash levels require investigation. Mechanistic studies should also be carried out in order to establish better understanding of processing occur during microwave treatment of biomass.

Up to this point, energy savings have been assumed due to the increased efficiency of lower operating temperatures, but a detailed study is necessary to ensure microwave processing of biomass does in fact offer improved energy efficiency over conventional processing. To this end, further potential energy outputs of the microwave processing of biomass were investigated. It has been found to be possible to produce a pyrolysis type bio-oil as a co-product as part of the char formation process (Chapter 4). This energy output will be discussed along with that of the char when constructing the overall energy balance of the system (Chapter 6).

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Chapter 4: Production of bio-oil through microwave treatment of biomass

Publications:
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.; Ross, A., The preparation of high-grade bio-oils through the controlled, low temperature microwave activation of wheat straw. *Bioresource Technology* 2009, *100* (23), 6064-6068.

4.1 Introduction

In 2008, petroleum derived fuels accounted for 98 % of transportation fuels. The associated carbon emissions and market insecurities bolstered interest in liquid biofuels. First generation biofuels, based on food crops, such as maize, have come under much negative attention due to the food versus fuel debate along with the high resource demand in the crop production. As a result, interest has grown in the production of second generation biofuels, i.e. those produced from lignocellulosic biomass.[1]

Chemical methods for production of biofuels are generally divided into biochemical and thermochemical processes.

Biochemical processing involves the conversion of biomass to fermentable sugars for the production of specific alcohols, such as ethanol and butanol. While the process has already been established for first generation biofuels, further progress is necessary to optimise biochemical transformation of cellulosic components of biomass.[1] The conversion also tends to be slow, requiring batch-wise manufacturing, and can only be used to convert polysaccharide components of biomass.

Thermochemical processing produces a range of products through the thermal decay and chemical reformation of biomass under differing concentrations of oxygen. In this way, it is possible to maximise on the fuel and chemical potential of biomass by acting on all components. Pyrolysis is a medium temperature thermochemical process (typically 350-500 ^{o}C) focusing on the liquefaction of biomass. Bio-oil produced from pyrolysis has potential applications as a hydrocarbon fuel, but faces challenges in fuel applications due to unfavourable properties such as high acidity and high water and alkali metal contents.[2] Therefore, there is a need to optimise a process for production of bio-oil with more favourable properties.

The use of microwave energy to activate biomass dates back to the 1970s.[3] Microwave treatment of biomass for the production of chemicals, in particular levoglucosan, has been reported.[4, 5] Thermochemical microwave treatment of biomass has also been investigated for fuel production. Both gasification and pyrolysis under microwave conditions have been reported at operating temperatures above 300 °C.[6-8] Following on from the results of the work reported in Chapters 2 and 3, here will be reported for the first time the possibility to produce bio-oils through microwave processing of biomass below 200 °C. By maintaining low temperatures, it has been shown that decomposition of the biomass is more controlled resulting in a bio-oil with improved fuel properties relative to fast pyrolysis bio-oil.[9]

4.2 Bio-oil from the microwave treatment of biomass

The widespread application of bio-oil as a fuel is dependent on its physical properties such as ash and alkali content, heating value and viscosity. Ash present in bio-oil can reduce the protective oxide surface of the engine, a process which may be accelerated by alkali metal sulfates and chlorides. The heating value and viscosity of bio-oil are heavily influenced by water content; therefore by controlling this it should be possible to improve the quality of the oil. These parameters have yet to be tuned to a satisfactory level using conventional processes.[10] As a result the application of microwave technology is being investigated due to the increased control it can offer.

The majority of reported investigations have focused on the microwave pyrolysis of biomass at temperatures within the standard pyrolysis range (350 – 600 °C). It has been shown that microwave technology is capable of producing bio-oils of similar or better properties than fast pyrolysis, but the energy demand associated with processing at these temperatures is still significant.[11-13]

The optimisation of microwave pyrolysis of cellulose and wood has been investigated for production of levoglucosan. [4, 5, 14] The influence of parameters such as power, irradiation time, particle size and biomass source was studied. While product distribution in terms of water, oil, gas and char were monitored and oil analysis carried out, the temperature of the process was not directly controlled, and therefore, appears not to have been recognised for its influence.

Menendez et al[8, 15-17] studied the calorific value of microwave pyrolysis products of biomass processed at temperatures above 500 °C. Microwave energy was used to pyrolyse sewage sludge at microwave power of 1000 W and a final reaction temperature of 1000 °C, aiming to optimise the fuel properties of the gas produced. It was found that microwave pyrolysis produced more gas and less oil than conventional pyrolysis. Notably, the amount of hydrogen in the gas mixture was much higher than under conventional conditions, suggesting a different degradation mechanism during microwave pyrolysis. The calorific values for char, oil and gas fractions were up to 7, 37 and 10 kJg^{-1} respectively. In comparison to typical values for coal, oil and gas with 32, 42 and 14 kJ/kg these values are lower, although, the highest yielding fraction, gas, compares favourably with the fossil fuel alternative.

Investigations described in this thesis (Chapter 3) showed it is possible to produce char from microwave treatment of biomass working at temperature between 120 and 300 °C, resulting in a significant saving in energy input. The co-production of an oil fuel product with char would further add to the value of the process. By operating at lower temperatures than traditional pyrolysis it should be possible to increase energy efficiency and process control in order to produce an oil with suitable properties for preparation of fuel.

4.2.1 Experimental set-up

As described in experimental section 7.2.5, bio-oil was produced by exposing the biomass sample to microwave irradiation in a Milestone ROTO-SYNTH Rotative Solid Phase Microwave Reactor (Milestone Srl., Italy) fitted with a VAC 2000 vacuum module in series (Figure 4.1). The maximum operating temperature was 200 °C.

As the biomass was heated within the rotating vessel in the microwave chamber, two liquid fractions were seen to be produced. Firstly, an aqueous fraction was evolved and collected at the water cooled condenser. Secondly, a dark pyrolysis-type bio-oil was evolved and collected separately in the pressurised condenser chamber. Remarkably, due to the nature of the process the bio-oil could be kept almost free of the water.

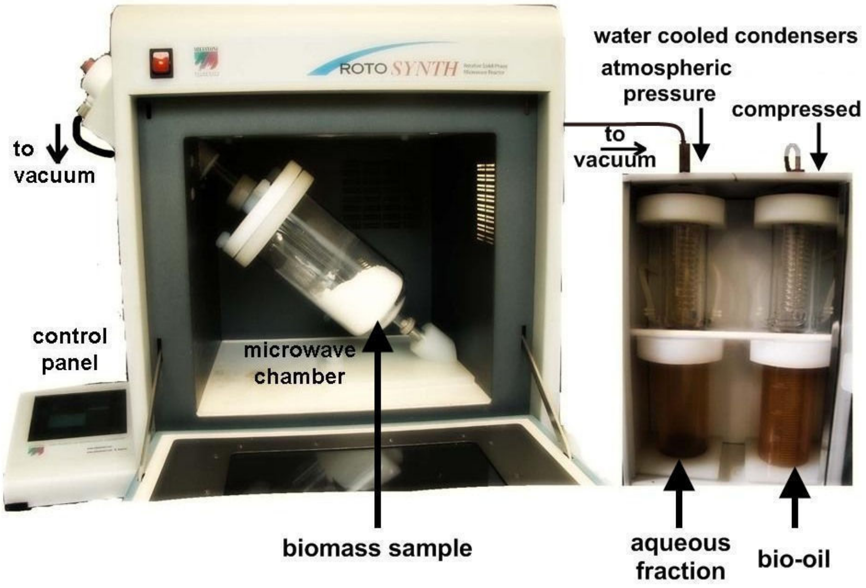


Fig. 4.1: Process for production of microwave bio-oil

Bio-oils were produced from several different types of biomass including wheat straw, miscanthus, cocoa husk, spruce wood and rolled oats. For the purpose of this thesis, the oils produced from the processing of wheat straw have been chosen as the main focus due to the availability of this feedstock in the UK and the ability to reach higher temperatures when processing pellets.

4.2.2 Microwave treatment of wheat straw for production of bio-oil [18]

Wheat straw pellets were exposed to microwave irradiation in the rotating reactor vessel of the Milestone SMPR. As can be seen from Figure 4.2, changes in the process pressure give clear indications of the release of volatile components from the biomass. Similar to the results presented in section 2.4.2, between 60-120 °C, an aqueous fraction is produced with a relatively high acid content (low pH) over a period of 5-10 minutes. Subsequently, while maintaining a relatively low temperature, an organic fraction of low water and low acid content is produced over a period of 1-2 minutes. As a result it is possible to collect two discrete liquid fractions through this *in-situ* separation process. As will be discussed in section 4.2.3, the second fraction was analysed in terms of water content, acidity, composition and calorific value (Experimental sections 7.3.11-14, 7.3.5, 7.3.1) to establish its suitability for use as a fuel. As discussed in Chapter 3, the sample could then be heated to higher temperatures to improve char properties but this was found not to impact on liquid yields or properties as no further liquid is evolved after the second peak.

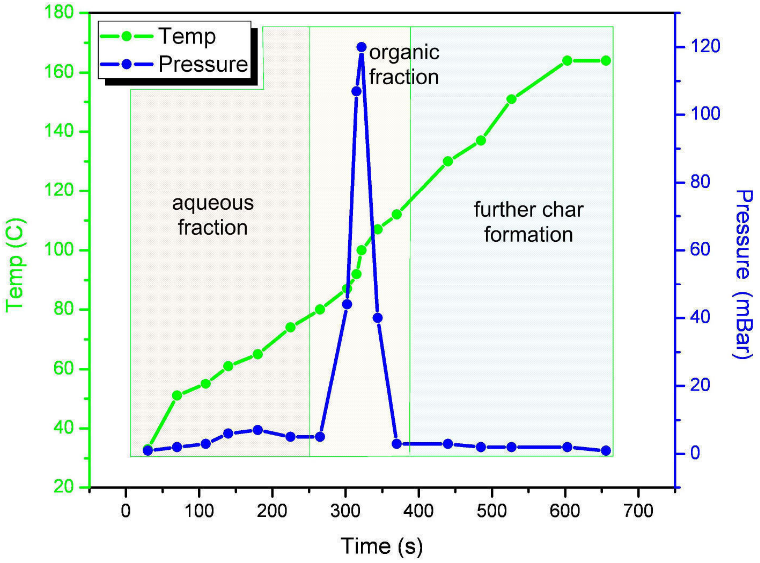


Fig. 4.2: Evolution of fractions during microwave treatment of wheat straw

4.2.3 Properties of wheat straw bio-oil

Bio-oil produced through the microwave treatment of wheat straw was compared to conventional pyrolysis bio-oil, crude petroleum and other reported microwave bio-oils (Table 4.1). It can be seen that the properties of the wheat straw bio-oil compares favourably to the typical properties of conventional pyrolysis bio-oils with comparable elemental composition. However, due to the in-situ separation of aqueous components the major impurities (sulfur, alkali metals and acids) are condensed in the aqueous fraction. This significant shift results in the levels of these being lowered substantially in the organic fraction of the microwave oils, making microwave bio-oil more suitable for upgrading for fuel use.[19]

Table 4.1: Comparison of key properties of crude petroleum and bio-oils produced from the conventional pyrolysis and microwave activation of biomass

Property	Crude petroleum[19]	[a]Conventional wheat straw pyrolysis oil[20-22]	Microwave oil production		
			[b]Coffee hull[8]	Corn stover[7]	Wheat straw
Yield (wt %)	-	41-51	7.9	30.16	21±2.3
Water (%)	<1	20-50	<1	15.2	<1
C (wt %)	85-87	43-55	67.3	60.1	58.9±0.2
H (wt %)	10-14	6.6-9	2.4	7.70	6.85±0.07
N (wt %)	0.1-2	0.1-1.25	3.1	2.02	1.15±0.01
O (wt %)	0.1-1.5	38-63	6.2	29.4	33.2±0.28
S (wt%)	0	0.1-0.3	0.3	0.15	0.02
Acid number (pH)[c]	<1	(3-4)	-	(2.87)	1.4
HHV (kJ/g)	42	11-21	24.3	17.5	19.01±2.7

[a] oils produced between 500 to 530 °C

[b] contains ~ 20 % ash

[c] values given in brackets refer to pH. Low acid number indicates low concentrations of both organic and inorganic acids in the oil, i.e. pH value close to 7

As microwave pyrolysis is a relatively new field, there is little data available for comparison in terms of properties. Yu et al.[7] reported production of bio-oil from corn stover with higher carbon and lower oxygen content than that produced under conventional conditions (54 % and 38 % respectively). The higher oxygen to carbon ratio (O/C) improves fuel properties although this improved quality came with a reduced yield relative to conventional pyrolysis which produced up to 70 % oil (including 15 % water).[23] Conventional pyrolysis of coffee hulls under conditions similar to those of the microwave pyrolysis showed little difference in the properties of the bio-oil.[8] As such, microwave pyrolysis was shown to be comparable to conventional pyrolysis; further optimisation of this process could possibly improve the microwave processing performance.

4.2.4 Composition of wheat straw microwave bio-oil

FTIR characterisation was used to determine groups present in the crude wheat straw microwave bio-oil (Figure 4.3 A). O–H stretching vibrations indicate the presence of phenols, alcohols or residual water. Symmetrical and asymmetrical C–H stretching vibrations at 2931 and 2959 cm^{-1}, together with C–H deformation vibrations around 1457 cm^{-1} correlate to the presence of alkane components. This is backed up by CH_3 bending vibrations at 1363 cm^{-1} and 1457 cm^{-1}. Skeletal vibrations in aromatic rings would be expected between 1500 and 1450 cm^{-1}, meaning overlapping peaks are probable. The C=O stretching vibration at 1712 cm^{-1} may correspond to ketone, aldehyde or carboxylic acid groups present within the complex mixture. C=C stretching bands can be seen around 1609 cm^{-1} indicating the presence of alkenes and aromatics. Weak absorbances below 1000 cm^{-1} may be as a result of some substituted aromatic groups.[24]

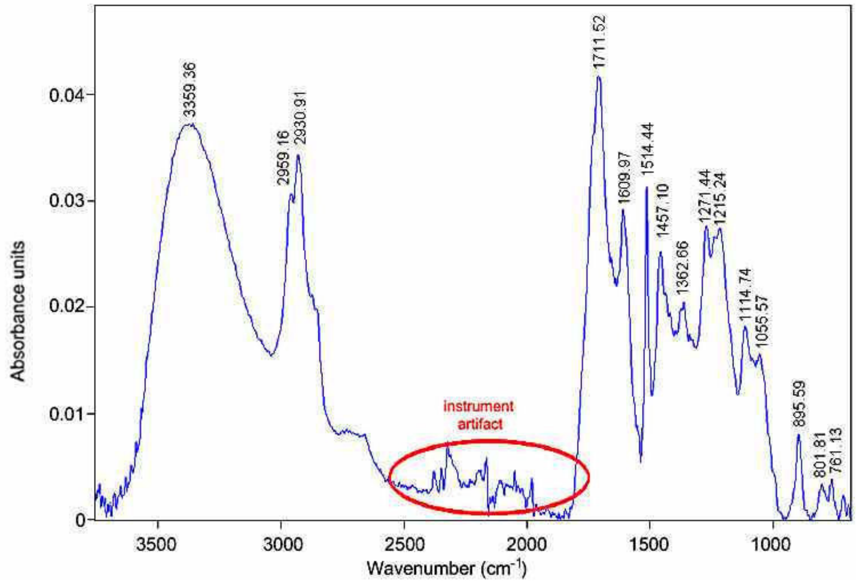
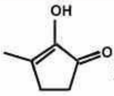
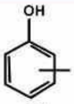
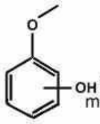
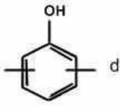
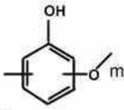
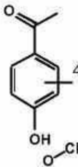
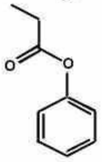
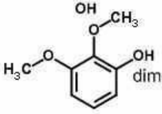
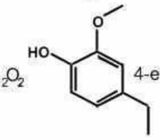
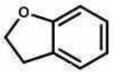
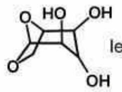


Fig. 4.3: A: FTIR spectrum and B: GC-MS trace of microwave pyrolysis wheat straw bio-oil

Qualitative GC-MS was carried out on the wheat straw microwave pyrolysis oil (Figure 4.4 B). Through comparisons with library spectra (National Institute of Standards and Technology 08 database), approximately 50 % of the total peak area was accounted for by 10 peaks listed in Table 4.2. While several smaller furans were present at low levels, substituted phenols accounted for the majority of components present according to GC-MS. Further characterisation via LC-MS, ICP-MS, atomic absorption and elemental analysis were attempted but the poor solubility and viscous nature made these extremely difficult.

Table 4.2: Most significant peaks in GC-MS of microwave wheat straw pyrolysis oil

Molecular mass	Empirical formula	Proposed structure	Molecular mass	Empirical formula	Proposed structure
112	$C_6H_8O_2$	 2-hydroxy-3-methyl-2-cyclopenten-1-one	108	C_7H_8O	 methylphenol
124	$C_7H_8O_2$	 4-hydroxyphenol mequinol (2 hydroxy)	122	$C_8H_{10}O$	 dimethylphenol
138	$C_8H_{10}O_2$	 methoxymethylphenol	150	$C_9H_{10}O_2$	 4-hydroxy-2/3-methyl-acetophenone
136	$C_8H_8O_2$	 phenylpropionate	154	$C_8H_{10}O_3$	 dimethoxyphenol
152	$C_9H_{12}O_2$	 4-ethyl-2-methoxyphenol	120	C_8H_8O	 2,3dihydrobenzofuran
			162	$C_6H_{10}O_5$	 levoglucosan

A separate comparison was carried out between the wheat straw pyrolysis oil prepared under microwave and conventional conditions (600 °C) (Figure 4.4). When analysed under identical conditions, conventional pyrolysis oils show the typical product distribution of a metal (e.g. in situ potassium) catalysed decomposition of a lignocellulosic biomass via an ionic mechanism (Figure 4.4 A).[25] This includes significant levels of furfural, acetic acid, phenols and methoxyphenols but only small quantities of sugars. Furfural and acetic acid were also detected in the microwave oil, but in much smaller relative amounts; with phenols, methoxyphenols and their dimers much more dominant. The most notable point of difference is in the yield of sugars such as levoglucosan and 1,4:3,6-dianhydro-D-glucopyranose, along with small amounts of long chain acids. The high level of levoglucosan visible in the microwave oil, has potential as a chemical or bio fuel intermediates (e.g. levoglucosan to glucose for ethanol[26]). Microwave processing affords milder conditions causing less decomposition and hence a greater amount of high molecular weight components in the bio-oil.

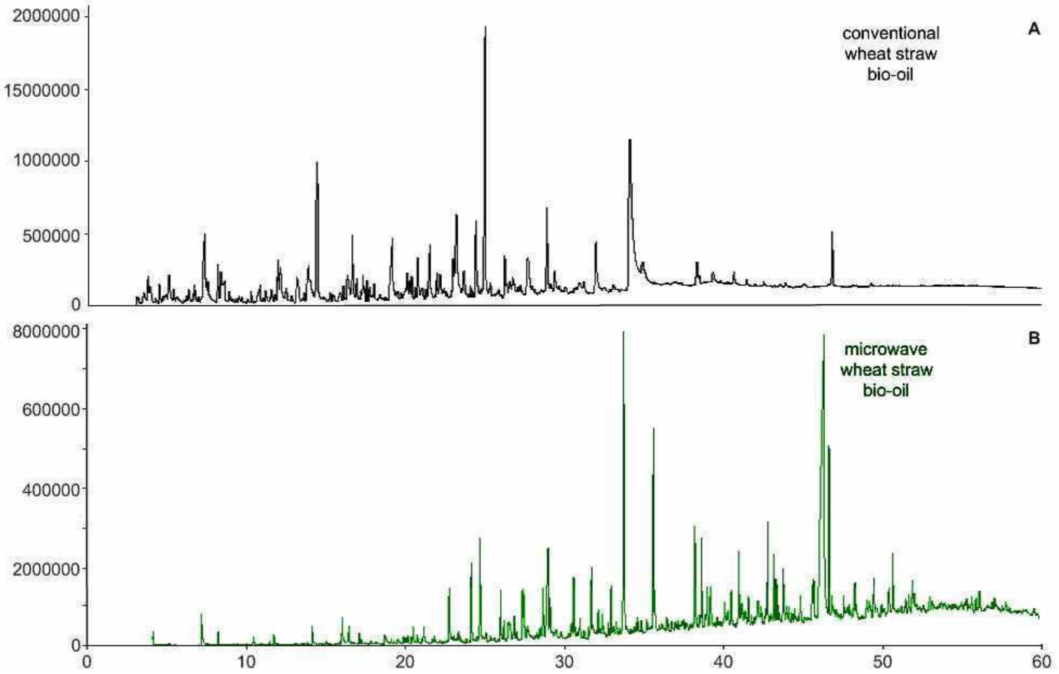


Figure 4.4: Comparison of GC-MS analysis of conventional (A) and microwave (B) pyrolysis oil from wheat straw pellets

4.2.5 Influence of additives on microwave bio-oil

As discussed in Chapter 3.4.3, inorganic additives are known to have an effect on the mechanism of biomass pyrolysis and as a result on the product distribution and properties. In this chapter, the effect of simple inorganic additives on the microwave bio-oil yield and properties was investigated. Sulfuric acid, hydrochloric acid and ammonia were chosen as simple inexpensive molecules which could easily be introduced in low concentrations. An equal concentration of each additive was mixed with the wheat straw pellets for several minutes and oven dried where necessary before microwave processing (Experimental section 7.2.6). The product distribution varied depending on the additive used (Table 4.3). As can be seen, sulphuric acid caused a significant decrease in the oil yield, to the advantage of char yield. Interestingly, the same quantity of hydrochloric acid had little effect on the oil yield, while NH_3 resulted in a greater char yield but had little influence on oil yield. The effect was found to rely on the additive itself, rather than acid/base properties as might be expected. It was noted that the calorific value of the bio-oil produced in the presence of additives varied little from that of the standard microwave bio-oil with all values falling within the error range.

Table 4.3: Mass balance of products from the low temperature microwave activation of wheat straw pellets including presence of additives [a]

	Wheat Straw	Wheat Straw + H_2SO_4	Wheat Straw + HCl	Wheat Straw + NH_3
Process temperature (^oC)	130	140	140	165
Calorific Value of bio-oil	19.3	23.2	24.7	22.8
Product Distribution (mass %)				
Char	29	44.4	31.8	40.7
Bio-oil	20.6	7.3	22.1	17.0
Aqueous Phase	36.4	32.9	27.1	22.3
Gas	14	15.4	19	20

[a] Results quoted are for highest yield of bio-oil recorded under these conditions.

It has been reported that inorganic components within biomass support the formation of gas and char over bio-oil.[27] In a study of the pyrolysis behaviour of twelve different biomass feedstocks, Raveendran et al reported that in the majority of cases, lowering mineral content resulted in lower char yields and increased oil yields.[28] The addition of inorganic species, such as NaCl, $ZnCl_2$, NaOH, $FeSO_4$ and KCl, has been subject to widespread study in terms of impact on the yield and composition of pyrolysis products.[12, 29-35] In agreement with the results shown above, it was found in all cases, that the additives resulted in increased char and gas formation to the detriment of liquid yields. As a result, the use of additives in oil production has little value in terms of yield, therefore the influence of additives on composition was investigated.

4.2.6 Influence of additives on bio-oil composition

It is to be expected that the use of additives will also affect the composition of bio-oils. Scott et al discovered the yield of anhydrosugars was significantly higher in the absence of inorganic species proposing two alternative mechanisms for the pyrolysis of cellulose. Accordingly, it was reported that in the absence of minerals, cellulose decomposes via depolymerisation steps forming levoglucosan as the major product. Alternatively, in the presence of minerals, low molecular weight compounds are formed as the major product of decomposition. These findings have been supported by further investigations although the exact mechanism and reason for the effect of inorganic content on degradation remains unclear. [36-38]

The compositions of the bio-oils produced from microwave pyrolysis of wheat straw were studied using ^{1}H NMR and GC-MS. The complex composition of the oils meant it was difficult to determine the exact composition although the abundance of specific groups of compounds was clearly demonstrated.

4.2.6.1 ^{1}H NMR studies of bio-oil

As described in Experimental section 7.3.14, proton NMR spectra were recorded for wheat straw bio-oils prepared in the presence and absence of additives. Although the spectra were too complex to allow identification of individual components (see Appendix 1), the integral values of selected regions were used to identify relative quantities of functional groups in the oils following the procedure of Mullen et al (Figure 4.6).[23]

Aliphatic protons, in the region of 0.5 to 1.5 ppm, account for approximately 14 % of the protons in the standard microwave wheat straw bio-oil, as is expected for grassy biomass.[23] Addition of either sulfuric acid and ammonia led to a reduction in this integral, while hydrochloric acid appears to have no influence.

Signals between 1.5 to 3.0 ppm correspond to protons on aliphatic carbons which are alpha to a heteroatom or unsaturation. This is one of the most populated regions for the standard microwave oil (27 %); in this case only sulphuric acid caused a notable change in this region (18 %). Water in the samples would also be likely to resonate in this region but as all the oils contain <1 wt% (measured according to procedure in Experimental section 7.3.12) it was assumed not to cause significant interference.

The next region of the spectrum, 3.0 to 4.4 ppm, contributed a similar proportion of the makeup of all the oils (~20 %) with hydrochloric acid showing the greatest increase at just 6 % higher. Protons in this area are likely to be bonded to carbons next to an aliphatic alcohol or ether group, or a methylene group bridging two aromatic rings. The latter would suggest a partial decomposition of lignin resulting in the presence of the oligomer in the sample.

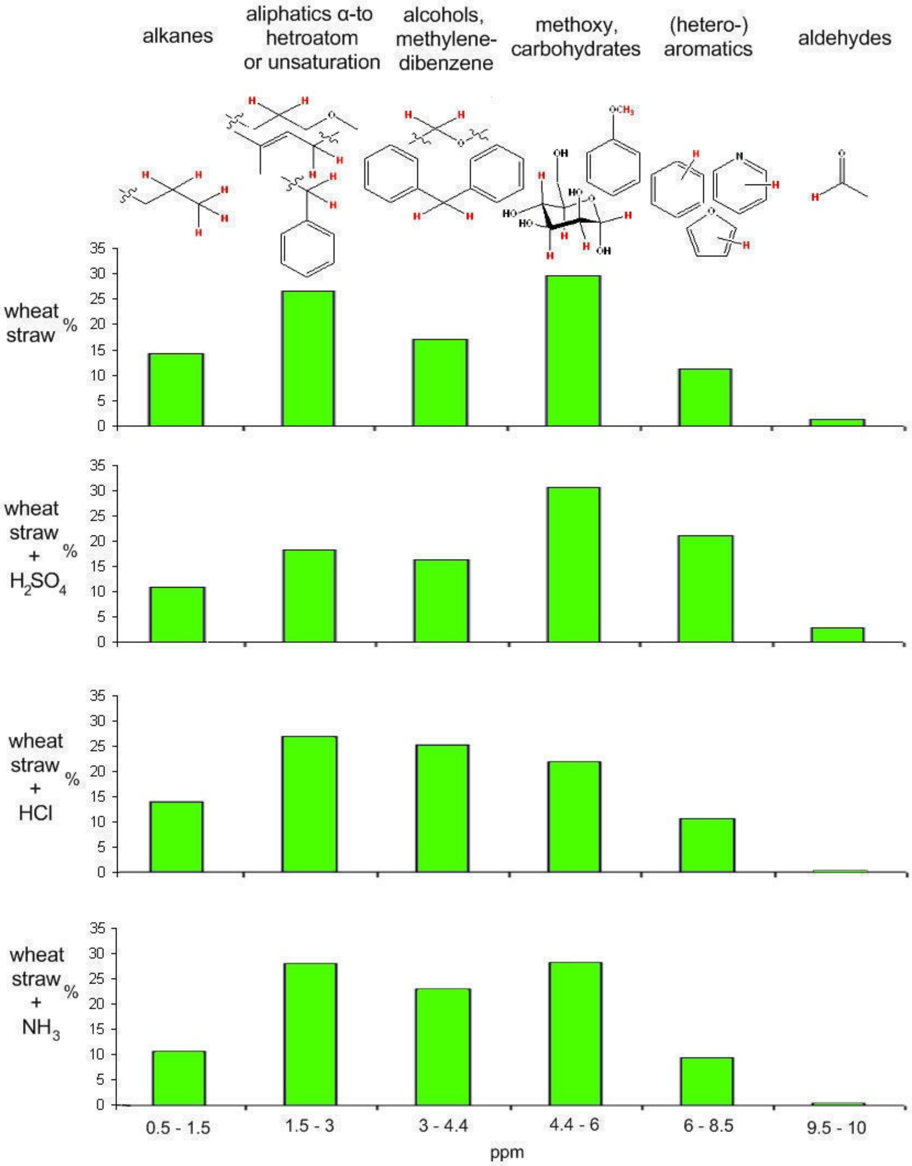


Fig. 4.6: Distribution of functional groups in bio-oil based on ^{1}H NMR analysis of bio-oil from microwave treatment of wheat straw pellets in the presence of additives. (Note: the structures shown are representative of groups which may be present rather than individual structures shown to be present.)

Proton signals between 4.4 and 6 ppm have been assigned to aromatic ether protons of lignin degradation products, or many of the protons in carbohydrate-like structures which would be expected. Again, this region saw little change except in the presence of hydrochloric acid where the yield dropped from ~30 % to 22 %.

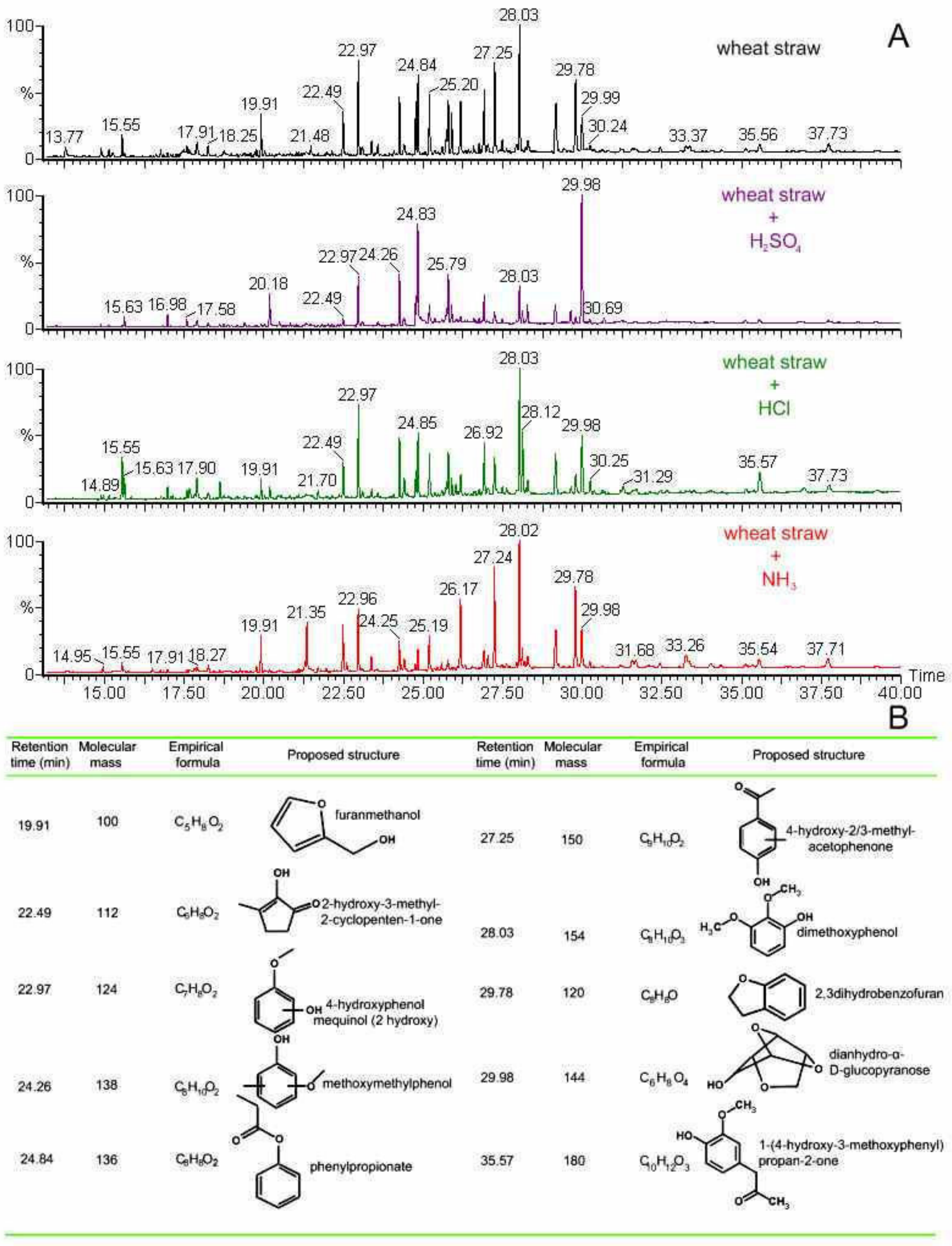
The aromatic region of the spectrum (6 – 8.5 ppm) contained ~10 % of the protons in all the bio-oils except that produced in the presence of sulphuric acid (21 %). The downfield region of the spectrum (9.5 to 10 ppm) contains the smallest portion of protons in all the bio-oils (0 to 3 %). This is to be expected as signals here correspond to aldehydes and certain carboxylic acids, both of which have been identified by IR as mainly condensing in the separate aqueous phase (Appendix 1 Figure 3).

It is clear from the NMR study that the use of additives not only affects yields, but also has an effect on the product distribution in the bio-oils. The possibility to control the distribution of components within bio-oil could potentially benefit further transformation and upgrading processes. GC-MS of the bio-oils obtained gave broadly similar profiles, but, in agreement with the ^{1}H NMR, some changes were evident (Section 4.2.6.2).

4.2.6.2 GC-MS studies of bio-oil

Figure 4.7 shows the GC-MS analysis of wheat straw microwave bio-oils. Due to the complex mixture of compounds present the GC-MS was interpreted in terms of the type of compound present, with absolute identification where possible.

H_2SO_4 results in a comparatively simpler product distribution than bio-oil produced in the absence of additives or in the presence of NH_3 and HCl. This is in agreement with the NMR data which showed over 30 % of the peaks falling between 4.4 and 6 ppm. The GC shows two main peaks along with fewer small peaks and noise. The peaks at 24.83 min and 29.98 min have been assigned respectively as a substituted phenyl and an anhydrosugar from the decomposition of cellulose.



Retention time (min)	Molecular mass	Empirical formula	Proposed structure	Retention time (min)	Molecular mass	Empirical formula	Proposed structure
19.91	100	$C_5H_8O_2$	furanmethanol	27.25	150	$C_9H_{10}O_2$	4-hydroxy-2/3-methyl-acetophenone
22.49	112	$C_6H_8O_2$	2-hydroxy-3-methyl-2-cyclopenten-1-one	28.03	154	$C_8H_{10}O_3$	dimethoxyphenol
22.97	124	$C_7H_8O_2$	4-hydroxyphenol mequinol (2 hydroxy)	29.78	120	C_8H_8O	2,3dihydrobenzofuran
24.26	138	$C_8H_{10}O_2$	methoxymethylphenol	29.98	144	$C_6H_8O_4$	dianhydro-α-D-glucopyranose
24.84	136	$C_8H_8O_2$	phenylpropionate	35.57	180	$C_{10}H_{12}O_3$	1-(4-hydroxy-3-methoxyphenyl) propan-2-one

Figure 4.7: A) GC traces from qualitative analysis of microwave wheat straw bio-oils in the presence and absence of additives. B) Assignment of key peaks

In the case of HCl, a peak at 28.03 min is significantly larger than that at 29.98 min, indicating an increased yield of the dimethoxyphenol over the anhydrosugars. This along with the overall product profile again suggests the salt influences reactions rather than pH. In order to fully understand the implications of these results, repeat experiments will be needed varying the concentration of additives in the samples.

4.3 Conclusions & Further work

Microwave activation of wheat straw provides a novel, low temperature route to bio-oils with excellent key properties in terms of bio-fuel suitability (i.e. low water and acid content, high calorific value). Relative to bio-oil prepared by conventional pyrolysis, this low sulphur and acid content of microwave bio-oils are particularly significant in increasing its suitability for fuel applications (Table 4.3). These results show for the first time, that the use of low temperature microwave pyrolysis gives a simpler product profile than conventional pyrolysis. These milder operating conditions prevent further polymerisation or break down of volatile fractions. Table 4.4 summarises the properties of the oils produced by microwave processing of wheat straw. The process has been applied to other biomass feedstocks including miscanthus, and proved to be versatile method for production of bio-oil. Initial investigations showed similar yields (21 % oil) as are reported for wheat straw although further optimisation and characterisation needs to be carried out (Appendix 1 Table 4).

Table 4.4: Overview of wheat straw microwave bio-oils

Additive	Oil yield (wt%)	Composition	Comments
None	20.6	Mainly aliphatic and aromatic or carbohydrate like products	Simpler product distribution than conventional pyrolysis
H_2SO_4	7.3	Predominantly aromatic or carbohydrate like products	Simplest product profile making it most suitable for purification or upgrading but yield is very low

HCl	22.1	Broad range of different compounds	Broad range of components may offer more options for upgrade although separation may be difficult
NH_3	17.0	Broad range of different compounds	Broad range of components may offer more options for upgrade although separation may be difficult

It is evident that the presence of additives has an influence on the products of microwave treatment of biomass. While it appears that this influence is independent of the pH of the additive, other factors such as volatility, the dehydrating ability of the species and its ability to interact with the microwave field may be involved. A mechanistic study on the interaction of biomass with microwave energy should be carried out in the future in order to form a proper understanding of the role of additives in production of bio-oil.

As mentioned in Chapter 3, it is essential to be aware of the overall energy balance when assessing the advantages of microwave processing of biomass. Chapter 5 describes the scale up experiments and the energy demand of increased scale processing of biomass. All of this data is drawn together in Chapter 6 to discuss the energetic merits of microwave processing of biomass compared to conventional pyrolysis.

4.5 References

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Chapter 5: Short Investigations

Publications:
Budarin, V. L.; Milkowski, K.J.; Shuttleworth, P.; Lanigan, B.; Clark, J.H.;
Macquarrie, D.J.; Wilson, A.J.; Patent Application: WO 2010/001137
Microwave torrefaction of Biomass, 2010.

5.1 Introduction

Throughout the course of the studies already described, some short term studies were also carried out in order to further investigate applications of microwave processing of biomass. This chapter covers two of the most interesting of these projects, a set of pilot-scale trials of microwave treatment of biomass, and new applications of lignin.

5.2 Microwave treatment of lignin for preparation of materials

Lignin is Nature's greatest store of aromatic molecules. Finding an efficient and environmentally benign way to unlock that store is a great challenge for chemists and biologists.[1]

Lignin is available in several forms as a waste product from a variety of wood handling processes. Traditionally seen as a by-product from the paper industry, as lignosulfonate and Kraft Lignin, lignin is now posing a challenge to the integrated biorefinery due to the difficulty in converting it into a valuable product stream. It is generated through acid or enzyme hydrolytic pre-treatment of lignocellulosic biomass, to isolate cellulosic material before fermentation for ethanol production. Currently there is little application for the lignin. While it is used as a stabiliser in drilling muds and emulsions, and as a dispersant in paints, dyes and clay, the majority of lignin is seen as waste and burnt for energy production.

In this section, the production of expanded materials from lignin was investigated as a novel use for the material.

5.2.1 Expanded Materials

According to IUPAC classification solids may be categorized as microporous, mesoporous and macroporous depending on the average pore diameter (Table 5.1).[2]

Table 5.1: IUPAC Pore Classification[2]

Pore Type	Pore Diameter
Micropore	0.5 – 2 nm
Mesopore	2 – 50 nm
Macropore	> 50 nm

Studies on the surface area and pore structure of a solid surface may be carried out by studying the adsorption of a gas or liquid onto the surface. When a solid in a closed space is exposed to a gas at a definite pressure the solid begins to adsorb the gas forming a monolayer on the surface. The fall in pressure in the system can then be used to calculate the mass of gas adsorbed.[3]

Of particular interest in this investigation was the production of mesoporous materials through expansion of lignin. Mesoporous materials have applications in fields including catalysis, sensors, adsorbents, separation media, waste remediation and shape selective electrodes.[4] Previous work in the group had shown the production of high surface area starches and carbonised starches, Starbon®[5, 6] which is currently being sold commercially by SigmaAldrich. Production of a mesoporous lignin could lead to several new applications for this waste product.

Figure 5.1 shows the preparation procedure for the formation of expanded materials from lignin which has been produced as a side product of bioethanol production. As outlined in Chapter 7.2.8, conditions were varied in order to identify the optimum procedure for gel formation.

5.2.2 Preparation of expanded material from lignin

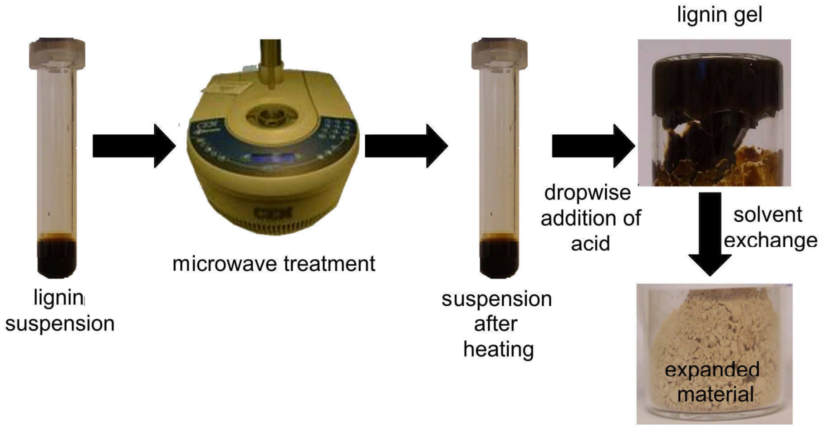

Fig. 5.1: Outline of Microwave Gel Preparation Procedure

Some conditions were found to only result in the formation of an emulsion, while other suspensions appeared completely unchanged after addition of acid. When a gel was successfully formed, the properties of the product after the solvent exchange process varied again. Table 5.2 shows the variation of product surface area in relation to preparation conditions.

Table 5.2: Surface area of materials produced through microwave treatment (200 W) of bioethanol lignin in the presence of NaOH (2 M)

Time	180 °C	190 °C	200 °C
5 min	9 m^2g^{-1}	21 m^2g^{-1}	23 m^2g^{-1}
10 min	12 m^2g^{-1}	14 m^2g^{-1}	58 m^2g^{-1}
15 min	18 m^2g^{-1}	18 m^2g^{-1}	44 m^2g^{-1}
20 min	19 m^2g^{-1}	45 m^2g^{-1}	69 m^2g^{-1}

Note: 1. Starting material surface area: Bioethanol Lignin < 1 m^2g^{-1}

2. Instrument accuracy dictates values < 10 m^2g^{-1} are equivalent to 0 m^2g^{-1}

3. Measurements made using Coulter SA3100 Surface Area and Pore Size Analyzer (Experimental section 7.3.15)

Increased time and temperature resulted in increased surface area. Raising the temperature by 20 °C (from 180 °C to 200 °C) resulted in surface area increases of up to 50 m^2g^{-1}, with the time increase (from 5 min to 20 min) resulting in an average increase of up to 46 m^2g^{-1}. The energy input of this process must be considered and balanced against the benefits higher temperatures and residence times bring to the product.

More in depth gas adsorption analysis of samples with surface area >20 m^2g^{-1} was carried out using a Micrometics ASAP 2010 Surface Area and Pore Size Analyzer. The amount of gas adsorbed by the solid sample depends on the equilibrium temperature and pressure. The relationship between the "amount adsorbed by unit mass of solid and the equilibrium pressure at a known temperature" is shown as an adsorption isotherm. IUPAC have defined six adsorption isotherms for gas physisorption as shown below.[2] Figure 5.2 shows a typical isotherm for the samples analysed. This type of isotherm indicates the presence of micropores, shown by the initial vertical climb, and some mesoporous properties, shown by the hysteresis loop.[2]

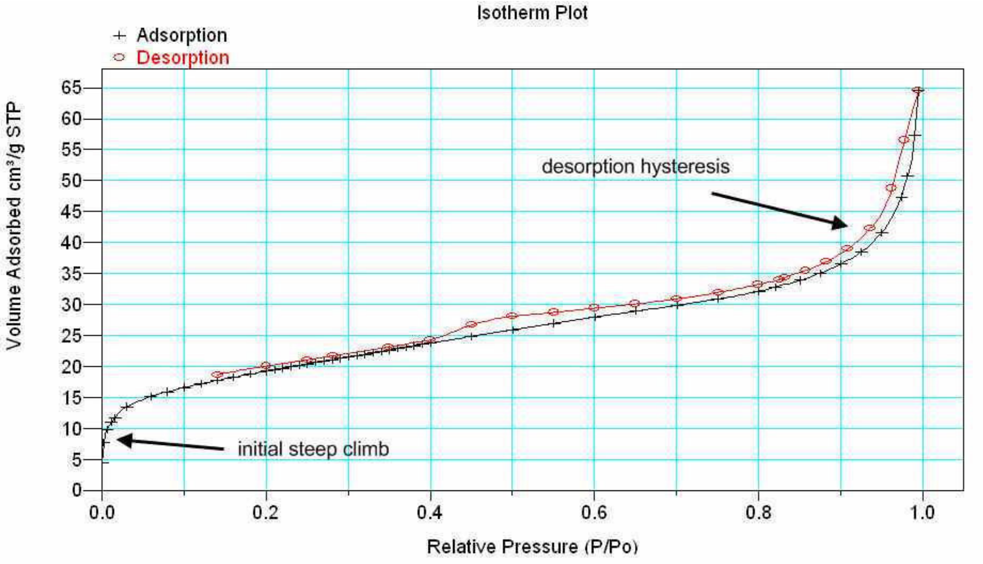

Fig. 5.2: N_2 Adsorption Isotherm Plot for expanded lignin sample (surface area 69 m^2g^{-1})

5.2.3 Application of mesoporous lignin

The use of expanded lignin as a stationary phase for column chromatography was tested by attempting to separate ferrocene/ acetylferrocene/diacetylferrocene on a column of unmodified lignin (surface area 0 m^2g^{-1}) and a column of the expanded material (surface area 58 m^2g^{-1}). This system was chosen due to the ease of visual and GC identification of the different fractions upon elution from the column (Figure 5.3). The columns were eluted with solvents of varying polarity and fractions collected. In the case of unmodified lignin, all components were removed from the column by the solvent, hexane, showing little affinity between it and the components to be separated. Modified lignin showed superior separation properties. Visual inspection of isolated fractions showed expected variation in the colours of the samples (Figure 5.3 C). The fractions were analysed by GC and showed good separation of components with each fraction containing a single major component (Figure 5.3 B).

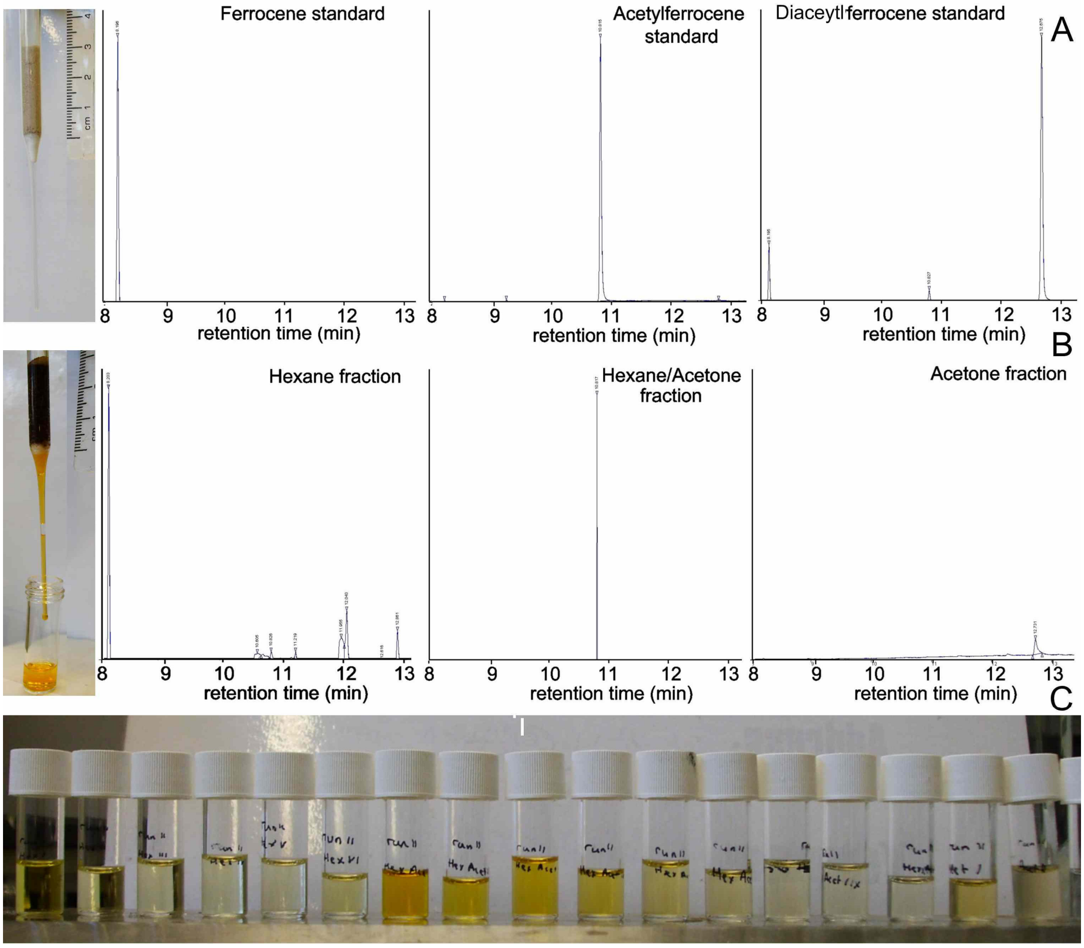

Fig. 5.3: Ferrocene / acetylferrocene / diacetylferrocene separation (A) Column of expanded lignin and GC trace of standards (B) Fraction during separation (C) Fractions collected from column

These initial investigations were seen as a promising application of the expanded material but no further work was carried out in this area due to issues with the reproducibility of the surface area properties of the expanded materials.

5.2.5 Reproducibility of Surface Area Results

In order to be able to draw conclusive results from this study it would have been necessary to achieve reproducible results. Several gels prepared using the same conditions resulted in different surface areas with differences of up to 50 m^2g^{-1} (Table 5.2). Elemental analysis of the material showed it to contain much lower levels of carbon than would be expected and spectroscopic analysis offered little indication of the makeup of the products. While the results included here were promising it was decided to conclude this investigation to focus on the thermal transformations of lignin and biomass in to fuel and chemicals (Chapters 2 to 4).

Possible future work in this area could look to further characterise the solid by determining inorganic content and microscopic structure. The composition of the solvent exchange washes should also be determined. This could provide an interesting insight into the fate of organic components, perhaps containing break down products of lignin which should be identified.

5.3 Pilot-scale trials of microwave treatment of biomass

The ideal biomass treatment process should be capable of handling large volumes continuously, yielding high calorific value products with minimum energy input (Figure 5.4).

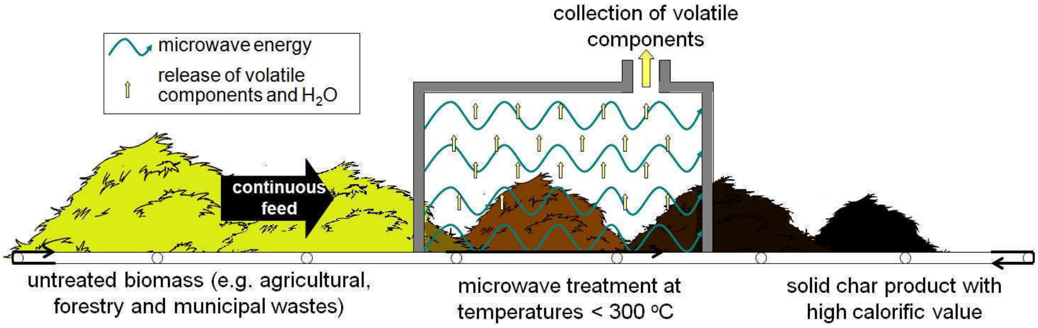

Fig. 5.4: Continuous processing of biomass for production of high calorific value products

Following the success of the lab work, funding was provided by Yorkshire Forward, the Regional Development Agency, to carry out pilot scale studies as part of a proof of concept project. Pilot-scale trials (5 – 25 kg of starting material) on the continuous microwave processing of biomass were carried out using facilities at Rotawave Ltd., Sandycroft, Deeside, Clwyd in August 2008 as described in experimental section 7.2.7. Samples of rolled oats, wheat straw pellets and miscanthus were processed for the isolation of oils and preparation of solid chars for fuels. Figure 5.5 shows the scale of the tests. Biomass samples were loaded into the microwave by bucket and products collected in similar quantities.

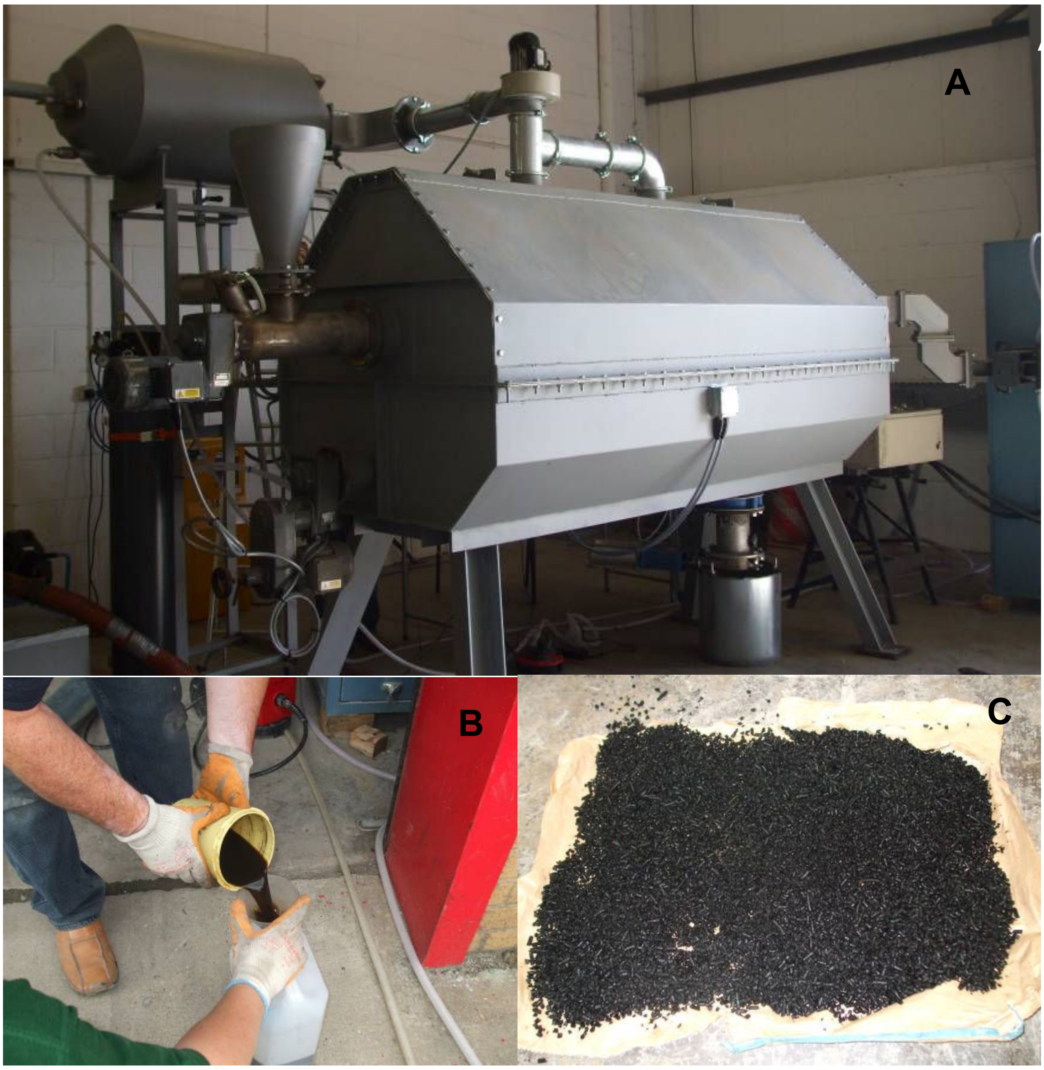

Fig. 5.5: Pilot scale biomass microwave trials. A: Rotawave trial microwave B: Wheat straw pyrolysis oil C: Wheat straw pellets after microwave treatment.

Figure 5.6 shows a schematic of the microwave processor. Before loading samples, the microwave chamber was flooded with nitrogen in order to provide an inert environment. The sample was then introduced into the chamber via a screw feed, where it was mixed and heated to between 80 – 100 ^{o}C before treatment in order to maximise the efficiency of the process.

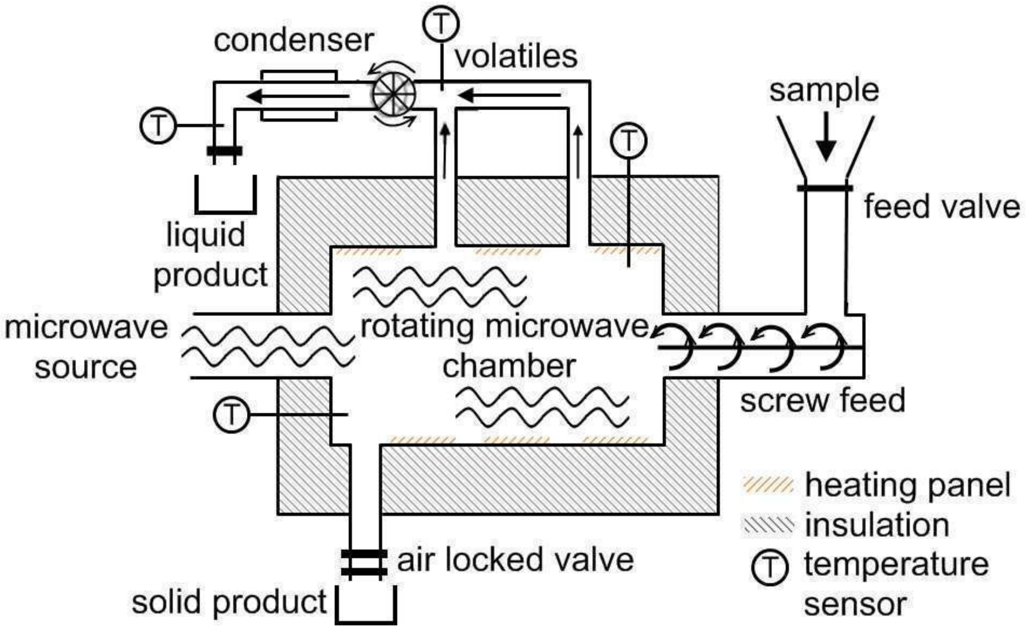

Fig. 5.6: Schematic of Rotawave microwave processor

The biomass remained in the microwave for an average residence time of 15 minutes before being discharged through an air locked valve. Due to the temperature of the char product, it was necessary to discharge into water to prevent risk of combustion upon exposure to air. This risk could be minimised in a purpose built system by discharging the solid through cooled air lock systems. Volatile components were drawn out and condensed via a water cooled condenser for collection. As the microwave was not designed for the trapping of such large volumes of liquid the condensation process was highly inefficient with significant amounts of product being lost as gases. The liquid fraction was also highly diluted by water used to clean the microwave between runs.

While the operating conditions were far from ideal, the scaled up studies produced chars of similar calorific value to those produced in the lab (Table 5.3) along with significant amounts of liquid which were not collected. These results showed low temperature microwave processing to be a versatile and scalable method for producing fuels from biomass.

Table 5.3 shows the preparation conditions and properties of the best chars produced (see Appendix 1 Table 5 for additional information). In agreement with the laboratory studies, the bulk properties of the biomass showed a strong influence on the efficiency of the microwave interaction. The dense wheat straw pellets absorbed the microwave energy well requiring a lower energy input to reach similar temperatures as the other biomass feedstocks, while the diffuse miscanthus straw required much higher energy inputs.

Table 5.3: Char preparation conditions and properties

Biomass Type	Mass (kg)	T (^{o}C)	Microwave energy expended		Bulk density	Char Calorific Value pilot scale (kJ g^{-1})	Char calorific value lab scale (kJ g^{-1})	Elemental composition (%)		
			kJ	kJ/kg				C	H	N
Wheat straw pellets	12	166 - 175	21,600	1,800	high	23.1	22.4	61	4	1.1
Miscanthus	2.4	160 - 165	8,550	4,800	low	22.4	24.6	52.7	3.2	1.1
Cocoa husk	4.3	151 - 190	14,520	3,400	medium	28.2	22.1	54	3	2.5

While the energy input is high when compared to other pre-treatment methods such as peletisation (250 kW h tonne^{-1} vs. 28 kW h tonne^{-1}), the production of additional liquid and gas products and further optimisation of the process should result in a favourable energy balance. Liquid fractions collected contained high levels of water, this along with a lack of suitable storage conditions made it difficult to accurately analyse the composition of the liquid fraction. The nature of the system did not allow for proper cleaning between trials. As a result, high levels of cleaning water and contaminants remained within the microwave and were carried over into the liquid fraction of the subsequent run. Figure 5.7 shows the fractionation of the collected liquid into various solvents as an approximation of the nature of the mixture. Over 75 % of the mixture partitioned in the first water washes, including dissolved water in the bio-oil. The resulting bio-oil was then washed sequentially with hexane, toluene, dichloromethane, chloroform and ethylacetate.

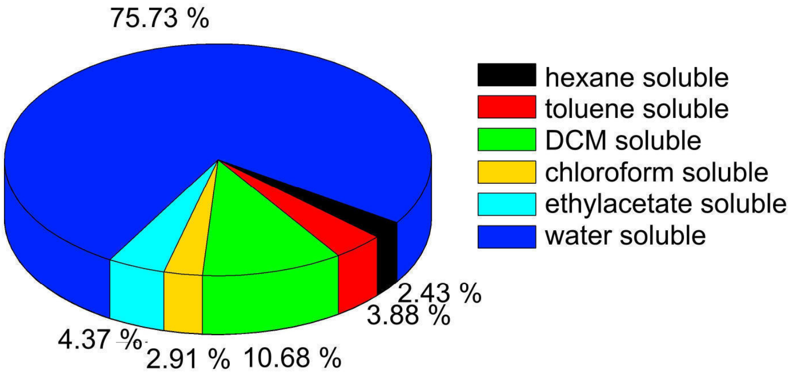

Fig. 5.7: Fractions of liquid product of microwave treatment of wheat straw

The lowest proportion was soluble in hexane, the most non-polar solvent, as is to be expected from the typical composition of bio-oils.[7] The remainder partitioned between the other solvents which varied in polarity from 2.4 (toluene) to 4.4 (ethylacetate) indicating the majority of components are polar in nature.[8]

Further optimisation of this process should provide a route to in-situ separation of water from organic components during bio-oil production.

Studies on the scalability of this process are being continued in the purpose-built microwave facility in the Green Chemistry Centre at the University of York.

5.4 References

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Chapter 6: Concluding remarks and future work

Biomass is a versatile and important source of energy, and a rich potential feedstock for the chemical industry. In an attempt to alleviate fossil fuel usage and reduce global CO_2 emissions, it has been cited as a strong alternative. Development of biofuels is being driven by worries over energy security, climate change mitigation, and agricultural and economic development targets.

In terms of commercialisation of lignocellulose-based biofuels, it is still difficult to determine which route will become most successful. The direct combustion of biomass is a simple and straightforward method of accessing energy stored in biomass, but material handling issues along with inorganic components and moisture pose obstacles to widespread industrial scale application. As a result, there is widespread interest in technology to upgrade the value of biomass as a fuel. It is likely to be the case that several technologies will come into widespread use depending on the regional situation. Climate and soil type will determine the crops that are utilised, while the end use of the fuel will influence the process.

Independent of all these factors will be the need to have a process which is versatile, scalable and suitable for continuous production, while also being energy efficient and environmentally benign. The patented work (Appendix 2) described in this thesis has shown for the first time the ability to produce high calorific value fuels from the microwave treatment of biomass at temperatures below 300 °C.[1-3]

This technology offers many advantages over current bioenergy systems. Microwave technology is relatively mature and suitable for implementation on a variety of scales.[4] The benefits of microwave technology for fuel production have been reported by many researchers,[4-13] but the work described in this thesis has gone beyond that previously reported by proving milder operating conditions can produce quality products.

Microwave processing of biomass components was shown in Chapter 2 to reduce the preparation temperature of high calorific value chars by up to 150 °C. Through interactions with groups within the amorphous region of cellulose, microwave-induced dipolar polarisation and ionic conduction leads to acid catalysed decomposition of the entire cellulose. Similar increases in calorific value of xylan chars were also observed at temperatures lower than those required under slow pyrolysis conditions.

Building on this knowledge, it was shown that microwave processing can be used to treat whole biomass to produce significant yields of high calorific value chars (Chapter 3) and oils (Chapter 4) at low temperatures. Results were reported for three diverse types of biomass available for use in the UK. Each one produced high calorific value chars through microwave processing at low temperatures. More in depth studies on microwave treatment of wheat straw showed it is possible to produce bio-oils similar to those produced through conventional fast pyrolysis. The success of the laboratory results led to scale up trials, which enabled further proof of the concept and its applicability (Chapter 5.2).

The improvements reported in this thesis not only offer energy savings by operating at low temperatures, but also reductions in capital costs as the system does not need to be capable of tolerating extremes of temperatures. The work has been shown scalable from less than 1 g to over 15 kg with minimal changes to the operating conditions or loss of product quality. The operation of microwave systems requires low skill training, with safety cut offs easily automated. As a result microwave processing of biomass is a safe, scalable option for the production of energy from biomass. The scalability also makes the technology suitable for distributed energy production (Figure 6.1), an option cited by many as being necessary to improve the overall economics of biofuel production.

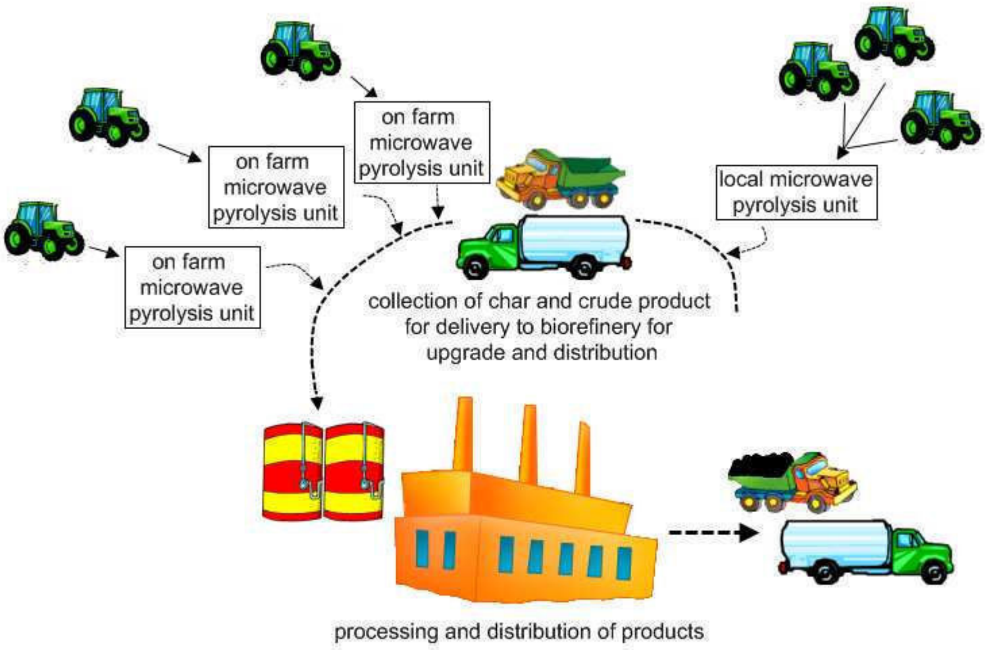

Fig. 6.1: Distributed energy production minimising energy used in transport of biomass

By processing biomass and producing biofuels close to the source, there is greater potential for economic benefits to be felt by the area. Implementation of distributed energy production also reduces energy spent transporting the moisture-rich low-density biomass. By transporting after processing, only components which add to the energy value of the product will be taken.

To demonstrate the economic viability and further validate the merits of the microwave system, a basic energy balance was calculated. Figure 6.2 shows the calculation boundaries which were limited to energy used for field production, storage and processing of the biomass but to exclude distribution of products to users (e.g. power plants or pyrolysis oil upgrading facilities).[14] The calculations were based on established norms, assuming transport of material up to 150 km before processing. The energy efficiency would be greater if distributed energy generation were to be implemented.

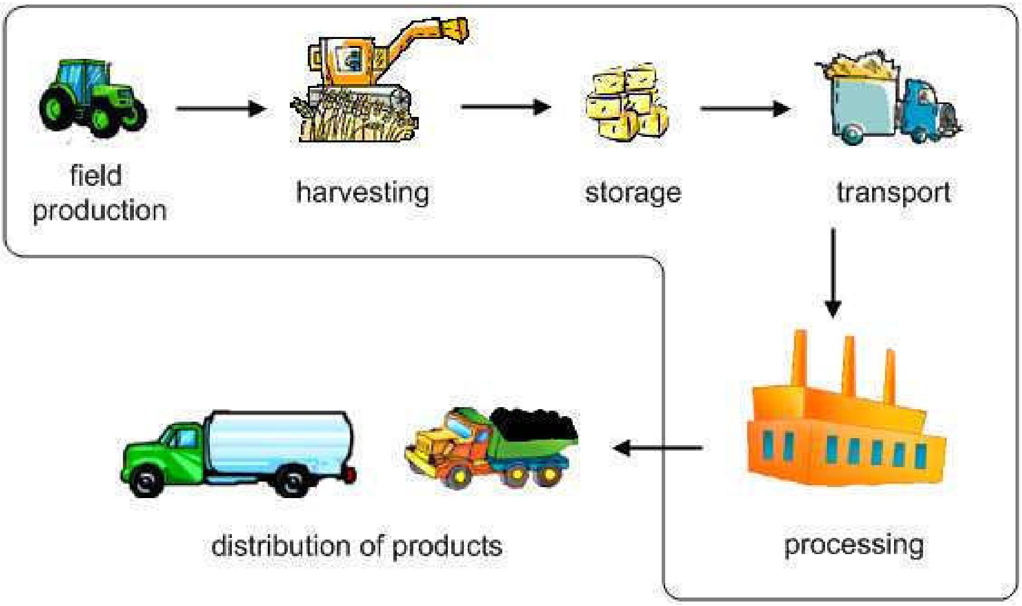

Fig. 6.2: Boundaries of energy calculations

Table 6.1 shows the results of the energy balance calculated on the basis of reported and experimental data (Appendix 1). These preliminary calculations show enormous benefit. The energy value of the product is over 20 times that of the energy inputs, with the final microwave processing stage contributing less than 5 % of the overall energy input. This final processing step produces a renewable solid fuel capable of being used as a direct substitute for fossil fuels, while the liquid fraction is of superior quality to conventional pyrolysis oil and suitable for direct use or upgrading into a hydrocarbon fuel. Energy inputs could be decreased further by processing the material on a local level.

Table 6.1: Energy balance for production of fuels from biomass using microwave processing

Energy (kJg^{-1})	Miscanthus	Wheat straw pellets
Inputs:		
Field production & harvesting	0.53	0.36
Processing & transport	0.36	0.42
Pellet production	-	0.1
Microwave energy for optimised char production (% of total)	0.043 (4.6 %)	0.0144 (1.6 %)
Total energy inputs	**0.933**	**0.894**
Char calorific value	**24.59**	**22.00**
Energy value of output/energy input (kJ/kJ)	**26.4**	**24.6**
Microwave energy for optimised char and oil production (% of total)	-	0.0086 (0.96 %)
Total energy inputs		**0.8886**
Char calorific value	-	21.2
Oil calorific value	-	15.9
Average calorific value of products		**18.9**
Energy value of output/energy input (kJ/kJ)		**21.3**

Data reported on the energy efficiency of conventional pyrolysis, puts the energy yield (energy value of output/energy input) at between 3 and 9 kJ/kJ depending on the biomass type and pyrolysis system used.[15, 16] As can be seen from table 6.1, this level is well below that found for the microwave processing of biomass described in this thesis (21 – 26 kJ/kJ).

This work described is only the initial development and understanding of this new process. These results have formed the basis of project proposals which have gained £1.5 million of funding for the Department of Chemistry at the University of York from the European Regional Development Fund, the Carbon

Trust and METRC (The N8 Molecular Engineering Translational Research Centre).[17-19] This money has supported the opening of a dedicated microwave facility with dedicated research staff. Future research will focus on further characterisation of pyrolysis products, in particular the bio-oil, in order to provide deeper understanding of the mechanisms occurring within the biomass during microwave treatment. A wider variety of biomass feedstocks must also be investigated to prove the versatility of the system. Non fuel applications of the products (e.g. high value chemicals) should be investigated along with new applications for lignin as added value product streams.

Mankind has an ever increasing thirst for energy. A secure supply of energy will be essential for development but must be realised with minimal environmental impact. Society will have to move from an economy based on fossil fuels to a more sustainable energy mix. This will require development of sustainable energy solutions and more efficient ways of producing them.

The work reported here has shown for the first time, that microwave irradiation at low temperatures can have a dramatic effect on the decomposition of major components in plant biomass. This influence has been proven both in terms of the temperature at which carbonisation occurs and the properties of the char and oil produced. The process yields high quality products, which can strengthen the case for the use of biomass for energy production both as a solid and liquid fuel. The process has low energy consumption and can be easily adapted to a variety of biomass. This technology has been proven as a green and flexible method of upgrading biomass for energy applications, supporting progress to a society which is no longer reliant on fossil fuels.

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Chapter 7: Experimental methods

7.1 Materials and reagents

Sample	Source	Properties	Characterisation
Miscanthus	Charles Jackson Ltd., Northampton	Milled Particle size: ≥ 4 mm Approximate moisture content on arrival: 27 %	Fig 3.4, 3.9
Wheat straw	Charles Jackson Ltd., Northampton	Milled Particle size: ≥ 4 mm Approximate moisture content on arrival: 19 %	Fig 3.4, 3.10
Wheat straw pellets	Charles Jackson Ltd., Northampton	8 mm pellets Approximate moisture content on arrival: 6 %	Fig 3.4
Cocoa husk	Nestlé UK	Non-uniform particles Approximate moisture content on arrival: 13 %	Fig 3.4, 3.11
Cellulose	SigmaAldrich	Form: fibres Particle size: medium	Fig. 2.8, Table 2.1, Fig. 2.12
Lignin	Processum Biorefinery & Umeå University, Sweden	Produced through acid hydrolysis of pine wood.	
Lignin (alkali)	SigmaAldrich	Mol wt: average ~10,000 total impurities: 4 % sulfur pH: 10.5 (3 wt. %)	
Xylan (from beech wood)	SigmaAldrich	>90% xylose residues	Table 2.3, Fig. 2.19, 2.21
sodium lauryl sulfate	SigmaAldrich	ACS reagent Assay: ≥99.0 %	

		Total impurities: ≤0.06 meq/g Titr. Base ≤8.0 % NaCl + Na2SO4 ≥96.0 % fatty alcohols <4.0 % unsulfated alcohols
Ethylene – diamine-tetraacetic acid disodium salt dihydrate	SigmaAldrich	ACS reagent Assay: 99.0-101.0 % total impurities: ≤0.005 % insoluble matter ≤0.1 % Nitrilotriacetic acid ([HOCOCH2]3N) pH: 4.0-6.0 (25 °C, 5 %)
disodium hydrogen phosphate	SigmaAldrich	ACS reagent Assay: ≥99.0 % total impurities: ≤0.002 % Chloride (Cl) ≤0.01 % insoluble matter ≤0.2 % loss on drying, 105 °C pH: 8.7-9.3 (25 °C, 5 % in solution)
sodium tetraborate decahydrate	SigmaAldrich	ACS reagent Assay: ≥99.5 % total impurities: ≤0.005 % insoluble matter pH: 9.15-9.20 (25 °C, 0.01 M in solution)

Analytical grade acetone, ethanol and dichloromethane were obtained from Fisher Scientific. Gases used for elemental analysis were high purity oxygen (BOC), with CP-grade He as the inert carrier gas (BOC).

Before use, biomass samples were oven dried at 110 °C until a constant weight was reached. Samples were then kept at atmospheric conditions before use resulting in an average moisture content of 4 – 7 %.

7.2 Sample preparation

7.2.1 Study of direct microwave effect on cellulose (Chapter 2)

Using a glass pipette, sealed at one end, a narrow closely packed column of cellulose was prepared. The upper half of the column was wrapped with aluminium foil to protect from microwave energy. The column was then placed in a microwave tube filled with tetradecane to ensure even distribution of heat throughout the tube (Figure 7.1). The microwave tube was placed in a CEM Discovery laboratory microwave (power: 300 W) and heated to 300 °C. The sample was visually examined after heating to determine any differences in behaviour due to exposure to microwave irradiation.

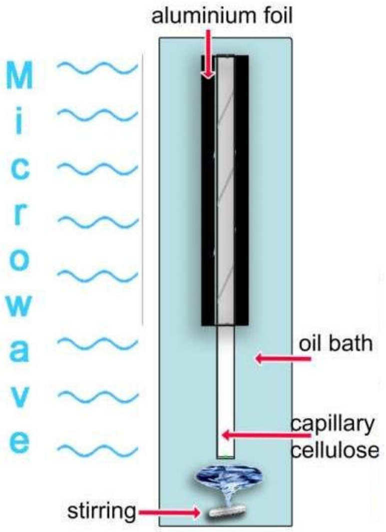

Fig. 7.1: Investigation of direct microwave effect

7.2.2 Microwave treatment of biomass for char production (scale: <1 g) (Chapter 2 & 3)

Biomass sample (200 mg) was weighed out into a microwave tube containing a magnetic stirring flea, and then sealed using the microwave tube lid. The sample was placed in a reaction tube in a CEM Discovery laboratory microwave. The sample was irradiated under constant power of 300 W to reach the target temperature (100-

300 ^{o}C) after which the sample was immediately cooled, Figure 7.2 shows a typical heating profile for cellulose. After microwave treatment, the sample was removed from the vessel and washed with acetone to remove condensed volatile components. The mass of solid lost as a result of microwave treatment was carefully monitored. The calorific value of the dried solid was measured using a *Stanton Redcroft* STA 625 as outlined in 7.3.1.

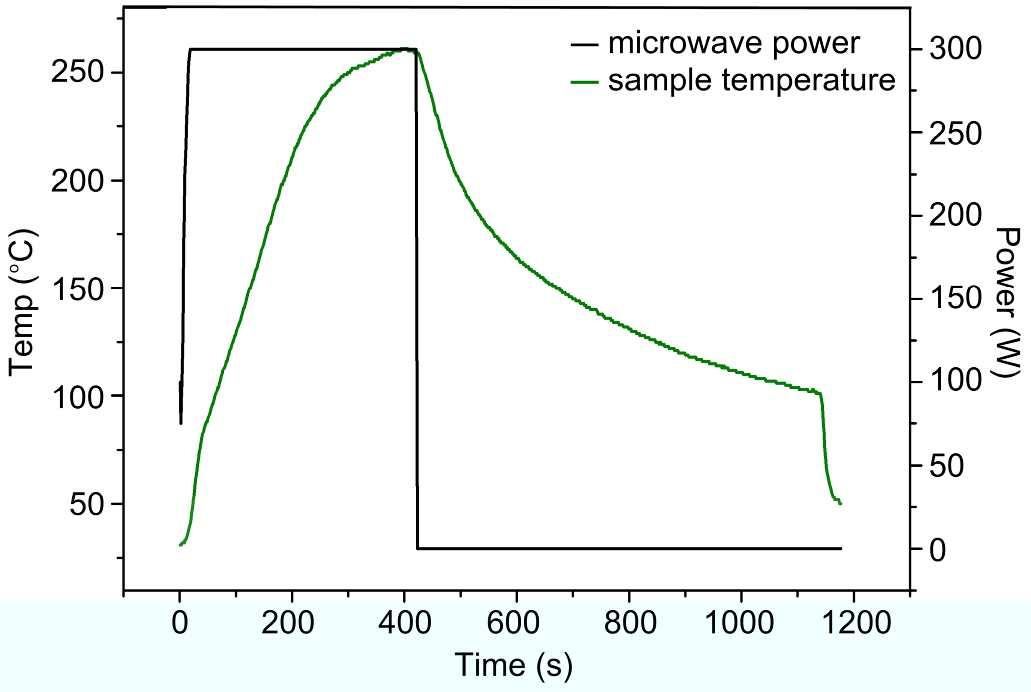

Fig. 7.2: Typical heating profile for preparation of cellulose sample in CEM discovery (scale < 1 g)

7.2.3 Preparation of conventional chars through slow pyrolysis and torrefation (Chapter 2 & 3)

Conventional chars were prepared in a Netzsch STA 409. The raw material was heated to a target temperature at a rate of 10 ^{o}Cmin^{-1} under a flow of N_2 (100 mLmin-1) in order to keep ramp rate similar to microwave preparation. The sample was cooled quickly by increasing the flow of N_2 to 500 mLmin^{-1}.

7.2.4 Microwave treatment of biomass for char and oil production (scale: 2-6 g) (Chapter 3)

The biomass sample (2-6 g) was weighed out into a round bottom flask. Using a system designed for this work, a two-necked adapter was attached to the round bottom flask with one inlet allowing a flow of nitrogen to ensure no oxidation of the materials during the run and the second connected to a water-cooled condenser to collect the volatile products evolved. A dichloromethane trap was connected in series with the round bottom flask to capture volatile components, as shown in Figure 7.3.

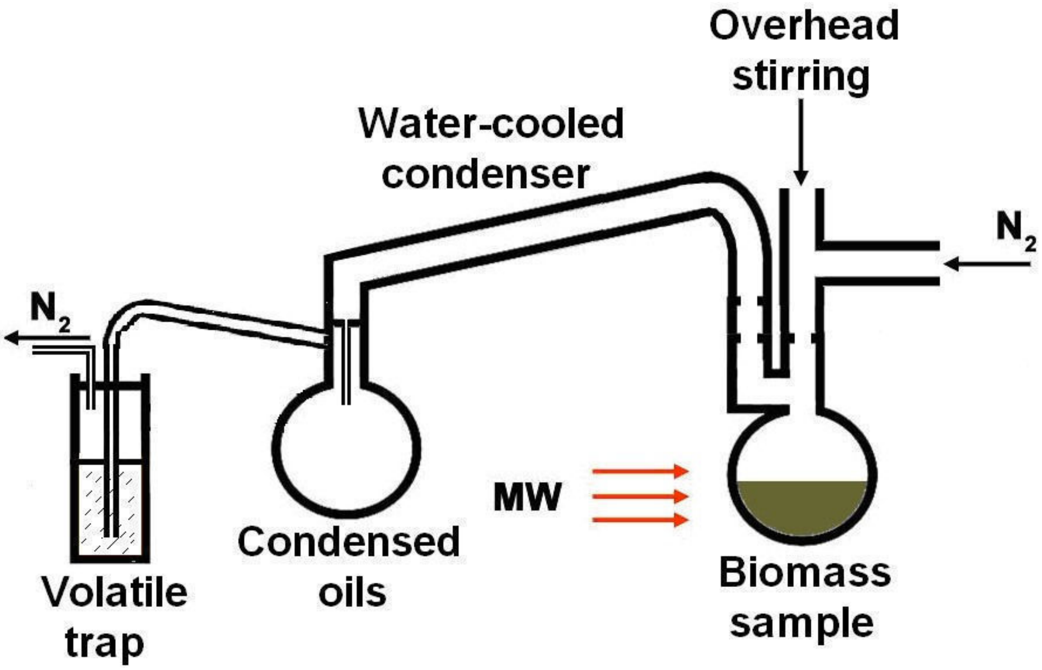

Fig. 7.3: Apparatus set-up for microwave processing on 2 – 6 g scale

7.2.5 Microwave treatment of biomass for char and oil production (scale: 8-500g) (Chapter 3 & 4)

Microwave treatment for samples greater than 8 g was carried out using a Milestone ROTO SYNTH Rotative Solid Phase Microwave Reactor (Milestone Srl., Italy) fitted with a VAC 2000 vacuum module in series which allows condensation and collection of volatile components (Figure 4.1). Temperature was measured via remote infrared sensor, and verified by thermocouple measurements during process development. Both temperature and pressure readings were monitored on the control panel.

Biomass (8 - 500 g) was weighed into the microwave vessel and placed in the microwave. The sample was heated under vacuum in the presence of nitrogen. Volatile components were collected after condensation in the vacuum unit. Operating conditions were typically: power: 400-1200 W, temperature: 50-250 ^{o}C.

7.2.6 Use of additives (Chapter 4.2)

H_2SO_4:

Wheat straw pellets were agitated in an aqueous solution of sulphuric acid (5 % w/w). The water was removed *in vacu* at 60 ^{o}C resulting in deposition of 5 % w/w H_2SO_4 on the wheat straw sample.

NH_3, HCl:

Ammonia and hydrochloric acid were introduced into the sample as gases produced following the equations (1) and (2). The gas flowed through the sample which was mixed repeatedly during the process to ensure even distribution throughout. The final concentration of additive on the wheat straw was approx 5 % w/w as determined by weighing the sample before and after process.

Equation (1): $NH_4Cl + NaOH \rightarrow NH_3 + NaCl + H_2O$

Equation (2): $2NaCl + H_2SO_4 \rightarrow 2HCl + Na_2SO_4$

7.2.7 Microwave treatment of biomass for char and oil production (scale: 5-50 kg) (Chapter 5.2)

Pilot scale processing of biomass was carried out using the facilities at Rotawave Ltd., Sandycroft, Clwyd. Biomass samples of up to 20 kg were fed into the rotary microwave system, through the feed valve. The sample enters between the 2 valves shown (Figure 5.6), where the system is flushed with N_2 before addition to the microwave chamber. The sample has an average residence time in the chamber of 15 minutes before discharge through a similar air locked system, maintaining an inert processing environment.

7.2.8 Formation of expanded materials from lignin (Chapter 5.1)

Suspensions of lignin (100 g/L) were prepared in NaOH (2 N). The aqueous mixture (4 mL) was heated in the microwave under various conditions (Temperature: 180 – 200 ^{o}C; Time: 5 – 20 min; Power: 100-300 W). Sulfuric acid (30% v/v) was added drop-wise to the resulting solution until a gel was seen to form. A solvent exchange was carried out on the stable gel to produce powder (Figure 5.1). Water was replaced with a lower surface tension solvent to prevent damaging the structure during drying, by sequentially washing five times with ethanol (30 mL) and three times with acetone (20 mL).[1] The product was thereafter dried under vacuum over night at 60 ^{o}C to yield a powder.

7.3 Characterisation of feedstocks and products

7.3.1 Measurement of calorific value (Chapters 2-5)

Calorific value (low heating value) measurements were carried out on a Stanton Redcroft Simultaneous Thermal analyzer, STA 625 using a method developed by Dr. V. Budarin and Dr. P. Shuttleworth. A 50:50 mixture of biomass and palladium oxide was heated at 5 ºC min^{-1} from 20 ºC to 625 ºC in a 50 mL min^{-1} flow of air and the low heating value was calculated by integrating the resulting thermogram. Figure 7.4 shows a typical thermogram, calorific value (CV) was calculated using the formula below:

$$\text{C.V. (J/g)} = \frac{\text{area under peak (mcal/mg)} * 4.1868}{\text{dry mass (\%)}}$$

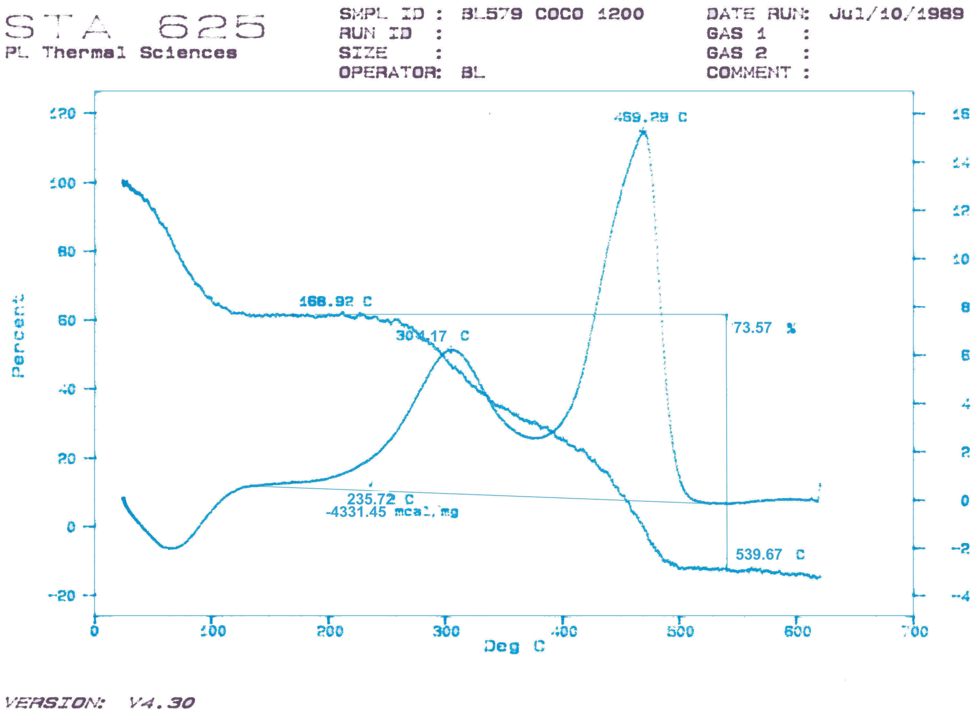

Fig. 7.4: Typical thermogram collected for measurement of calorific value

Worked example:

Using the data shown in Figure 7.6, the calorific value can be calculated as:

$$\left(\frac{4331.45 * 4.1868}{0.7357}\right) \Big/ 1000 = 24.65\ \mathrm{kJg^{-1}}$$

The method was calibrated through measurement of calorific value of standard carbohydrate materials and validated through comparison with external measurements on twin samples (see Appendix 1 for external analysis data).

7.3.2 Infra-red analysis (Chapters 2 – 5)

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded on a Bruker EQUINOX-55 instrument equipped with a liquid N_2 cooled MCT detector. The samples for DRIFT studies were prepared by grinding the analyte to a fine powder using a pestle and mortar. Typically 0.2-0.5 wt % of sample in KBr (as a diluent) was ground together. 1024 scans were used to compile each spectrum with a resolution of 2 cm^{-1}.

DRIFT spectra were recorded for samples of cellulose at 10 - 15 ^{o}C temperature intervals between 120 and 230 ^{o}C. The samples were loaded in a controlled temperature chamber and measurements made under a flow of N_2 using the spectrometer setting listed above. The crystallinity index of samples was calculated from the ratios of the absorbance bands A_{1430}/A_{898}.[2, 3]

7.3.3 Deuteration of cellulose for analysis (Chapter 2)

Cellulose samples were stirred overnight in D_2O in a sealed vessel at 180 ^{o}C, the temperature at which all hydroxyl groups in the amorphous region are replaced by deuterium atoms.[4] The cellulose was cooled, filtered and dried under vacuum before use.

7.3.4 FTIR analysis of volatile components released during microwave treatment (Chapter 2)

Cellulose was exposed to microwave irradiation using in the CEM Discovery open vessel mode. Experiments were done under microwave power 300 W. As shown in Figure 7.5, volatiles were captured and carried through a heated tube at 200 °C to a heated cell within a Bruker EQUINOX-55 FTIR instrument equipped with a liquid N_2 cooled MCT detector. 32 scans were used for spectrum recording.

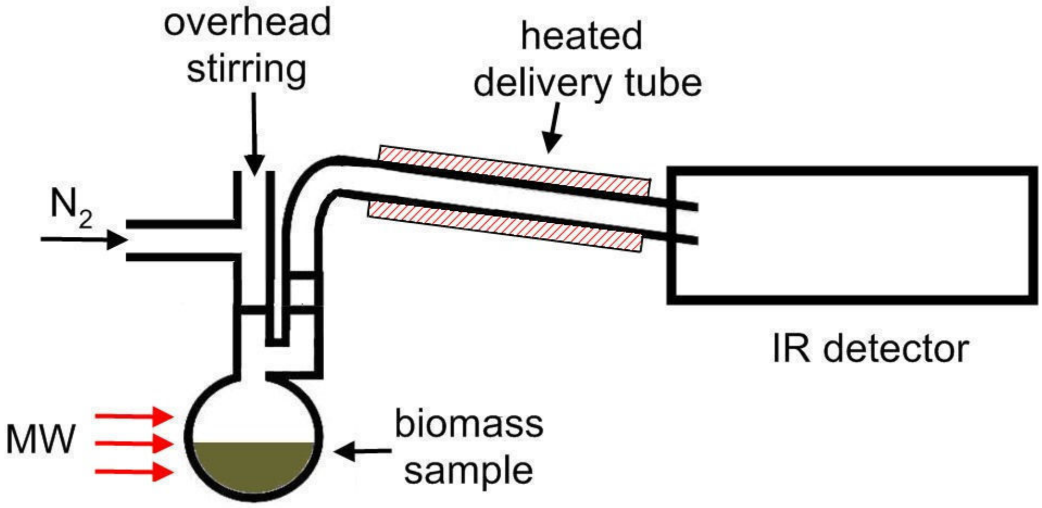

Fig. 7.5: Schematic of experimental set-up

7.3.5 Elemental analysis of biomass and chars (Chapters 2 – 5)

Elemental analysis based on carbon, hydrogen and nitrogen content was carried out through the departmental service using an Exeter Analytical (Warwick, UK) CE440 Elemental Analyser, calibrated against acetanilide with a S-benzyl-thiouronium chloride internal standard.

7.3.6 Modulated differential scanning calorimetry (Chapter 2)

Cellulose samples were weighed and sealed in T-Zero aluminium DSC pans topped with lids containing a pin hole to allow loss of water vapour. The samples were equilibrated at 5 °C for 10 min in the DSC chamber and then heated to 240 °C under the following modulated conditions: underlying heating rate, 5 ºC/ minute, an amplitude of ± 2 ºC, and a period of 60 seconds. The sample size used was between 15 and 20 mg.

7.3.7 Solid-state ^{13}C CP MAS NMR analysis of cellulose and cellulose chars (Chapter 2)

^{13}C CP MAS NMR spectra were obtained using a Varian VNMRS spectrometer operating at 100.56 MHz for ^{13}C. Referencing for all spectra presented is made with respect to tetramethylsilane, and was obtained at ambient temperature. Analysis was performed under standard ^{13}C CP MAS spectral acquisition was performed using a ^{1}H $\pi / 2$ pulse of 40.0 μs length and 5.0 s recycle, at a spin rate 6.7 kHz. A 4.0 mm zirconia rotor was used.

7.3.8 Characterisation of biomass composition (Chapter 3)

Ethanol-soluble components were determined by two sequential 250 mL ethanol soxhlet extractions of 50 g of biomass. The amount extracted was determined by removal of ethanol *in vacu* and measurement of the mass of the remaining residue.

Plant cell wall constituents were determined following the procedure outlined by Soest *et al*. A neutral detergent solution was prepared by adding to 1 L of distilled water: 30 g of sodium lauryl sulphate, 18.61 g ethylene diamine tetra acetic acid sodium salt, 6.81 g sodium tetraborate decahydrate, 4.56 g sodium phosphate dibasic and 10 mL 2-ethoxy ethanol. The solution was between pH 6.9 – 7.1. 100 ml of the neutral detergent solution was added to 1 g of biomass in the presence of 2 ml decahydrate naphthalene and 0.5 g sodium sulfite and refluxed for 1 hour. The solid was the removed by filtration, washed repeatedly with hot water and dried in the oven overnight. The mass of solid was taken to be equal to the total mass of cell wall components and ash in the biomass.[5]

Ash content was determined by decomposing the residue in the presence of air at 550 ^{o}C until a stable mass was reached.

All values were represented as percentage mass of the starting material. Analysis was done in duplicate and the average taken.

X-ray Fluorescence (XRF) analysis of feedstocks was carried out by compressing (~1g) of ground samples of straw or char into a holder and analysed on a Horiba XGT 7000 X-ray analytical microscope using a standardless independent parameters method. Each measurement was repeated five times and the average was taken.

7.3.9 Analysis of conventional pyrolysis oil (Chapter 4)

Fast pyrolysis oil was prepared from wheat straw and analysed in-situ. For each pyrolysis run, approximately 1 mg of sample was place in a 20 mm quartz silica tube using quartz wool plugs and heated in the pyroprobe in a purge of helium at 20 °C min^{-1} to the desired temperature (600 °C). The pyroprobe was held at maximum temperature for 20 s.

GC was performed using a CDS Analytical Pyroprobe 2000 interfaced to an Agilent Technologies 6890N Gas Chromatograph, using a CDS 1500 Interface. The oven was fitted with a 61.3 m, 0.25 mm i.d., 0.25 μm phase (14% cyanopropylphenyl, 86% dimethyl polysiloxane) thickness Rtx 1701 capillary column. An Agilent Technologies 5975B Inert XL Mass Selective Detector was coupled to the GC. The oven temperature was held at 40 °C for the first 2 minutes of each run, then heated at 4 °C min^{-1} to 250 °C, then held at final temp for 30 min, with a total run time of 84.50 minutes. Products were identified by comparison with NIST 08 library.

7.3.10 GC-MS analysis of microwave oils (Chapter 4)

Microwave oils were diluted in methanol (10 mg/ml)for GC analysis and automatically injected on to the GC using an Agilent 7683 Gas Chromatograph (injector temperature: 300 ^{o}C, volume: 1 μl). The oven was fitted with a Chrompack

CP-WAX 57 CB polar column for improved separation. The oven temperature was held at 60 °C for the first 2 minutes of each run, then heated at 6 °C min^{-1} to 150 °C, and at 5.6 °C min^{-1} to 290 °C then held at final temp for 14 min, with a total run time of 66 min. GC-MS characterisation was carried out under similar conditions using electron ionisation techniques.

7.3.11 Elemental composition of microwave oils (Chapter 4)

Elemental composition was carried out as outlined for the starting material (7.3.5).

7.3.12 Microwave oils water content (Chapter 4)

Water content was determined using an automated Karl Fisher Coulometer (Mettler Toledo DL32) by comparison to Karl Fischer Standard reagent (Fluka Chemicals). Samples were diluted tenfold in methanol before being added to the reaction cell.

7.3.13 Determination of acid number (Chapter 4)

Acid number was measured as the mass of potassiumhydroxide (mg) required to neutralise 1 g of analyte. The analyte was dissolved in methanol and titrated against KOH of known concentration in the presence of phenolphthalein. The end point was indicated by the colour change of colourless to pink. Due to the dark colour of the analyte it was difficult at times to determine the exact end point. pH measurements were made using universal indicator paper to validate acid number values.

7.3.14 ^{1}H NMR of microwave oils (Chapter 4)

Samples were prepared for ^{1}H NMR analysis by dissolving approximately 10 mg of sample in 2 mL of deuterated solvent (D_2O and $(CD_3)_2CO$) . Spectra were recorded on a JEOL 270 MHz NMR spectrometer using 128 scans in order to improve the signal to noise ratio. The spectra were interpreted based on integrals of the areas between 0.5 – 1.5 ppm, 1.5 – 3 ppm, 3 – 4.4 ppm, 4.4 – 6 ppm, 6 – 8.5 ppm and 9.5 – 10 ppm.[6] A typical NMR spectrum is shown in Figure 7.6; the spectrum was reintegrated in the chosen ranges using JEOL Delta software. The integral values within specified chemical shift ranges are shown in Appendix 1.

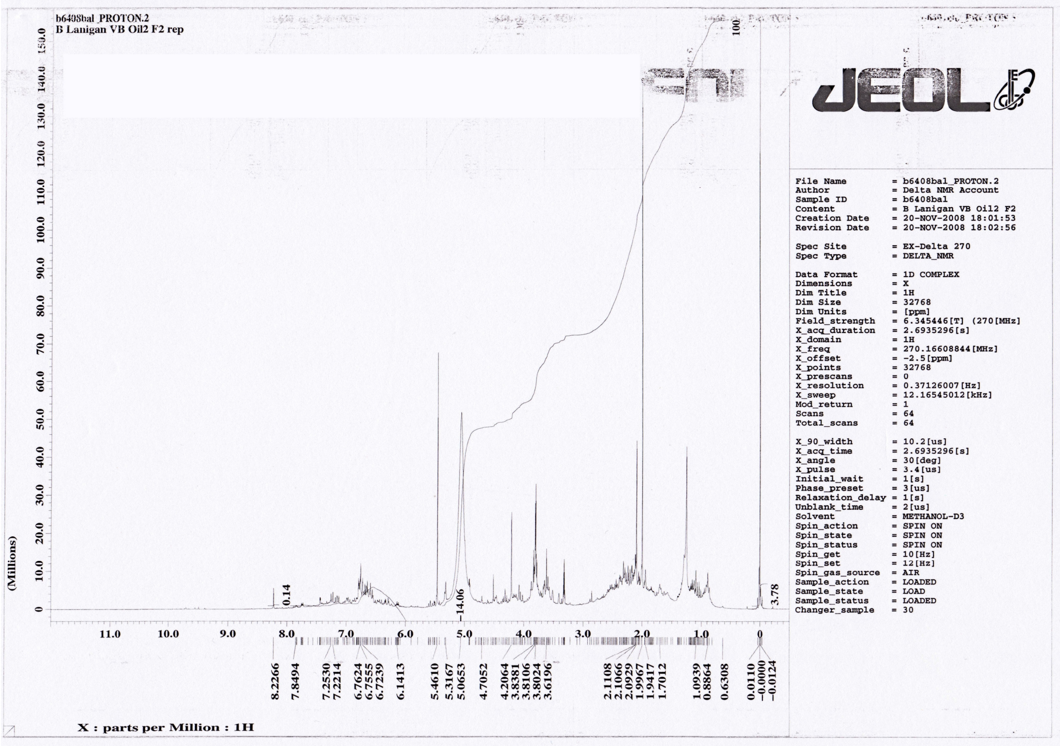

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Fig. 7.6: ^{1}H NMR of microwave wheat straw bio-oil

7.3.15 Surface area measurements (Chapter 5)

Surface area measurements were made using a Coulter SA3100. All samples (20-100 mg) were degassed at 60 °C prior to analysis. Nitrogen adsorption studies were carried out at 77 K and analysed using the BET method to determine surface area of the material. Further analysis was carried out on samples with surface area > 50 m^2g^{-1} using a Micromeritics ASAP 2010 under similar analysis conditions.

7.4 References

1. J. H. Clark, V. Budarin, F. E. I. Deswarte, J. J. E. Hardy, F. M. Kerton, A. J. Hunt, R. Luque, D. J. Macquarrie, K. Milkowski, A. Rodriguez, O. Samuel, S. J. Tavener, R. J. White and A. J. Wilson, *Green Chem.*, 2006, **8**, 853-860.
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4. Y. Horikawa and J. Sugiyama, *Cellulose*, 2008, **15**, 419-424.
5. P. J. Van Soest and R. H. Wine, *Journal of the Association of Official Analytical Chemists*, 1967, **50**, 50-55.
6. C. A. Mullen, G. D. Strahan and A. A. Boateng, *Energy & Fuels*, 2009, **23**, 2707-2718.

Appendices

Chapter 2

Table 1: Elemental composition of cellulose and chars

Material	Preparation Temperature (^{o}C)	C (%)	±	H (%)	±	N (%)	Rest (%)	±
Starting material		42.77	0.01	6.03	0.01	0.01	51.21	0.02
Microwave char								
	150	43.9	0.04	6.14	0		49.97	0.06
	200	44.51	0.03	6.00	0.02	-0.04	49.53	0.03
	225	45.43	0.05	5.90	0	-0.07	48.75	0.06
	250	50.10	0.04	5.38	0.03	-0.04	44.56	0.06
	270	64.25	0.01	4.34	0.01	0.01	31.39	0.04
	300	68.41	0.01	4.11	0.01		27.37	0.02
Conventional char								
	220	43.60	0.03	6.11	0.05		50.3	0.01
	296	43.79	0.02	6.05	0		50.17	0.03
	305	44.19	0.02	6.05	0.01	-0.02	49.79	0.03
	324	46.99	0.07	5.76	0.01	-0.06	47.31	0.07
	334	51.81	0.02	5.41	0.02	-0.07	42.85	0.04
	364	68.72	0.08	4.24	0.02	-0.03	27.08	0.1
	450	75.33	0.09	2.5	0.05	0.03	22.15	0

Table 2: Elemental composition of xylan and chars

Material	Preparation Temperature (°C)	C (%)	±	H (%)	±	N (%)	Rest (%)	±
Starting material		39.5	0.04	5.90	0.04	-0.01	54.61	0.08
Microwave char								
	180	43.36	0.07	5.70	0.05	-	50.95	0.07
	200	46.30	0.13	5.62	-	-0.03	48.11	0.1
	220	52.48	0.06	5.39	0.03	0.02	42.11	0.08
	240	56.3	0.05	5.15	0.01	0.04	38.51	0.05
	260	61.43	0.72	4.95	0.10	0.04	33.57	0.64
	300	66.66	0.05	4.72	0.03	-0.03	28.65	0.12
Conventional char								
	200	43.18	0.01	5.72	0.05	-	51.12	0.01
	220	42.04	0.04	5.74	0.05	-	52.23	0.03
	240	43.82	0.08	5.56	0.02	0.02	50.6	0.08
	270	47.49	0.2	5.55	0.05	-	46.95	0.2
	285	53.83	0.02	5.36	0	-	40.8	0.01
	300	60.48	0	5.07	0.01	0.08	34.45	0.02
	400	69.23	0.12	4.68	0.01	0.09	26	0.13
	360	63.98	0.01	4.84	0.01	-	31.12	0.02

Chapter 3

Table 3: Elemental composition of biomass and chars

Material	Preparation Temperature (^{o}C)	C (%)	±	H (%)	±	N (%)	Rest (%)	±
Miscanthus								
Starting material		41.88	0.32	5.29	0.02	0.7	52.18	0.59
Char								
25 min 800 W	125	48.38	0.11	4.62	0.05	0.93	46.08	0.13
25 min 1200 W	152	50.16	0.1	4.40	0.01	0.92	44.53	0.08
conventional	640	59.38	0.68	1.86	0.05	0.76	38.01	0.69
Wheat straw								
Starting material		40.21	0.23	5.34	0.12	0.7	53.76	0.5
Char								
Pellet 5 min 1200 W	182	54.86	2.03	3.90	0.164	0.91	40.34	2.18
WS 07 25 min 1200 W	171	54.38	0.19	4.58	0.31	0.63	40.41	0.17
WS 08 25 min 1200 W	164	49.80	0.1	4.81	-	0.76	44.63	0.13
conventional	640	67.46	0.05	1.97	0.05	0.93	29.64	2.15
Cocoa husk								
Starting material		42.24	0.2	5.4	0.01	2.9	49.4	0.14
Char								
25 min 1200 W	143	47.35	0.32	4.38	0.08	3.32	44.96	0.42
conventional	640	59.21	0.01	1.8	0.01	2.29	36.7	0.05

Chapter 4 & 7

Integration of NMR for Figure 4.6

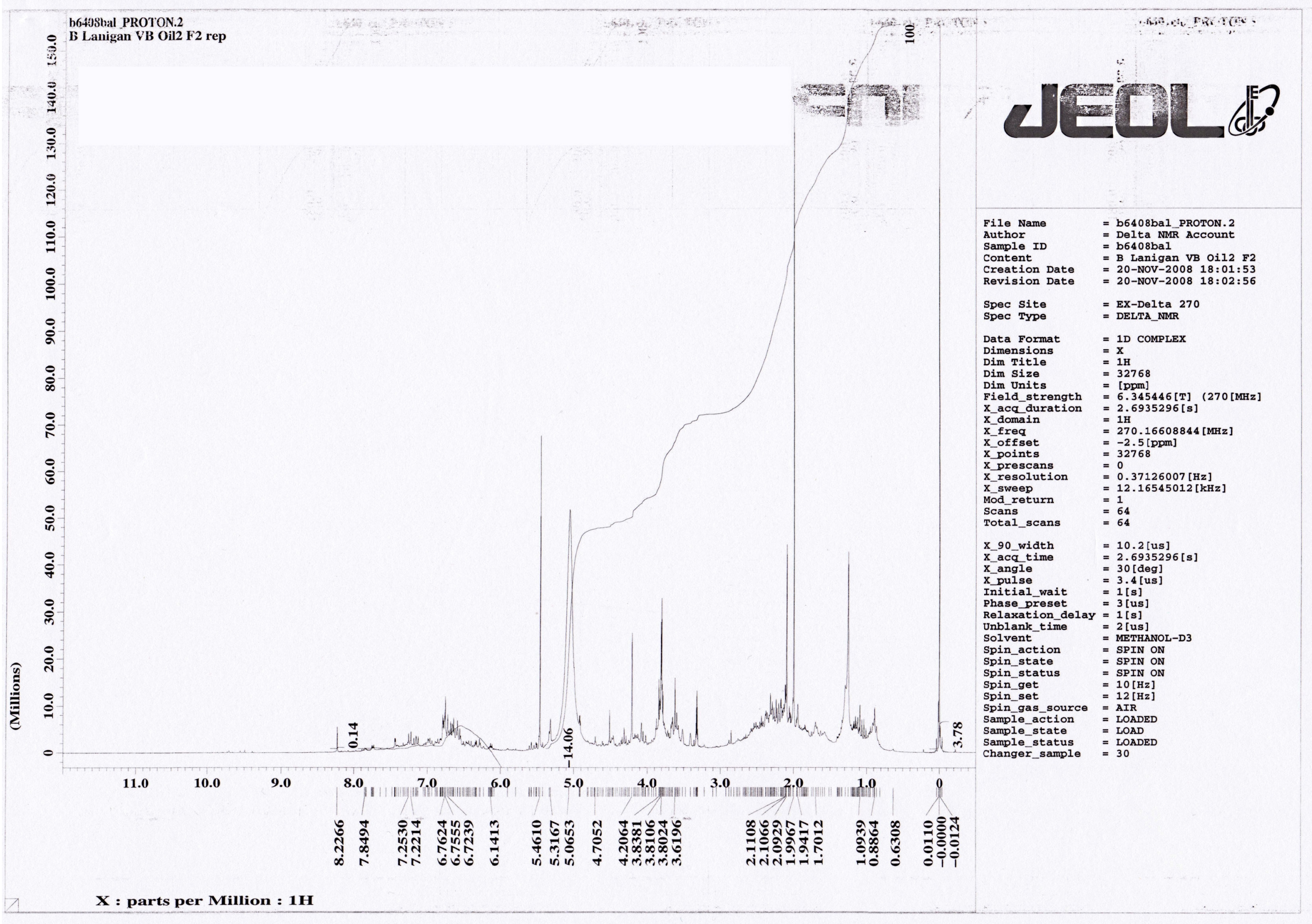

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Fig. 1: ^{1}H NMR of microwave wheat straw bio-oil

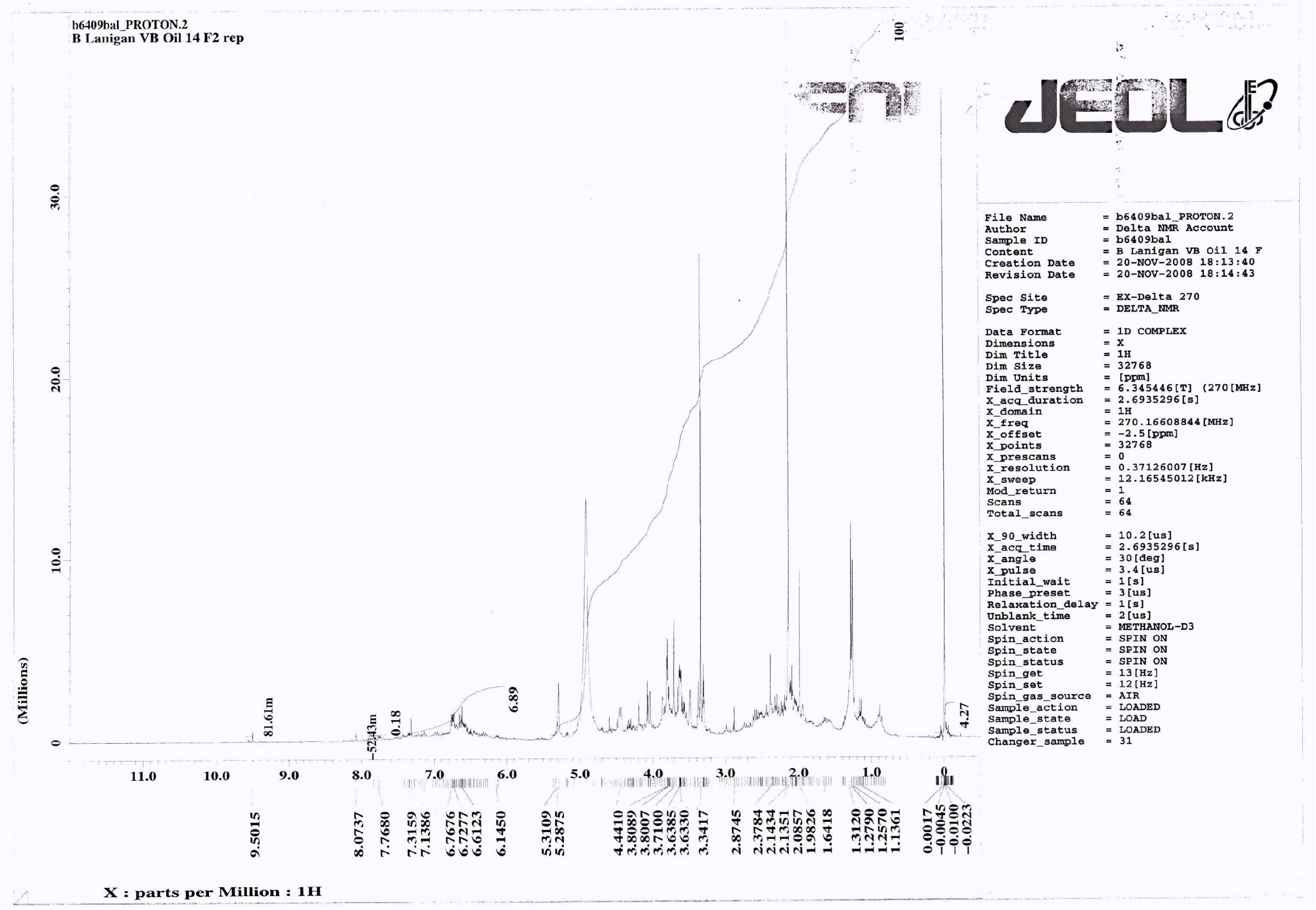

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Fig. 2: ^{1}H NMR of microwave wheat straw bio-oil in the presence of HCl

Table 4: Integral values within specified chemical shift ranges

Sample	0.5-1.5 ppm	1.5-3 ppm	3-4.4 ppm	4.4-6 ppm	6-8.5 ppm	9.5-10 ppm
Wheat straw microwave bio-oil	0.55	1.02	0.65	1.13	0.43	0.0489
Wheat straw + H_2SO_4	53.36	89.87	79.74	150.34	102.83	13.73
Wheat straw + HCl	38.53	74.96	70.2	60.4	29.36	0.94
Wheat straw + NH_3	33.44	87.94	72.28	88.42	29.54	1

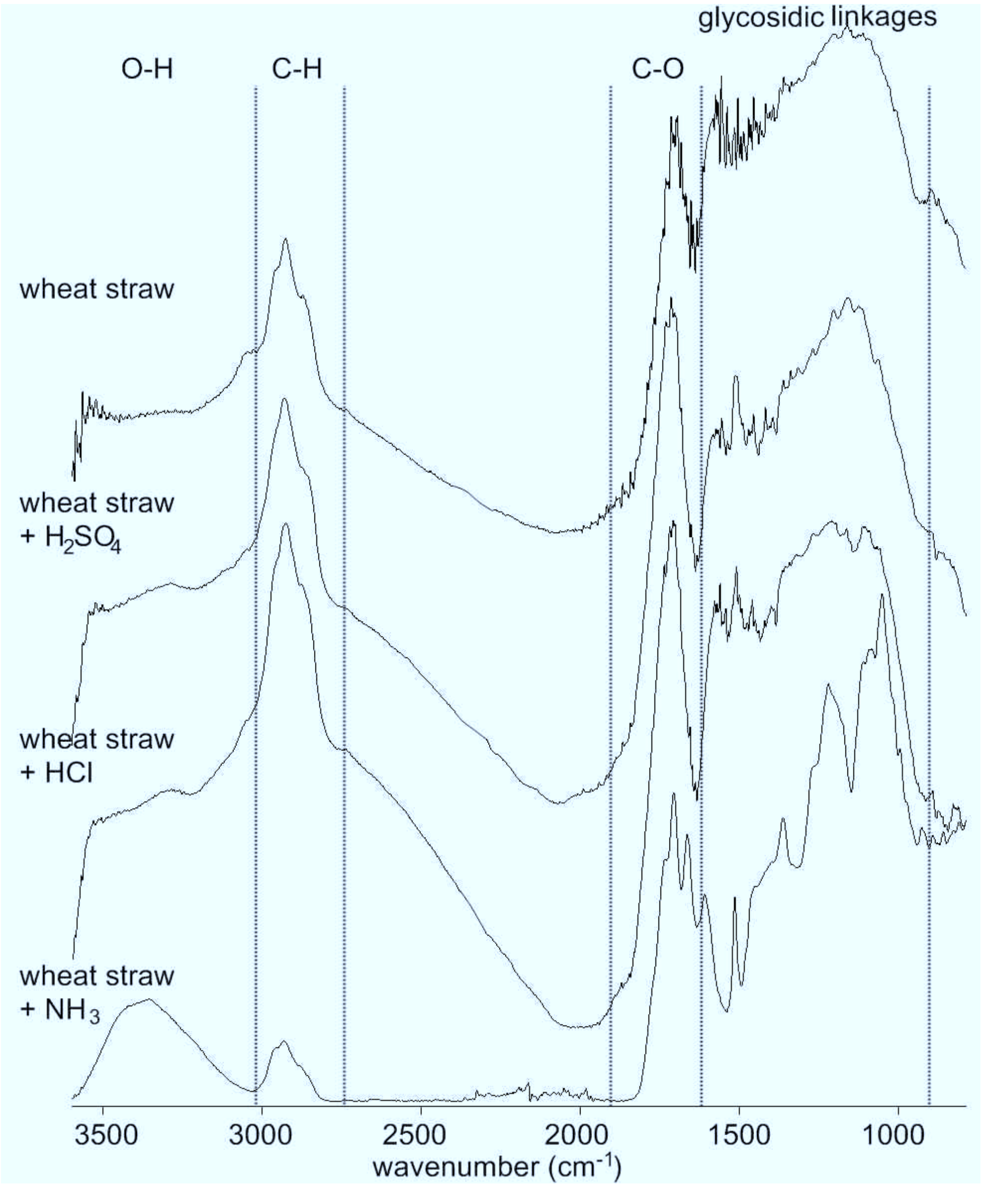

Fig. 3: FTIR analysis of bio-oil from microwave treatment of wheat straw pellets in the presence of additives

Table 5: Preliminary results of microwave processing of miscanthus and spruce for production of bio-oil

Sample	Mass (g)	Microwave power (W)	Processing temperature (^{O}C)	Yield			
				Char	Aqueous	Oil	Gas*
Spruce	100	1200	140	32.7	35.8	18.1	13.4
Miscanthus	100	1200	100	29.4	17.7	21.3	31.6

*Gas yield calculated by difference

Table 6: Pilot scale microwave treatment of biomass: available operating conditions, yields and characterisation

Biomass sample	Mass processed (kg)	Oil yield[a] (% w/w)	Water content[b] (% w/w of oil)	Operating temperature (°C)	Microwave energy (kW)	Elemental analysis of char (%)			
						C	H	N	Rest
Wheat straw pellets	12	29	87	166 – 175	3 - 6	61.1	3.95	1.1	33.85
Oats	4.5 (+ 0.5 kg H_2O)		92	117 – 122	5				
Oats	5 (+ 0.75 kg H_2O)			109 – 130	2.5 – 4.5				
Oats	10.5			105 - 118	4.5				
Miscanthus	2.4	17	86	160 - 165	3.5 - 6	52.67	3.21	1.1	42.01
Cocoa husk	4.3			151 - 190	4.6 – 7.5	53.9	2.99	2.5	40.62

Note: a) Approximate value (where given). Residues were trapped within system

b) High water content values due to residual water from system washes.

Yield of char was not recorded as samples were discharged into water

Chapter 6

Assumptions[1, 2]*:*

Field production:

- Field operations, agrochemical inputs, and levels of production described are typical of the UK.
- For agrochemical inputs the sum of the energy used in the manufacture and distribution are taken into account.
- Regular non-annual activities are given a proportional value in the annual C balance.
- Energy used in the manufacture and distribution of the machinery and replacement parts is included.
- For all calculations it is assumed that 1 L of diesel fuel delivers 51.5 MJ and emits 1.13 kg C on combustion (accounting for fuel used in the distribution of diesel).
- A factor of 3.67 to convert from kg C to kg CO_2.

Harvesting:

- 10 year average yield of miscanthus was assumed to be 12.3Mgdry matter (DM) ha^{-1}.
- The crop was harvested using agricultural mowers and baled using Hesston-type machinery producing bales of approximately 500 kg each prior to transportation.
- Wheat straw removal is recovered through baling and carting of straw.

Postharvest processing and transport:

- Emissions of 10.5 Mg h^{-1} are assumed for using a telescopic handler to load bales prior to transportation.
- Energy use of 110 MJ Mg^{-1} straw or 8.001 kg CO_2 Mg^{-1} biomass was assumed for transportation over an average distance of 150 km using a large truck carrying 16 Mg of straw and an average fuel consumption of 32.8 L $100km^{-1}$.

Standard conversions[3]: 1kW h = 3.6 MJ

Miscanthus:

Yield[1] = 12.3 Mg ha^{-1} of dry matter y^{-1} (taken as average over 10 year growth cycle)

Energy inputs:

Pre-treatment:

Field production (including planting, harvesting, baling and storage)[1]
$= 6505\ \mathrm{MJ\ ha^{-1}\ y^{-1}}$
$= (6505/12.3)\ \mathrm{MJ\ Mg^{-1}}$
$= 528.86\ \mathrm{MJ\ Mg^{-1}}$
$= 0.53\ \mathrm{kJ\ g^{-1}}$

Transport (average distance 150 km) and processing[1]
$= 4430\ \mathrm{MJ\ ha^{-1}\ y^{-1}}$
$= (4430/12.3)\ \mathrm{MJ\ Mg^{-1}}$
$= 360.13\ \mathrm{MJ\ Mg^{-1}}$
$= 0.36\ \mathrm{kJ\ g^{-1}}$

Microwave processing:

Following the procedure outlined in 7.2.4, 50 g of miscanthus was exposed to microwave irradiation for 30 min at a constant power of 1200 W to produce a char of calorific value 24.59 $\mathrm{kJg^{-1}}$.

$(1200\ \mathrm{W})(0.5\ \mathrm{hr}) = (0.6\ \mathrm{kW\ h})(3.6) = (2.6\ \mathrm{kJ})/(50\ \mathrm{g}) = 0.043\ \mathrm{kJ\ g^{-1}}$

Wheat straw:

Yield[1] = 5.68 Mg ha^{-1} of dry matter y^{-1}

Energy inputs:

Field production (including harvesting, baling and storage)[1] = 2024 MJ ha^{-1} y^{-1}
= (2404/5.68) MJ Mg^{-1}
= 356.3 MJ Mg^{-1}
= 0.36 kJ g^{-1}

Peletisation[2] = 28 kW h tonne^{-1}
= (28)(3.6) MJ tonne^{-1}
= 100.8 MJ tonne^{-1}
= 0.1 kJ g^{-1}

Transport (average distance 150 km) and processing[1]= 2410 MJ ha^{-1} y^{-1}
= (2410/5.68) MJ Mg^{-1}
= 424.29 MJ Mg^{-1}
= 0.42 kJ g^{-1}

If peletisation is done prior to transport ~2.5 times less energy is used per tonne due to the increased bulk density.[4] As a result, the energy used for transport of wheat straw pellets is (0.42/2.5) = 0.16 kJg^{-1}.

Following the procedure outlined in 7.2.4, 50 g of wheat straw pellets were exposed to microwave irradiation for 10 min at a constant power of 1200 W to produce a char of calorific value 22.0 kJg^{-1}.

(1200 W)(0.166 hr) = (0.2 kW h)(3.6) = (0.72 kJ)/(50 g) = 0.014 kJ g^{-1}

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Fuel Analysis Report

Test Report: 08-000
Our Ref: CSL8073 SC3371
Supplier: Drax Power Ltd
Grade: Pyrolisis Char
Date Sampled: 24.01.08
DPL10-08

Test Date: 30/01/2008
Date Reported: 03/03/2008
Sampling: Samples taken by Client
Procedures used: As Method

				Results Basis			
Method Reference			Units	As Received	As Analysed	Dry	Dry Ash Free
calP/01	Moisture	Total	%	3.7	-	-	-
cplP/05		Free	%	0.54	-	-	-
calP/03		Inherent	%	-	3.16	-	-
calP/01		Analysis	%	-	3.14	-	-
calP/02	Proximate	Ash	%	17.5	17.6	18.1	-
calP/04		Volatile Matter	%	22.7	22.9	23.6	28.8
calP/26		Fixed Carbon	%	56.1	56.4	58.3	71.2
calP/01	Ultimate	Total Sulphur	%	0.54	0.54	0.56	0.68
calP/06		Chlorine	%	0.01	0.01	0.01	0.01
astmD5373		Carbon	%	66.4	66.8	68.9	84.2
astmD5373		Hydrogen	%	2.28	2.29	2.36	2.89
calP/25		Hydrogen (calc.)	%	3.52	3.54	3.65	4.46
astmD5373		Nitrogen	%	5.84	5.87	6.06	7.40
calP/07	Calorific Value	Gross	kJ/kg	26028	26175	27024	33003
calP/25		Net(H calc.)	kJ/kg	25144	-	-	-
calP/25		Net(H det.)	kJ/kg	25407	-	-	-
-		Energy	MWh/t	7.058	-	-	-

T180	>8000

Hardgrove Index	Unsuitable Sample

Trace Element Analysis		
Element	Result mg/kg	Limit mg/kg
Arsenic*	0.10	5
Cadmium*	<0.01	3
Chromium*	0.4	30
Copper*	5.7	50
Lead*	0.1	20
Mercury*	<0.01	0.10
Nickel*	0.4	30
Vanadium*	0.1	20
Zinc*	67.9	80
Boron*	14	-
Fluorine*	3455	-

Report Authorised by……………………………………………………
G Maloney Oil and Fuel Laboratory Head

Note:
Tests marked* are externally sourced analysis
Test results relate solely to the samples tested
The sampling, sample preparation, tests and associated comments in this report are not UKAS accredited

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Aspects of Applied Biology 90, 2008
Biomass and Energy Crops III

Microwave processing as a green and energy efficient technology for the production of energy and chemicals from biomass and energy crops

By B LANIGAN, V BUDARIN, J CLARK, F DESWARTE, P SHUTTLEWORTH and A WILSON

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Summary

There is increasing interest in the use of renewable means of energy production to meet society's growing energy demands in a sustainable manner. Among the several options available, a lot of attention has been focused on the production of energy through the co-firing of biomass with coal in existing power stations. The largest coal fired power plant in the UK, Drax Power Ltd, aim to produce 10% of their energy output from the combustion of biomass by 2009. The use of biomass in electricity production faces challenges due its high moisture content, comparatively low calorific value, relative to coal, and material handling issues. Here we show that low temperature mobile microwave technology can be used as an energy efficient method to significantly improve the fuel properties of biomass feedstocks including calorific value, moisture content and grindability.

Keywords: Biomass, microwave, calorific value, co-firing

Introduction

Conventional electricity production relies on the combustion of fossil fuels, resulting in the release of carbon which has been stored in the earth for several millennia, which is contributing to the heating of the planet's atmosphere and hence climate change. Of all sources of CO_2, the burning of fossil fuels for electricity production is responsible for the greatest proportion of emissions; therefore the replacement of fossil fuels is vital for the reduction of our impact on global warming. The partial replacement of fossil fuels with biomass can be done with minimal changes to conventional burners and results in a reduction of the net CO_2 released during energy production. The CO_2 released during combustion of biomass is seen as being equivalent to that captured through photosynthesis during growth, as illustrated in Fig. 1, reducing the carbon footprint of energy production.

The use of biomass in energy production faces challenges due its low calorific value when compared to oil or coal. Whilst biomass is a cleaner fuel than coal, generally with lower sulfur content, the corrosive properties of biomass ash and the formation of tar during combustion can result in damage of burners and fouling of down stream systems (Prins *et al*., 2006). The inherent high moisture content and highly oxygenated nature of biomass means that the efficiency of energy production is not optimised when used for direct combustion. Biomass also raises material handling issues and is energy inefficient to transport in its raw state due to the low energy density, and high water content (Demirbas, 2004, Prins *et al.*, 2006).

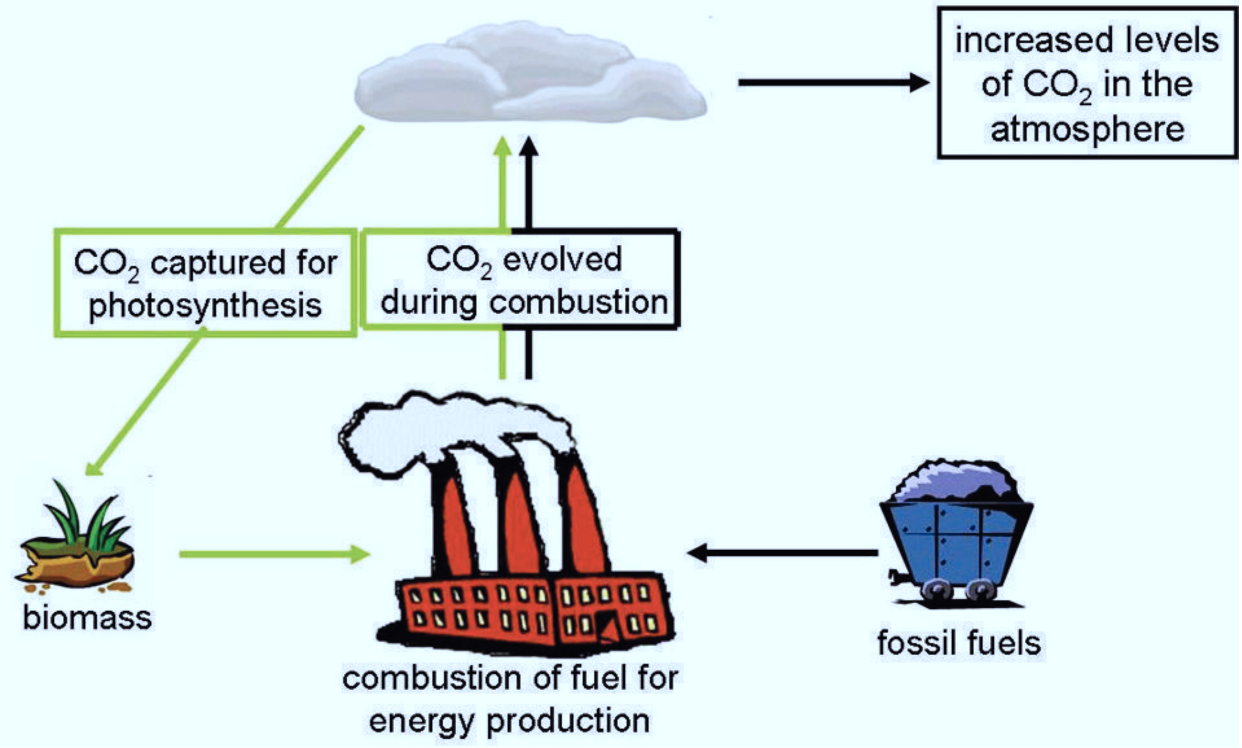

Fig. 1. Carbon cycle.

When focussing on pre-treatment methods for biomass, there are three main thermal processes of energy densification, namely: gasification, pyrolysis and torrefaction. Each process converts the biomass to a preferred form which may then be used for energy production as outlined in Fig. 2.

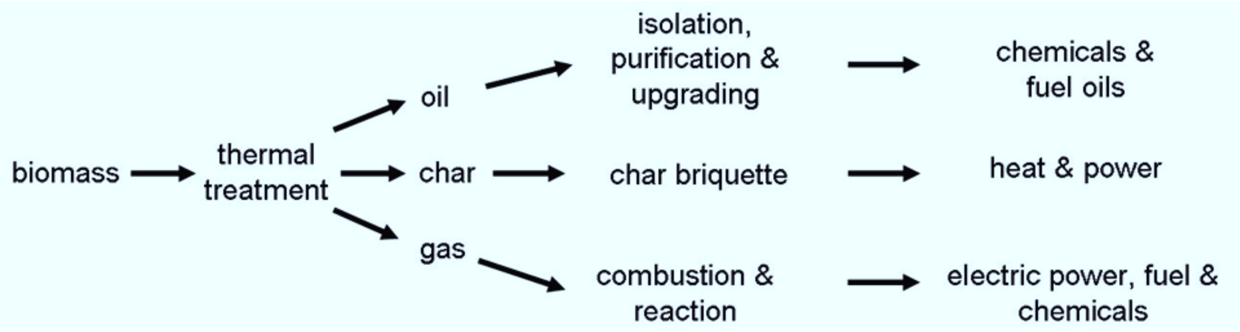

Fig. 2. Thermal transformations of biomass for energy production.

Co-firing of biomass requires the feedstock to be transformed into a solid with physical characteristics to coal, and preferably with a higher calorific value than is usually associated with biomass. The energy consumed in the upgrading procedure is also a vital consideration, ensuring more energy is not used in the treatment process than is gained from the increased calorific value of the final fuel.

Microwave processing has been examined as a possible method of preparation of fuels from biomass. Microwave chemistry offers many advantages over conventional methods of heating. Overall the process is more energy efficient as microwave irradiation heats the whole volume of a sample while conventional heating heats the sample in contact with the reaction vessel before the bulk (Kappe, 2004). The application of microwave technology in high throughput reactions such as flow reactors has proven the large scale applicability of microwave technology (Roberts & Strauss, 2005; Wilson *et al.*, 2004).

Microwave pyrolysis of biomass has been carried out on a variety of substrates. The majority of work which has been carried out focuses on high temperature processes generally between 500–1000°C, producing char, oil and gas products with calorific values up to 7, 37 and 10 kJ g^{-1} respectively, while the typical values for petroleum derived fuels with 32, 42 and 14 kJ kg^{-1} for coal, oil and gas (Domínguez *et al.*, 2007, Domínguez *et al.*, 2006; Menendez *et al.*, 2007, Yu *et al.*, 2006).

In our work we chose to focus on low temperature processing of biomass for the production of solid fuel for use in energy production.

Materials & Methods

Char preparation

Chars were prepared using a CEM Discovery laboratory microwave. The biomass was processed in the "open vessel" mode under a flow of N_2, with adequate stirring. Volatile components evolved during processing were collected through a water cooled condenser connected in series to the system. (U.K. Patent Application)

Measurement of calorific value

The calorific value of the resulting char was measured using a Stanton Redcroft STA 625. Solid residue (~ 20 mg), that had been subjected to microwave irradiation, was weighed out. To this sample, palladium oxide (~ 20 mg) was added. The mixture was ground using a pestle and mortar until a very fine powder was formed. Approximately 2.5 mg of the mixture was added to an aluminium STA sample cup, and then placed in the STA for analysis. The conditions of analysis were 20 to 625ºC at 5ºC per minute in a flow of air (50 mL min^{-1}).

Measurement of energy usage

Choosing cellulose as the key component of biomass, chars were prepared as outlined above on a scale varying from 2–8 g of starting material in a CEM discovery microwave. Samples between 20–200 g were treated under similar conditions using a Milestone SPMR (Solid Phase Microwave Reactor) System fitted with a VAC 2000 vacuum module in series which allows condensation and collection of volatile components. The energy demand of the process was measured using a domestic power metre.

Results

The results of microwave treatment of rape meal are outlined in Fig. 3. As is the standard procedure for rape seeds, initial physical crushing produced a primary oil with possible application in production of biodiesel. The resulting rape meal, which is usually used as animal feed, was extracted via microwave steam-distillation at 100 °C to yield another portion of similar quality oil along with residual water. Further processing of the rape meal at higher temperatures yielded a secondary oil and char with higher calorific value than the starting material.

Analysis of rape meal char showed it to contain up to 17.5% ash, 3.7% moisture and all minerals present were below safe levels.

The energy consideration for the microwave processing was monitored for char preparation on varying scales. Fig. 4 shows the energy spent per gram of biomass processed at 280°C for the production of a high calorific value char. The energy used per gram is shown to drop dramatically with increased mass of sample.

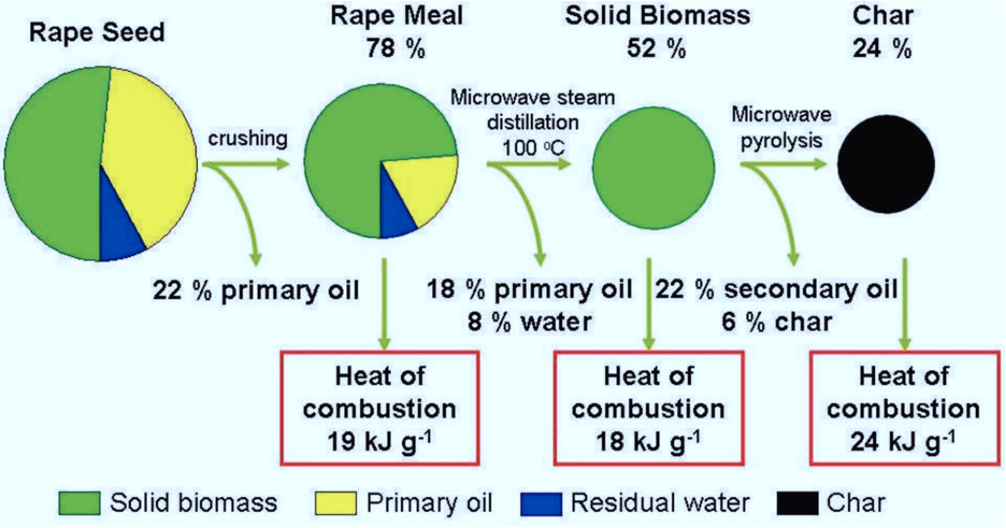

Fig. 3. Results of microwave treatment of rape seed.

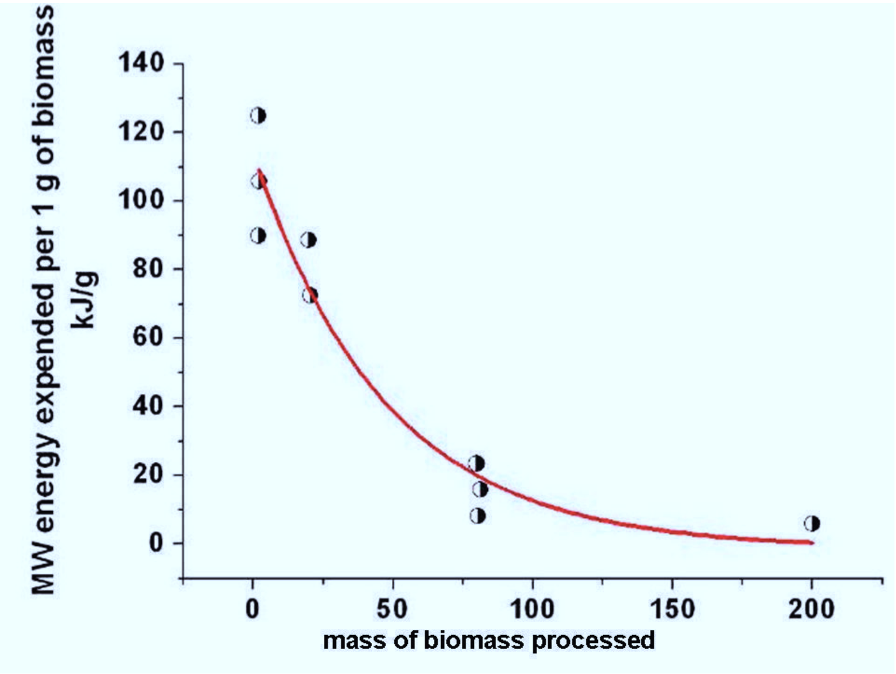

Fig. 4. Energy usage for char preparation per gram of starting material.

Discussion

As outlined in Table 1, the fuel product of our process possesses many advantages over untreated biomass in terms of suitability for use co-firing with coal. Untreated biomass not only is a poor fuel due low energy content per unit mass, but also as a result of the associated material handling issues. Biomass fuels are known to self-heat during long-term storage, releasing harmful volatile vapours which poses risks through inhalation and self ignition (Lehtikangas; 2000, Arshadi *et al.*, 2007). The diverse character of biomass in terms of its physical form may necessitate feedstock-specific procedures when used untreated, as a result power plants may be tied to a specific feedstock leaving them susceptible to seasonal variations in crop properties and yields. The final solid product of our procedure is a dry fuel suitable for pelletisation and/or micronistation. The suitability of the final product for micronisation is independent of feedstock, therefore offers flexibility to the end user in terms of feedstocks used.

Table 1. *Advantages of biomass treatment for production of a solid fuel*

Disadvantages of biomass as solid fuel	Advantages of treated biomass as solid fuel
High water content	Low water content
Low energy density	High calorific value
High O/C ratio	Low O/C ratio
Poor long term stability	Stable for long term storage
Risk of self-ignition on storage	Stable for long term storage
Feedstock-specific material handling	

Analysis of rape meal char was carried out in terms of the suitability of the char for fuel usage, grindability, elemental composition, ash content and moisture content (Table 2). From the perspective of materials handling, the solid was deemed suitable for co-firing with coal. The calorific value, 24 kJ g^{-1}, compares favourably to other fuels (Table 3).

Table 2. *Properties of biomass char*

Moisture content	3.7 %
Ash content	17.5 %
Sulphur	0.54 %
Chlorine	0.01 %

Table 3. *Calorific value of selected solid fuels(Environmental Agency, 2008)*

Fuel	Calorific Value kJg^{-1}	Energy MWh/t
Wood chips (30 % moisture)	12.6	3.5
Wood Pellets	18–20	5–5.6
House coal	27–31	7.5–8.6
Anthracite	33	9.2
Oil	42	11.7

The use of rape meal as a feedstock for fuel production also compares well from a financial point of view as the cost of coal increases (Table 4). The cost of processing the rape meal to improve the energy density of the char will add to the price of the solid fuel but this price is negated by the saving in transport of the densified fuel.

Table 4. *Price Comparison for Power Generation (Environmental Agency, 2008)*

Fuel	Price per tonne[a]	Cost per kWh
Wood chips (30 % MC)	£ 60	1.7 p/kWh
Wood Pellets	£ 170	3.5 p/kWh
Coal	£420	5.3 p/kWh
Rape meal	£200[b]	2.8 p/kWh

[a] Price quoted June 2008.

[b] Does not include cost of microwave processing

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The preparation of high-grade bio-oils through the controlled, low temperature microwave activation of wheat straw

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ABSTRACT

The low temperature microwave activation of biomass has been investigated as a novel, energy efficient route to bio-oils. The properties of the bio-oil produced were considered in terms of fuel suitability. Water content, elemental composition and calorific value have all been found to be comparable to and in many cases better than conventional pyrolysis oils. Compositional analysis shows further differences with conventional pyrolysis oils including simpler chemical mixtures, which have potential as fuel and chemical intermediates. The use of simple additives, e.g. HCl, H_2SO_4 and NH_3, affects the process product distribution, along with changes in the chemical composition of the oils. Clearly the use of our low temperature technology gives significant advantages in terms of preparing a product that is much closer to that which is required for transport fuel applications.

1. Introduction

The replacement of fossil resources with sustainable (renewable) sources of carbon is one of the major routes to a low carbon solution for future global energy and chemicals supplies. The transition to a renewable based society brings with it substantial environmental, economic and social benefits.

Several national and trans-national legislation, policy and incentives have been set to increase the proportion of biomass being used for energy production (Williams et al., 2006). Biomass is a fully renewable, widely distributed resource that should increasingly be used for the production of heat and power, liquid fuels, chemicals and many (e.g. polymeric) materials. One way to exploit the energy potential of biomass such as wheat straw is through combustion. However, direct combustion is inefficient due to low energy density and high water content (Demirbas, 2004).

Various biochemical and thermochemical processes have been researched for the upgrading of biomass for fuel use. While both methods of processing can be used to produce fuels and chemicals, thermochemical processing can be seen as being the easiest to adapt to current energy infrastructure. Pyrolysis is a medium temperature process resulting in the liquefaction of the biomass into a complex mixture of organic compounds. The pyrolysis products face challenges in terms of fuel application due to unfavourable properties such as high acidity, high water and alkali metal contents making them difficult to exploit as fuels (Mohan et al., 2006).

It is clear that new, clean and efficient biomass conversion technologies are needed if we are to better exploit the carbon potential of biomass.

Microwave technology has been shown to be an energy efficient method for chemical processing and has become widely accepted as a mild and controllable processing tool (Gronnow et al., 2005). Microwaves are not only useful as alternative methods of heating; there is also a good body of evidence to suggest they can cause specific molecular activations (De la Hoz et al., 2005). Microwave processing has now been shown to be effective at pilot scale and at large continuous processing scale, for example in waste treatment (Clark and Sutton, 1996).

The use of microwaves to activate biomass dates back to the 1970s (Allan et al., 1980). Microwave reactors for on-farm processing (to reduce transportation costs) have also been highlighted as a future possibility. Among the published studies, the optimisation of wood pyrolysis to maximise production of levoglucosan, a useful chemical intermediate, has been described (Miura et al., 2001). Optimising the calorific value of biomass pyrolysis products has also been studied but reasonable values for bio-oils have inevitably been at the cost of yield (Ruan et al., 2008). Almost all of the

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published work in this area has been carried out at temperatures above 350 °C with reported benefits including high rates of pyrolysis, good energy efficiency and better controllability than conventional pyrolysis (Yu et al., 2007; Dominguez et al., 2007). In order to maximise process efficiency and examine the possibility of improved process control our studies focussed on microwave processing at temperatures below 350 °C.

Low temperature microwave-induced pyrolysis has rarely been reported and we report here our results from a study of the low temperature microwave activation of wheat straw to produce bio-oils. By working at low temperatures and by running the process with continuous separation we hope to get better control over the biomass decomposition and separate the undesirable water and water-soluble components and thus get closer to fuel-ready oils than has previously been achieved.

2. Methods

2.1. Raw materials

Wheat straw pellets were obtained from Charles Jackson Farms, UK. Initial analysis of the pellets as received showed a moisture content of approximately 10%. Elemental analysis based on carbon, hydrogen and nitrogen content was carried out using an Exeter Analytical (Warwick, UK) CE440 Elemental Analyser, calibrated against acetanilide with a S-benzyl-thiouronium chloride internal standard. CHN wt% of the starting material was 40.21%, 5.34% and 0.7% respectively.

2.2. Use of additives

Wheat straw pellets were mixed in an aqueous solution of sulphuric acid (10% w/w) to ensure even distribution throughout the sample. The water was removed *in vacu* at 60 °C. Ammonia and HCl (3% v/v) were introduced into the sample as a gas. As previously, the sample was mixed thoroughly.

2.3. Microwave processing of materials

The microwave treatment of wheat straw pellets was carried out using a Milestone ROTO SYNTH Rotative Solid Phase Microwave Reactor (Milestone Srl., Italy) fitted with a VAC 2000 vacuum module in series. Average sample mass was between 150 and 200 g. Samples were exposed to a maximum microwave power of 1200 W. The sample was heated at a rate of 17 °C/min to a maximum temperature of 180 °C, as measured by in situ temperature probes. Process pressure was monitored at all times. Liquid fractions were collected via the vacuum unit, which collected and condensed vapours produced during the process (Fig. 1).

2.4. py-GC–MS of wheat straw

Pyrolysis-GC was performed using a CDS Analytical Pyroprobe 2000 interfaced to an Agilent Technologies 6890 N Gas Chromatograph, using a CDS 1500 Interface. The oven was fitted with a 61.3 m, 0.25 mm i.d., 0.25 μm phase (14% cyanopropylphenyl, 86% dimethyl polysiloxane) thickness Rtx 1701 capillary column. An Agilent Technologies 5975B Inert XL Mass Selective Detector was coupled to the GC.

For each pyrolysis run, approximately 1 mg of sample was place in a 20 mm quartz silica tube using quartz wool plugs and heated in the pyroprobe in a purge of helium at 20 °C m^{-1} to the desired temperature (600 °C). The pyroprobe was held at maximum temperature for 20 s. The oven temperature was held at 40 °C for the first 2 min of each run, then heated at 4 °C min^{-1} to 250 °C, then held at final temp for 30 min, with a total run time of 84.50 min. This process yields approximately 84% volatiles of the wheat straw sample which is carried onto the column and 16% char (remaining in the quartz silica tube).

2.5. Characterisation of liquid fractions

For GC–MS analysis of the microwave oils, approximately 1.0 g of each oil was diluted in 15 ml of methanol. About 5 μl of this solution was then automatically injected onto the GC column using an Agilent 7683 series autosampler. The oils in solutions were analysed using the same column and operating under the same oven heating regime as described above. Elemental composition was carried out as outlined for the starting material. Acid number was determined by titration. Water content was determined using a Karl Fisher Coulometer (Mettler Toledo DL32) by comparison to Karl Fischer Standard reagent (Fluka Chemicals).

3. Results and discussion

3.1. Yields of bio-oils

We have developed an improved microwave process for production of oils from biomass. Taking advantage of a microwave reactor equipped for continuous extraction we have found that,

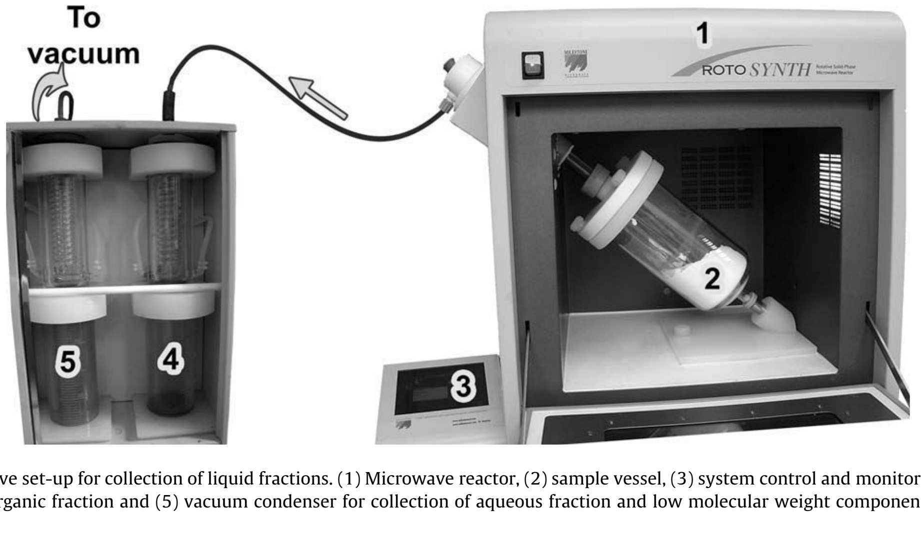

Fig. 1. Schematic of microwave set-up for collection of liquid fractions. (1) Microwave reactor, (2) sample vessel, (3) system control and monitoring console, (4) water cooled condenser for collection of organic fraction and (5) vacuum condenser for collection of aqueous fraction and low molecular weight components.

by exposing the biomass to microwave energy within a rotating reactor vessel, even distribution of the microwave energy within the sample volume can be ensured. We also found that by operating under a vacuum it is possible to fractionate the liquid products obtained from the process, as shown in Fig. 1. Unexpectedly though, we have discovered that under these conditions, two separate processes of volatiles production occur.

By monitoring peaks in the process pressure, we can clearly see the point at which the volatiles are released (Fig. 2). As a result it is possible to collect two liquid fractions. The first pressure change can be seen between 60 and 120 °C and has been correlated to the evolution of an aqueous fraction containing relatively high levels of acid. Thereafter, and while maintaining a relatively low temperature, an organic fraction of low water and low acid content is produced at temperatures as low as 120 °C (dependent on biomass type and presence of additives) and in a very short period of 1–2 min. Microwave processing of wheat straw pellets under these conditions has yielded up to 21% of this organic fraction (water content < 1%). We have concluded from our work that heating the sample to further elevated temperatures has no positive influence on oil yields or properties.

3.2. Composition and properties of the bio-oils

The key parameters of the microwave bio-oils were measured and compared to those of conventional pyrolysis as well as to those of crude petroleum (Table 1). The differences between our oil and the pyrolysis oil are striking. When compared with conventional pyrolysis oil, microwave processing of biomass has allowed for an alternative distribution of minerals between the liquid fractions. As a result major impurities such as sulphur, alkali metals and acids are collected in the aqueous fraction. The subsequent levels of these impurities are all substantially lower in the organic fraction of the microwave oils than in conventional pyrolysis oil (less than 10% of the value in all cases). The lower levels of impurities result in a bio-oil which is more amenable to fuel use, (e.g. for blending in with petroleum after upgrading). Comparisons with petroleum are not as favourable, although the acidity and alkali metal content are favourable, both of which are important factors when considering engine fouling. The microwave oil may also be seen as a potential source of chemicals as it is rich in aromatics and anhydro-sugars.

The preparation of bio-oils using microwave treatment at temperatures within the normal pyrolysis range has been reported. Comparison of the properties and composition of our oils with others generated by microwave activation shows that the use of elevated temperatures is unnecessary and possibly detrimental for the production of bio-oil for fuel use. The bio-oil reported by Yu et al. (2007) displays a similar carbon content to ours (60.1%), but has a sulphur content that is seven times higher and a very high acidity (reported as a pH of 2.87). The bio-oil produced by Dominguez et al. (2007) while having a higher carbon content (75%) and a good calorific value (34.4 kJ/mol) has a very high sulphur content (over thirty times ours) and was obtained in very small yields (3%); no acidity value was reported.

Comparison of pyrolysis-GC–MS analysis on samples of wheat straw using conventional high temperature (600 °C) pyrolysis conditions and GC–MS analysis of our low temperature microwave processing of wheat straw has shown noteworthy differences. The volatile composition from the former shows a typical product distribution for a metal (e.g. in situ potassium) catalysed decomposition of a lignocellulosic biomass via an ionic mechanism (Nowakowski et al., 2007). This includes large amounts of furfural and acetic acid (from the cellulosic components), and phenols and methoxyphenols (from the lignin) but only small quantities of sugars. For our microwave oil furfural and acetic acid are also present, but in much smaller relative amounts; phenols, methoxyphenols and their dimers are more prominent. We also obtain relatively high yields of the sugars levoglucosan and 1,4:3,6-dianhydro-D-glucopyranose, along with small but significant amounts of long chain acids including hexadecanoic acid. The microwave-generated oil generally shows a smaller number of prominent peaks and a remarkable one third of the total peak area can be assigned to the two compounds levoglucosan and 2,3-dihydrobenzofuran, both of which have value as chemical or bio fuel intermediates (e.g. levoglucosan to glucose or citric acid (Zhuang et al., 2001; Helle et al., 2007)) (Table 2).

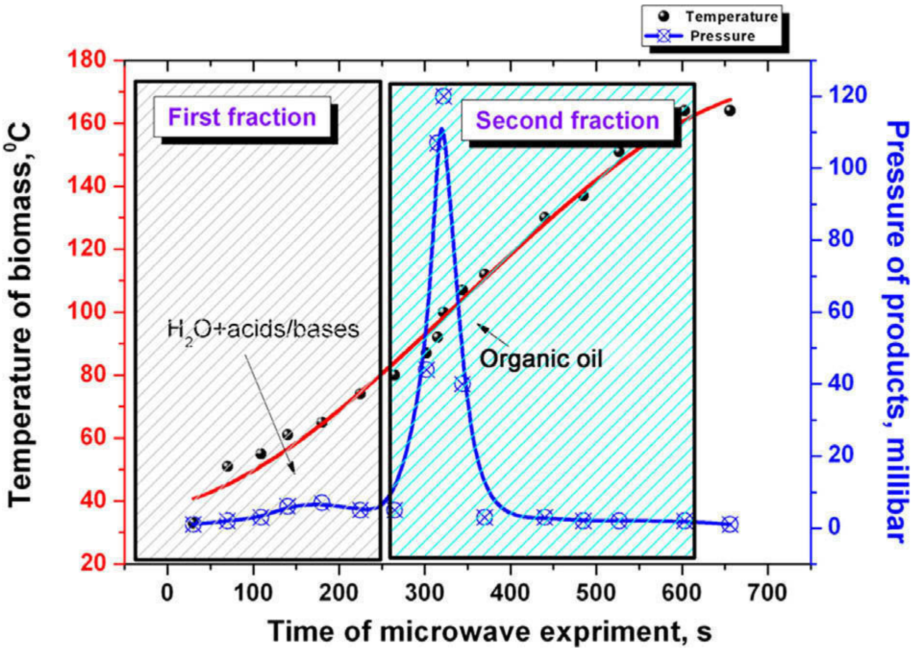

Fig. 2. Stages of liquid product formation during microwave process.

Table 1
Comparison of the key parameters of petroleum and bio-oils produced from the conventional pyrolysis and microwave activation of wheat straw.

Property	Crude oil Nexant Ltd. (2008)	Pyrolysis oil Nexant Ltd. (2008)	Microwave oil		
			Dominguez et al. (2007)	Yu et al. (2007)	Current work
Water (%)			–	15.2	<1
C (wt%)	85–87	45–55	74.8	60.1	58.9
H (wt%)	10–14	6–7	8.3	7.70	6.85
N (wt%)	0.1–2	0.3	7.8	2.02	1.15
O (wt%)	0.1–1.5	40–50	8.5	29.4	33.2
S (wt%)	0	0.5–5	0.6	0.15	0.02
Specific gravity	0.8–1.0	1.2–1.3	–	–	1.2
Acid number	<1	70–150	–	pH 2.87	1.4
Alkali metal	50	100	–	7.6	5.71
LHV (kJ/g)	42	16–21	34.4	17.4	16–22

Table 2
Chemical composition of wheat straw MW-pyrolysis oil.

Compound	Percentage area	Retention time (min)
Acetic acid	0.84	7.194
Furfural	0.50	14.194
2-Furanmethanol	0.57	16.057
1,2-Cyclopentanedione, 3-methyl-	1.64	22.769
Phenol	2.00	24.154
Phenol, 2-methoxy-	2.73	24.703
Phenol, 2-methyl-	1.16	26.002
Phenol, 3-methyl-	1.23	27.370
Phenol, 4-methyl-	1.50	27.455
Phenol, 2-methoxy-4-methyl-	1.38	28.657
Phenol, 4-ethyl-2-methoxy-	1.57	31.701
1,4:3,6-Dianhydro-α-D-glucopyranose	1.27	32.943
Benzofuran, 2,3-dihydro-	10.66	33.715
Phenol, 2,6-dimethoxy-	4.54	35.586
Phenol, 2-methoxy-4-(1-propenyl)-	2.84	38.196
Vanillin	1.13	38.980
Hydroquinone	1.44	39.185
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.92	41.566
4-Methyl-2,5-dimethoxybenzaldehyde	2.45	42.779
Homovanillyl alcohol	1.62	43.174
Levoglucosan	27.87	46.309
Phenol, 2,6-dimethoxy-4-(2-propenyl)	3.71	46.636
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	1.07	49.456
Desaspidinol	1.30	50.641
n-Hexadec0anoic acid	0.75	51.871

Table 3
Mass balance of products from the low temperature microwave activation of wheat straw including presence of additives.

	Wheat straw pellets	Wheat straw pellets + H_2SO_4	Wheat straw pellets + HCl	Wheat straw pellets + NH_3
Process conditions				
Microwave power	1000	1200	1200	1200
Process temperature	130	140	140	165
Product distribution (mass%)				
Char	29	44.4	31.8	40.7
Organics	20.6	7.3	22.1	17.0
Water	36.4	32.9	27.1	22.3
Gas	14	15.4	19	20
Composition of oil (%)[a]				
Desaspidinol	1.3	2.21	2.05	2.74
1,4:3,6-Dianhydro-α-D-glucopyranose	1.27	6.69	3.11	1.22
Levoglucosan	27.87	20.64	35.46	46.44
Levoglucosenone	–	23.63	1.51	–
2-Methoxy-4-vinylphenol/benzofuran, 2,3-dihydro-	10.66	1.06	2.80	10.23
Phenol, 2,6-dimethoxy-	4.54	0.54	4.3	3.93
Phenol, 2,6-dimethoxy-4-(2-propenyl)	3.71			
Phenol, 2-methoxy-	2.00	2.25	2.57	1.69

[a] Based on peak area in GC.

3.3. Influence of additives on the composition and properties of the bio-oils

We have found it possible to affect oil properties through the use of simple additives which can also affect the oil yield (Table 3). This effect has been found to be dependent on the additive itself, rather than on properties such as pH as may be expected. For example, the addition of sulphuric acid to the sample before processing results in a significant decrease in the oil yield, to the benefit of char yield. Interestingly, the addition of the same quantity of hydrochloric acid has minimal effect on the oil yield. On the other hand, ammonia can be seen to behave in a similar manner to sulphuric acid, resulting in a sacrifice of oil yield for greater quantities of char.

GC–MS of the microwave-generated oils obtained from processes with HCl, H_2SO_4 and NH_3 as additives gave broadly similar profiles but some significant changes were evident. The amount of levoglucosan remained high in all cases but the relative yield was seen to increase remarkably in the oil obtained by microwaving wheat straw in the presence of ammonia. We believe that these results support our proposition that by decomposing the biomass at unusually low temperatures, we have been able to obtain significantly different chemical products and simpler mixtures which in one case leads to a mixture containing almost 50% of one compound, a potentially important observation for future sustainable chemical manufacturing.

3.4. Energy balance for the low temperature microwave process

The energy balance has been calculated for a production unit operating at 6000 kg/h. The energy input includes straw drying and low temperature activation (pyrolysis). These have been calculated on the basis of energies required to heat the different components of the biomass (including water evaporation for the drying stage) plus, in the case of the pyrolysis stage, the evaporation of the organic compounds. The total energy input has been calculated on the basis of an energy requirement of 474 kJ for the initial drying along with 1302 kJ for the microwave pyrolysis. The energy value of the oil produced based on a yield of 20.2% and a worst case calorific value of 16,000 kJ/kg is 8.98 MJ, over five times the energy input for the process, 1.78 MJ.

This clearly shows the favourable energy balance for the process based only on the oil produced. When the energy of the char and the gas is included the overall energy balance is considerably more favourable.

4. Conclusions

The low temperature microwave activation of wheat straw provides a novel, energy efficient route to bio-oils with excellent key properties for use as bio-fuels. Low sulphur, acid and alkali metal content are particularly significant for fuel applications. Compositional analysis shows further differences with conventional pyrolysis oils including simpler chemical mixtures. The microwave oil also possesses large percentages of a small number of compounds with value as fuel and chemical intermediates. Simple additives can be used to further change the oil properties and composition with HCl causing a small increases in oil yields and NH_3 causing a notable process selectivity to yield large amounts of a single chemical.

Clearly the use of our low temperature technology gives significant advantages in terms of preparing a product that is much closer to that which is required for transport fuel applications, both when compared to conventional pyrolysis oils and when compared to bio-oils produced by high temperature microwave processing. By working at lower temperatures we can also expect to see major differences in chemical structure and content and with an eye on possible higher value, chemical applications.

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We thank Rotawave Ltd. for assisting in the energy balance calculations based on their large-scale continuous microwave processor.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2009.06.068.

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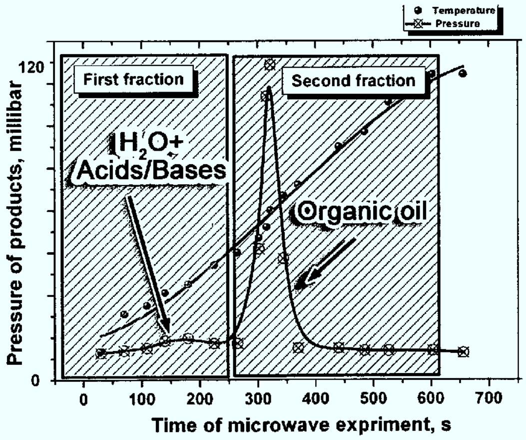

Figure 1.2. Separation of aqueous and organic fraction based on microwave time.

(57) Abstract: There is described a processor for use in the microwave torrefaction of biomass material which comprises, a micronised biomass char material and a method of producing a biomass char material, and a method of producing L-glucosan.

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MICROWAVE TORREFACTION OF BIOMASS

FIELD OF THE INVENTION

The present invention relates to the processing of biomass, such as microwave torrefaction of biomass, and the invention provides microwave technology based on a range of acid/base additives which will be able to control mass ratio between different products (char/oil/gas), char properties and oil composition.

Moreover, this aspect of the invention provides a novel process to certain biomass derived products, such as L-glucosan.

Furthermore, the present invention relates to the processing of biomass to produce a micronisable biomass char which is useful, *inter alia*, as a biofuel, by the use of microwave technology. This aspect of the invention in particular provides microwave assisted torrefaction of polysaccharide rich plant biomass, and non-lignocellulosic biomass.

In addition, the present invention pertains to a processor for microwave torrefaction of materials, in particular, but not exclusively biomass. We define the biomass as organic matter available on a renewable basis. Biomass includes forest and mill residues, agricultural crops and wastes, food wastes, wood and wood wastes, animal wastes, livestock operation residues, aquatic plants, fast-growing trees and plants, and municipal and industrial wastes.

BACKGROUND OF THE INVENTION

The use of biomass for isolation of bio-oils, biochar and for energy production faces several problems due to, *inter alia*, its low energy density as a fuel.

The influence of chemical active additives on high temperature microwave pyrolysis, though not torrefaction, of biomass has been investigated just by few teams. For example, the effect of additives such as, sodium hydroxide (NaOH), sodium formate (HCOONa), sodium bicarbonate ($NaHCO_3$), silicon dioxide (SiO_2) and calcium hydroxide ($Ca(OH)_2$) on the microwave processing of biomass has been studied by Barbara Krieger-Brockett in 1994[1]

M. Chen *et al* [2] investigated eight inorganic additives (NaOH, Na_2CO_3, Na_2SiO_3, NaCl, TiO_2, HZSM-5, H_3PO_4, $Fe_2(SO_4)_3$) in terms of their catalytic effects on the pyrolysis. Experiments were carried out at ca. 470°C under dynamic nitrogen atmosphere. It was found that all additives have significantly increased yields of solid products; however yield of liquid wasn't changed substantially. They also found that additives can change the composition of the organic products. Furfural and 4-methyl-2-methoxy-phenol have been identified as the two dominant organic components in the liquid products obtained from MW pyrolysis of acid (H_3PO_4 and $Fe_2(SO_4)_3$) treated samples. Notably L-glucosan (levoglucosan) was not found or found only in trace amounts in the liquid products from pyrolysis of sawdust by microwave heating both in control microwave experiment and in the presence of inorganic additives. Furthermore, calorific values of bio-char and acid number of bio-oil have not been estimated.

Furthermore, conventional fuel furnaces, such as those used in coal fired power stations require the fuel to be pulverized or micronised. For example, coal for burning in a power station furnace will usually be pulverised to increase the fuel surface area. This also provides more efficient combustion, more complete burnout, lower emissions, and better heat liberation rates.

One particular disadvantage identified with the use of biomass in energy production is that whilst the biomass may be shredded is has thus far not been possible to achieve micronised particles sizes of biomass or biomass char which would be suitable for use in conventional furnaces and or for burning when admixed with conventional fuels, such as coal.

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[1] B. Krieger-Brockett, "Microwave pyrolysis of biomass", Res. Chem. Intermed., 1994, **20** ,39-49

[2] Chena M., Wanga J.,Zhanga M., Chena M., Zhub X., Mina F. and Tanc Z. "Catalytic effects of eight inorganic additives on pyrolysis of pine wood sawdust by microwave heating", Journal Of Analytical And Applied Pyrolysis 2008, **82** , 145-150.

Several options are available for the valorisation of biomass for energy production although none can result in increasing the overall energy available from the biomass. The three core options are seen as

1. gasification, a high temperature process of degradation of biomass to produce gases which can then be used for energy production;
2. pyrolysis, a medium to high temperature process where the biomass is degraded to yield mainly oil products for energy production; and
3. torrefaction, a low temperature process for the production of solid fuels with an increased energy density than the original biomass.

Under conventional heating conditions gasification is carried out between 750 – 1800°C, pyrolysis generally above 400°C and torrefaction between 200 and 300°C.

In terms of method of production of an improved fuel, each of these has inherent problems. Gasification is an endothermic process and occurs at very high temperature so requires significant energy input to drive the process. The major product of pyrolysis processes is oil, with typical yields of 60 – 70%. The so-called “bio-oil” is easier to transport than the gas products of gasification but suffer reduced fuel efficiency due to high water content, phase separation and corrosive properties which make long-term storage an issue. Although torrefaction offers the lowest energy demand of all these processes, as it operates at the lowest temperature, and offers a product which burns cleanly there are several problems associated with the process.

- In conventional processes difficulties arise in strict control of operating temperature, it is necessary to ensure the process does not go above 300°C.
- The maximum achievable calorific value is usually much lower than that of coal, expected to be from 18 to 23 kJ/g (8000 to 10000 Btu/lb).[2]
- The production costs are high.

These problems have, along with a complex system, prevented torrefaction of biomass for fuel from practical commercial use. Various routes such as catalysis have been investigated in order to improve the process but still the process has not been optimised to a point where it can perform on a commercial scale. As a result of the problems faced in conventional torrefaction we have chosen to investigate microwave torrefaction as an easily controlled mobile technology and for increasing the energy density of biomass for use as fuel.

Microwave torrefaction, as defined here, has not been reported in literature. The following is a review of the current state of the art of microwave gasification and pyrolysis which are generally carried out at temperatures above 300°C.

Microwave irradiation is defined as "electromagnetic irradiation in the frequency range of 0.3 to 300GHz". Similar to domestic microwaves, specialised chemistry microwave reactors operate at 2.45GHz. Microwave radiation is used in several applications including radar, communications, radiometry, medicine, physics, chemistry, and cooking food. Compared to conventional heating techniques a microwave process is advantageous in terms of shorter reaction times, higher heating efficiencies and greater control. The advantages of microwave technology in terms of mobility of small scale processors and value in waste reduction applications have been highlighted by Ruan et el.[1] The use of microwaves is well established in many industrial and commercial applications. Microwave treatment of biomass is used before and or during extraction processes. The use of microwave for extraction of oil is gaining significantly in terms of commercial importance and wide spread utilization. It is employed in extraction of primary plant oils as well as extraction of petroleum oils from drilling muds, tar and sands. Microwave ovens have gained acceptance as a mild and controllable processing tool. Microwaves allow simple, rapid and low solvent consuming processes. Microwaves are already widely used for extraction of oil from solid to liquid (CEM-2005). The use of microwaves is also growing in the processing of materials. Microwave processing is now being used for "the production of advanced ceramics, the deposition of thermal barrier coatings, and the remediation of hazardous wastes" with new applications constantly being researched.

The use of microwaves for treatment of biomass is relatively new and dates back to the early 1970's. However, previous focus on microwave treatment of biomass has always been on high temperature pyrolysis, gasification and liquefaction of the starting material. Pyrolysis of biomass is usually conducted at temperatures above 350°C. Examples of substrates employed in this type of pyrolysis are numerous and include plant biomass such as wood or agricultural residues, plastics and municipal waste.

Low temperature pyrolysis, also known as torrefaction, is a thermal treatment usually carried out between 200 and 300°C. Torrefaction is a mild biomass pre-treatment process for upgrading the quality of biomass as fuel for combustion and gasification applications. Torrefaction can also be referred to as roasting, slow and mild pyrolysis and high temperature drying.

Conventional (non-microwave) torrefaction of biomass materials such as wood is well known. Torrefied wood has the moisture and most volatile organic compounds (VOC's) driven out resulting in a high percentage of carbon content. In addition, the chemistry and structure of the wood itself is converted into a new form by continued exposure to heat. Torrefaction of other biomass materials, such as those of plant origin, e.g. prunings and/or mown grass, or waste materials is also known.[2] However, the micronisation or pulverisation of such torrefied materials has proved unsatisfactory.

Use of additives

In typical microwave pyrolysis one of the key requirements is the presence of dielectric materials which are good absorbers of microwave energy and transfers heat directly. Examples of additives include inorganic oxides, carbons (e.g. carboniferous additives, such as graphite) and/or water. Biomass is largely transparent to microwaves, meaning that it is not easy to heat it directly. The use of absorbers overcomes this limitation and enables fast heating rates. In addition it is important to note that as pyrolysis proceeds, more carbon is generated from the biomass and the microwave heating becomes progressively more effective.

The use of additives was also investigated by F.Yu,R. Ruan et al.[3] who employed char and NaOH and showed increased yields of oil and syn-gas respectively. They also observed variations in gas composition at elevated temperatures.

Microwave gasification of biomass

Miura et al[4] and A.M. Sarotti et al[5] looked at the optimisation of microwave pyrolysis of cellulose and wood for production of levoglucosan. They investigated particle size, power and irradiation time and source of biomass on the distribution of products in terms of water, oil, gas and char and they also conducted chemical analysis of their oil. However, neither investigated the calorific (heating) value of the wood based biomass or the biomass components. The temperature of the process was not directly controlled and was only determined as a result of the microwave power input and sample residence time. In our work, we have found that the control of the process temperature along with the power input was vital for the production of products with reproducible properties.

Calorific value of microwave pyrolysis products of biomass have, however, been investigated by Menendez et al[6] who have investigated the effects of microwave irradiation for pyrolysis above 500°C. They used microwave energy to pyrolyse sewage sludge at irradiation of 1000W and a final reaction temperature of 1000°C, with the aim to optimise the fuel properties of the gas produced. They found that microwave pyrolysis produces more gas and less oil than conventional pyrolysis and additionally the amount of hydrogen in the gas mixture is much higher especially at temperatures 500°C. The calorific values of the collected fractions were up to 7, 37 and 10 kJ/g for char, oil and gas respectively. In comparison to typical values for petroleum derived fuels with 32, 42, 14 kJ/kg for coal, oil and gas these values are relatively lower. However although heating values were higher for oils their yield was relatively small, meaning that the greatest percentage of energy was accumulated in the gas fraction, with the oil fraction containing the lowest relative percentage of the energy.

They also tried to optimise the calorific value of char from biomass prepared between 500 – 1000°C by microwave pyrolysis. They were unable to affect the calorific value with increased temperature. Moreover the calorific value of the char was similar to that prepared at the same temperature under conventional conditions (around 24 kJ/g).

Surprisingly, we have been able to produce char and oil fuel products from microwave torrefaction of biomass working at temperature between 120 and 300°C, resulting in a significant saving in energy input. The production of solid and oil fuel products is seen as favourable due to the ease of transport of the final product and their simple integration into current energy production systems. The decomposition of the biomass occurred at lower temperature and yielded a solid char of increased calorific value, comparable with coal.

Microwave pyrolysis of biomass for liquefaction

Ruan et el[1]. and Heyerdahl et al. have investigated microwave biomass pyrolysis for the production of a liquid fuel. They worked at temperatures between 260-600°C, with optimum process conditions for liquefaction in the region of 350 and 600°C. Under these optimised conditions it was found that 50% of the biomass energy can be condensed into liquid products, just 20% in the char and the remaining 30% in the gas phase. The fuel properties of the char were not fully investigated. Analysis of the pyrolysis oil in terms of water content, density, pH, viscosity, elemental analysis and calorific value (CV) were reported. The properties reported, including calorific values, were in the range of similar bio-oils produced by conventional pyrolysis process and they were also similar to those disclosed in the present invention at around 19kJ/g. However no discussion of how the properties of the oil product varied with processing conditions such as time, temperature, power or use of microwave activated additives was given. The authors reported that at elevated temperatures char yields could be decreased resulting in increased yields of hydrogen gas.

Microwave pyrolysis of biomass for char production

More recently, microwave induced pyrolysis has been investigated by Huang et al. They looked at pyrolysis of rice straw and have identified solid liquid and gaseous products. As they were unable to control temperature independently to power input, a calibration curve for a defined sample mass was prepared between for 50W to 500W, corresponding to a temperature interval of 105 – 563°C. The conditions for experimentation were set between 266 – 563°C. The calorific value of the rice straw solid residue results obtained was no more than 20 kJ/g, and no better than those achievable by conventional methods in this temperature range. They also found no correlation between the calorific value of the char and the microwave power/temperature. As a result of the poor calorific value of the char they investigated alternative applications for the solid, e.g. as absorbent (surface area up to

270 m^2g^{-1}). In our work we have found that it was possible, at temperatures lower than those reported, to prepare a char of higher calorific value, with the possibility to optimise the calorific value by control of microwave power and temperature. The char which we have produced is also physically different to those reported by Huang et al, with negligible measured surface area.

Although microwave pyrolysis of biomass above 300°C from different sources has been investigated by other researchers the lower temperature process of microwave torrefaction for the production of a high calorific char has not been.

In microwave assisted torrefaction or pyrolysis of biomass a number of factors such as microwave power, reaction temperature and time, type of substrate and its moisture affect the efficiency of the process. However, as this disclosure demonstrates there may be additional factors which influence the efficiency of the process, for example, biomass densification and pre-treatment temperature.

These two aforementioned factors form the basis of the process disclosed in this invention and are a key advantage over existing microwave-assisted pyrolysis processes.

At a basic level density and size of biomass govern processing quantities, handling volumes and materials logistics. With increasing utilisation of biomass for renewable energy generation, densification techniques such as pelletisation and briquetting have become an essential prerequisite in biomass pre-processing. However, densification also influences the efficiency with which materials interact with microwaves. As demonstrated in Example 1.D densification enhances the efficiency of absorption of microwave energy and allows greater processing rates, which are essential in commercial application of this technology. Typically, simple densification techniques start with pulverisation of biomass followed by compacting the pulverised material into pellets, briquettes or continuous rods or logs. The compacting process involves pressing particles into desired shapes, for example, by means of a press wheel (pellets) or screw extrusion into a dye of determined shape. Heat is generated during the compression as a result of increasing pressure. This causes the lignin (plus other components) in the biomass to melt and/or flow to envelop and bind the particles in the desired final shapes. In some instances adhesives or adhesion promoting compounds may be added to affect the binding or particles may be heated in the process to cause the flow or setting of the binder. The resulting products, for example, pellets, briquettes or rods, exit the processor, or stage of processing, hot and it is this heat that is utilised in the process disclosed herein.

Biomass pre-heating in microwave-assisted pyrolysis of biomass is an important factor of this disclosure. A number of preceding inventions suggest preheating of biomass to minimise microwave power input.

For example, the disclosure of US Patent No. 5,084,141 suggests preheating organic material with a heated gas stream to temperatures above 250°C and preferably between 300 and 500°C. However, this disclosure does not provide an informed explanation why these temperatures might be beneficial. Carbohydrate based biomass and, in particular, lignocellulosic plant biomass, does not interact well with microwaves to generate efficient heating. Many microwave absorber additives such as graphite have been explored in the patent and scientific literature to indirectly induce heating to non-absorbing substrates to overcome this shortfall. However, as this disclosure demonstrates, heating is an important pre-requisite to microwave-assisted biomass torrefaction.

At elevated temperatures, the main components of biomass interact more efficiently with microwave irradiation. At about 180°C cellulose, typically the major component of plant biomass, undergoes a physical transition which increases the mobility of the cellulose polymer chains. This allows better charge transfer interactions between hydroxyl and/or other functionalities on the chains (or hydrogen-bonding network) and tends to increase electric conductivity. This in turn enhances interaction with the electromagnetic field of the microwave irradiation. Furthermore, it also affects the chemical reactions pathways involved in the decomposition of cellulose by altering the activation energies associated with charge transfer and other reactions as a result of proximity of functional groups in more mobile polymeric systems. This, coupled with the increased polarity of functional groups, is responsible for the different chemical composition of the resulting products observed in microwave-assisted processes compared to conventional pyrolysis systems. Similar physical changes occur for hemicellulose, but typically at lower temperatures of around 160°C. Physical transitions in lignin can occur at lower temperatures, but in a broader, less defined, manner. Additionally, the extended three dimensional structural network, as well as fewer hydroxyl functionalities, means that the activation effect is less pronounced for lignin.

Lignin, hemicellulose and cellulose are the main structural components of biomass, with the latter usually representing the largest proportion. In order to fully take advantage of the activation phenomenon, biomass should be preheated to around 180°C. At this temperature all structural components are activated and a relatively low power of microwaves and/or short irradiation time (within seconds) is required to affect the decomposition reactions and carbonisation. Furthermore, under these conditions the fast rates of reaction enable homogeneous decomposition of the samples. Lower temperatures are acceptable, but do not take full advantage of the activation phenomenon across all components and thus reaction rates are slower. The resulting chars are less homogeneous under comparable irradiation times with charring occurring from inside out. Furthermore, at lower temperatures fractions of volatiles are significantly lower and the calorific values of the resulting chars are poor. Higher pre-treatment temperatures are unnecessary and uneconomical, and too high a temperature in excess of 300°C can cause premature thermal degradation and/or undesirable decomposition reaction pathways.

The process utilised in the present invention takes full advantage of the densification and preheating phenomena. It integrates two elements: densification and microwave torrefaction equipment in a continuous fashion.

The first element compresses the sample(s) to maximise throughput and/or the amount of material available for absorption of microwave energy. In the process the sample(s) are preheated due to mechanical friction and compression (and potentially additional chamber, wheel or screw heating, depending, *inter alia*, on the equipment design and type of biomass), but rather than dissipate that heat, as in conventional processes, the energy is directly utilised for the second element of the process: microwave decomposition. In this manner the first element not only provides densification, but also an efficient preheating method. Preheating has been described in other patents, such as, US Patent No. 5,084,141 for preheating biomass, but the use of gas, infrared or other methods requires additional energy and is less efficient, in particular for larger particles. Because the thermal diffusivity of biomass is poor these methods largely preheat the surface and not the core of the particle. In the invention disclosed herein heat is transferred to individual particles which are then compressed to the desired size/shape and, although a temperature gradient between the core and the surface is likely, it is still a more effective way of preheating the sample and it utilises the "waste" heat of the first process rather than requiring additional heating energy.

US Patent No. 7,101,464 discloses using heat generated from the pyrolysis process for preheating waste tyres prior to microwave pyrolysis, but this process does not integrate densification and is less applicable to biomass where (1) anaerobic conditions are required to suppress burning and thus large volumes of inert gas is needed; and (2) the exhaust gasses from pyrolysis, which contain valuable chemical products, can be lost or exposed to prolonged heating and microwave irradiation.

The importance of maintaining low temperatures during microwaving of biomass to produce chemically functional oils has been highlighted in US Patent No. 3,843,457 which employs low temperature microwave induced plasma under vacuum for pyrolysis of waste (largely carbohydrates). This helps to preserve chemical functionality and produce higher value chemical products. In the invention disclosed herein the processing temperature for the microwave assisted pyrolysis may be low, i.e. between 100 and 300°C. Additionally, the biomass may be fed into the microwave chamber through a narrow feed tube with one or more outlets for gas (Figure 1.1) and liquid decomposition (Figure 1.1) products. The outlets are placed at the point at which the decomposition reaction occurs enabling immediate removal of products from the microwave chamber thus preventing prolonged heating and exposure to microwaves.

A number of biomass microwave processor designs are reported in the patent literature. For example, US Patent No. 4,795,300 describes a processor where microwaves are used to dry the biomass prior to pyrolysis, but the pyrolysis itself is initiated with a powerful laser and occurs at temperatures in excess of 400°C. The process utilises a screw feed or an auger to mix and propel the materials through the process. Use of this material conveying method for biomass is the most popular in the existing designs. International Patent application No. WO 2006/057563 utilises an auger screw to transport materials and mix them to ensure even irradiation with microwaves which are irradiating the chamber from one side. A similar design is reported in US Patent application No. 2008/0063578 which describes generation of carbonaceous materials. In addition to mixing and propagation of the feed materials and products, an auger may enable contact heating of the material to be processed, as described in Canadian Patent No. 2,577,684.

An alternative method of feeding materials into and through the microwave chamber involves conveyor belts. US Patent Nos. 5,330,623 and 3,843,457 both employ a conveyor belt to transport organic materials through a microwave chamber. However these systems do not allow easy mixing of the material which might be unevenly irradiated. US Patent No. 4,631,380 discloses a design for sterilisation of grain whereby a number of microwave sources are arranged across and around a central cylindrical passage way thus irradiating the material evenly as it passes through. The material can be conveyed by an auger or a belt conveyor and the passage way is constructed using a microwave transparent material.

An alternative approach is proposed in International WO 2007/007068 whereby the whole chamber is rotated around its axis much like in a tumble dryer. The material is mixed and irradiated with microwaves through the chamber. This design is also equipped with vents in the inner wall of the chamber for venting gasses and the rotating action prevents the material from falling through these vents.

Open chambers or vents are used to enable the removal of pyrolysis vapours. However, the microwave processing chambers in these existing designs are typically large, leaving significant void spaces where vapours and/or residues can collect and continue to be heated and/or reacted. The vapours can react with themselves or the feedstock and condense on the walls of the chamber where they can further react to form heavier fractions such as tars. The deposits can potentially block microwave radiation windows/inlets affecting the irradiation of samples. Even with a flow of carrier gas or a vacuum, which is commonly employed, a large void volume is a disadvantage in that it allows secondary reaction after pyrolysis or torrefaction. Furthermore, larger microwave chambers will require larger amounts of inert gases and/or more powerful vacuum to (1) ensure the necessary anaerobic conditions are maintained throughout the pyrolysis/torrefaction reactions; and (2) ensure that the vapours are removed from the chamber.

Furthermore, fractionation of pyrolysis/torrefaction products according to the residence time of materials in the microwave is disclosed as part of the present invention. The system described herein enables fractionation of the liquid and gaseous products obtained from the degradation process. It may be controlled by altering outlet positioning, rate of feed, microwave power and/or positioning. This is a key advantage of the present invention over existing processors.

A similar principle can be utilised for additives which can be injected into the processor at different points to affect desired reactions. This may additionally enhance the flexibility and control of the process.

The present invention overcomes these disadvantages having a material carrier tube which is transparent to microwaves and closely surrounds the biomass material so as to reduce voids. Careful positioning of the outlet ports on the processor can help to remove gaseous, vaporous or liquid products as soon as they are formed. Additionally because of the close fit of the feed in the processor any char deposited on the inner walls of the processor can be wiped off/cleaned by the forward moving materials ensuring that the enclosure remains transparent to microwaves. Additionally, none of the prior known designs take advantage of the densification of biomass to maximise the absorption efficiency of the microwave energy nor the preheating generated through that process.

Densification of biomass can be achieved in a number of ways, for example: pelletising, briquetting or screw extrusion. A combination of screw extrusion and microwave irradiation is known and has been applied in food processing (DE3237267: Process for extruding a foodstuff with the use of microwaves) and extrusion of plastics and rubber articles (US 1,493,836: Extrusion Process). However, it has only been used to warm or melt materials, but it has not been applied in preheating and/or pyrolysis/torrefaction of biomass.

European Patent Application No. 1978086 discloses a process for the production of biogas or bioethanol from water and lignocellulosic biomass in which an extruder is used to premix powdered lignocellulosic material and water to form a paste for microwaving, but this process involves hydrolysis and not pyrolysis/torrefaction of biomass and additionally does not benefit from densification and temperature increase, but merely from improved mixing between components.

SUMMARY OF THE INVENTION

Thus, according to a first aspect of the invention we provide a processor for use in the microwave torrefaction of biomass material which comprises;

(1) a material densifier, optionally including means for preheating the biomass material; and

(2) a microwave unit adapted to conduct microwave-assisted torrefaction of the biomass material, the unit comprising a feed pipe for material transfer fitted with gas and/or liquid outlets to enable rapid removal of gas and/or liquid formed during the process.

The biomass may be pulverised and dried before feeding to the densifier. The drying can optionally be conducted with heat generated by the microwave process utilising a heat exchanger described herein. Pulverisation should be carried out by equipment suitable for the biomass to be processed. Typically a hammer mill or chopper used in standard biomass densification technologies can be used although other appropriate means can also be employed.

The pulverised material is then fed into a material densifier. The material densifier may be, for example, a pelletiser, a briquetter, a screw extruder, etc. Thus, the material densifier may be known to the person skilled in the art. The object of the densifier is to increase the density of the biomass material which makes the process more efficient. It also enables the biomass material to be preheated to the desired processing temperature. The densifier can be a standard commercially available pelletiser, or a briquetter but is preferably one capable of producing continuous rods which can be fed into the microwave chamber. Screw type extruders capable of continually feeding material are also appropriate and preferred. If appropriate liquid additives, such as, but not limited to those used in typical densification processes, e.g. glycerol or waste glycerol, or others, such as, ammonia, hydrochloric or sulphuric acid, etc., can be mixed in to help material processing into a dense rod. The density of the extruded material that can typically be achieved by commercial processors, but typically, not essentially, higher densities (in excess of 600kg/m^3 are preferred). The densifier should be preferably, but not essentially, equipped with means of temperature and processing rate control, to allow flexibility and control of the system and to allow for variability in the feed material. The material should normally be preheated during mechanical processing but, where additional heating is necessary, auxiliary heating can be supplied by a heat exchanger, which removes heat from the sample after the microwaving stage. The preheating temperature should be between 100 and 300°C, preferably 120-250°C, more preferably 160-220°C and most preferably 180-200°C. Optionally, the densifier can be fitted with an outlet for exhaust gasses and/or liquids generated in the pressing processes.

Additionally, the densifier should be fitted with a gas inlet near the point the densified material is fed into the microwave chamber for feeding gases which suppress flame formation and/or assist removal of vapours, gasses and liquids generated in the microwave assisted degradation process. These can include, but are not limited to, for example, nitrogen, hydrogen, carbon dioxide, acidic or basic vapours or other additives which can help to catalyse certain processes.

The compressed feed material together with the gas may be fed directly into a carrier tube which feeds into and runs through the microwave chamber. If the biomass material is prepared in short pellets, rather than a continuous feed, a means of propulsion should be integrated into the densifier to ensure feeding and continuous passage of the material through the carrier tube whilst overcoming friction between the carrier tube and the densified material. The carrier tube feeds material directly into and through the microwave chamber and takes the bio-char out at the end of the degradation process.

The carrier tube should be constructed of a strong material, which is transparent to microwaves, heat resistant to at least 300°C and capable of withstanding mechanical pressure of the feed materials as along with the pressure of the evolved gasses during the process. It should also have low friction to allow smooth transfer of material within close contact to the sides. Construction materials can, for example, include glass, toughened or Pyrex® glass, or other suitable non-metallic material. The choice of a suitable construction material can allow online monitoring such as, but not limited to, NIR probes, laser probes or UV-Vis measurements, which can aid control of the process.

Although the tube may be any conventional shape, it is desirably substantially cylindrical with a substantially uniform diameter throughout. It will be understood that the diameter of the tube may be governed by, *inter alia*, the size of the extruded/pressed biomass material and its density as well as the penetration ability of microwaves which depend on wave parameters and power. Thus, the tube diameter may typically be less than 50cm to ensure that the biomass sample is irradiated uniformly throughout and sizes of about 0.5-10 cm in diameter are most preferable. It is also desirable that the tube or chamber is dimensions to correspond to the amount of biochar being processed. Thus, the chamber closely surrounds the biomass material so as to reduce the size of any void(s) remaining and therefore reduce the undesirable reactions that can be a consequence of excessive voids. The carrier tube may comprise an irregular shape, for example, a tube with a conical shape, e.g. with a progressively smaller diameter following the degradation reaction to account for the resulting mass loss, may be desirable. The exact specification of the reduction in size will depend upon, *inter alia*, the reaction conditions employed, biomass used and the pre-treatment employed. Similarly the length of the tube will depend upon, *inter alia*, process parameters, including the diameter of feed material, the rate of feed, microwave power, number of microwave irradiation points used, etc.

The pressed material is fed into the microwave chamber. The use of the microwave processor to conduct microwave-assisted torrefaction of the material is so as to yield a higher calorific value char, decomposition oils and/or gasses. The chamber should be fitted with at least one microwave irradiation source, if more than one irradiation source is used they can optionally be shielded from each other to allow better control of the reaction. A simple low power microwave source is typically required as reactions are very rapid. Typically a 15mm biomass cylinder can be charred in around 10 seconds at 300W power input, a larger volume of, for example 35mm can take around 200 seconds, but this relationship is not linear. Higher power microwave generators, or more sequenced generators might be required for high throughput rates. The process conditions can easily be controlled by altering the feed rate from the densifier. The microwave irradiation can be focused around the carrier tube or reflected around the chamber. The microwave source should be located in any geometry which is perpendicular or angled along the carrier tube in some cases use of reflective mirrors might be beneficial to ensure uniform sample irradiation.

Inside the chamber the carrier tube is desirably fitted with exhaust tubes to enable the removal of degradation vapours and liquids placed preferably adjacent the top and/or bottom of the tube respectively. The removal of volatile or liquid products will be promoted by the mixed gas (e.g. nitrogen) and/or can be assisted by vacuum. The exact positioning of the outlet tubes will depend on process parameters, but flexibility is built into the process through control of the feed rate, density, microwave power and other aspects to enable optimisation. Typically the one or more outlets will be placed in direct proximity to the area where pyrolysis/torrefaction occurs. The one or more outlets can be angled relative to the flow of the material in the tube to minimise particulate matter entering the outlet holes. Additionally, the one or more outlets can be fitted with traps for any particulate or early condensing matter and/or appropriate filters. The length of the outlet tubes within the microwave chamber should be kept to a minimum to ensure material is removed from the degradation environment as soon as possible to avoid secondary reactions, unless these are particularly required by the application. Once outside the chamber, the volatile and/or liquid products can be treated in conventional ways.

Significantly, this design has sufficient flexibility built in to enable fractionation of the degradation products. Thus, a number of outlets can be used to facilitate the process and can be spaced according to the progress of reaction(s) along the carrier tube. This can be used in conjunction with sequential microwave sources to allow for better process control. For example, at an early stage water vapour can be removed followed by more organic fractions and chars. Fractionation of the degradation products is an important and innovative aspect of the present invention. It enables users to take full advantage of the low temperature employed in the process to preserve chemical functionality and offers an opportunity for the users to maximise the value of their chemical products resulting from the degradation.

At the end of the pyrolysis/torrefaction the remaining bio-chars can be removed from the microwave chamber into a cooling area. At the end of the microwave process the bio-char can reach temperatures in excess of 300°C, to avoid potential for fires the bio-char must be cooled. At this stage, optionally, a heat exchanger can be used whereby the heat dissipated from the char can be transferred to drying and/or preheating the feed material in the pulverisation and/or densification stage. Use of a heat exchanger can significantly improve the energy footprint of the process. Additionally, other elements of the process should preferably be insulated to avoid loss of valuable heat energy.

We also provide a process for the microwave torrefaction of biomass material which comprises the steps of;

(1) densifying the material;
(2) optionally preheating the biomass material;
(3) torrefying the material in a microwave processor; and
(4) collecting gas and/or liquid formed during the process.

The process takes advantage of densification and heat pre-treatment, both of which are important in efficient microwaving of biomass.

The process allows flexibility and control to accommodate a variety of samples such as, but not limited to biomass.

In the process, the biomass may be pulverised and dried. Pulverisation should be carried out by equipment suitable for the biomass to be processed. Typically a hammer mill or chopper used in standard biomass densification technologies can be used although other appropriate means can also be employed. The drying can optionally be conducted with heat generated by the microwave process.

Liquid additives, such as, but not limited to those used in typical densification processes, e.g. glycerol or waste glycerol, can be mixed in to help material processing into a dense rod.

When the process includes the optional pre-heating step, the pre-heating temperature may be from 100 to 300°C, preferably 120-250°C, more preferably 160-220°C and most preferably 180-200°C.

The process conditions can easily be controlled by altering the feed rate of the biomass from the densifier. The microwave irradiation can be focused around the carrier tube or reflected around the chamber.

The vaporous and liquid products of the process may be treated in conventional ways. In addition, the degradation products may themselves be fractionated as part of the process of the present invention. For example at an early stage water vapour can be removed followed by more organic fractions and chars. Fractionation of the degradation products is an important and innovative aspect of this invention. It enables users to take full advantage of the low temperature employed in the process to preserve chemical functionality and offers an opportunity for the users to maximise the value of their chemical products resulting from the degradation.

Thus, according to one aspect of the invention we provide a method of producing L-glucosan which comprises the microwave torrefaction of a biomass material in the presence of ammonia or hydrochloric acid (HCl).

We especially provide a method of producing L-glucosan in which ammonia is used. When ammonia is included in the reaction, the amount of ammonia present in the reaction of the invention may vary depending upon, *inter alia*, the nature of the biomass, the temperature of the torrefaction, etc. However, desirably, the amount of ammonia should be 5% or less based on the weight of the biomass, e.g. from 0.2 to 5% w/w or from 1 to 3% w/w. Ammonia could be introduced to biomass either from dry gas phase or from solution.

In the production of L-glucosan when HCl is included in the reaction instead of ammonia, the amount of acid present in the reaction of the invention may vary depending upon, *inter alia*, the nature of the biomass, the nature of the acid, the temperature of the torrefaction, etc. However, desirably the amount of acid should be low than 30%, preferably less than 5% based on the weight of the biomass, e.g. from 0.5 to 5% w/w or from 1 to 3% w/w.

In the production of L-glucosan the nature of the acid may also vary, although preferred acids are those acids that are readily available in large scale and commodities, such as hydrochloric or sulphuric acid. The nature of the acid has been shown to have an influence on the product of microwave torrefaction. For example, hydrochloric acid increases the amount of oil and the yield of L-glucosan despite the fact that sulphuric acid decreases the amount of oil, significantly increases yield of L-glucosenone and does not significantly change L-glucosan yield.

HCl could be introduced either from dry hydrochloric acid in a gas phase or from solution. The concentration of acid should be lower than 100%w/w, preferably ≤30% w/w, more preferably ≤10% w/w and especially ≤5%w/w. In the process of the invention the use of 5% or less of ammonia produces L-glucosan as a major component of the oils production from microwave torrefaction. The amount of L-glucosan in the oil may be as much as 50% and thus the bio-oil is significantly simplified.

The production of L-glucosan is especially advantageous since it has been shown that L-glucosan may be enzymatically digested to glucose and consequently may be useful in the production of biofuels, such as bioethanol. Thus, in a further aspect of the invention we provide a process for the manufacture of glucose, suitable for the bioethanol production, which comprises:

(i) microwave torrefaction of a biomass material to in the presence of ammonia or HCl to produce L-glucosan; and

(ii) hydrolysis of the L-glucosan of step (i) to produce glucose.

We have further found that the addition of sulphuric acid dramatically decreases the yield of organic oil, but, importantly, simultaneously produces a significant increase in the char yield. Therefore, the use of sulphuric acid may have the ability to dramatically reduce the amount of waste in bio-char production. Sulphuric acid may desirably be introduced from solution, for example, sulphuric acid could be adsorbed from an aqueous solution.

Thus, according to further aspect of the invention we provide a method of producing bio-char which comprises the microwave torrefaction of a biomass material in the presence of sulphuric acid.

We have found that the presence of an acid, such as sulphuric acid, increases the yield of solid, i.e. char, product greatly (see Figure 3.1A). For example, in the presence of 3% of sulphuric acid, we have found that char yield is 50% higher than the yield of char under standard conditions, i.e. microwave torrefaction in the absence of sulphuric acid. Furthermore, the calorific value of the char produced by microwave torrefaction is increased in the presence of acid/base additives by up to 50%.

The amount of sulphuric acid present in the reaction of this aspect of the invention may vary depending upon, *inter alia*, the nature of the biomass, the nature of the acid, the temperature of the torrefaction, etc. However, desirably the amount of acid should be 5% or less based on the weight of the biomass, e.g. from 0.5 to 5% w/w or from 1 to 3% w/w.

Although it is often considered desirable to maximise the amount of oil produced, in certain circumstances a decreased oil yield is preferred. For example, in the operation of furnaces, e.g. in power generation, oil is generally considered a waste product and it is the char that is the desired product. Thus, the fact that the use of sulphuric acid as hereinbefore described may reduce the amount of oil produced may be seen as significantly beneficial in the generation of power from biomass/char.

However, this contrasts with the use of hydrochloric acid insofar as, whilst hydrochloric also increases the yield of bio-char, it also increases the yield of organic oil simultaneously with an increase in the char yield.

Thus, according to further aspect of the invention we provide a method of producing bio-char which comprises the microwave torrefaction of a biomass material in the presence of hydrochloric acid.

The bio-char may comprise one or more of a lignocellulosic char, a cellulosic char or a hemicellulosic char and mixtures thereof.

In this aspect of the invention the method comprises a method of producing bio-char and bio-oil.

We have also found that the use of amines other than ammonia, for example, trialkylamines, such as tri-n-butylamine increase the wax produced from wheat straw.

Thus, according to a yet further aspect of the invention we provide a method of producing a bio-wax which comprises the microwave torrefaction of a biomass material in the presence of a trialkylamine.

Microwave irradiation is defined as "electromagnetic irradiation in the frequency range of 0.3 to 300 GHz". Similar to domestic microwaves, specialised chemistry microwave reactors operate at 2.45 GHz. Microwave radiation is used in several applications including radar, communications, radiometry, medicine, physics, chemistry, and cooking food. Compared to conventional heating techniques a microwave process is advantageous in terms of shorter reaction times, higher heating efficiencies and greater control. The advantages of microwave technology in terms of mobility of small scale processors and value in waste reduction applications have been highlighted by Ruan et el.[7] The use of microwaves is well established in many industrial and commercial applications. Microwave treatment of biomass is used before and or during extraction processes. The use of microwave for extraction of oil is gaining significantly in terms of commercial importance and wide spread utilization. It is employed in extraction of primary plant oils as well as extraction of petroleum oils from drilling muds, tar sands. Microwave ovens have gained acceptance as a mild and controllable processing tool. Microwaves allow simple, rapid and low solvent consuming processes. Microwaves are already widely used for extraction of oil from solid to liquid (CEM-2005). The use of microwaves is also growing in the processing of materials. Microwave processing is now being used for "the production of advanced ceramics, the deposition of thermal barrier coatings, and the remediation of hazardous wastes" with new applications constantly being researched.

Low temperature pyrolysis, also known as torrefaction, is a thermal treatment usually carried out between 200 and 300°C. Torrefaction is a mild biomass pre-treatment process for upgrading the quality of biomass as fuel for combustion and gasification applications. Torrefaction can also be referred to as roasting, slow and mild pyrolysis and high temperature drying. Thus, by the term "microwave torrefaction" we mean a mild pyrolysis carried out in the presence of microwave irradiation, and in particular a treatment process carried out at a temperature of between 100 and 300°C, for a variety of biomass materials. Particular temperature ranges may be used depending upon, *inter alia*, the nature of the biomass, thus ranges which may be suitable are preferably between 100 – 220°C for hemicellulose and hemicellulose rich biomass, 200-300°C for cellulose and cellulose rich biomass, and above 250°C for lignin and lignin rich biomass.

Conventional (non-microwave) torrefaction of biomass materials such as wood is well known. Torrefied wood has the moisture and most volatile organic compounds (VOC's) driven out resulting in a high percentage of carbon content. In addition, the chemistry and structure of the wood itself is converted into a new form by continued exposure to heat. Torrefaction of other biomass of materials, such as plant origin, e.g. prunings and/or mown grass, or waste materials is also known.[8] However, the micronisation or pulverisation of such torrefied materials has proved unsatisfactory.

The biomass used in the present invention may comprise untreated biomass, pre-treated biomass, biomass fractions, and components and mixtures thereof.

The bio-char will generally be a lignocellulosic char material and it is advantageous in that, *inter alia*, it is suitable as a fuel, for example, in the generation of power. Therefore, advantageously the bio-char of the invention may be mixed with other fuels, such as coal. Therefore, according to a further aspect we provide a fuel comprising a bio-char material according to the invention. We further provide a fuel as hereinbefore described which comprises the bio-char material in admixture with other conventionally known fuels, such as a polysaccharide or coal (e.g. pulverised coal).

The process of the present invention is especially advantageous in that by the use of relatively low temperatures and control of the power input, *inter alia*, it provides the torrefaction of naturally occurring products in a biomass, such as cellulose, hemi-cellulose and/or lignin.

Therefore, according to a further aspect of the invention we provide a method as hereinbefore described of selective microwave torrefaction of hemicellulose from a biomass between 100 – 200°C.

Furthermore, we provide a method as hereinbefore described of microwave torrefaction for the production of breakdown products of cellulose, between 200 – 250°C.

Furthermore again, we provide a method as hereinbefore described of microwave torrefaction for the production of breakdown products of lignin, above 250°C in the presence of ammonia. The amount of ammonia should be 5% or less based on the weight of the biomass, e.g. from 0.5 to 5% w/w or from 1 to 3% w/w.

According to a further aspect of the invention we provide a method as hereinbefore described in which the irradiation power is between 100 and 1200W when using a CEM Discover^{TM} (available from CEM Microwave Technology Ltd. Buckingham, UK) and Millstone Microwave. As is well known in microwave processing the power input depends on the size of the microwave cavity and the cavity geometry, therefore, it would be understood by the person skilled in the art that scale-up of the process will include irradiation powers >1200W.

In the methods of the invention any conventionally known biomass materials may be used, such as waste material, or biomass material grown from plants, including, corn, hemp, miscanthus sugarcane and switch grass, etc., wood, such as poplar or willow, fungal species and marine resources, such as algae.

The method also discloses the use of other additives. Such additives may comprise one or more microwave absorbers, which not only act to absorb the microwave energy but can be used at higher ratios as activators for earlier or alternative decomposition pathways. Although a variety of conventionally known microwave absorbers may be used a preferred microwave absorber is a carboniferous absorber, such as graphite. The catalytic role of the absorber is important. It is well known that graphite and such materials act as absorbers of microwave energy, but we have surprisingly found that at higher ratios (up to 10% graphite/absorber) it is possible to change the properties of the products produced, in a manner contrary to that reported previously, in particular, increased char yields.

The amount of microwave absorber used may also vary, although generally small amounts are necessary. Thus for example the ratio of absorber: biomass may be 1:99 to 10:90. Use of char/graphite differs from those previously reported in that rather than increasing the amount of oil it improves the yield of char and thus can be used to affect the distribution of the three products in a different way.

Alternatively, an additive may comprise a humectant, such as glycerol, glycerine or other such materials, to help extract primary oil, minimize acidity of secondary oil, catalyse the transformation of the biomass and improve properties of secondary oil.

The invention will now be described by way of example only and with reference to the accompanying figures.

Table 3.1 shows that the yield of char depends on the nature of feedstock and additives. The change in yield of char and oil in comparison to those produced under the same conditions in the absence of additives are shown in Figure 3.1. All of the additives increase yield of solid product greatly (Figure 3.1A). In the presence of 3% of sulphuric acid char yield is 50% higher than the yield of char in the standard experiment. Calorific value of the microwave produced char is increased in the presence of acid/base additives up to 50%.

The temperature at which the oil is released from the biomass in the presence of additives is lower than the temperature at which it is released in the control microwave experiment (see Table 3.1). As shown in Figure 3.1B, the organic oil yield depends heavily on the nature of the additives. For example, addition of hydrochloric acid to wheat straw increases oil yield by 5% (from 21.1 up to 22.1). In contrast, addition of sulphuric acid dramatically decreases oil yield from 21.1% down to 7.3%.

Composition of the organic oils produced in the presence of microwave irradiation (see Figures 3.3 to 3.6 and Tables 3.2 to 3.5) is different from composition of oil produced during the fast pyrolysis (see Figure 3.7). As an agricultural residue, wheat straw is high in the main plant nutrients, especially potassium.[3] Potassium is a well-known catalytic metal for the pyrolysis process, and the product distribution is typical for a catalysed decomposition of the lignocellulose via an ionic mechanism.[4] Thus, low yields of sugars and high yields of furfural and acetic acids are observed from cellulose and hemicellulose decomposition (see figure 7).[5] A mixture of phenols and methoxyphenols is produced from decomposition of the lignin component of the biomass.[6] Figure 3.3 and Table 3.2 display the GC-MS of the oil produced in the process of microwave torrefaction from wheat straw (control experiment). While catalysed decomposition product markers (furfural and acetic acid) are observed in the microwave oil, the product distribution contains higher relative yields of phenols, methoxyphenols, diphenols and di-methoxyphenols, and high relative yields of the primary cellulose decomposition products (28% of L-glucosan and 1.3% of 1,4:3,6-dianhydro-α-D-glucopyranose), possibly due to the milder temperatures experienced in this case. Thus, qualitatively, it appears that the bio-oil produced in the process of microwave torrefaction has a higher relative yield of aromatics and primary sugars compared to the fast pyrolysis oil. M. Miura *et al* proved that microwave heating of

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[3] E.g. Jenkins B.M., Baxter L.L., Miles Jr. T.R., Miles T.R. Combustion Properties of Biomass. Fuel Proc Technol. 54 (1998) 17-46i

[4] Evans R.J., Milne T.A. Molecular Characterisation of the Pyrolysis of Biomass. 1. Fundamentals. Energy & Fuels, 1 (1987) 123-137

[5] Nowakowski D.J., Jones J.M. Uncatalysed and potassium-catalysed pyrolysis of the cell-wall constituents of biomass and their model compounds. J. Anal. Appl. Pyrol. 83 (2008) 12-25.

[6] Fahmi R., Bridgwater A.V., Thain S.C., Donnison I.S., Morris P.M. Yates N. Prediction of Klason lignin and lignin thermal degradation products by Py–GC/MS in a collection of *Lolium* and *Festuca* grasses. J. Anal. Appl. Pyrol. 80 (2007) 16-23.

cellulose and wood increased L-glucosan yield.[7] Also, A.M. Sarotti *et al* have demonstrated that cellulose can be pyrolysed under microwave irradiation to produce L-glucosenone.[8] Neither of these teams has done any investigation of acid/base influence on the L-glucosan and L-glucosenone yields.

The influence of acid additives on the composition of microwaved oil is shown in Figures 3.4 and 3.5 and Tables 3.3 and 3.4. Bases increase the relative concentration of sugar derivatives in the bio-oil in comparison with a control microwave experiment. Microwave torrefaction of biomass in the presence of H_2SO_4 gives a narrower range of products, predominately sugar derivatives, such as L-glucosenone, in the bio-oil. The high concentration of L-glucosenone could be explained because it is well known that acid catalysed rearrangement/dehydration of cellulose during the pyrolysis.[9,10] It can be seen that the yield of sugars is increased in the presence of hydrochloric acid from 29.3% to 41% in comparison with control microwave experiment. In contrast to sulphuric acid, concentration of L-glucosenone in the oil is insignificant (1.5%). A major component in this case is L-glucosan (35.5%). The effect of ammonia on the composition of the oil is shown in Figure 3.6 and Table 3.5. L-glucosan (46%) and 2,3-dihydro-benzofurane (10.2%) are two major components of this oil.

It is significant that during the microwave-low-temperature torrefaction chem-adsorbed water, accompanied by low molecular mass acids/bases, is released separately from the organic oil (Figure 3.8). As a result, neither additives influence water content nor the acid number of the organic oil obtained during the microwave experiment. In the typical low temperature microwave experiment the water content is lower than 1% of the oil mass and the acid number is lower than 10. These

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[7] M. Miura, H. Kaga, T. Yoshida, K. Ando "Microwave pyrolysis of cellulosic materials for the production on anhydrosugars" J. Wood. Sci. 2001, 47, 502-506.

[8] A.M. Sarotti, R.A. Spanevello and A.G.Suarez "An efficient microwave-assisted green transformation of cellulose into levoglucosenone. Advantages of the use of an experimental design approach" Green Chemistry, 2007, 1137-1140.

[9] Nowakowski D.J., Woodbridge C.R, Jones J.M, Phosphorus catalysis in the pyrolysis behaviour of biomass. J. Anal. Appl. Pyrol. 83 (2008) 197-204.

[10] Di Blasi C., Branca C., Galgano A., Thermal and Catalytic decomposition of wood impregnated with sulfur- and phosphorus-containing ammonium salts. Polymer Degrad. Stabil. 93 (2008) 335-346.

parameters are much better than those for the typical fast pyrolysis oil[11] and the oil obtained at the high temperature microwave pyrolysis[12].

In a further aspect of the present invention it is demonstrated that the effects of microwave irradiation on the decomposition of each of the major constituent components: cellulose, hemi-celluloses and lignin. The invention also demonstrates that this process of decomposition in the presence of microwave irradiation can be successfully carried out at temperatures lower than those used in conventional conditions and in the presence or absence of additives as hereinbefore described. As a result of the alternative production method it is possible to prepare new materials with novel properties, such as high calorific value char and previously unreported yields of oils with controllable properties. Furthermore, the lignocellulosic char produced is advantageous in that, *inter alia*, it may be micronised or pulverised which renders it more suitable as a fuel. We also demonstrate that the control of, *inter alia*, irradiation power and temperature have independent effects on the product distribution and product properties.

Therefore, according to a further aspect of the invention we provide a micronised biomass char material. The biomass char material is suitably derived from a lignocellulosic biomass material using processes hereinafter described. By the term micronised we mean generally comminuted or pulverised char material. Thus, the particle size of the micronised biomass material, e.g. a lignocellulosic char material, may be from 10 to 1,000μm, preferably from 10 to 500μm, more preferably from 10 to 250μm and more preferably from 10 to 100μm. It should be understood that the present invention contemplates the preparation of a lignocellulosic char material which is suitable for micronisation.

As hereinbefore described, the micronised lignocellulosic char material is advantageous in that, *inter alia*, it is suitable as a fuel, for example, in the generation of power. Therefore, advantageously the micronised char of the invention may be

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[11] Report 40661. The Exploitation of Pyrolysis Oil in the Refinery Main Report. Prepared For: The Carbon Trust. March 2008.

[12] Yu F., Deng S., Chen P, LIU Y., Wan Y., Olson A., Kittelson D., and Ruan R. "Physical and Chemical Properties of Bio-Oils. From Microwave Pyrolysis of Corn Stover", *Applied Biochemistry and Biotechnology*, 2007, **136–140**, pp 957-950.

mixed with other fuels, such as coal. Therefore, according to a further aspect we provide a fuel comprising a micronised lignocellulosic char material according to the invention. We further provide a fuel as hereinbefore described which comprises the micronised lignocellulosic char material in admixture with other conventionally known fuels, including one or more of cellulosic char, hemicellulosic char, polysaccharide and coal (e.g. pulverised coal).

According to a yet further aspect of the invention we provide a method of producing a micronised biomass char material which comprises the steps of;

(i) microwave torrefaction of a biomass material to produce a char; and
(ii) micronising the char of step (i).

The process particularly provides a method of producing a micronised lignocellulosic biomass char material. In addition, we provide a method of producing a lignocellulosic char material which comprises of microwave torrefaction of the biomass.

By the term "microwave torrefaction" we mean a mild pyrolysis carried out in the presence of microwave irradiation, and in particular a treatment process carried out at a temperature between 100 and 300°C, for a variety of biomass. In particular preferably between 100 and 220°C for hemicellulose and hemicellulose rich biomass, 200 and 300°C for cellulose and cellulose rich biomass, and above 250°C for lignin and lignin rich biomass.

The process of this aspect of the present invention is especially advantageous in that by the use of relatively low temperatures and control of the power input, *inter alia*, it provides the torrefaction of naturally occurring products in a biomass, such as cellulose, hemi-cellulose and/or lignin.

Therefore, according to a further aspect of the invention we provide a method of selective microwave torrefaction of hemicellulose from a biomass between 100 and 200°C.

Furthermore, we provide a method of microwave torrefaction for the production of breakdown products of cellulose, between 200 and 250°C.

Furthermore, we provide a method of microwave torrefaction for the production of breakdown products of lignin, above 250°C.

The present disclosure demonstrates that the decompositions for hemicelluloses and cellulose can be lower by up to 150°C compared to thermal methods by employing the disclosed microwave method. This means that the microwave induced torrefaction disclosed in the present invention can now extend to include cellulose decomposition at temperatures below 300°C and can yield decomposition oil resulting not only from decomposition of hemi-cellulose but also cellulose.

The present disclosure also offers energy savings over conventional torrefaction methods due to the notable energy efficiency of microwave technology and minimum energy losses during the condensation of the biomass energy in char, oil and gas.

The disclosed method enables the decomposition of biomass components: cellulose and hemi-cellulose in biomass mixture or individually at temperatures at least 100°C lower than in conventional thermal pyrolysis methods.

Therefore, according to a further aspect of the invention we provide a method as hereinbefore described in which the temperature selectively affects the different components. Thus, from 100 to 220°C predominantly provides hemi-cellulose decomposition; from 200 to 300°C predominantly provides cellulose decomposition; and >250°C predominantly provides lignin decomposition.

According to a further aspect of the invention we provide a method as hereinbefore described in which the irradiation power is between 100 and 300W when using a CEM Discover^{TM} (available from CEM Microwave Technology Ltd. Buckingham, UK). As is well known in microwave processing the power input depends on the size of the microwave cavity and the cavity geometry, therefore, it would be understood by the person skilled in the art that scale-up of the process will include irradiation powers >300W.

The process of the present invention is also advantageous, *inter alia*, because it yields char and/or oil with calorific values at least 10 % higher than obtainable by conventional pyrolysis methods and known microwave pyrolysis methods. The yield of oil has also been found to be greater when compared to known methods under similar conditions.

The calorific values of torrefaction oils reported in the present invention are up to 19 kJ/g. Char obtained by the method of the present invention, and especially the micronised char of the invention, has a calorific value of up to 32 kJ/g, which is higher than char produced by conventional methods or as reported in high temperature microwave methods. Importantly, this value is comparable to that obtained from coals (27 to 32 kJ/g).

Therefore, according to a further aspect of the invention we provide a method of manufacturing a high calorific value char which comprises microwave torrefaction of a biomass optionally in the presence of hydrochloric acid as hereinbefore described and optionally followed by micronisation of the char. It will be understood that bio-char suitable for, *inter alia*, micronisation may be manufactured according to the method of the present invention without the use of additives, such as hydrochloric acid.

We also provide a torrefied biomass char which can be easily micronised wherein the char has a calorific value from 20 to 32 kJ/g.

Furthermore, we provide a torrefied biomass char which is suitable for grinding and/or micronisation prior use for energy production.

By the term “high calorific char” we mean a char that has a calorific value comparable to coal. We especially provide a method of manufacturing a high calorific value char which comprises microwave torrefaction of cellulose optionally in the presence of hydrochloric acid. Alternatively, we provide a method of manufacturing a high calorific value char which comprises microwave torrefaction of hemi-cellulose. In a further alternative, we provide a method of manufacturing a high calorific value char which comprises microwave torrefaction of lignin.

Furthermore, the microwave torrefaction of individual biomass components using the disclosed procedure also yields higher values than obtainable with conventional methods. Values up to 45 kJ/g were obtained for hemi-cellulose pyrolysed by the disclosed method compared to 39kJ/g for conventional pyrolysis. For cellulose the maximum values attained were 34 compared to 30 kJ/g for the disclosed microwave and conventional methods respectively. The calorific values of other biomass samples can similarly be maximised to a similar extend with the individual components giving proportional contributions to the overall calorific value of whole biomass.

Furthermore, the microwave torrefaction of biomass which is not rich in hemicellulose, cellulose and lignin, such as algae and biomass rich in other polysaccharides, also yields chars of high calorific value.

Therefore, we also provide a torrefied cellulose char wherein the char has a calorific value of up to 34 kJ/g.

We also provide a torrefied hemi-cellulose char wherein the char has a calorific value of up to 45 kJ/g.

We also provide a torrefied biomass derived oil with a calorific value up to 20 kJ/g, and a gas which may also be used for energy production.

The use of microwave radiation to produce a char and oil from cellulosic material as hereinbefore described is also advantageous in that the use of low temperatures, e.g. in 120°C produces oils with a pH of 3-4. This compares with a pH range of 1-2 when a higher temperature e.g. 150°C was used.

Thus, according to a yet further alternative aspect of the invention we provide a method of producing an oil from a biomass material without the use of an additive as hereinbefore described, wherein the oil has a pH of from 3 to 4, wherein the method comprises the low temperature microwave torrefaction of a biomass material. The method of this aspect of the invention is especially advantageous in the production of, *inter alia*, secondary oils.

Furthermore, the use of microwave radiation to produce a char and/or oil from cellulosic material is also advantageous in that the use of low temperatures, e.g. about 120°C, produces oils with a water content of 10% w/w or less. This may be compared with oils with a water content of up to 30% w/w when a higher temperature e.g. 150°C, was used.

Thus, according to a yet further aspect of the invention we provide a method of producing an oil from a biomass material, wherein the oil has a water content of 10% w/w or less, wherein the method comprises the low temperature microwave torrefaction of a biomass material, optionally in the presence of an additive as hereinbefore described. The method of the invention is especially advantageous in the production of secondary oils.

Furthermore, the method enables independent control of temperature and microwave power to selectively affect different components in the biomass and thus control the distribution and/or elemental and/or chemical composition of decomposition products: solids, liquids and gases. Specifically, oils prepared at the same temperature using different powers can be shown to display different properties, and also oils prepared at different temperatures using the same microwave power can be differentiated.

In the method of the invention any conventionally known biomass materials may be used, such as waste material, or biomass material grown from plants, including, corn, hemp, miscanthus sugarcane and switch grass, etc., wood, such as poplar or willow, fungal species and marine resources, such as algae.

The method also discloses the use of additives as hereinbefore described. Such additives may comprise one or more microwave absorbers, which not only act to absorb the microwave energy but can be used at higher ratios as activators for earlier or alternative decomposition pathways. Although a variety of conventionally known microwave absorbers may be used a preferred microwave absorber is a carboniferous absorber, such as graphite. The catalytic role of the absorber is important. It is well known that graphite and such materials act as absorbers of microwave energy, but we have surprisingly found that at higher ratios (up to 10% graphite/absorber) it is possible to change the properties of the products produced, in a manner contrary to that reported previously, in particular, increased char yields.

The amount of microwave absorber used may also vary, although generally small amounts are necessary. Thus for example the ratio of absorber: biomass may be 1:99 to 10:90. Use of char/graphite differs from those previously reported in that rather than increasing the amount of oil it improves the yield of char and thus can be used to affect the distribution of the three products in a different way.

Alternatively, an additive may comprise a humectant, such as glycerol, glycerine or other such materials, to help extract primary oil, minimize acidity of secondary oil, catalyse the transformation of the biomass and improve properties of secondary oil.

The method of the invention is advantageous because, *inter alia*, we achieve:

- Much higher yields of pyrolysis oils at low temperatures (<300°C)
- Control of properties of the oil at <350°C (variable power and temperature)
- Greater degree of chemical functionality of the oils through use of lower temperatures
- Use of graphite to control composition of oil and the oil/char/gas balance
- Use of glycerol (and other additives) to control oil composition and the oil/char/gas balance
- Higher calorific value chars from biomass, and components and fractions thereof.
- Highest calorific value chars from cellulose and hemi-cellulose
- First demonstration of selective activation of cellulose and to a lesser extent hemi-cellulose
- More energy efficient method of biomass processing through use of microwave technology

- Low temperature production of a high calorific value char with physical properties suitable for direct use in energy production.

The biomass used in any of the aspects of the invention may comprise untreated biomass, pre-treated biomass, biomass fractions, and components and mixtures thereof.

The invention will now be described by way of example only and with reference to the accompanying figures, in which;

Figure 1.1 is a schematic representation of a microwave processor;

Figure 1.2 is a graph illustrating the separation of aqueous and organic fraction based on microwave time;

Figure 1.3 is a schematic representation of apparatus set-up for simultaneous microwave-IR experiment;

Figure 1.4A) is a Gram-Schmidt trace for isotherm pyrolysis of pelletised biomass and 1.4B) is an IR spectrum of the fractions;

Figure 1.5 is a graph illustrating the relationship of the specific microwave energy (amount of microwave energy per unit mass which the biomass absorbs) with the degree of densification of wheat straw;

Figure 2.1 is a schematic representation of the apparatus set-up for the microwave extraction of volatiles from rape meal;

Figure 2.2 is a graph of the microwave profile for the extraction of volatiles from Rape Meal;

Figure 2.3A is a Differential Scanning Calorimetry analysis of the rape meal oil extract and 2.3B a Thermogravimetric analysis of the rape meal extract;

Figure 2.4 is a FTIR spectrum of the liquid organic compounds extracted from rape meal;

Figure 2.5is a schematic representation of the apparatus set-up for microwave co-extraction of volatile organic compounds with water from pine wood;

Figure 2.6 is a graph of the microwave profile for the extraction of volatiles from pine wood pellets;

Figure 2.7 is a FTIR analysis on the volatile extracts from pine wood obtained at the different irradiation power;

Figure 2.8 is a graph of the microwave profile of rape meal extracted with n-pentanol;

Figure 2.9 is a FTIR spectrum of extracts from rape meal with pentanol and water;

Figure 2.10 is a schematic representation of the apparatus set-up for microwave extraction of secondary oil from biomass with capture of highly volatile components;

Figure 2.11 is a FTIR spectrum of extracts from cellulose, miscanthus, rape meal and Norway spruce;

Figure 2.12is a graph illustrating the calorific value of cellulose chars produced by conventional pyrolysis and microwave irradiation at different temperatures;

Figure 2.13 illustrates the direct microwave effect on cellulose;

Figure 2.14 is a FTIR of different types of biomass before and after microwave irradiation;

Figure 2.15 is a C^{13} NMR of cellulose chars of same elemental composition produced by conventional pyrolysis and microwave irradiation;

Figure 2.16 is a graph illustrating the calorific value of hemicellulose chars produced by conventional pyrolysis and microwave irradiation at different temperatures;

Figure 2.17 is a graph illustrating the heat of oxidation values for biomass samples before and after MW irradiation;

Figure 2.18 is a STA (Simultaneous Thermal Analysis) profile of barley dust mixed with PdO as an oxidant to measure heat of combustion;

Figure 2.19 is a STA profile of barley dust after microwave processing;

Figure 2.20 is a STA profile of rape meal;

Figure 2.21 is a STA profile of rape meal after microwave processing;

Figure 2.22 are thermogravimetric IR spectra of volatiles at temperature 330^0C for rape meal before and after microwaving;

Figure 2.23 are thermogravimetric IR spectra of volatiles at temperature 390^0C for rape meal before and after microwaving;

Figure 2.24 is a graph illustrating the influence of graphite on the product distribution in microwave thermal treatment;

Figure 2.25 is a STA profile of pine wood before microwave treatment;

Figure 2.26 is a STA profile of pine wood after microwave treatment;

Figure 2.27 is a graph illustrating the percentage energy per gram of starting material maintained in the char;

Figure 2.28 is a graph illustrating the energy input for microwave torrefaction at 270°C for different sample masses;

Figure 3.1 is a graph illustrating the influence of acid/base additives on the relative change of A) char yield and B) oil yield from wheat straw in microwave torrefaction;

Figure 3.2 is a schematic representation of a microwave experiment;

Figure 3.3 is a GC-MS trace of wheat straw microwave pyrolysis oil

Figure 3.4 is a GC-MS trace of wheat straw microwave pyrolysis oil prepared in the presence of H_2SO_4;

Figure 3.5 is a GC-MS trace of wheat straw microwave pyrolysis oil prepared in the presence of HCl;

Figure 3.6 is a GC-MS trace of wheat straw microwave pyrolysis oil prepared in the presence of ammonia; and

Figure 3.7 is a GC-MS trace for the fast pyrolysis of wheat straw at 600°C.

Example 1

Example 1.A

Biomass Processor

The schematic layout of the processor is illustrated as an example in Figure 1.1. The biomass is fed at point (1) where, as necessary, it can be pulverised and dried. The drying can optionally be conducted with heat generated by the microwave process utilising a heat exchanged at point (7). Pulverisation should be carried out buy equipment suitable for the biomass to be processed. Typically a hammer mill or chopper used in standard biomass densification technologies can be used although other appropriate means can also be employed.

The pulverised biomass is then fed into a densification chamber (2). This can be a standard commercially available pelletiser, or a briquetter but preferably one capable of producing continuous rods which can be fed into outlet (3). Screw type extruders capable of continually feeding material are also appropriate and preferred. If appropriate liquid additives, such as, but not limited to those used in typical densification processes, e.g. glycerol or waste glycerol, or other known additives, such as, ammonia, hydrochloric or sulphuric acid, etc., can be mixed in to help material processing into a dense rod. The density of the extruded material that can typically be achieved by commercial processors, but typically, not essentially, higher densities (in excess of 600 kg/m3 are preferred). The densifier (2) should be equipped with temperature and processing rate control to allow flexibility and control of the system to allow for variability in the feed material. Optionally it can be fitted with an outlet for exhaust gasses generated in the pressing processes. Additionally the densifier (2) should be fitted with a gas inlet near outlet (3) for feeding gases which suppress flame formation and/or assist removal of vapours, gasses and liquids generated in the microwave assisted degradation process. These can include, but are not limited to nitrogen, hydrogen, carbon dioxide, acidic or basic vapours or other additives which can help to catalyse certain processes. The material should be preheated in the process either through mechanical compression, auxiliary heating (which can be utilised from the heat exchanger at point (7)) or both. The preheating temperature should be between 100 and 300°C, preferably 120-250°C, more preferably 160 -220°C and most preferably 180 -200°C.

The compressed feed material together with the gas is fed into outlet (3) into a carrier tube (4). If the material is prepared in short pellets rather than a continuous feed a means of propulsion should be integrated into the densifier (2) to ensure feeding and continuous passage of the material through the carrier tube (4) whilst overcoming friction between the carrier tube and the densified material. The carrier tube (4) feeds material directly into and through the microwave chamber and takes the bio-char out at the end of the degradation process.

The carrier tube should be constructed of a strong material, which is transparent to microwaves, heat resistant to at least 300°C and capable of withstanding mechanical pressure of the fed materials as along with the pressure of the evolved gasses during the process. It should also have low friction to allow smooth transfer of material within close contact to the sides. Construction materials can for example include glass, toughened or Pyrex glass, or other suitable non-metallic material. Choice of a suitable construction material can allow online monitoring such as, but not limited to, NIR probes, laser probes or UV-Vis. measurements, which can aid control of the process.

The tube (4) can be cylindrical with a uniform diameter throughout. The diameter of the tube will be governed by the size of the extruded/pressed material and its density as well as the penetration ability of microwaves which depend on wave parameters and power. Tube diameter should typically be less than 50 cm to ensure sample is irradiated throughout and sizes of about 0.5-10 cm in diameter are most preferable. The carrier tube can also optionally be irregular in shape having a conical shape with a progressively smaller diameter following the degradation reaction to account for the resulting mass loss. The exact specification of the reduction in size will depend on the reaction conditions employed, biomass used and the pre-treatment employed. Similarly the length of the tube will depend on process parameters, including the diameter of feed material, rate of feed, microwave power, number of microwave irradiation points used and others.

The pressed material is fed into the microwave chamber the chamber should be fitted with at least one microwave irradiation source, if more than one irradiation source is used they can optionally be shielded from each other to allow better control of the reaction . A simple low power microwave source is typically required as reactions are very rapid. Typically a 15 mm biomass cylinder can be charred in around 10 seconds at 300W power input, larger volume of, for example 35mm can take around 200 seconds, but this relationship is not linear. Higher power microwave generators, or more sequenced generators might be required for high throughput rates. The process conditions can easily be controlled by altering the feed rate from the densifier. The microwave irradiation can be focused around the carrier tube (4) or reflected around the chamber. The microwave source should be located in any geometry which is perpendicular or angled along the carrier tube (4) in some cases use of reflective mirrors might be beneficial to ensure uniform sample irradiation.

Inside the chamber the carry tube should be fitted with exhaust tubes to enable the removal of degradation vapours (5) and liquids (6) placed preferably on top and bottom of the tube respectively. The removal of volatile or liquid products will be promoted by the mixed gas (e.g. nitrogen) and/or can be assisted by vacuum. The exact positioning of the outlet tubes will depend on process parameters, but flexibility is build into the process through control of feed rate, density, microwave power and other aspects to enable optimisation. Typically the outlets will be placed in direct proximity to the area where pyrolysis occurs. The outlets can be angled along the flow of the material in the tube to minimise particulate matter entering the outlet holes. Additionally these can be fitted with traps for any particulate or early condensing matter and/or appropriate filters. The length of the outlet tubes within the microwave chamber (9) should be kept to the minimum to ensure material is removed from the degrading environment as soon as possible to avoid secondary reactions, unless these are particularly required by the application. Once outside the volatile and liquid products can be treated in conventional ways.

Significantly, this design has sufficient flexibility built in to enable fractionation of the degradation products. A number of outlets can be used to facilitate the process spaced according to the progress of reaction(s) along the carrier tube. This can be used in conjunction with sequential microwave sources to allow for better process control. For example at an early stage water vapour can be removed followed by more organic fractions and chars. Fractionation of the degradation products is an important and innovative aspect of this invention. It enables users to take full advantage of the low temperature employed in the process to preserve chemical functionality and offers an opportunity for the users to maximise the value of their chemical products resulting from the degradation.

Furthermore, in addition to the outlets, the feed pipe may contain inlets for injecting additives such as ammonia or other gaseous, liquid and potentially solid additives, as hereinbefore described, at a controlled point in the process to affect particular reactions.

At the end of the pyrolysis the remaining bio-chars are pushed out of the microwave chamber into a cooling area (7). At the end of the microwave process the bio-char can reach temperatures in excess of 300°C, to avoid potential for fires the bio-char must be cooled. At this stage, optionally, a heat exchanger is used where by the heat dissipated from the char can be transferred to drying and/or preheating the feed material in the pulverisation stage or densification. Use of a heat exchanger can significantly improve the energy footprint of the process. Additionally other elements of the process should preferably be insulated to avoid loss of valuable heat energy.

Example 1.B

Influence of microwave time on cellulose decomposition products under vacuum

Pyrolysis of cellulose under vacuum was carried out. 50g of cellulose was preheated at 80°C and placed inside a Milestone microwave. Microwave irradiation with power

1200W was applied to the sample during 12 minutes. The typical pressure profile for organic volatiles produced from cellulose under microwave conditions is shown in Figure 1.2. As it is indicated in Figure 1.2 there are minimum two stages of volatile compounds production: 1) broad low temperature peak around 120°C and 2) rapid process (narrow peak) at temperature around 180°C. These two fractions were separated by time and analysed. It was shown that the first fraction consists essentially of water which contains acetic and formic acids in combination with formaldehyde and acetaldehyde. This demonstrates that under these conditions (initial preheating temperature below optimum of 180°C) it is possible to collect two liquid fractions. Firstly, an aqueous fraction is collected with a relatively high acid content at temperatures as low as 60-120°C and in a period of 3-5 minutes. Thereafter, and by maintaining low temperature control, an organic fraction of low water and low acid content is produced at temperatures around 180°C within 1-2 minutes. The organic fraction has been collected in yields of up to 21 % (water content <1 %) from the microwave processing of cellulose. So, simple positioning of outlet tubes, e.g. extraction tubes, along the microwave carrier tube enables the separation of aqueous and organic fractions.

Example 1.C

Influence of microwave time on decomposition of preheated biomass pellets under nitrogen flow.

Thermal decomposition of canary grass pellets under nitrogen atmosphere was carried out as shown in Figures 1.3 and 1.4. The apparatus included a microwave and IR gas cell for monitoring off gases.

5g of canary grass pellets was preheated at 180°C and placed inside CEM microwave. Microwave irradiation with power 300W was applied to the sample during 6 minutes. The typical Gram-Schmidt profile (which was calculated as integral of IR gas spectrum) for organic volatiles is shown in Figure 1.4. There are at least three stages during the period of microwave decomposition occurring sequentially in time:

1) removal of water with and low boiling aldehydes and acids;

2) removal of CO_2 and CO accompanied by organic compounds; and

3) removal of compounds containing hydroxyl groups.

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Short Communication

Microwave assisted decomposition of cellulose: A new thermochemical route for biomass exploitation

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ABSTRACT

A microwave assisted low temperature decomposition process has been developed for production of high quality fuels from biomass. 180 °C was identified as key in the process mechanism, as the amorphous region of cellulose softens allowing a microwave induced rearrangement. Proton transfer is then possible under the microwave field resulting in acid catalysed decomposition. This low temperature process has been shown to be suitable for scale-up, producing a high quality char for use as a coal replacement and bio-oil suitable for upgrading to liquid fuel.

1. Introduction

The world is facing an energy crisis due to increasing concern related to fossil fuel use (environmental impact, finite availability, security of supply); consequently it is vital to optimise the potential of biomass to power the future. Any future bio-refinery processes, which are required, have to be more efficient and flexible in using a variety of feedstocks in the same installation and have the possibility to provide up to 30% of world fuel demand on the base of lignocellulosic biomass without interfering with food supplies.

Here we show that through understanding the mechanism of microwave (MW) activation of key plant structural components an energy efficient, low-temperature MW process (<200 °C) can be used to enhance the energy value of biomass. The process converts biomass into two energy concentrated fuels, a solid char which has properties comparable with coal, and oils with properties superior to those achievable with conventional methods. Due to the improved process efficiency and the high quality of the products this research offers the opportunity for significant economic and environmental benefits, with adaptable technologies which can be installed close to source (Ruan et al., 2008).

Microwave technology has gained acceptance as a mild and controllable tool, allowing simple and rapid processing. Industrial scale treatment of food and materials at temperatures below 200 °C has been established as a continuous tonne-scale process with increased process selectivity (Clark and Sutton, 1996). Microwave treatment of biomass has previously been reported for the production of fuels. The processes, which were carried out at temperatures associated with conventional pyrolysis (>350 °C), result in gasification or liquefaction of the starting material to produce fuels (Menendez et al., 2007). It is our belief that the high temperatures and heating rates in previous microwave pyrolysis studies may be masking important lower temperature processes.

At low temperatures, the efficiency of microwave processes depends greatly on the nature of the material being processed, in terms of its physical form (structural arrangements, conductivity and dielectric properties) (Kappe, 2004). Lignocellulosic biomass consists of three structural polymers along with various extraneous components (Saha, 2004). In this study cellulose, the major component was chosen as the focus. In order to choose the parameters for microwave investigations it is important to know the temperature points at which structural and molecular changes occur within cellulose.

2. Methods

2.1. Materials

Fibrous cellulose (medium) (Sigma Aldrich cat. No. C6288-250G), deuterium oxide and potassium bromide (spectroscopic grade) were used as received from Sigma Aldrich.

2.2. Microwave treatment for char production

Biomass sample (300 mg) was weighed out into a microwave tube containing a magnetic follower, and then sealed using the

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microwave tube lid. The sample was placed in a CEM Discovery laboratory microwave. The sample was irradiated under varying conditions (100–300 W, 100–300 °C). The mass of solid lost was carefully monitored by weighing the sample before and after microwave treatment.

2.3. Modulated differential scanning calorimetry

The methodology was carried out in the same manner as (Picker and Hoag, 2002).

2.4. FTIR analysis

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded on a Bruker EQUINOX-55 instrument equipped with a liquid N_2 cooled MCT detector. The samples for DRIFTS studies were prepared by mechanically grinding all reactants with KBr. Spectra were recorded using 1024 scans at a 4 cm^{-1} resolution.

2.5. Measurement of calorific value

Calorific value (Low heating value) measurements were carried out on a Stanton Redcroft Simultaneous Thermal analyzer, STA 625. A 50:50 mixture of biomass and Palladium oxide was heated at 5 K min^{-1} from 20 °C to 625 °C in a 50 ml min^{-1} flow of air and the low heating value was calculated by integrating the resulting thermograms.

2.6. Deuteration of cellulose

The procedure was carried out in the same manner as (Horikawa and Sugiyama, 2008).

3. Results and discussion

In order to differentiate between any specific and non-specific microwave effects an experimental set-up was designed to allow the homogeneous exposure of biomass to microwave irradiation. The experiment was based on a narrow packed column in a well stirred oil bath within the microwave chamber with the top portion of the cellulose protected from microwave irradiation using aluminium foil (Fig. S1A). The cellulose which had been exposed to microwave irradiation visibly began to decompose, while the area above shows little or no decomposition (Fig. S1B). A range of experiments were carried out between 150 and 220 °C. It was found that after 180 °C cellulose started decomposing to a greater extent producing a solid char along with an oily liquid fraction.

The effects of temperature on amorphous and crystalline regions of medium fibre cellulose were followed by modulated differential scanning calorimetry (MDSC). The MDSC trace showed an overall heat flow signal and both a reversing and non-reversing heat flow signal (see Supplementary material Fig. S2). In the non-reversing heat flow signal, which accounts for the kinetic component of the total heat flow, an endothermic deviation in the base line starts around 100 °C, and peaks at 134 °C. This process may be attributed to the evaporation of any residual moisture within the sample. From 170 °C there is a continual decrease in the heat flow of this signal which we believe is due to depolymerisation of the material. This event coincides with a glass transition (T_g) starting at 185 °C and returning to a steady state at 220 °C, with the point of inflection at 197 °C (Fig. 1A). This transition is masked in the total heat flow from the continual depolymerisation in the non-reversing signal.

To verify the MDSC data, changes in the crystallinity of cellulose were monitored by DRIFT, using a temperature controlled apparatus. The crystallinity index was calculated based on the ratio of peaks at 1430 and 894 cm^{-1} (Oh et al., 2005). It was found that the crystallinity index rapidly decreased at around 180 °C which correlates well with the MDSC information. With the increased molecular motion within the amorphous region, as illustrated by the glass transition, a cooperative stress is induced on the crystalline region resulting in a reduction in the level of crystallinity.

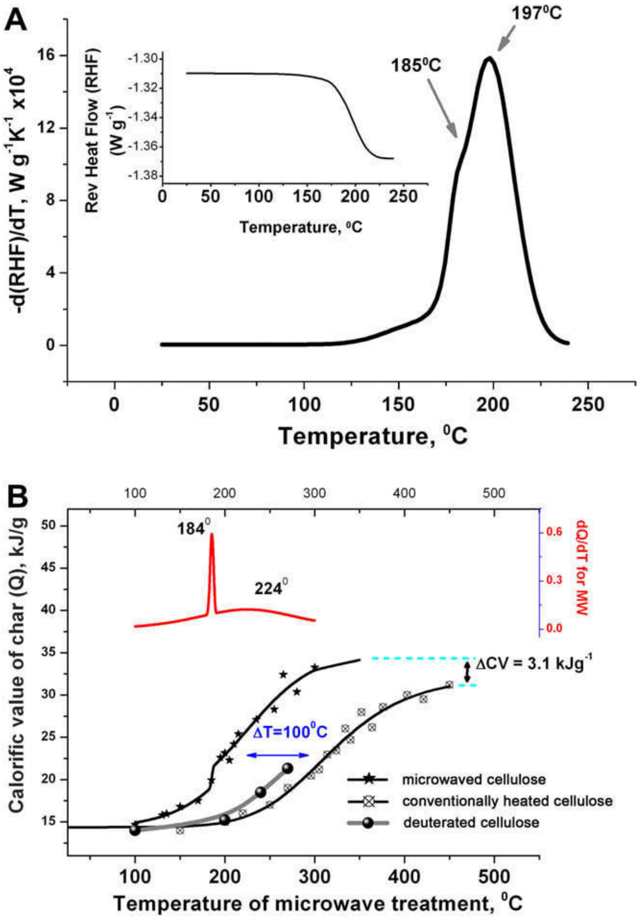

Fig. 1. (A): Reversing heat flow signal from the MDSC of cellulose showing the true glass transition (inset), and the derivative of the reversing heat flow signal. (B): Calorific value of char obtained from cellulose processed conventionally and in the presence of microwaves. Also cellulose that was initially deuterated and then microwave treated is shown. The calorific value derivative of the microwave treated cellulose is shown emphasising a peak at 184 °C.

To understand the mechanism of the MW effect on cellulose, the influence of microwave temperature on the production of char was investigated in parallel with conventional pyrolysis experiments. By measuring calorific value, it can be seen that chars could be produced at temperatures 100 °C lower than those produced using conventional pyrolysis (Fig. 1B). The rate of increase in calorific value of the microwave chars showed a jump ca. 180 °C, in agreement with our earlier observations. It is also important to note that the maximum calorific value of the char obtained in the microwave experiments is ca. 10% greater than those produced using conventional heating.

In order to further investigate the mechanism, the amorphous region of cellulose was partially deuterated and chars produced analysed as for ordinary cellulose. As can be seen in Fig. 1B, the deuterated cellulose activated by microwave, decomposes slower than the protonated form. This decreased rate of decomposition on deuteration stresses the importance of the amorphous region for microwave processing.

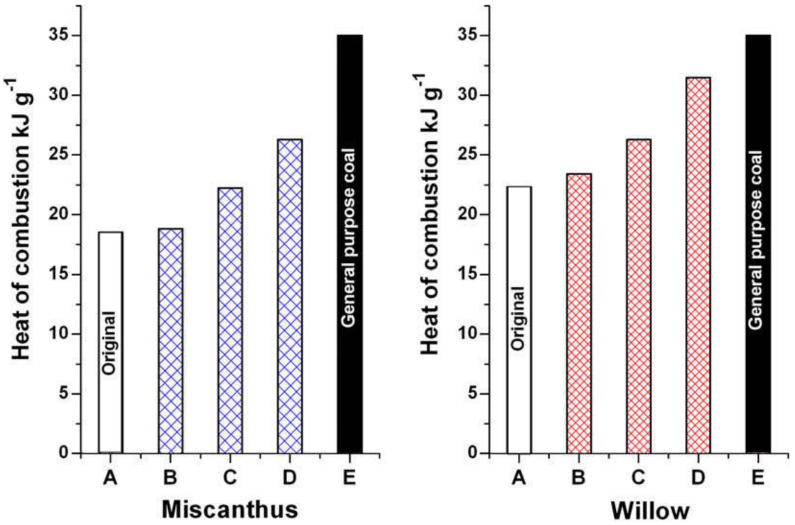

Fig. 2. Changes in the calorific value (kJ g^{-1}) of biomass species after heating to 280 °C conventionally and with microwave irradiation. (A) Original biomass. (B) After conventional heating. (C) After MW activation. (D) General purpose coal.

DRIFT studies were carried out on the char samples prepared at a range of temperatures using microwave activation. Crystallinity rapidly increased at 180 °C, which again indicates the amorphous region is more affected by microwave irradiation, and decomposes in preference to the crystalline region, leading to more rapid loss of signals from the amorphous cellulose fraction than from the crystalline regions.

The temperature of 180 °C has been identified as a key turning point in the microwave degradation of cellulose; this understanding allows the production of fuels at dramatically lower temperatures than would be required under conventional conditions. Thermal analysis, using MDSC has correlated the temperature to a glass transition in the polymer. Above this temperature, the specific microwave effect becomes pronounced and the rate of degradation of cellulose increases significantly. The combination of experimental techniques proves that the MW degradation starts within the amorphous region. The enhanced molecular freedom within this region resulting from the glass transition allows improved interaction between the microwave energy and cellulose. The interaction depends on a process termed dipolar polarization which involves the alignment of polar groups with the oscillating MW field (Kappe, 2004). Below 180 °C the polar groups in cellulose have less freedom so cannot rotate easily, resulting in a poorer interaction. Above 180 °C, as the number of groups capable of rotating increases particularly, but not exclusively, in the amorphous region the rate of decomposition increases.

It could be considered that the softer material can decompose faster. If this were the case the same increase in rate of decomposition would be seen in the conventional pyrolysis chars after 180 °C. The fact that there is no increase in rate at this temperature under conventional conditions strengthens the argument for a specific non-thermal MW effect.

It is known that the structure of cellulose within the cell wall of plants exists in a fibrillar form. Within these fibres the amorphous and crystalline regions alternate at a period of approximately 15 nm (Fig. S3). Crystalline cellulose contains a very ordered hydrogen bonded network within which a proton transport network is possible in the presence of an electromagnetic field (Fig. S4). The temperature coefficient of the electrical conductivity of amorphous polymers increases greatly above the glass transition temperature. This phenomenon can be interpreted qualitatively in terms of the ionic current which is known to increase remarkably between 150 and 180 °C due to activated segmental motion of the amorphous chains (Takahashi and Takenaka, 1983). Below 180 °C the hydrogen bond network within the amorphous regions is relatively small and localized. For these reasons cellulose fibres could be represented as alternating ionic conducting (crystalline) and non-conducting (amorphous) regions. When the crystalline region is placed within an electromagnetic field it will polarize, generating a charge on the crystalline interface (overall charge will be zero).

The MW treatment of cellulose produces chars at significantly lower temperatures than conventional pyrolysis (Fig. 1B). The presence of acid has been found to promote char formation (Mamleev et al., 2009). It is our belief that after 180 °C the acidity in the amorphous region is increased as the softening of the T_g allows movement of protons from the crystalline region causing acid catalyzed decomposition of cellulose (Figs. S3 and S4). Acid catalysed pyrolysis is also reported to increase the yield of 1,6-anhydrosugars in bio-oil (Dobele et al., 2003). Analysis of liquid fractions produced from our microwave treatment has shown significant levels of such products along with the furans and substituted phenols associated with conventional pyrolysis (Budarin et al., 2009). The production of these components will further plasticise the amorphous region exacerbating the enhanced MW effect. Increasing temperature and acidity will eventually disrupt the crystalline regions of cellulose aiding its degradation to char and volatiles.

In terms of an industrial process, this procedure can be easily adapted to a variety of biomass (see Fig. 2) producing a uniform char which can be handled with ease by the end user. In order to achieve sustainable development mankind needs to move away from petrochemical feedstocks to renewable alternatives. Microwave processing of biomass may be the route to solid and liquid fuel for the development of a society which is no longer reliant on fossil fuels.

4. Conclusion

The interaction of cellulose with microwave irradiation has been investigated and a mechanism involving a phase transition in cellulose was proposed. Our results show for the first time, that microwave irradiation has a dramatic effect on the rate of decomposition when cellulose softens; yielding products which would require much higher temperatures (100 °C higher) to produce under conventional conditions. The mechanism of the specific microwave effect helps explain the low temperature at which carbonisation occurs, in the maximum calorific value of the final char, and in the properties of oils produced.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2009.12.110.

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Use of green chemical technologies in an integrated biorefinery

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A new concept is demonstrated for an integrated close to zero waste wheat straw biorefinery combining two novel green technologies, CO_2 extraction and low temperature microwave pyrolysis, to produce a variety of products, including energy and CO_2 which can be internally recycled to sustain the processes. CO_2 adds value to the process by extracting secondary metabolites including fatty acids, wax esters and fatty alcohols. Low temperature microwave pyrolysis (<200 °C) is shown to use less energy and produce higher quality oils and chars than conventional pyrolysis. The oils can be fractionated to produce either transport fuels or platform chemicals such as levoglucosan and levoglucosenone. The chars are appropriate for co-firing. The quality of the chars was improved by washing to remove the majority of the potassium and chlorine present, lowering their fouling potential. The economic feasibility of a wheat straw biorefinery is enhanced by intergrating these technologies.

Introduction

Since the 1990s, decreasing fossil reserves, rising oil prices, concerns over the security of supply, environmental impacts and sustainability have led to a global policy shift back towards the use of biomass as a local, renewable and low carbon feedstock. The biorefinery concept that has emerged is analogous to today's petroleum refineries, integrated facilities for the conversion of biomass into multiple value-added products including energy, chemicals and materials.[1] However, many of these focus on single technologies and feedstocks such as starch or vegetable oils that could compete with food or feed.[2] Improvements are needed to create flexible, zero waste networks, applicable to a variety of low value local feedstocks. Biorefineries will then be able to challenge the current status quo and develop novel interconnecting webs of products that can meet the demands of existing and new industries.

There are a large variety of lignocellulosic materials containing varying compositions of waxes, lignin, cellulose, hemicellulose and inorganics that are ideal feedstocks for a biorefinery. Agricultural residues, and in particular straw, are a major source of available biomass in the UK.[3] In order to simplify our system and focus on how different innovative technologies can interact with each other using one particular lignocellulosic feedstock, wheat straw was chosen as a representative material.

The main technologies available to the biorefinery can be classified as extraction, biochemical and thermochemical processes. Currently, these methodologies are usually studied independent of one another, with each jostling for primacy as the biorefinery technology of the future. However, it is essential that the strengths and weaknesses of all the technologies available are recognised to enable the integration and blending of different technologies and feedstocks to best maximise the diversity of applications and products formed.

An integrated close to zero waste system exploiting a sequential process including extraction, followed by a combination of biochemical and thermal processing, with internal recycling of energy and waste gases is viewed as a model system (Fig. 1), although we recognise the limits of the model without a more complete process design study. Extraction of valuable phytochemicals, prior to their destruction during biochemical and thermal treatments, can significantly increase the overall financial returns.[4]

Biochemical routes offer advantages in terms of typically low processing temperatures, and high selectivity and specificity of components targeted and products generated. However, they generally require pre-treatment of biomass,[5] long processing times, large amounts of space for batch systems, and difficult

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Broader context

We demonstrate a new concept for an integrated zero waste wheat straw biorefinery combining two novel green technologies, CO_2 extraction and low temperature microwave pyrolysis, to produce a variety of products, including energy and CO_2 which can be internally recycled to sustain the processes. CO_2 adds value to the process by extracting secondary metabolites including fatty acids, wax esters and fatty alcohols. Low temperature microwave pyrolysis (<200 °C) is shown to use less energy and produce higher quality oils and chars than conventional pyrolysis. The oils can be fractionated to produce either transport fuels or platform chemicals such as levoglucosan and levoglucosenone. The chars are appropriate for co-firing. The quality of the chars was improved by washing to remove the majority of the potassium and chlorine present, lowering their fouling potential.

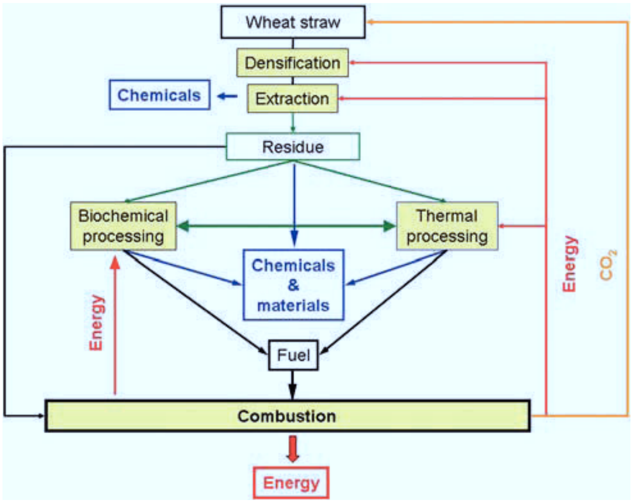

Fig. 1 Proposed model for integration of extraction, biochemical and thermochemical processes into a single biorefinery internally recycling the energy and extraction solvent required.

lignin treatments and downstream processing such as distillation which may be energy intensive.[6] Alternative thermochemical routes include gasification, pyrolysis and direct combustion to produce oils, gas, char or ash. They are fast and typically continuous systems.[7] However, they are non-specific, affect all components, and generally require high operating temperatures (>500 °C), which reduce their energy efficiency and increase capital investment. It is therefore clear that the strengths of biochemical and thermochemical processing complement each other and in an integrated system can deliver significant advantages in terms of specificity of products, flexibility and efficiency.

Herein, we demonstrate the development of an integrated wheat straw biorefinery through the use of green technologies which can bring added benefits either through cost, flexibility, controllability or energy efficiency. This study focuses on the integration of two green technologies, extraction using supercritical CO_2 ($scCO_2$), and low temperature microwave pyrolysis, highlighting the mutual benefits of each and the potential for linking them with biochemical processes. We draw comparisons with traditional technologies and show how the concept of a near to zero waste biorefinery leads to a diverse and intricate web of products for different markets.

Experimental

Raw materials

Wheat straw (Claire, 2007) pellets were obtained from Charles Jackson Farms, UK. Initial analysis of the pellets (7 mm diameter) as received showed a moisture content of 10% and a density of 1.2 g cm^{-3}.

Supercritical carbon dioxide extraction

Supercritical carbon dioxide ($scCO_2$) wax extractions were carried out on air dried milled straw (30 g) using a Thar Technologies $scCO_2$ rig at various temperatures (40–100 °C) and pressures (100–300 bar) for 2 hours with a 40 g min^{-1} flow rate.

Microwave processing of materials

The microwave treatment of wheat straw pellets was carried out using a Milestone ROTOSYNTH Rotative Solid Phase Microwave Reactor (Milestone Srl., Italy) fitted with a VAC 2000 vacuum module in series. Average sample mass was between 150 and 200 g. Samples were exposed to a maximum microwave power of 1200 W with an operating microwave frequency of 2.45 GHz (wavelength 12.2 cm) under fixed power conditions. The process temperature was maintained below 180 °C as measured by *in situ* and infrared temperature probes. These measurements showed no significant difference between the temperatures throughout the whole sample. The process pressure was monitored at all times. Liquid fractions were collected *via* the vacuum unit, which collected and condensed vapours produced during the process.

Use of additives

Wheat straw pellets were agitated in an aqueous solution of sulfuric acid (10% w/w). The water was removed *in vacuo* at 60 °C. Ammonia and HCl were introduced into the sample as a gas. As previously, the sample was mixed thoroughly.

Char demineralisation

Microwave pyrolysed wheat straw char (~20 g, variety Claire) was mixed with distilled water (150 ml) and heated in a Milestone RotoSYNTH microwave at 100 °C for 10 minutes. The resulting mixture was stirred overnight in a sealed bottle, filtered and stored. The leached char was dried at 40 °C under vacuum.

Elemental analysis

Elemental analysis based on carbon, hydrogen and nitrogen content was carried out using an Exeter Analytical (Warwick, UK) CE440 Elemental Analyser, calibrated against acetanilide with an *S*-benzyl-thiouronium chloride as internal standard. CHN wt% of the starting material was 40.21, 5.34 and 0.7 respectively.

Characterisation of gas fraction

The apparatus for thermal decomposition of wheat straw pellets consisted of a microwave connected to IR gas cell for monitoring of gases, with the IR cell and transfer pipe heated at 200 °C. 5.0 g of wheat straw were placed inside the microwave reactor and 300 W of microwave power applied during the experiment (six minutes).

Characterisation of liquid fractions

Pyrolysis–GC was performed using a CDS Analytical Pyroprobe 2000 interfaced to an Agilent Technologies 6890 N Gas Chromatograph, using a CDS 1500 Interface. The oven was fitted with a 61.3 m, 0.25 mm id, 0.25 μm phase (14% cyanopropylphenyl, 86% dimethylpolysiloxane) thickness Rtx 1701 capillary column. An Agilent Technologies 5975B Inert XL Mass Selective Detector was coupled to the GC.

For GC-MS analysis of the microwave oils, approximately 1.0 g of each oil was diluted in 15 ml of methanol. About 5 μl of this solution were injected into the GC column. The oils in solutions were analysed using the same column and operating under the same oven heating regime as described above. TG-IR analysis demonstrates that about 70 wt% of liquid fractions have a boiling point below 250 °C and could be detected by the GC method. Elemental composition was carried out as outlined for the starting material. Acid number was determined by titration. Water content was determined using a Karl Fischer Coulometer (Mettler Toledo DL32) by comparison to Karl Fischer Standard reagent (Fluka Chemicals). pH measurements of solutions were performed using a Jenway 3505 pH meter.

Simultaneous thermal analysis

Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were carried out simultaneously on a PL Thermal Sciences STA 625. Milled wheat straw or ground char (1.5 mg) was accurately weighed into an aluminium cup and analysed against an empty aluminium reference pan from 20 °C to 625 °C at a heating rate of 5 K $\min^{-1}$ under a 60 ml $\min^{-1}$ flow of air. For calorific value analysis powdered palladium oxide (35 mg) was added to cover the surface of the straw or char to ensure complete oxidation occurred. All chars were washed and dried prior to analysis. Analyses were carried out in duplicate. The calorific content was calculated using the following equation:

$$\text{Joules gram}^{-1} = [4.18 \times (100 - \text{residual\%}) \times \Delta Q]/\Delta m$$

X-Ray fluorescence

Ground samples of straw or char (~1 g) were compressed into a holder and analysed on a Horiba XGT 7000 X-ray analytical microscope using a standardless independent parameters method. Each measurement was repeated five times and the average was taken.

X-Ray diffraction

Finely ground char was analysed using a Bruker-AXS D8 Advance diffractometer with a Kristalloflex 760 X-ray generator. Scans were taken with a step size of 0.007 from 10–75 2θ. The evaluation programme EVA and the Bruker CDS database were used to identify the phases.

Inductively Coupled Plasma (ICP)

Inductively Coupled Plasma Atomic Emissions Spectroscopy (ICP-AES) was carried out by Yara Analytical Services, York and was analysed for 39 inorganic elements.

Results and discussion

Extraction with supercritical CO_2

The first stage of our integrated biorefinery is the extraction of valuable secondary metabolites. These are traditionally extracted from straw using volatile organic solvents, which are environmentally and toxicologically problematic, as well as being highly unselective. CO_2 combines effective isolation and fractionation of valuable components with low environmental impact. It has previously been demonstrated that the waxy cuticle layer of straw can be selectively extracted using supercritical CO_2 ($scCO_2$).[8] In addition, $scCO_2$ extraction leaves no solvent residue, meaning that products are suitable for use in food, personal care or pharmaceutical applications, giving it major commercial advantages over traditional extraction methods. Industrial scale use of $scCO_2$ should be applicable within the biorefinery as it has already been employed commercially for hop extraction, decaffeination of coffee and dry cleaning.[15]

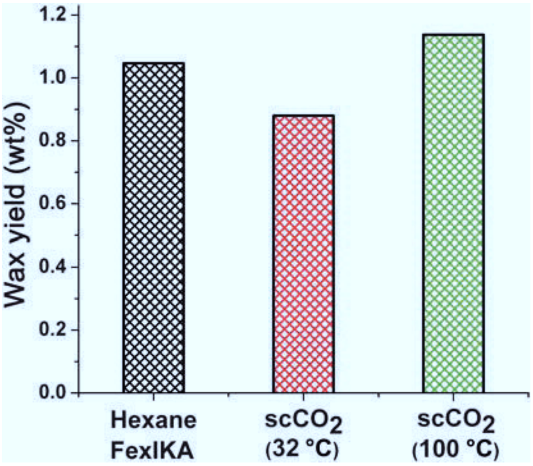

Fig. 2 Wax yield from wheat straw using different solvents and conditions ($scCO_2$ at 300 bar and 40 g $\min^{-1}$). The utilisation of this technology within the biorefinery also enables the recycling of the internally generated clean CO_2 from the biochemical treatment of sugars.

We studied $scCO_2$ extraction under varying temperatures and pressures in comparison with hexane, a traditional solvent of similar polarity. This revealed comparable wax yields (Fig. 2) and composition (Table 1) for both solvents. Although, the

Table 1 Identification and application of main compounds found in hexane and $scCO_2$ extracted wheat wax

Identification	Groups of compounds	Application	Ref.
6,10,14-Trimethyl, 2-pentadecanone	Fatty acid	Soaps, detergents, lubricating grease/oils, cleaning compounds/ polishes	9,10
Palmitic acid			
Linoleic acid			
Oleic acid			
Stearic acid			
Nonacosane	Alkanes	Paraffin waxes (can replace petrochemical derived)	11
Octadecanal	Aldehydes	Food flavourings	
Hentriacontane	Alkanes	Paraffin waxes (can replace petrochemical derived)	
Fatty alcohol (branched and/or unsaturated)		Surfactants, cosmetics	12
14,16-Hentriacontanedione	Diketones	Metal chelators	13
14,18-Tritriacontanedione	Diketones	Metal chelators	
Octacosanyl hexadecanoate	Wax esters	Hard polishes, coatings, cosmetics, plasticisers	14

chemical composition of the hexane and supercritical extracts does not vary greatly, the proportions of unwanted co-extracted components such as pigments, polar lipids and free sugars are well-known to be far greater in hexane extracts than from $scCO_2$.

The components that were identified in the wax extracts included fatty acids, alkanes, aldehydes, diketones and wax esters. These all have potential commercial applications including uses as lubricants, food flavourings or replacements to paraffin waxes or in cosmetics (Table 1). Although, supercritical carbon dioxide extraction is an energy intensive process, use of combined heat and power from the combustion of microwave gas or chars could make the use of this extraction technique a perfect green technology for incorporation into a wheat straw biorefinery.

Low temperature microwave pyrolysis

An increasing number of patents in microwave (MW) assisted biomass pyrolysis demonstrate that this technology is mature and highly scalable. A significant body of this research has focused on high temperature (>350 °C) microwave-mediated pyrolysis, gasification and liquefaction of biomass. Microwave technology may offer advantages over pyrolysis relying on convection heating including increased decomposition rates, better controllability, higher energy efficiency and better selectivity in terms of the ratio of solid, can occur at much lower temperatures than previously reported.[15] This low temperature microwave process is scalable, energy efficient and generates five major types of products from lignocellulosic biomass.

(1) A high quality char with properties superior to those achieved by most conventional methods and with an enhanced energy value, feedabiliy and grindability, making it suitable for use as a coal replacement.

(2) Bio-oil suitable for upgrading to liquid fuel.

(3) An aqueous solution of organic acids and aldehydes.

(4) An aqueous solution of sugars.

(5) A gas fraction containing combustible organic compounds, which could be used for energy production.

In the microwave pyrolysis of the original untreated wheat straw, gas was the lowest yielding fraction (*c.a.* 14 wt%), with bio-oil and char yields of 20 and 30 wt% respectively, whilst the aqueous fraction gave the highest yield (*c.a.* 35 wt%). The significant amounts of water produced indicate a substantial reduction of organic matter during the process. All of these products have an important function within our biorefinery concept.[15,16] The flexiblity and controllabilty of this technology as well as its portability and relative ease of installation at source may present significant economic and environmental benefits.[17] Furthermore, it has been shown that certain microwave assisted reactions can take significantly less time and can occur at comparatively lower temperatures.[18–21] Our research in this area shows that MW assisted degradation of wheat straw and biomass in general products has an important function within our biorefinery concept.

Gas fraction

Although it is the lowest yielding fraction, the gas formed could have an indispensable role by providing some or all of the internal energy required for both the $scCO_2$ extraction, microwave processing and additional biochemical modification.

In situ FTIR analysis of the volatiles formed during MW pyrolysis clearly shows two major fractions being released (Fig. 3). The first fraction at temperatures lower than 110 °C (points I and II, Fig. 3A) contains low molecular weight carboxylic acids and other aqueous soluble components (FTIR

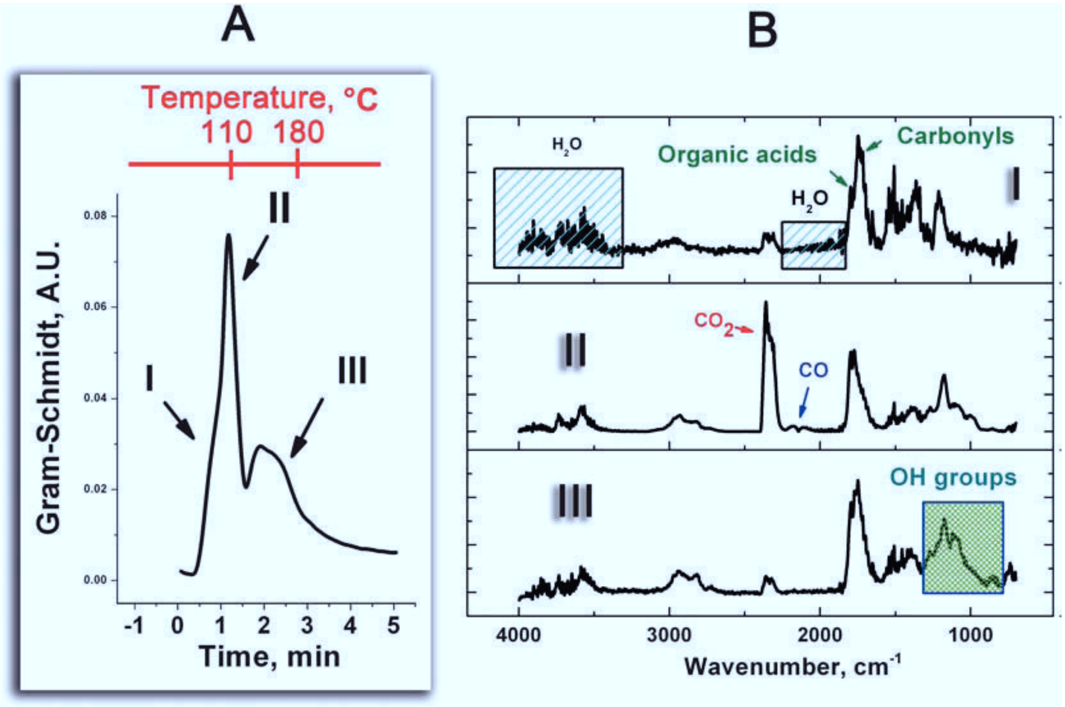

Fig. 3 *In situ* FTIR analysis of volatiles during pyrolysis.

spectrum I and II, Fig. 3B), whilst the second (point III, Fig. 3A), peaking around 180 °C, corresponds mainly to an organic fraction with low water content (FTIR spectrum III, Fig. 3B). In addition, it was proved by FTIR spectroscopy that MW irradiation produces uncompressible gases such as carbon dioxide, carbon monoxide and methane. The latter two could be recycled internally for power generation. 180 °C was previously identified as a key temperature in the degradation mechanism of cellulose during microwave pyrolysis as at this point the amorphous region of cellulose softens and increased mobility and polarity of the cellulose molecules enhance susceptibility to microwaves.[15] These data, showing the low temperature decomposition of wheat straw around 180 °C, could indicate that cellulose is the active component in MW pyrolysis of wheat straw.

Aqueous fraction

Our unique process understanding enables the separation of the low temperature aqueous fraction from the organic matter. The main components present in this fraction were identified by GC-MS as formic acid, formaldehyde, acetic acid and acetaldehyde, all of which are potential platform molecules for downstream processing to valuable products. Alternative direct applications could include use as a disinfectant or as a preservative for wood thanks to the anti-bacterial and -microbial properties of formaldehyde.[22,23] The *in situ* separation of the aqueous fraction also improves the quality of the bio-oil formed.

Bio-oil

Bio-oil is potentially one of the most valuable products of wheat straw microwave pyrolysis, as it has the potential to partly replace crude oil for the production of transportation fuels and chemicals.

Our previous work indicates that the low temperature microwave bio-oil is much more similar in composition to crude oil than other pyrolysis oils.[16] It has a significantly decreased water content than that observed for either higher temperature microwave processes or conventional pyrolysis oils (including water fraction), an improved acid value (pH 7) compared to typical pyrolysis oils (pH 2.9) and a reduced metal concentration (Fig. 4).[24]

This is due to the lower processing temperatures which prevent rapid evaporation of water, resulting in the deposition of the alkali metals in the char rather than in the organic oil. The calorific value (CV), carbon and hydrogen content of the bio-oil produced during the low temperature MW process are at the top of the range of typical pyrolysis and microwave bio-oils. Although the energy content is still not as high as for crude oil, Menendez *et al.* have demonstrated that this can be improved dramatically by judicious selection of process parameters.[25] All of the factors above indicate that low temperature microwave bio-oil should need less downstream processing in comparison to thermal convection pyrolysis oils to be upgraded as a replacement for crude oil to produce fuels and chemicals.

An understanding of the chemical composition of the oils is also essential to evaluate the potential for producing valuable chemicals in the biorefinery. The composition of MW bio-oil is significantly different from conventional pyrolysis (Fig. 5). In the bio-oil obtained by fast pyrolysis, at a temperature of 600 °C, furans and phenols dominate.

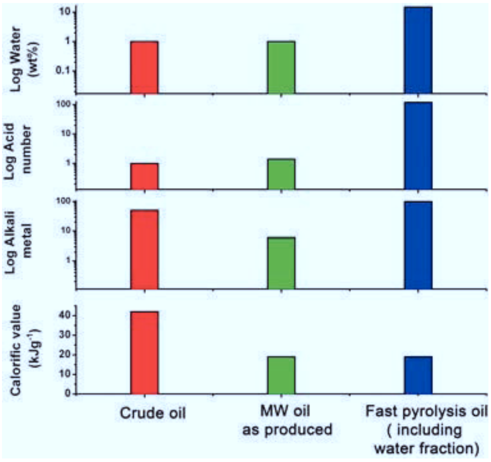

Fig. 4 Comparison of microwave oil characteristics with competing fuel technologies.[24]

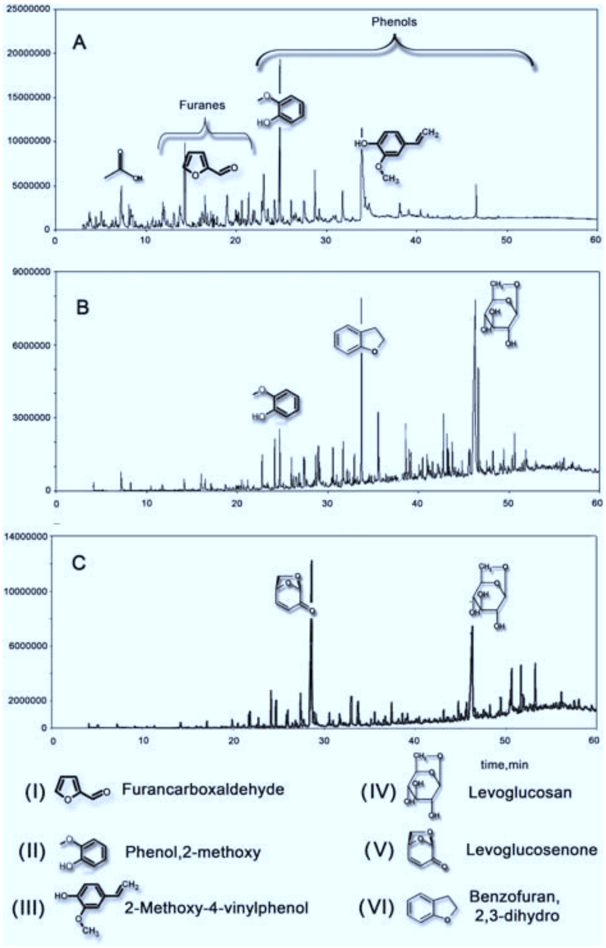

Fig. 5 Gas chromatograms of oils generated by pyrolysis in a conventional fast pyrolysis system at 600 °C (including water fraction) (A) compared to a microwave system (B) and microwave pyrolysis in the presence of 5% of sulfuric acid (C).

The major hydrocarbon component in the MW pyrolysis oil is benzofuran, 2,3-dihydro (Fig. 5, structure VI). Noteworthy is the high yield of monosaccharides, such as levoglucosan (Fig. 5, structure IV), generated during MW pyrolysis. The former are useful in the pharmaceutical industry as therapeutic or prophylactic agents,[26] as inhibitors for lipoperoxide production[27] and as cytoprotective agent.[28] It was found that the sugars could be separated from the pyrolysis oil by simple water extraction into a second aqueous fraction. This opens up the possibility of taking sugars from the pyrolysis oil and upgrading them using more specific biochemical routes. Levoglucosan (Fig. 5, structure IV) is attractive for use directly or indirectly as a feedstock for the fermentation industry. It has been shown that levoglucosan produced by pyrolysis of cellulose can be fermented to citric acid by *Aspergillus niger* CBX-209.[29] Furthermore, levoglucosan itself has been identified as a key renewable platform molecule due to the anhydro group which makes the ring structure much more rigid than that of a normal glucose molecule, allowing for more selective chemistry on the remaining free hydroxy groups.[30] Levoglucosan is an important starting material for the synthesis of stereoregular polysaccharides possessing biological activity, such as the anti-human immunodeficiency virus and blood anticoagulants. The derivatives of the stereoregular polysaccharides can be used for chiral stationary phases in high-performance liquid chromatography.[31]

Additives. Acid and base additives were tested to observe their influence on both the fractionation of the major products and the composition of the bio-oil. It was possible to adsorb HCl and NH_3 from the gas phase onto the straw, improving diffusion and mixing, preventing the need for drying the biomass/additive mixture.

Furthermore, the use of acid and base additives strongly influenced the mass balance between the different product groups (Table 2). For example, sulfuric acid reduces the bio-oil yield by three times, in favour of biochars, and ammonia increases the char fraction by nearly 40%. These results could be explained by polymerisation of bio-oil in the presence of acid–base catalysts.

The use of additives therefore adds flexibility to this technology, enabling some controllability over the distribution of the desired products and composition of the oil to permit adjustments of outputs from the biorefinery depending on the markets.

The additives had a strong impact on the distribution of chemical compounds in the bio-oil. Under acidic conditions, levoglucosenone (Fig. 5, structure V) was formed, with the highest relative content achieved on addition of sulfuric acid (Fig. 5C). Levoglucosenone has previously been utilised as a starting material in the synthesis of 2,3-dideoxyribose, used as a medicine,[32] serricornine (sex pheromone of the tobacco beetle),[33] hydroxylactones (an appetite satisfying ingredient),[34] and optical active compounds.[35] It is significant that in the presence of sulfuric acid the benzofuran concentration in the MW oil is reduced whilst the concentration of the high boiling point phenolic compounds is increased.

Table 2 Influence of 3% w/w of additives on mass balance of pyrolysis

	Products characteristics						
	Char		Organic fraction		Aqueous fraction		Gas
Additive	Yield (%)	CV/kJ g^{-1}	Yield (%)	CV/kJ g^{-1}	Yield (%)	pH	Yield (%)
Original	29	27.2	21	15.9	36	4.1	14
H_2SO_4	44	29.7	7	16.4	33	3.7	16
HCl	35	28.6	16	17.9	35	2.8	14
NH_3	41	26.5	17	17.7	22	4.6	20

Under basic conditions the product distribution within the bio-oil is simple and clean, with the levoglucosan content double than without additives. Ammonia did not influence the benzofuran concentration, but significantly reduced the quantity of phenolic compounds.[21]

Char

As indicated in Table 2, char is one of the major products of microwave pyrolysis and can be increased as a percentage of the product by the use of additives. It is a source of energy *via* combustion. This can provide the internal energy for the biorefinery as well as the carbon dioxide for the $scCO_2$ extraction process. However, the large amounts of alkali ash remaining in the microwave char following pyrolysis could cause problems. The high potassium and chlorine content of wheat straw has created problems in commercial combustion boilers[36–38] due to the formation of glassy deposits[39] and corrosion of surfaces by alkali salts[40] reducing the lifetime of combustion equipment. We believe that a demineralization step could be a valuable addition to the wheat straw biorefinery to improve the performance of combustion. Char washing was chosen, due to the low energy requirement for drying, based on previous studies on extraction of conventional pyrolysis chars.[41]

Knowledge about the extraction of microwave chars and the influence of this demineralization on char combustion properties, final ash structure and the nature of extracts formed is limited. Therefore, to complement our wheat straw biorefinery concept we carried out initial studies into these processes. Leaching was carried out on chars directly following microwave pyrolysis of wheat straw at elevated temperatures in water. Significant changes are observed in the total ash content and combustion profiles of the microwave pyrolysis chars before and after leaching (Fig. 6). Demineralisation by aqueous extraction appears to reduce the ash residue by a third. In addition, both char oxidation peaks (>350 °C) are shifted to higher temperatures in the char washed sample, which is generally associated with the removal of potassium, reducing its catalytic effect, in studies of washed straw.[42] The presence of two char oxidation peaks could imply some char heterogeneity and the changes in the relative contributions of the two char oxidation peaks to the combustion profiles might suggest different decomposition pathways depending on the inorganic content of the char.

Analysis of the changing elemental nature of the chars confirms the predominant removal of potassium, along with chlorine and minor amounts of other elements, following aqueous extraction (Fig. 7B).

The inorganic content of the chars compared to the original straw was calculated by normalizing the element percentage to the relative ash content. Minor reductions in the ash content

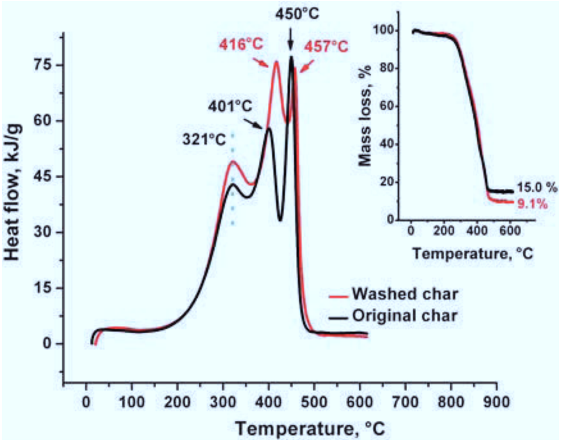

Fig. 6 STA profiles of char before and after washing showing the changes in energy on combustion and the mass loss profile (inset).

correspond to a reduction in chlorine content, as HCl or in association with the organic phase.[1] Following the char wash, 50% of the potassium, 80% of the chlorine and 35% of the sulfur are extracted, whilst only minor amounts of calcium and silicon are removed, as confirmed by ICP analysis. This indicates that the major elements indicative of problems in biomass combustion, potassium and chlorine, have been significantly reduced by char demineralisation.

Also of great importance is the effect of washing on the calorific value of the chars (Fig. 7A). Unsurprisingly, the chars show a much increased calorific value relative to the straws, whilst removal of inorganics also slightly improves the heating value by increasing the concentration of combustible organic material in the sample. In addition, the extraction of wax improves the energy content of the straw slightly by removing a lower calorific component and some of the moisture content of the straw.

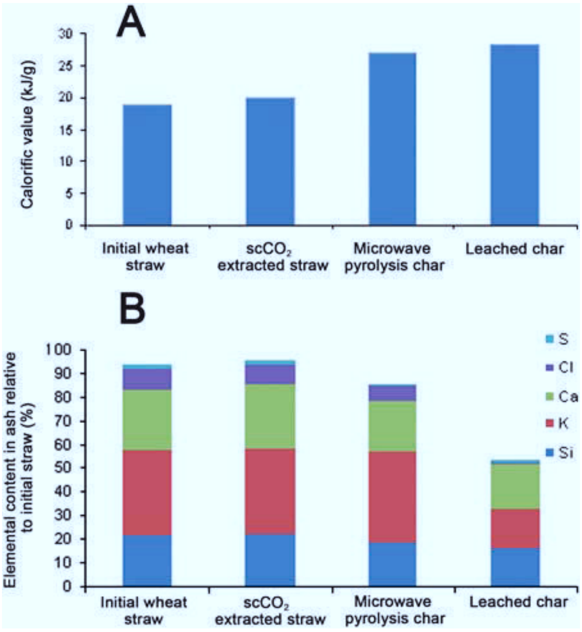

Fig. 7 Calorific value (A) and elemental content (B) of straws and chars initially, after scCO$_2$ extraction and after washing.

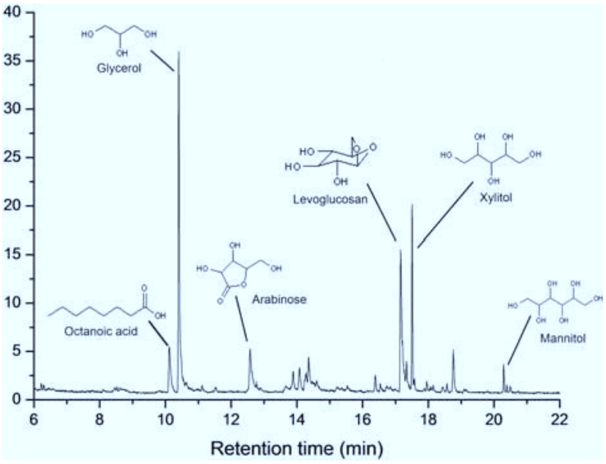

Fig. 8 Gas chromatograms of silylated compounds in leached microwave char solution.

The extraction solution was found to be strongly coloured, indicating the possible solubilisation of sugar components along with the mineral salts. GC-MS analysis of the silylated extracts (done by standard procedure[43]) suggested the presence of several lipid, hemicellulose and cellulose decomposition products (Fig. 8). Octanoic acid and glycerol are both products of fatty acid decomposition which could be present due to the breakdown of lipids from the intracellular walls of the straw. Levoglucosan is a product of the decomposition of cellulose[44] as observed in the bio-oil formed from microwave pyrolysis, whilst arabinose and xylitol are both precursors of hemicellulose. The extracted solution had a neutral pH of 7.4, which indicates that it could be used directly as a fermentation broth for the selective modification of the predicted fatty acid and sugar derived compounds present. This again provides another opportunity to add value to the biorefinery and reduce waste by the incorporation of biochemical processes to specifically target these components for modification.

These results show that the washing of microwave pyrolysis chars removes potassium, chlorine and remaining decomposition products. This has benefits for the straw/lignocellulosic biorefinery, increasing the calorific value of the char, modifying the combustion process and reducing the main inorganic components responsible for slagging and corrosion in the boiler and producing a solution potentially suitable for direct fermentation to produce higher value chemicals.

Process economics and energy efficiency

Extraction of wheat straw with supercritical CO$_2$ produces a high quality wax. Removal of co-extracted water produces a material almost devoid of any other extractives and exhibiting a narrow melting point range.[45] In contrast, the removal of hexane is a high cost and hazardous step and further purification is required to obtain a wax of equivalent quality to that obtained with scCO$_2$. Direct comparison of extraction costs between hexane and supercritical CO$_2$ is rarely possible as the

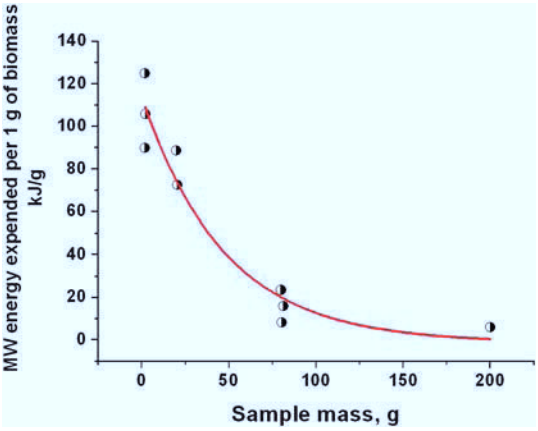

Fig. 9 Energy required per gram of sample for pyrolysis with increasing sample size.

total cost of extraction and subsequent removal of solvent and product purification varies depending on the raw material and product of extraction. A number of products have been the subject of economic studies[46] and in some instances the use of supercritical CO_2 has been shown to be significantly cheaper than using hexane.[47] This is almost always as a result of expensive post-extraction steps including solvent removal and purification for hexane rather than the direct extraction costs. As part of an integrated biorefinery the use of CO_2 could be an appropriate choice of solvent being captured as a product of fermentation and the process energy may be obtained by combustion of other solid waste streams or liquid biofuels. Although it is undoubtedly true that the capital cost of a supercritical CO_2 extractor of equal capacity to a hexane extractor is significantly higher, the lower operating costs should result in a shorter payback time and the greener credentials of the technology should encourage investment.

The microwave process is very tolerant of water compared to conventional pyrolysis and is suitable for most biomass types without pre-drying. Preliminary energy balance calculations based on the thermodynamic properties of the structural components of wheat straw during the decomposition process indicated a energy requirement of 1.8 kJ g^{-1} for microwave pyrolysis compared to 2.7 kJ g^{-1} for thermal convectional pyrolysis. Experimentally we proved that the microwave energy requirement decreased from 100 kJ g^{-1} to 2.2 kJ g^{-1} as the sample mass increased from 0.2 g to 200 g wheat straw (Fig. 9). Pilot scale studies (30 kg h^{-1}), showed a further increase in energy efficiency, requiring as little as 1.9 kJ g^{-1} biomass. Low temperature microwave pyrolysis therefore produces better quality oils and chars than conventional pyrolysis at 1.5 times the energy efficiency.

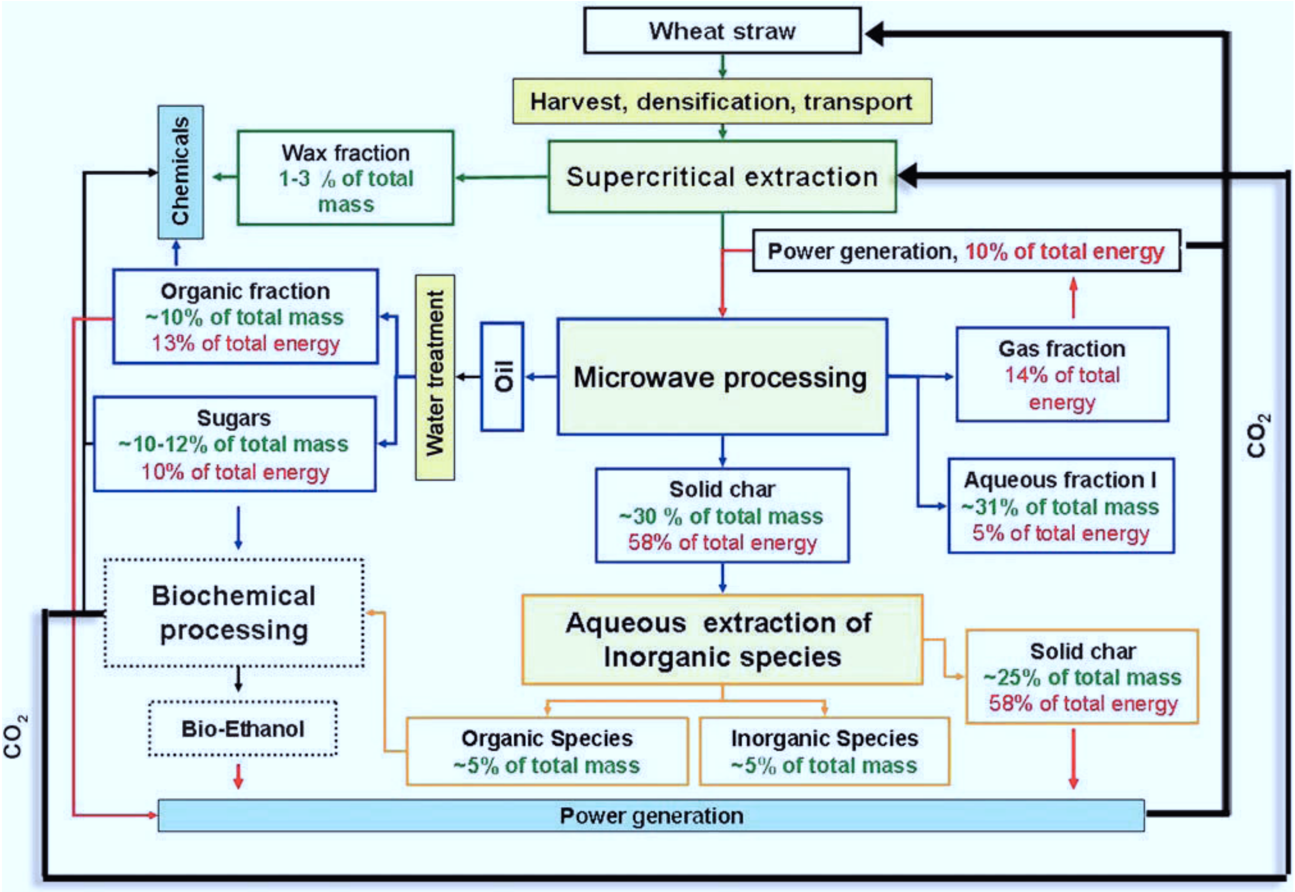

Fig. 10 Integrated wheat straw biorefinery utilising supercritical CO_2 and low temperature microwave pyrolysis to produce a range of products and showing the mass balance of the system.

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Conclusions

We have shown the potential for developing a zero waste wheat straw biorefinery (Fig. 10) incorporating two green chemical technologies, supercritical CO_2 and low temperature microwave pyrolysis. In addition, we recognised the potential impact of the presence of inorganic components in the products, and as such incorporated a new aqueous extraction process to improve combustion properties of the pyrolysis char and generate further useful products.

The external wax on the surface of the straw is extracted prior to processing, adding economic value to the system.

Low temperature microwave pyrolysis generates four major product fractions. The main aqueous fraction has possible uses as a disinfectant or antifungal agent. While the solid char and bio-oil can both be upgraded by water treatment, solubilising sugars and inorganic components, to increase end value. The remaining organic bio-oil may be a suitable starting material for the production of transportation fuels. Gaseous streams from the processing of biomass and combustion of the char can internally generate the CO_2 required for $scCO_2$ extraction and the energy for the whole system. The use of additives is shown to further increase the flexibility of the system.

Overall, we demonstrate the possibility to integrate several green processes to transform a single starting material into a large variety of products at different levels of the value-volume pyramid.

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Abbreviations

The following abbreviations are included in the text in addition to the Mendeleev periodic table symbols and SI units.

BERR	Department of Business, Enterprise and Regulatory Reform
CCC	Committee on Climate Change (Independent UK government advisors)
DECC	Department of Energy and Climate Change (UK)
DRIFT	Diffuse reflectance infrared fourier transform
EU	European Union
FT	Fourier transform
GC	Gas chromatography
GC-MS	Gas chromatography coupled with mass spectrometry
ICP-MS	Inductively coupled plasma coupled with mass spectrometry
IR	Infra-red
IPIECA	Global oil and gas industry association for environmental and social issues
IUPAC	International Union for Pure and Applied Chemistry
LC-MS	Liquid chromatography coupled with mass spectrometry
$MtCO_2e$	Megatonne carbon dioxide equivalents
NMR	Nuclear magnetic resonance spectroscopy
ppm	parts per million
SEM	scanning electron microscopy
STA	Simultaneous thermal analysis
UNFCCC	United Nations Framework Convention on Climate Change
WS	Wheat straw