DOCTOR OF PHILOSOPHY

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Charles Greenhalf

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Aston University

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CHARLES EDWARD GREENHALF

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## THESIS SUMMARY

The projected decline in fossil fuel availability, environmental concerns, and security of supply attract increased interest in renewable energy derived from biomass. Fast pyrolysis is a possible thermochemical conversion route for the production of bio-oil, with promising advantages.

The purpose of the experiments reported in this thesis was to extend our understanding of the fast pyrolysis process for straw, perennial grasses and hardwoods, and the implications of selective pyrolysis, crop harvest and storage on the thermal decomposition products. To this end, characterisation and laboratory-scale fast pyrolysis were conducted on the available feedstocks, and their products were compared. The variation in light and medium volatile decomposition products was investigated at different pyrolysis temperatures and heating rates, and a comparison of fast and slow pyrolysis products was conducted. Feedstocks from different harvests, storage durations and locations were characterised and compared in terms of their fuel and chemical properties. A range of analytical (e.g. Py-GC-MS and TGA) and processing equipment (0.3 kg/h and 1.0 kg/h fast pyrolysis reactors and 0.15 kg slow pyrolysis reactor) was used.

Findings show that the high bio-oil and char heating value, and low water content of willow short rotation coppice (SRC) make this crop attractive for fast pyrolysis processing compared to the other investigated feedstocks in this project. From the analytical sequential investigation of willow SRC, it was found that the volatile product distribution can be tailored to achieve a better final product, by a variation of the heating rate and temperature. Time of harvest was most influential on the fuel properties of miscanthus; overall the late harvest produced the best fuel properties (high HHV, low moisture content, high volatile content, low ash content), and storage of the feedstock reduced the moisture and acid content.

Key words: sequential pyrolysis, selective pyrolysis, Py-GC-MS, thermogravimetric analysis, biomass storage.

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# 1 INTRODUCTION

The aim of this chapter is to introduce the key concepts of interest for the present research programme and to provide background information regarding the project, placing the project objectives within the wider context. The context refers to the role of biomass as a renewable energy source in relation to universal economic and environmental factors and to specific European Union objectives. The narrower context of the project refers to the SUPERGEN Bioenergy Project, which is a large-scale programme that encompasses the present research. This discussion is followed by an overview of biomass and its components and the introduction of the crops of interest to this thesis. Finally, the project aims and objectives are outlined, along with a brief overview of the main sections of the thesis.

The projected decline in fossil fuel availability, concerns over the environment, and security of supply have attracted increased interest in renewable energy; in particular energy derived from biomass. This has received considerable attention worldwide since the oil crisis in the 1970's. In 2009, the European Commission projected that biomass will contribute to approximately two thirds of the renewable energy requirements by 2020 (DECC, 2011). To achieve this goal, biomass supplies in the UK will need to be increased, sustained and further sourced. Dedicated high yielding energy grasses and hardwoods will need to be utilised, alongside other waste forms of biomass, such as agricultural crop residues, e.g. straws.

The perennial grasses, such as switch grass (*Panicum virgatum*), reed canary grass (*Phalaris arundinacea) and* miscanthus (*Miscanthus x giganteus*) have been identified as suitable dedicated energy crops for the northern hemisphere (Christian et al., 1999; Clifton-Brown et al., 1999; Clifton-brown et al., 2004). Switch and reed canary grass are sown from seed and can produce high yields with low establishment costs and inputs. Miscanthus is established from rhizomes and is capable of higher yields (Christian et al. 2008), but the establishment costs are higher. Hardwoods, e.g. willow short rotation coppice (SRC), have also gained particular interest as suitable dedicated energy crops, and this is also because of their high yields and low establishment costs (SAC, 2008). Agricultural crop residues, such as wheat (*Triticum aestivum*), barley (*Hordeum vulgare*), maize (*Zea mays*) and rape (*Brassica napus*) straws have also gained particular interest because of their high abundance within the UK and EU (Copeland and Turley, 2008). Currently there is no commercial market for the straw from rape straw, but wheat straw does however have a low grade commercial market in the animal husbandry sector and is also used for power generation in dedicated straw combustion plants. Scarlat et al. (2010) estimated that the total amount of crop residues produced for all 27 European Union states (EU27) was on average 258 Mt (on dry basis) per year with wheat straw being the highest contributor (42% of 258 Mt), barley and maize straw tie second (18.85 of 258 Mt) and rape straw (7% of 258 Mt) in fourth place. Their study showed that on average, based on a lower heating value of 17.5 MJ/kg dry matter, the amount of crop residue available for the bioenergy sector within all European Union member countries was on average 1530 PJ/year, and this is representative of 3.2% of the EU27 yearly energy consumption.

Fast pyrolysis is a possible thermochemical conversion route that offers promising advantages and is of particular interest. This is because bio-oil, the main pyrolysis product (on dry basis up to 75 wt.% for woods (Bridgwater, 2004); 52 wt.% for perennial grasses (Hodgson et al., 2010); 38 wt.% for straw (Tsai et al., 2006)), offers greater versatility in its storage, transport and application and can be used as either a source of energy or chemicals (Bridgwater, 2004; Bridgwater, 2011). Compared to orthodox liquid fuels, bio-oil has a number of distinct environmental advantages. This is because biomass derived liquids have a near carbon-neutral footprint and have insignificant levels of sulphur; therefore no sulphur oxide emissions are generated (Mohan et al., 2006). The thermal-conversion of biomass by pyrolysis to produce bio-oil usually results in the production of a higher energy density fuel that contains a complex mixture of potential valuable chemicals which could be extracted.

A comprehensive review of the principles of fast pyrolysis and application of its products has been carried out by Bridgwater (2011). This thermal conversion process requires a high heat transfer, a stable pyrolysis temperature, high heating rates (>1000 $^{o}$C/s), short hot vapour residence times (<2 s) and rapid cooling of the vapours (Bridgwater and Peacocke, 2000). Continuously fed bubbling fluidised bed reactors are able to meet these requirements and this technology has been investigated thoroughly (Gerdes, 2001). The absence of rotating internal parts within the reactor is advantageous to their use because they are not subjective to wear and sealing issues.

In order to meet the European Commission projection (66% renewable energy by 2020 from biomass), the availability of biomass will have to be increased. For use of biomass in the UK, there are a number of challenges to overcome; these are stated below:

I. Limited availability of biomass

According to the study conducted by Whittaker and Murphy in 2008, UK biomass resources will need to be increased by 43.5 Mt by 2030, and this is based on the maximum assumption. Of the two biomass resources investigated to obtain this estimate, agricultural derived biomass (including energy grasses) is expected to make the highest contribution to this increase, from 13.5 Mt to 43 Mt in 2030 (based on the maximum assumption).

II. Competition for high value land and crops

As the demand for biomass increases (mentioned above) the available biomass resources will also need to be increased. Due to the rising population, depleting fossil fuel reserves and concerns for the environment, it is expected that land use will become more competitive for higher value products, such as fuels and chemicals, other than food. This has the potential to result in higher food prices if not managed properly.

III. Scale - not commercially attractive due to the distributed nature of biomass

The transportation distances can have an impact on the feasibility of the biomass to be used. In order to generate significant amounts of energy from biomass, large areas of land are required. If the distributed nature of the biomass in question is too extensive, i.e. spread over large amounts of land, the economics and energetics of the entire process can become non-commercially attractive (Herzog et al., 2001).

IV. Biomass properties - further research and refinement of biomass and its processing facilities is required

The current application of bioenergy products in some conventional systems, e.g. combustion engines, is still somewhat problematic and a further insight is required to develop this technology further.

## 1.1 BACKGROUND OF THE PROJECT

### 1.1.1 SUPERGEN

The research programme reported here is part of a large-scale project, known as SUPERGEN. SUPERGEN was created by the Engineering and Physical Sciences Research Council (EPSRC) in the UK, to help develop sustainable power generation and supply derived from renewable resources. Of the four original consortia setup (ten setup in total) by the EPSRC, the present research falls within the biomass and biofuels consortium and this is under the SUPERGEN Bioenergy II Project. The SUPERGEN Bioenergy II Project was setup as a continual to the SUPERGEN Bioenergy I Project, with the aim to develop and support the UK bioenergy sector. To achieve this main aim, the project focus was to contribute to the development of a competitive science and technology sector, and further establish the UK as a recognised centre of excellence in technological innovation.

In contribution to this, the bioenergy project has focussed attention towards the agronomy and thermal conversion of biomass. The project itself is based on 8 integrated and coordinated themes which are shown in Figure 1.1. The project involves collaboration between ten academic institutions and eleven industrial partners.

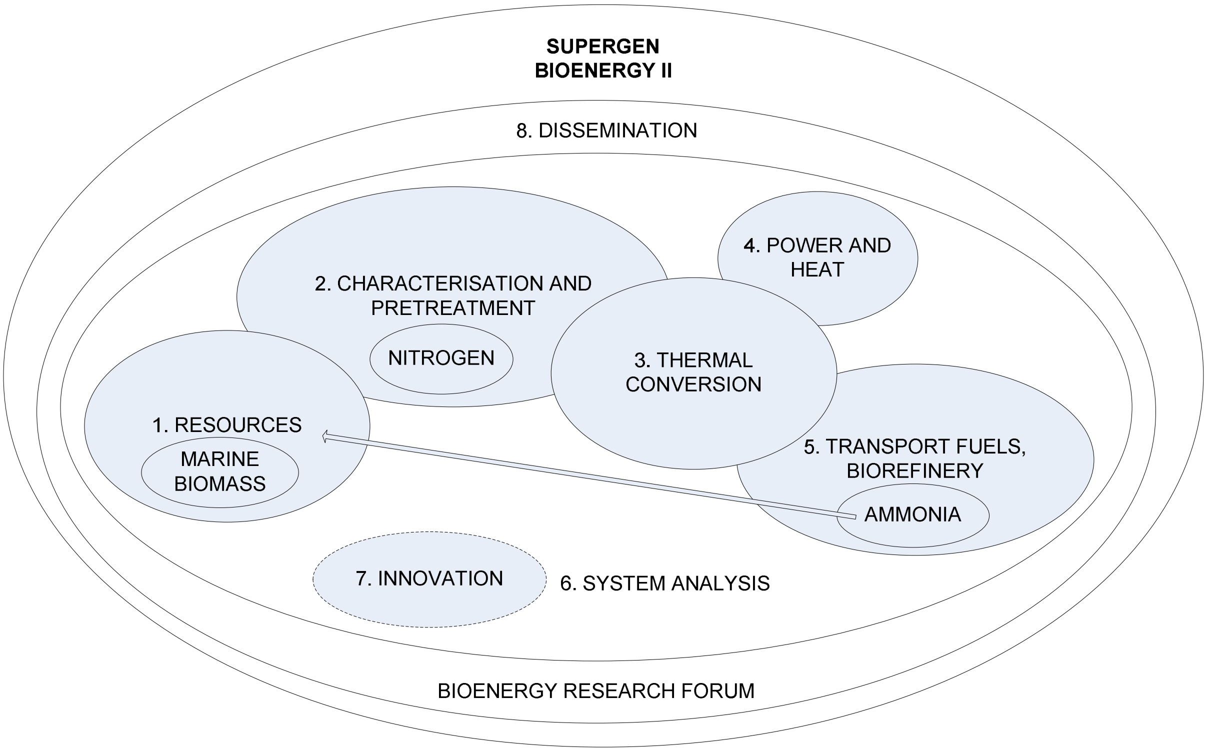


Figure 1.1 – Supergen Bioenergy II Project

The Rothamsted Research Institute (Theme 1) is a leading research centre in plant-based agriculture and land-based management within the UK. Rothamsted has a unique genetic resource of 1300 accessions of willow, and was the first in the UK to conduct work on perennial grasses in terms of their potential to become a dedicated crop for biofuel production. The Institute of Grassland and Environmental Research (formally known as IGER, now called IBERS; also part of Theme 1) in collaboration with Rothamsted, has actively been involved in the breeding of various miscanthus genotypes and other perennials grasses. Three of the five feedstocks investigated in the present research were supplied by the Rothamsted Research Institute. The present project falls under Themes 2 and 3 of the SUPERGEN project.

### 1.1.2 BIOMASS

The aim of this section is to investigate the main components found in biomass. It is of high importance to develop an understanding into the chemistry of biomass, because products derived from the thermal conversion process will be influenced by this. Herbaceous plants and grasses and woody plants are of primary interest to work carried out in the proceeding chapters. According to the Biomass Energy Centre, biomass is defined as a biological material obtained from living or recently living organisms, and usually refers to plant derived materials, but this definition is equally applicable to material derived from animals (BEC, 2012). Biomass is composed of oxygen rich carbon based polymeric material that contains small quantities of inorganics. According to McKendry et al. (2002), biomass can be classified into any of the following four categories, or a combination of these:

1) herbaceous plants and grasses, 2) woody plants, 3) aquatic plants and 4) manure. Figure 1.2 shows the composition of plant biomass obtained from categories 1 and 2 mentioned above.

The three main components of the cell wall are; hemicellulose, cellulose and lignin, fall under the macromolecular substances heading, and cellulose and hemicellulose are sub-headed under polysaccharides. The organic extractives, such as resins, fatty acids, alcohols, phenolics, sucrose, fructan, etc, and the inorganics fall under the low molecular weight substances category. The three main components, organic extractives and inorganics present in biomass are discussed in this section. Cellulose, hemicellulose and lignin are the three main components found in these categories (1 and 2). There is a considerable difference in the chemical structure found in each of these components. The differences, including the organic extractive and inorganic content, should be taken into consideration because this will influence the thermal conversion process, e.g. conversion by fast pyrolysis, and ultimately alter the pyrolysis product yields and their chemical composition.

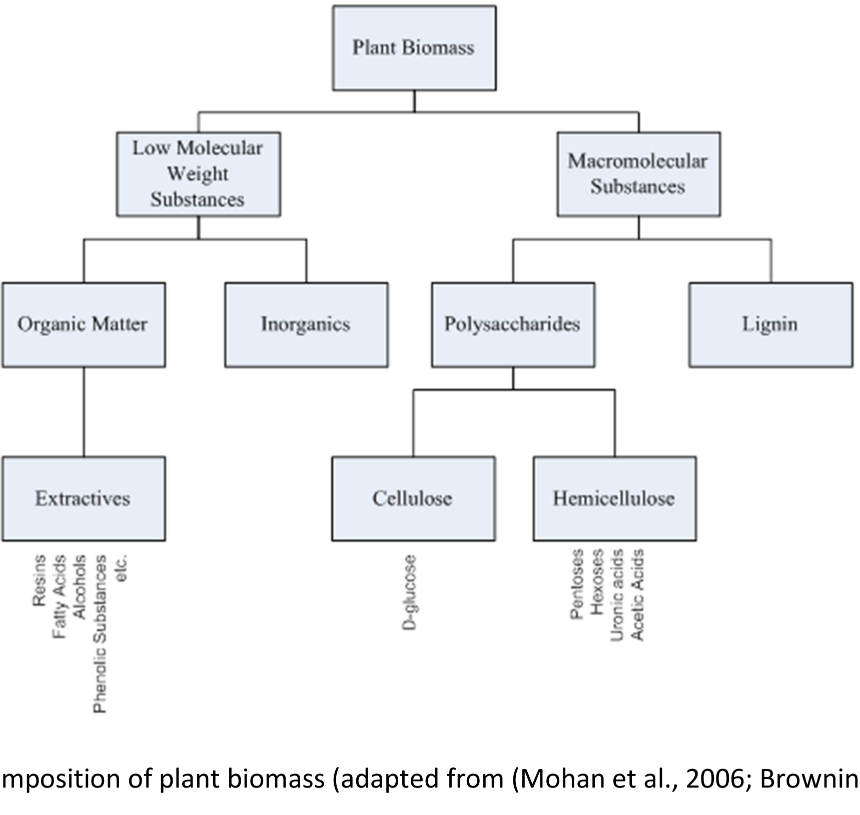


Figure 1.2 - Composition of plant biomass (adapted from (Mohan et al., 2006; Browning, 1967))

#### *1.1.2.1 Cellulose*

The most abundant organic compound in the biosphere is cellulose, and this is synthesised and degraded at the rate of $\sim 10^{15}$ kg annually (Berg et al., 2002). Cellulose is an unbranched glucan polymer (linear homopolysaccharide) of β-D-glucopyranose moieties joined by (β–1,4)-glycosidic bonds (Berg et al., 2002; Alén et al., 1996; Wu et al., 2009). Cellulose consists of a two sugar repeating unit known as cellobiose, and is able to form straight chains due to the β-1,4 linkages. The partial structure of cellulose and its repeating unit are shown in Figure 1.3.

Figure 1.3 - Partial Structure of Cellulose and its Repeating Unit Cellobiose (Alberts et al., 2002)

The cellulose chain is hydrophilic along its sides and hydrophobic on its end. Interaction between cellulose chains by intermolecular hydrogen bonding allows chains to adhere to one another and form ordered crystalline material, known as microfibril (Alberts et al., 2002). Hydrogen bonding occurs between the aliphatic hydrogen atoms and the principle functional groups, the hydroxyl groups (Huber et al., 2006). Microfibrils are connected and held together by cross-linking glycan molecules to form fibres. The degree of polymerisation ranges between 1,000 and 15,000 (Zhang, 2006; Rowell et al., 2005), with an average molecular weight of 100,000 (McKendry, 2002). Most wood-derived cellulose is approximately 35% amorphous (Rowell et al., 2005). The crystalline surfaces and amorphous regions of cellulose are thought to be most accessible to water, chemicals and microorganisms (Zhang, 2006). The central crystalline region has very limited accessibility because of the tight chain packing.

#### *1.1.2.2 Hemicellulose*

Hemicellulose is an inhomogeneous glycan (heteropolysaccharide) composed of two or more monomer units, namely hexoses (D-glucose, D-mannose and D-galactose) and pentoses (D-xylose and L-arabinose) (Alén et al., 1996; Wu et al., 2009; Berg et al., 2002). Hemicellulose is a cross-linking amorphous glycan that binds together cellulose microfibrils, and this contributes to its structural integrity (Alberts et al., 2002). The degree of polymerisation found in hemicellulose is significantly lower than that of cellulose, ranging from 100 to 200 (Rowell et al., 2005). The hemicellulose backbone is usually made up of a single monomer that is hydrogen-bonded to the cellulose microfibrils (Alberts et al., 2002). The backbone and the protruding short sugars side chains vary with plant species and age. Hemicellulose is classified according to its compositional units, molar ratios and linkages. Galactoglucommans (5–15 wt. %) and arabinoglucuronoxylan (7–10 wt.%) are common types of hemicellulose found in softwood, and hardwood hemicellulose usually contains both glucuronoxylan (15–30 wt. %) and glucomannan (2–5 wt. %) (Zhang, 2006).

### *1.1.2.3 Lignin*

Lignin is the main binder for cellulosic components and is considered an encrusting material (Rowell et al., 2005; Mohan et al., 2006). Lignin is has an amorphous highly cross linked three dimensional structure consisting of a non-regular arrangement of phenyl propane units (Alén et al., 1996; Wu et al., 2009; Grabber, 2005). The precursors of lignin are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Rowell et al., 2005). The structure of the lignin precursors can be seen in Figure 1.4. Confieryl alcohol and sinapyl alcohol are both methoxylated. The methoxyl content of hardwoods is higher than that of softwoods. This is because the main precursors for hardwoods are coniferyl alcohol and sinapyl alcohol. The main precursors in softwoods are coniferyl alcohol and minor amounts of p-coumaryl alcohol (Rowell et al., 2005), and p-coumaryl alcohol is commonly found in grasses (McKendry, 2002).

Figure 1.4 - Lignin, 1) p-coumaryl alcohol; 2) coniferyl alcohol; 3) sinapyl alcohol (Rowell et al., 2005)

### *1.1.2.4 Organic Extractives*

The extractive content varies with plant species and stage of development. Extractives are generally classified according to the extraction solvent used to extract them, e.g. water soluble, ethanol soluble, etc. (Rowell et al., 2005). Typical extractives include waxes, fats, proteins, pectin's, starches, etc. (Mohan et al., 2006).

#### *1.1.2.5 Inorganics Minerals*

According to Raveendran et al. (1995), elements such as Si, Ca, K, NA and Mg are commonly found in woody biomass, with smaller or trace amounts of elements such as S, P, Fe, Mn or Al also being seen. These elemental constituents are normally found in the form of inorganic minerals, e.g. oxides, silicates, carbonates, chlorides and phosphates. The ash content is representative of the inorganic minerals within the biomass.

### 1.1.3 PROJECT CROPS

This section introduces the feedstocks investigated and compares their compositional content, harvest yields and estimated production costs.

The feedstocks to be investigated are as follows:

- Straw
    - Wheat Straw (*Triticum aestivum*)
- Perennial grasses
    - Miscanthus (*Miscanthus x giganteus*)
    - Switch grass (*Panicum virgatum*)
- Hardwoods
    - Willow SRC (*Salix viminalis*)
    - Beech wood (*Fagus sylvatica*)

The perennial grasses and straw were provided by Rothamsted Research Institute (who contribute towards theme 1) to support other themes within the SUPERGEN project. The hardwoods, willow SRC and beech wood, were purchased from external suppliers. Table 1.1 shows the crop composition, harvest yields and estimated production costs of these feedstocks. The cellulose content is seen to be highest for the perennial grass miscanthus and the hardwood willow SRC. In comparison to the other crops, willow SRC has the lowest hemicellulose content. The lignin content is generally reported to be highest for the hardwoods. Wheat is commercially grown for its grain and the remaining straw (approximately half the original crop by weight), could be available for bioenergy use. Consequently, the yield per hectare and the associated production cost is significantly lower than that of the other dedicated energy crops. However, wheat straw does have a low-grade commercial market which may interfere with its sole use for bioenergy, as mentioned earlier. Although yields and costs are higher for dedicated energy crops, such as perennial grasses and hardwoods (e.g. willow SRC), the additional land requirement could be potentially problematic in the future. Hardwoods, such as beech wood, are less desired bioenergy feedstocks, because of their long growth periods. Beech wood has been used here as a reference material for comparison with the other feedstocks in this work.

Table 1.1 - Crop Composition, Harvest Yields and Estimated Production Cost

| | Yield and costs | | Composition | | | | |
|---|---|---|---|---|---|---|---|
| | Harvest yields | Cost to produce | Cellulose | Hemicellulose | Lignin | | |
| | [t/ha/y on dry basis] | [£/t] | | [wt.% d.b] | | References | Additional comments |
| Wheat Straw | 3.10* | ~20.00** | 33.20 | 24.00 | 15.10 | (DEFRA, 2010; Karp and Shield, 2008) | |
| | - | - | - | - | 7.50 | (Fahmi et al., 2008) | |
| | - | - | 39.90 | 28.20 | 16.70 | (Hague, 1998 ) | |
| | - | - | 45.37 | 28.28 | 18.74 | (Wang et al., 2011) | |
| | - | - | 41.30 | 30.80 | 7.70 | (Bridgeman et al., 2008) | |
| | | | 38.20 | 24.70 | 23.40 | (Fengel and Wegenaar, 1989) | |
| Switch grass | 5.40-9.60 | 30.00-57.00 | 36.00 | 31.60 | 6.10 | (Riche, 2006; Karp and Shield, 2008) | |
| | - | - | - | - | 8.56 | (Fahmi et al., 2007a) | |
| | - | - | 44.90 | 31.40 | 12.00 | (Fengel and Wegenaar, 1989) | Late cut |
| Miscanthus x giganteus | - | - | 54.00 | 23.90 | 14.94 | (Hodgson et al., 2010) | Treatment 1 |
| | 10.00-15.00 | - | - | - | - | (Lewandowski et al., 2000) | |
| | - | - | 52.13 | 25.70 | 12.50 | (Hodgson et al., 2011) | |
| | 17.69 | - | - | - | - | (Christian et al., 2008) | Mean: 2002 |
| | - | 30.24 | - | - | - | (CALU, 2006) | local use (12.5 t/ha/y) |
| Willow SRC | - | - | 49.30 | 14.10 | 20.00 | (Bridgeman et al., 2008) | |
| | ~10.00 | - | - | - | - | (Wilkinson et al., 2007) | |
| | - | - | - | - | 19.00 | (Fahmi et al., 2007a) | |
| | - | - | - | - | 19.60 | (Fahmi et al., 2008) | |
| | 8.00 | 31.00 | - | - | - | (SAC, 2008) | |
| Beech wood | - | - | 43.30 | 31.80 | 24.40 | (Carpita and McCann, 2000) | |
| | - | - | 40.10 | 26.80 | 23.20 | (Hague, 1998 ) | |

d.b: on dry basis

*straw (on average - wheat straw ~45% of whole crop (Scarlat et al., 2010))

**main cost of production allocated to the production of the grain, hence its low cost (bailing, carting and fertiliser

## 1.2 PROJECT AIMS AND OBJECTIVES

The main aims of this research project, as part of the SUPERGEN project framework, fall within Themes 2 and 3, and these are to:

A. Characterise a diverse range of feedstocks and assess their fast pyrolysis product potential for fuels and chemicals;
B. Develop a better relationship between biomass properties, pyrolysis conditions and pyrolysis product properties;
C. Investigate the influence of harvest time and storage duration on fast pyrolysis product properties.

In order to address the above aims three experimental studies were conducted, each of which focused on one or more of these set aims. Each experimental study has its own subset of objectives that collectively address the respective main objective the study deals with, and this is shown at the start of each experimental study (Chapters 4, 5 and 6). The thesis objectives are to:

[I]. Characterise and conduct laboratory-scale fast pyrolysis processing of feedstocks available for this project, and compare their products and yields;
[II]. Investigate how light and medium volatile decomposition products vary with different pyrolysis temperatures and heating rates using analytical equipment, and compare fast and slow pyrolysis products and yields;
[III]. Characterise and compare feedstocks from different harvests, storage durations and storage locations, in terms of their fuel and chemical properties.

The underlying purpose of all experiments is to extend the understanding of the fast pyrolysis process for different feedstocks, the implications of selective pyrolysis, crop harvest and storage on the thermal decomposition products and to develop, where possible, a better understanding of the process in order to optimise the products derived from various types of biomass. Such an undertaking has the potential to contribute towards the objectives regarding renewable energy and to help meet the European Commission's targets for 2020.

## 1.3 ORGANISATION OF THESIS

The thesis is divided into four sections: literature review, methodology, experimental studies and discussion. Inevitably there is a certain degree of overlap in the particular areas of investigation of the three experimental studies. Additionally, several aspects of each study are replicated in the other studies in order to provide further evidence in support of the experiments' findings and their generalisability. The thesis is organised into the following chapters:

**Literature Review:**

**Chapter 2**: Pyrolysis of Biomass

A literature review is carried out to investigate the principles of fast and slow pyrolysis, factors influencing product yields and pyrolysis products, with particular emphasis on the main fast pyrolysis product bio-oil. A critical review of the literature underlying the experimental work is also covered in this chapter.

**Methodology:**

**Chapter 3**: Experimentation Methodology

This chapter describes and details the methodology used to obtain the feedstocks investigated and undertake the experimental work that is reported in Chapters 4, 5 and 6.

**Experimental Studies:**

**Chapter 4**: A Comparative Study of Straw, Perennial Grasses and Hardwoods in Terms of Fast Pyrolysis Products

This chapter investigates the fast pyrolysis processing of straw, perennial grasses and hardwoods available to the project, and compares and assesses their potential for use as fuels and chemicals. Feedstocks selected included in this chapter are wheat straw (Triticum aestivum), switch grass (Panicum virgatum), miscanthus (Miscanthus x giganteus), willow short rotation coppice (Salix viminalis) and beech wood (Fagus sylvatica). The experimental work is divided into two parts, analytical analysis with and without close-coupled analysis and laboratory scale processing , using a continuous bubbling fluidised bed reactor with a capacity of up to 1 kg/h, with decoupled liquid and char analysis. Py-GC-MS was used to simulate fast pyrolysis heating rates, in order to study potential key light and medium volatile decomposition products found in these feedstocks.

**Chapter 5**: Sequential Pyrolysis of Willow SRC at Low and High Heating Rates – Implications for Selective Pyrolysis

This chapter investigates sequential pyrolysis using two different heating rates, 25 and 1500$^{o}$C/min, over eight different pyrolysis temperatures in a step sequence ranging from 320 to 520 $^{o}$C by Py–GC–MS. Fast pyrolysis was carried out using a 1 kg/h continuous bubbling fluidized bed reactor and slow pyrolysis using a 0.15 kg batch reactor. The bio-oil chemical composition was analysed and compared by GC with mass (MS).

**Chapter 6**: The Influence of Harvest and Storage on the Fuel Properties of Miscanthus x giganteus

This chapter investigate the impact of harvest time, storage duration and storage location on the pyrolysis product properties. The crop was harvested at three different times as follows: early (October 2009), conventional (May 2010) and late (June 2010). Once harvested the crop was baled and stored. The thermochemical properties were investigated using a range of analytical equipment including thermogravimetric analysis (TGA) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). Fast pyrolysis processing was undertaken using a continuous fed bubbling fluidised bed reactor with a capacity of 0.3 kg/h.

**<u>Discussion:</u>**

**Chapter 7**: General Discussions

**Chapter 8**: Conclusion and Recommendations

**<u>References, Appendices and Publications:</u>**

**Chapter 8**: References

**Chapter 9 and 10:** Appendices

**Chapter 11**: Publications

# 2 PYROLYSIS OF BIOMASS

This chapter begins with a description of the principles of fast and slow pyrolysis. It then discusses factors influencing pyrolysis products and yields, with particular emphasis on the main fast pyrolysis product, bio-oil, and it reports on extant findings of the feedstocks to be used. The recommended methodology for bio-oil analysis and end user requirements are also investigated. Then, a review of the thermal degradation of biomass is provided, and the implications of crop harvest and storage on crop properties are addressed. This explores the impact of process parameters on the thermal degradation mechanisms and what influence harvest time, storage duration and storage location have on the pyrolysis products and yields. Finally, research gaps from findings within this literature review are identified, and these inform the experimental work carried out in the proceeding chapters.

## 2.1 PYROLYSIS OF BIOMASS

This section outlines the fast pyrolysis principles, pre-requisite processing requirements, products, factors influencing product yields and current findings of crops investigated here. "Pyrolysis of biomass can be described as the direct thermal decomposition of the organic matrix in the absence of oxygen to obtain an array of solid, liquid and gas products" (Yaman, 2004: pg.653). The solid, liquid and gas product yields are influenced by the conditions of pyrolysis. The different conditions of pyrolysis are classified in modes. The table below gives an example of the pyrolysis modes for wood on dry basis (Table 2.1):

Table 2.1 - Different Modes of Pyrolysis for Wood

| Mode | Conditions | Liquid [%] | Char [%] | Gas [%] |
|---|---|---|---|---|

[Taken from (Bridgwater, 2011)]

### 2.1.1 Principles of Fast Pyrolysis

This section introduces the principles and operating conditions required for fast pyrolysis processing. Various reactor configurations have been investigated in the literature, with particular emphasis placed on the continuous bubbling fluidised beds, because of their use in this work. The purpose here is to explore the different modes of heat transfer and specific advantages and disadvantages of different reactors that could also be used. In addition, the problematic issues related to the poor thermal conductivity of biomass and its required high heating rates are discussed. Findings from this section will inform and be complemented by the laboratory fast pyrolysis experimental methodology carried out in Chapter 3 and this will help to carry out experimental work in Chapters 4, 5 and 6.

The fast pyrolysis of biomass is an endothermic process that requires high heating rates, typically between 10 - 200$^{o}$C/s (Bahng et al., 2009), in order to meet typical processing conditions (~ 500$^{o}$C, short hot vapour residence time of ~ 1 s ). This is due to the low thermal conductivity of biomass, which is 0.1 W/mK along the grain and ca 0.05 W/mK cross grain (Bridgwater et al., 1999), The high heating rate requirement is one of the most significant engineering challenges for the future development of pyrolysis equipment (Bridgwater, 2011). However, this can be reduced by minimising the feedstock particle size.

The reactor temperature is typically set between 525 and 550$^{o}$C to achieve a pyrolysis temperature, (or reaction temperature) of approximately 500$^{o}$C. Because of the effects of heat transfer and temperature gradients, the reactor temperature is set higher than the required pyrolysis temperature. For woody biomass a reaction temperature maximum of between 480 and 520$^{o}$C is necessary to achieve suitable high liquid yields (Bridgwater, 2004).

A number of different types of reactors can be used for fast pyrolysis. The reactor configurations and characteristics are well documented and an extensive review has been published by Bridgwater (2003). For the bubbling fluidised beds, a carrier gas ($N_2$) is passed through a distribution plate, situated in the reactor, at fluidising velocities suitable to suspend an inert fluidising medium, e.g. quartz sand. Quartz sand is a good heat transfer medium because it has a high solid density. The quantity and particle diameter of the quartz sand, within the reactor, is of significant importance to further enhance heat transfer. Some “ablation by attrition” from the fluidising medium within the reactor can occur, and this results in finer char particles (Bahng et al., 2009). Ablation by attrition is low in comparison to circulating fluid beds, because the mean char particle size resembles the initial biomass particle (Bridgwater et al., 1999). Due to the low thermal conductivity of biomass the particle size should not exceed 5.0 mm. The main mode of heat transfer for bubbling fluidised beds is by thermal conduction (90% conduction, 9% convection, 1% radiation (Bridgwater et al., 1999)). The technology behind the bubbling fluidised bed is well understood, since most of the research and development in the field has focused on the reactor and good control over the process temperature (Bridgwater, 2003).

Circulating fluid and transported beds are slightly different from bubbling fluidised beds. For the circulating fluid and transport beds the transfer medium, usually quartz sand, is normally re-circulated and heated in a separate reactor. The second reactor needs to be carefully controlled to match the high heating rate and process temperature requirements. The circulating sand can cause attrition to the char particles due to higher gas velocities and can cause further erosion problems within the reactor (Bahng et al., 2009; Bridgwater, 2011). Consequently, finer char particles are produced and this can lead to further difficulties in char separation. The residence time of the char particle is similar to the pyrolysis vapours, unlike the bubbling fluidised bed which has longer char residence times. The hydrodynamics are also more complex because of higher gas velocities within the system. The main mode of heat transfer is by thermal conduction (80% conduction, 19% convection, 1% radiation (Bridgwater et al., 1999)).

The ablative pyrolysis process is unique in comparison to fluid beds, because the process is driven mechanically and there are no inert gas requirements. Unlike fluid bed reactors, which have a maximum biomass particle size requirement of 5.0 mm, the ablative reactors rate of the reaction is not restricted by heat transfer through the biomass particle, but by heat supply to the reactor surface (Bridgwater, 2007). This is achieved by pressurised high velocity impact on a hot reaction wall, by either centrifugal or mechanical forces (Bahng et al., 2009). This causes abrasion to the produced char, thus exposing a fresh biomass surface (Bridgwater et al., 1999). The rate of the pyrolysis reaction is influenced by four factors; namely 1) the pressure exerted on the particle, 2) the velocity of the biomass material, 3) the heat exchange surface and 4) the reactor surface temperature (Bridgwater, 2007). The main mode of heat transfer is by thermal conduction (95% conduction, 4% convection, 1% radiation (Bridgwater et al., 1999)).

The rotating cone reactor operates mainly under centrifugal forces without the requirement for fluidising gas. The centrifugation process drives hot sand, typically quartz sand, and biomass upwards in a heated rotating cone. Pyrolysis vapours exit the reactor, and char and sand are transported into a riser for sand recycling and finally to the secondary reactor, i.e. bubbling bed combustor, where the char is used to reheat the sand (Bridgwater, 2007).

Fast pyrolysis gaseous products consist of a mixture of vapours, aerosols and non-condensable gases. Rapid cooling is an essential fast pyrolysis feature to condense the condensable vapours and reduce secondary reactions. Condensation of aerosols requires further coalescence and agglomeration, and this can be achieved by the use of an electrostatic precipitator (ESP). The ESP essentially nucleates the aerosol with a negative charge, and this causes the aerosol to attract to the ESP wall, a positively charged plate on the wall of the ESP, resulting in further condensation. Cyclones (cyclonic separation – vortex separation) are commonly used to separate char from gaseous products. Using cyclones, large particles (>10 μm) can be separated from gaseous products (Lu et al., 2009). The removed char is collected in a char pot(s) beneath the cyclone. Thermal insulation of the reactor, cyclones and transition pipe work is used to reduce heat loss and this is achieved using adiabatic materials (Liu et al., 2009).

### 2.1.2 Principles of Slow Pyrolysis

In contrast to fast pyrolysis, the slow pyrolysis process occurs at lower temperatures (300 – 550°C) and heating rates (0.01 – 80.00°C/min) (Williams and Besler, 1996), and has longer vapour residence times (that can last minutes, hours or even days) (Bridgwater, 2011). Pyrolysis product yields of the solids, liquids and gases are approximately equal in ratio on a dry wood basis (Bridgwater, 2004). Although the slow pyrolysis process has a lower energy requirement, lower liquid yields are attained when compared with fast pyrolysis. Slow pyrolysis is of specific interest because of the implications of heating rates on product distribution and product yields; this can be investigated through comparisons of lower and higher heating rates, i.e. fast pyrolysis conditions. The direct application of fast pyrolysis bio-oil in engines is still somewhat problematic (Paradela et al., 2009), and further fundamental studies could be advantageous when comparing liquid products under different heating rates, to help develop a better understanding.

### 2.1.3 Factors Influencing Pyrolysis Product Yields

This section reviews the effects of different pyrolysis processing parameters and feedstock characteristics on pyrolysis products and their yields. Operating parameters, such as process temperature, residence time, heating rate and flow rate, and the impact of gas recirculation are investigated. Additionally the impact of feedstock characteristics, such as water content and particle size, are addressed. This is of high importance for the selection of the appropriate operating parameters and feedstock characteristics, that are required to carry out fast pyrolysis work (Chapter 4, 5 and 6), and the selected parameters are detailed in Chapter 3, which discusses the experimental methodology.

Regarding the effects of fast pyrolysis process temperatures and residence times on pyrolysis products, the work of Piskorz et al. (1998) sheds some light on the relationships between these parameters in the study of three crops. Piskorz et al. (1998) investigated the influence of fast pyrolysis process temperatures (400 – 550°C) and residence times (222 – 703 ms) on product yields of sweet sorghum, sweet sorghum bagasse (residue after sugar removal by pressurised hot water washing) and deionised sweet sorghum bagasse. It was reported that variable liquid yields, between organic liquids and product water, could be achieved by a variation of process temperature. For sweet sorghum, the maximum organic yield (52%) was obtained at a process temperature of 427°C. A reduction in organic yields was seen with further temperature increases. The yield of product water was found to increase from 10% at a process temperature of 427°C to 21% at 550°C. As expected, an inverse relationship with temperature increase was found for gas and char yields. The maximum char and gas yield were found at 395°C and 555°C respectively. Residence time variations were found to have a minor influence; longer residence times resulted in a small reduction in organic yields, and increase in yields of char, gas and product water. It was seen that higher organic yields (max. 58.8%) were attainable from the sweet sorghum bagasse at a process temperature of 520°C. Deionisation of sweet sorghum bagasse, using dilute acids to remove alkaline cations, was found to further increase organic yields (max. 61.4%) and reduce gas yields.

Wei et al. (2006) explored how fast pyrolysis gas yields could be increased, with a particular focus on hydrogen-rich gas production by in-situ steam reforming, with varying process temperatures (500 – 800°C) and particle sizes (0.10 -1.20 mm). Under normal conditions, without steam application, gas yields were found to continually increase with process temperature, while yields of organics, product water and char decreased. Particle size was found to have a significant effect on gas evolution. The char and gas yields are affected by particle size: in particular for smaller particle sizes there is an increase in gas yields and a decrease in char yields. Char yield is unaffected by a particle size below 0.20 mm, because of the reduced heat and mass transfer issues, thus resulting in a decreased "internal heat transfer conduction resistance". Temperature gradient increases with particle size (>0.20 mm). Gas evolution can occur within the central regions of the particle. Volatiles exit through the pores of the particle structure matrix, and secondary polymerisation reactions can occur resulting in deposition of volatiles on the pores. This will result in reduced gas yield and increased char yield. Non-condensable gases, such as hydrogen, carbon monoxide and methane, all increased with process temperature. An exception was found for carbon dioxide because yields steadily decreased with increasing process temperature. In-situ steam application resulted in elevated yields of hydrogen and carbon dioxide, while yields of carbon monoxide and methane decreased. Wei et al. (2006) explain that hydrogen production increases due to reactions in the vapour phase at high process temperatures.

Tsai et al. (2007) investigated the variation of fast pyrolysis process parameters on product yields. The process parameters investigated include: processing temperature (400 – 800°C), heating rate (100 to 500°C/min.), nitrogen flow rate (500 – 1500 cm$^3$/min.), condensation temperature (0 -20°C) and particle size (0.17 to 0.50 mm). The experimental work was split into three sections, each section complementing the next. The first section investigated the influence of process temperature and heating rate on pyrolysis product yields of rice husk. The heating rate evaluation was only investigated at a process temperature of 500°C. It was reported that the optimum process temperature for rice husk biomass (particle size >0.50 mm) to generate maximum oil yields was at 500°C, at a nitrogen flow rate of 1000 $cm^3$/min., a condensation temperature of 10°C and heating rate of 200°C/min.. The maximum oil yield was obtained at a heating rate of 200°C/min. The second experimental section investigated the nitrogen flow rate and product condensation temperature, using the optimal processing and heating rate temperatures from section one. Tsai et al. (2007) found that variation in the flow rate had no significant effect on product yields, and they suggested that a larger variation than those used would significantly alter product yields. Product condensation temperature was found to have no effect below -10°C. The third experimental section explored the influence of particle size using the optimal conditions from experimental sections one and two. Findings were similar to those reported by Wei et al. (2006), that is when process temperature and particle size were changed product yields were effected.

Demirbas (2007) explored how the variation in pyrolysis process temperature (heating rate of 10°C/min. and residence time of 45 – 55 s to reach process temperature) influenced bio-oil compound distribution. The process temperature was varied between 350 – 600°C. The maximum liquid yield was obtained at process temperatures between 480 – 530°C, for the four feedstocks investigated. It was reported that feedstock's containing high lignin content, group 1 - olive husk and hazelnut shell, produced larger liquid yields. This was most evident when comparing yields with feedstock's containing lower lignin content, group 2 - spruce and beech wood. The variation in lignin content is approximately 2:1 between groups 1 and 2, and the increase in liquid yields between groups is approximately 5%.

He et al. (2009) undertook a three by three factorial experiment, using pyrolysis process temperatures of 450, 500 and 550°C and feedstock moisture contents of 5, 10 and 15 %, to investigate fast pyrolysis yields, using switch grass as a feedstock. The results show that when the moisture content was kept constant and the process temperature was increased, organic liquid yield decreased and the water content increased. The maximum and minimum organic liquid yields were obtained at a process temperature of 450°C and 550°C, with a feedstock moisture content of 10% and 5% respectively. When the moisture content was increased and the process temperature kept constant, it was reported that in general char and water yield increased.

Heo et al. (2010) explored how variation of fast pyrolysis process parameters (process temperature 350 – 550°C, particle size 0.3 – 1.3 mm, gas flow rate, feed rate and recirculation of product gas) influenced product yields for Miscanthus sinensis. The maximum yield of bio-oil was obtained at

450$^{o}$C and this had a water content of 34.5 %. Similar trends were reported with respect to the influence of particle size on pyrolysis yields as those mentioned above. Non-condensable product gases were used, by recirculation, to investigate their influence on product yields. It was found that the bio-oil yield increased by approximately 7 %.

Duman et al. (2011) compared fast and slow pyrolysis and the implications of process temperature on product yields. For the slow pyrolysis experiments, results show that product distribution was essentially unaffected by process temperature increases above 300$^{o}$C. A steady decrease in char yield was observed with temperature increase, and it was reported that gas yields increased. Fast pyrolysis experiments showed that product distribution varied considerably with increases in process temperature. This was most evident when comparing the ratio of oil to the aqueous phase between fast and slow pyrolysis experiments. This ratio essentially remained constant when looking at the slow pyrolysis experiments. Of the two feedstocks studied, it was found that the feedstock high in lignin produced more bio-oil.

### 2.1.4 Fast Pyrolysis Products

This section reports the pyrolysis products generated by fast pyrolysis. Particular emphasis was placed on the main pyrolysis product, liquid bio-oil, because of the high yields generated as compared with the other pyrolysis products. The chemical and physical characteristics of the bio-oil are investigated in order to gain a better insight into its complex nature. An understanding of the bio-oil multiphase structure and its stability is critical to further experimental analysis, and its use and potential for upgrading. Additionally the recommended methodology for bio-oil analysis, sample analysis guidelines, and end user requirements are detailed. The char and gas by-products were also investigated.

#### *2.1.4.1 Liquids*

Bio-oil is a thermal degradation liquid product derived from the pyrolysis of biomass. It consists of a complex mixture of compounds with a molecular weight ranging from 18 to 5000 g, and has an average molecular weight of between 370 and 1000 g/mol (Lu et al., 2009). Bio-oil as a whole can be divided into a number of different compound classes as shown in Figure 2.1.

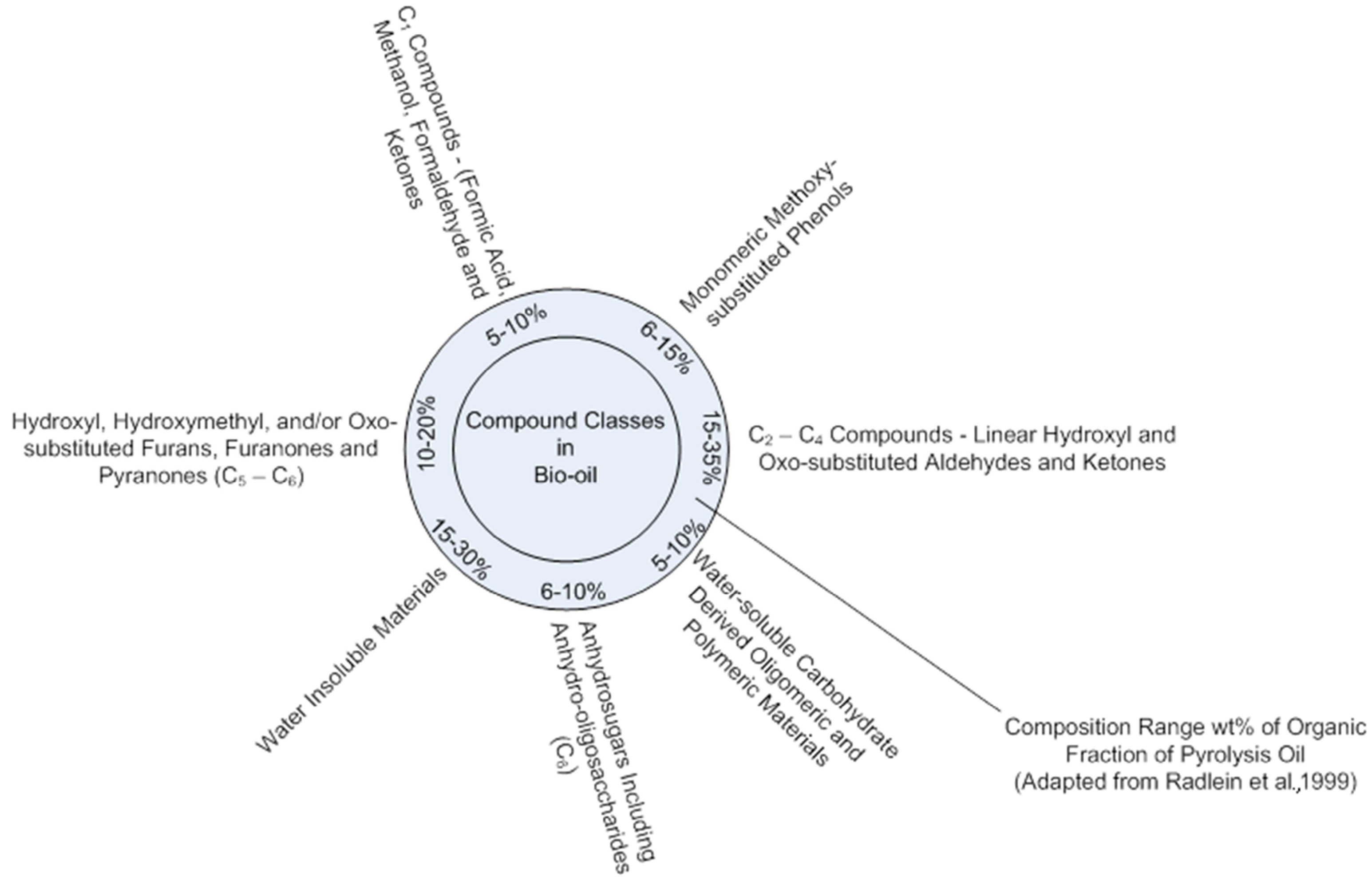


Figure 2.1 - The Different Compound Classes found in Bio-oil [adapted from (Bridgwater and Peacocke, 1999)]

A detailed review of the fuel properties of biomass derived from fast pyrolysis liquids has been undertaken by Lu et al. (2009) and some of the findings are reported below:

I. Water is the main component in bio-oil (typically ranging between 15 and 30 wt.%). This is functionally related to the initial feedstock moisture content and number of dehydration reactions. The most favourable arrangement for water within bio-oil is expected to be through hydrogen bonding with polar compounds.
II. The water could react to form aldehyde hydrates; this is formed by the union of water and aldehyde-containing compounds.
III. The oxygen content within bio-oil is typically between 35 and 60 wt.% on as-received basis. This is due to the high water content and a large variety of oxygen rich compounds. It is expected that the oxygen content will be higher in the bottom phase for phase separated bio-oil, because most oxygenated compounds are polar.
IV. The char content within the bio-oil is typically less than 3 wt.% and this can vary depending on the method of char separation. The char particle size ranges between 1 and 200 μm (mean particle size 10 μm). Most inorganic compounds are found within the char particles.
V. Bio-oil typically has a lower heating value (LHV) of between 14 and 18 MJ/kg and a density of approx. 1.2 g/mol. In comparison to conventional fossil fuels, the volumetric energy density is between 50 and 60%.

#### 2.1.4.1.1 Bio-oil Multiphase Structure

Bio-oil is usually found as a macroscopic homogeneous liquid consisting of microscopic multiphase structures (Lu et al., 2009). According to Radlein (2002), bio-oil can be considered as a micro-emulsion that is formed as a result of polarity differences between compounds. This can lead to the formation of micelles, whereby non-polar compounds form aggregates within the bio-oil continuous aqueous phase. The continuous aqueous phase consists of water and water-soluble compounds. Multi-polar compounds act as bridging agents to stabilize the dispersed and continuous phase. Phase separation can occur due to differences in polarity, solubility and density of the bio-oil.

Garcia-Perez et al. (2006) investigated the multiphase structure of bio-oil. It was reported that the microscopic analysis of the bio-oil confirms that large droplets (Ø 20 – 80 μm) and aqueous droplets (Ø 5 – 10 μm) exist in an oily matrix. The large droplets contain crystals, approximately 20 μm in length, and may be formed from fatty and resin acids, fatty alcohols and sterols (avg. $C_{20\text{-}40}$). Bio-oil that is phase-separated is commonly associated with biomass rich in extractives. The typical composition of extractives is similar to that found in the large droplets. From the microscopic analysis, it is clearly evident that the bio-oil top phase is rich in waxy material and that the bottom phase contains very minimal amounts. Garcia-Perez et al. (2006) also investigated the influence of temperature on the top and bottom phase of the bio-oil. The top phase is seen to progressively solubilise with increasing temperature; the large droplets solubilise between 25 and 42°C and the aqueous droplets at approximately 53°C. During the cooling process, at a cooling rate of 0.5°C/min., the waxy material from the large droplets precipitates to form crystals (approx. length 10 µm). The process of crystal re-growth by nucleation occurs at 37.3°C. The bottom phase characteristics differ to the top because at 54.5°C movement is seen in the aqueous droplets. This is thought to be due to the weak hydrogen bond interaction in the top phase. At 70°C, the bottom phase becomes soluble and only one homogeneous matrix is seen. It was also reported that char particles concentrate at the interface between the two phases of a phase-separated bio-oil. This may be due to a stabilising effect at this interface. Differential thermal calorimetry further confirms the melting of the waxy material in the top phase of the bio-oil (Garca-Prez et al., 2006). This can be split into two regions, the low and high crystalline point fractions. The high crystalline point fraction corresponds to the temperature of solubilisation seen in microscopic studies, and has an endothermic energy requirement of approximately 3.45 J/g which is only seen in the top phase. The influence of surface tension with temperature was also investigated. It was reported that a major reduction in surface tension at the wax melting temperature was seen, from 33 to 25 mN/m for the whole bio-oil. Steady rheological studies indicate that viscous flow activation energy is reduced upon progressive solubility of the waxy material. This is most evident in the whole bio-oil and top phase bio-oil. The bottom phase viscous flow activation energy remains constant with temperature increase. All liquids (bottom, top and the whole bio-oil) have Newtonian fluid behaviour above a temperature of 45°C. Below 45°C the top phase shows non-Newtonian fluid behaviour; this is because the liquid is not independent of shear stress. The interaction between waxy crystals gives this phase elastic behaviour.

Oasmaa et al. (2002) investigated bio-oil phase separation and reported that feedstocks rich in extractives, i.e. forestry and agricultural residues, produced a phase separated bio-oil. Extractive content consists mainly of hydrophobic compounds and some of these compounds are shown in Figure 2.2. As a result of phase separation, different compound classes can be found in the different phases. The top phase, for extractive rich biomass, does not normally exceed 20 wt.% of the whole bio-oil yield, and the extractives content within this phase is approximately 30 wt.%. Most hydrophobic compounds are within the top phase, and this is due to their lower density and differences between solubility and polarity with other compounds in different classes. The bottom phase typically consists of hydrophilic compounds that are water soluble. Water insoluble compounds, e.g. pyrolytic lignin compounds, can also be found in the bottom phase, and their content typically varies between 3 and 4 wt.%. Water insoluble compounds are thought to exist as micro-emulsions that are stabilised by acids. The micro-emulsion can be destabilised by the addition of water. This is because water addition reduces the interaction between the acid and the micro-emulsion, resulting in a change in solubility and subsequent precipitation. The water content should not exceed 30 wt.% in order to avoid precipitation of the hydrophobic compounds. However, this can be prevented by reducing the feedstock moisture content prior to processing. The calorific value of the top phase is higher than the bottom phase due to the lower oxygen content. It was reported that efficient phase separation of bio-oil results in a reduction in the calorific value, viscosity and solid content of the bottom phase. Newtonian liquid behaviour was found in the bottom phase, which is in agreement with the observations of Garcia-Perez et al. (2006).

Ba et al. (2004) investigated the thermal chemical properties associated with water soluble and water insoluble fractions obtained from extractive rich bio-oil. Thermogravimetric results show that the maximum rate of degradation is lower for the water soluble fraction than for the water insoluble fraction.

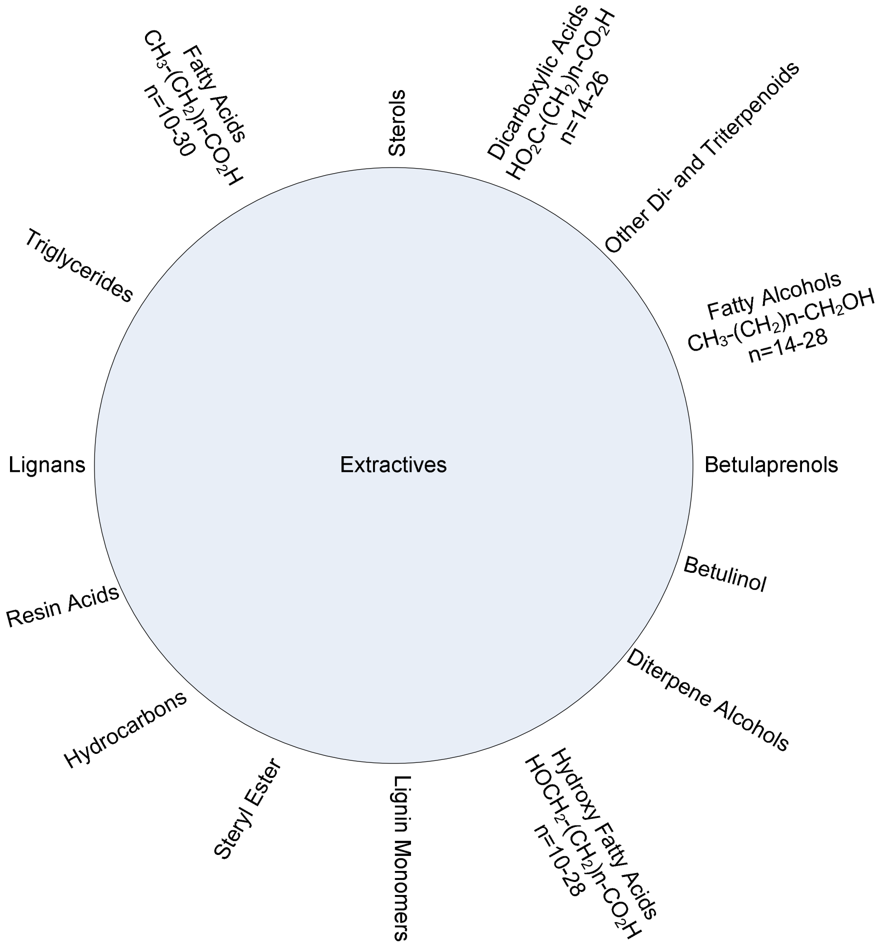


Figure 2.2 - Compounds Typically Found in Extractives Rich Bio-oil [adapted from (Oasmaa et al., 2002)]

The differential thermogravimetric analysis of the bio-oil reveals the presence of three different groups with specific thermal degradation temperatures. The first group, consist of compounds with a low activation energy (light volatiles), the second group has higher activation energy high molecular weight compounds, and the third group contains high molecular weight water insoluble compounds. It was reported that thermogravimetric analysis could be used to predict the water insoluble content and Conradson Carbon Residue value. This is because the water insoluble weight percentage attained at separation is equal to the initial point of degradation on the decomposition curve; and because the bio-oil residue remaining after thermal analysis is comparative to the value of the Conradson Carbon Residue. Microscopic analysis of the bio-oil shows that heating to $70^{o}$C causes phase separation. This is due to the effects of Brownian motion because the droplets, aqueous and waxy, are able to move and coalesce. Elemental analysis of the water soluble and insoluble fractions shows that the carbon to hydrogen ratio is higher in the water insoluble fraction.

Oasmaa et al. (2003) investigated the compositional content of heterogeneous bio-oil obtained from extractive rich biomass. The top phase was high in extractives and low-molecular weight lignin. High molecular weight lignin and aldehydes, ketones and lignin monomers were reported to be evenly distributed between the two phases. The bottom phase contained high levels of water, sugar constituents, acids and alcohols. The ratio of acetic and formic acid contributes significantly to the pH of the bio-oil; this is normally the case when comparisons are made between different bio-oils.

#### 2.1.4.1.2 Storage Stability

The storage stability of pyrolysis liquids has been addressed by a number of researchers (Oasmaa and Kuoppala, 2003; Ba et al., 2003; Fratini et al.; 2005). Aging generally increases the viscosity and water content and decreases the volatile content of bio-oil. Oasmaa and Kuoppala (2003) investigated the influence of storage on the thermochemical properties of bio-oil, derived from green forestry residue. The chemical content was explored using solvent separation techniques to determine the weight percentage of different fractions, due to their solubility in different solvents. Findings from the twelve month storage period are as follows:

I. Viscosity increased with storage duration, increasing most during the first few months ~50 % and a further increase of ~50 % by month twelve (12 months: 20 – 40 cST at $40^{o}$C). The viscosity increased pour point and affects general usability.

II. Water content increased most during the first month. This may be due to condensation reactions that produce water as a by-product. An increase in water content will normally reduce the calorific value.

III. High molecular mass (HMM) lignin approximately doubled during the first few months with a further increases of approximately 40% by month twelve (12 months: 8 – 19 wt.%).

IV. Ether soluble compounds (aldehydes, ketones, furans, phenols and guaiacols) were found to decrease with storage time. Compounds containing aldehyde and ketone groups decreased most with storage time (hydroxyacetaldehyde and 1-hydroxy-2-propanone). The content of furfurals (5-hydroxymethyl-2-furaldehyde, 2-furaldehyde and 5-methyl-2-furaldehyde) and furans (5H-furan-2-one and 2,3-dihydro-5-methylfuran-2-one) were also found to be reduced. A reduction in the light volatile content will increase the flash point.

V. Sugar compounds (ether insoluble: anhydrosugars, anhydrooligomers and hydroxyl acids; main compound: levoglucosan) reduced most during the first six months and slightly increased during the last six months. Acid hydrolysis of sugars could result in an increase in levoglucosane and y-butyrolactone, thus contributing to an increase in ether insoluble compounds.

VI. The content of carboxylic acids and alcohols remained constant throughout the twelve-month trial.

Weight percentage correlations were found between the high molecular mass lignin, and ether soluble ($r^2$=0.8512 over 12 months) and ether insoluble ($r^2$=0.8653 over 6 months) compounds. The correlation between ether soluble and high molecular mass lignin compounds may indicate the presence of joint reactions. The ether insoluble correlation is thought to exist due to the change in solubility brought about by condensation and polymerisation reactions. Ether insoluble compounds would then be found in the high molecular mass fraction. Similar trends were found for other biomass feedstocks (I – VI). Accelerated aging tests display similar results to the twelve-month study. Oasmaa et al. (2002) reported that no further phase separation occurred in bio-oil after 24 h at 35$^{o}$C.

#### 2.1.4.1.3 Recommended Methodology for Bio-oil Analysis

Oasmaa and Meier (2005) undertook a “round robin test” with twelve participating laboratories, to compare the accuracy of bio-oil analysis techniques. This was previously undertaken by the International Energy Agency-European Union (IEA-EU) in 2000. It was reported that poor results could be obtained if good laboratory practice was not followed. Sample handling and storage guidelines were submitted to each participating laboratory in the round robin test. The researchers were instructed that the sample should be stored in a refrigerator (at approximately 5$^{o}$C), used within one week for stability tests and one month for all other analyses. The sample should also be well shaken and at room temperature when the analysis is conducted. Findings from the study were as follows:

- Karl Fisher titration is a suitable method for the determination of water content. The system should be calibrated using the appropriate water standards and sample analysis should be carried out in triplicate.
- pH can be undertaken with reasonable accuracy (±0.1), and it is necessary to ensure re-calibration after each sample.
- Nitrogen content should be carefully tested in triplicate due to low concentration levels. The maximum possible sample size should be used as this will increase accuracy.
- Determination of solid content by measurement of ethanol insoluble, using filter paper with a pore size of 1 µm, is suitable for white woods. For extractive rich biomass a mixture of different polarity solvents, i.e. methanol and dichloromethane, should be tested.
- GC-MS quantification of compounds can be problematic and it may be necessary to use calibration standards.
- Kinematic or dynamic viscosity measurements are most accurate at 40$^{o}$C for homogeneous bio-oil samples that exhibit Newtonian liquid behaviour. Newtonian behaviour of extractive rich biomass should be investigated using a closed-cup rotaviscotester.
- The stability index test, using viscosity measurement at 40$^{o}$C, should be carried out in exactly the same way between samples, and only be used as an internal comparison when comparing liquids generated from the same process. Results should be excluded if weight loss of >0.1 wt.% occurs during the test.
- The determination of the water-insoluble content was found to be unreliable and further improvements are required to achieve a suitable degree of accuracy.

#### 2.1.4.1.4 Bio-oil Standard Requirements

Oasmaa et al. (2005) investigated the end-user specification requirements for fast pyrolysis liquids derived from biomass. The principle objective was to determine norms and standards for fast pyrolysis liquids with respect to end-user fuel quality requirements. It was found that sufficient data was not available to allow for full norms and standards. The specifications required for pyrolysis liquids vary with application and unit size. The general consensuses between end-users of their main fuel requirements are as follows: water content <27 wt.%; solid content <0.01 wt%; inorganics <0.01 wt%; homogeneity – single-phase; max. 100 % increase in viscosity at 80$^{o}$C over 24 h. Values for calorific content, pH, viscosity, flash point and lubrication requirements were not detailed.

### ***2.1.4.2 Char***

Char is commonly referred to as bio-char and is the solid phase, or product, left behind after the loss of volatiles and re-arrangement in structure (Asadullah et al., 2010). In contrast to the main fast pyrolysis product, the bio-oil, char has a lower H:C and O:C atomic ratios and this is indicative of increased carbon-carbon bonds (McKendry, 2002). The char ash content is typically higher than the initial feedstock because the non-volatile inorganics will mainly remain within the char particle. The feedstock particle size has been reported, for fast pyrolysis conditions, to have an impact on the char yield and structure (Asadullah et al., 2010). Char is a valuable by-product that could be used as a heat source to fuel the fast pyrolysis process.

#### *2.1.4.3 Gases*

In addition to the by-product char, non-condensable gases are also generated and these are mainly composed of light hydrocarbons $C_1$-$C_4$. The produced gas could be recirculated to improve efficiency by recycling the fluidising gas. The gas could also be used, in addition to the char, to fuel the process and help produce a lower cost effective process.

### 2.1.5 Fast Pyrolysis Findings of Feedstock Investigated

This section details reported fast pyrolysis processing yields of the feedstock investigated here using different processing capacity continuously fed bubbling fluidised bed reactors. The compositional content, harvest yields and the associated production cost of the investigated feedstocks, wheat straw, miscanthus, switch grass, willow SRC and beech wood, have already been mentioned in Chapter 1 - Table 1.1.

Table 2.2 shows reported findings of the fast pyrolysis product yields, at a process temperature of approximately 500$^{o}$C, from varies past studies using reactors with capacities ranging from 0.15 – 5.00 kg/h from various past studies. The reported product yields vary considerably between studies, and this is thought to be mainly related to differences in the experimental set-up, capacity and source of the feedstock. A number of similarities and differences can be seen when comparing the reported results presented in Table 2.2. Gas content was highest for wheat straw and beech wood, and char content was reported to be highest for wheat straw. A large variation can be seen when comparing the yields of char for the same feedstock. The reactor set-up and feedstock sources are thought to be the main causes for this variation. The variation of the bio-oil and organic content were seen to be much lower were reported. A more accurate comparison between the different feedstock (using the same laboratory scale processing equipment and operating parameters) would further improve current findings.

Table 2.2 - Reported Findings of Fast Pyrolysis Product Yields

| | Fast Pyrolysis Reactor[a] | | | Product yields | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Liquid | | | | Char | Gas | |
| | Reactor capacity | Process temperature | Biomass processed | Bio-oil | Organics | Reaction water | Total water content | | | |
| | [kg/h] | [°C] | [kg] | [wt.% w.f] | [wt.% d.b] | [wt.%] | [wt.%] | [wt.% d.b] | [wt.% d.b] | References |
| Wheat straw | 0.15 | 509 | 0.07 | - | 24.9 | - | 47.4 | 31.9 | 15.6 | (Fahmi et al., 2008) |
| | 1.5 | 505 | - | 60.6 | | - | - | 21.7 | 17.1 | S Run 4 (Jendoubi et al., 2011) |
| Switch grass | 0.15 | 500 | 0.10 | - | 51.5 | - | 24.7 | 24.7 | 7.9 | (Fahmi et al., 2008) |
| | 5 | 500 | 5 | - | ~40.0 | - | 23.1 | ~25.0 | - | 10% moisture (He et al., 2009) |
| | 2.5 | 480 | 1.65 | 60.7 | - | - | 23 | 12.9 | 11.3 | (Boateng et al., 2007) |
| | 0.1 | 500 | - | 60.2 | - | - | - | 18.8 | 13.6 | Run 1 (Agblevor and Besler, 1996) |
| Miscanthus | 0.15 | 500 | 0.08 | - | 52.4 | 8.93 | 17.7 | 19.17 | 11.1 | Treatment 1: (Hodgson et al., 2010) |
| Willow SRC | 0.15 | 507 | 0.06 | - | 52.9 | - | 17.4 | 20.9 | 9.3 | (Fahmi et al., 2008) |
| Beech wood | 1.5 | 498 | - | 67.8 | - | - | - | 12.6 | 13.3 | B run 2 (Jendoubi et al., 2011) |
| | 1.5 | 500 | - | 65 | - | - | 35.0 - 40.0 | 15.9 | 17.7 | (Wang et al., 2005) |
| | 1 | 500 | - | 62.5[d.b] | - | - | 11.3 | 17.02 | 17.4 | (Harms et al., 2010) |

a: Continuous bubbling fluidised bed reactor; d.b: Dry basis; w.f: Wet feed

## 2.2 THERMAL DEGRADATION OF BIOMASS

The aim of this section is to investigate the thermal degradation of biomass and explore the impact of process parameters on the thermal degradation mechanisms and their products and yields. This section builds on from Chapter 1 which gives a background of the chemical composition of biomass and compliments experimental work carried out in Chapter 5. The literature review investigates some of the main pyrolysis products generated from the main biomass components; hemicellulose, cellulose, lignin, organic extractives and inorganics. In addition, this section explores the impact of inorganics and some of the proposed models used to account for the decomposition nature of cellulose at different heating rates.

The understanding of the thermal degradation of biomass by fast and slow pyrolysis is largely not well understood. A large number of studies have been conducted to investigate pyrolysis decomposition pathways for biomass. Alén et al. (2006) reported that the thermal decomposition products of hemicellulose, cellulose and lignin can be divided into major groups (Alén et al., 1996). The major groups for cellulose include: (1) Light volatiles (i.e. carbon monoxide, carbon dioxide, methanol, acetaldehyde and hydroxacetaldehyde); (2) Anhydroglucopyranose (1,6-anhydro-b- D -glucopyranose); (3) Anhydroglucofuranose (1,6-anhydro-b-D-glucofuranose); (4) Dianhydroglucopyranose (1,4:3,6-dianhydro-a-D-gludopyranose; (5) Furans (i.e. (2H)-furan-3-one and 5-hydroxymethyl-3-furaldehyde); and (6) Other products (mainly pyrans). From their study, they concluded that the main products formed between 400 and 600°C were anhydrosugars (groups 2, 3 and 4), mainly levoglucosan. At higher temperatures (600–1000 °C), light volatiles were predominantly formed (group 1). Thermal decomposition of cellulose is extremely complex, but initial break-down starts with the polymer chain prior to the cracking of glycosidic bonds between neighbouring pyrans, due to weak bonds (Wu et al., 2009). This can be seen in Figure 2.3.

A number of models have been proposed to account for the decomposition mechanism of pure cellulose at high and low temperatures. A good example is the Waterloo model (Radlein et al., 1991), and the Piskorz model (Piskorz et al., 1998), which is a more recent modification of the Bradbury model (Bradbury et al., 1979). Another well-known model is the Broido-Shafizadeh model (Bradbury et al., 1979), recently adapted and updated by Liao et al. (2004) to include further modifications. It should be emphasised that these models primarily concentrate on the more immediate decomposition products of pure cellulose, but that secondary decomposition pathways play an important role on the final product distribution. For example, an increase in hot vapour residence time during pyrolysis, will result in an elevated low molecular weight gas yield (Liao et al., 2004), as a result of increased secondary decomposition reactions.

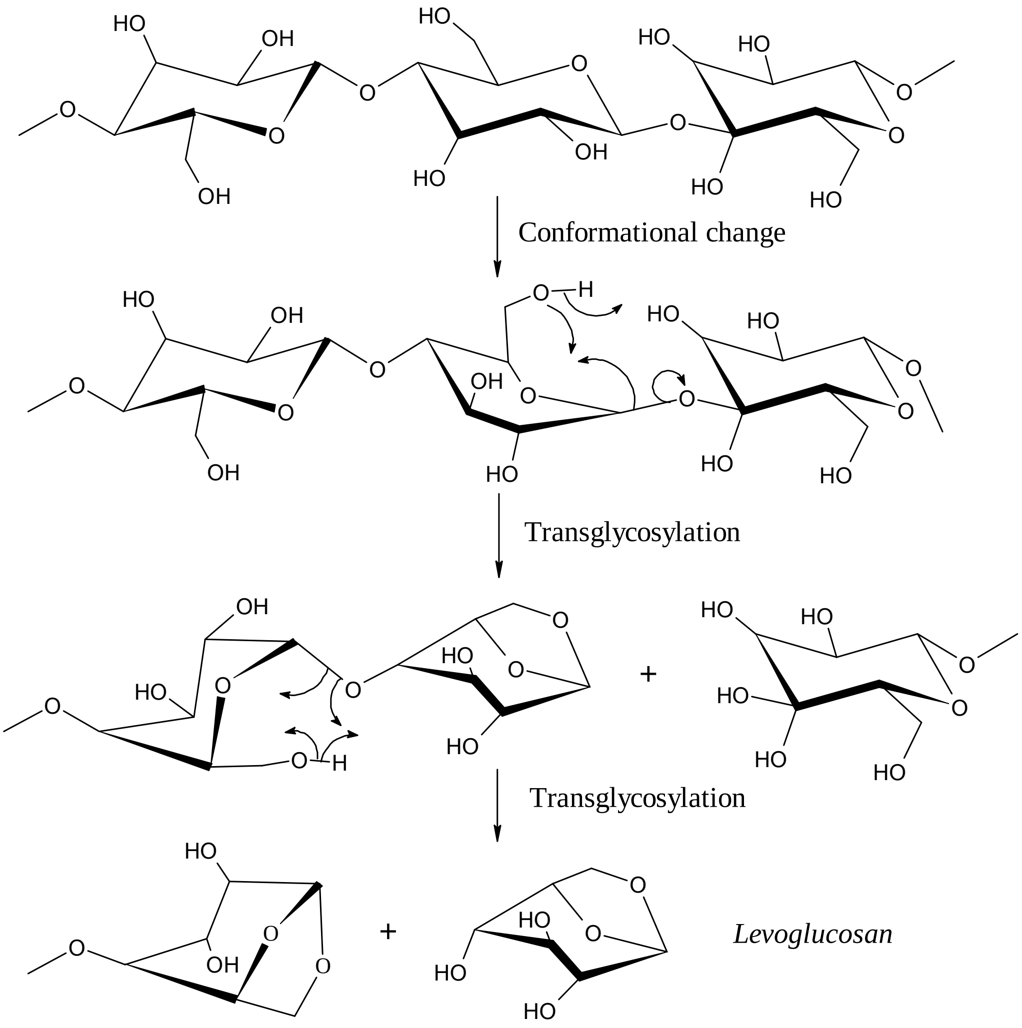


Figure 2.3 - Pyrolytic Formation of Levoglucosan from Cellulose

Further details of these models can be found in the literature (Radlein et al., 1991; Piskorz et al., 1998; Bradbury et al., 1979; Liao et al., 2004; Antal and Varhegyi, 1995; Antal et al., 1985; Antal, 1982; Ponder and Richards, 1994). The general consensus among these investigators with respect to the thermal decomposition of cellulose can be found in Figure 2.4, and this shows two competing pyrolytic decomposition routes.

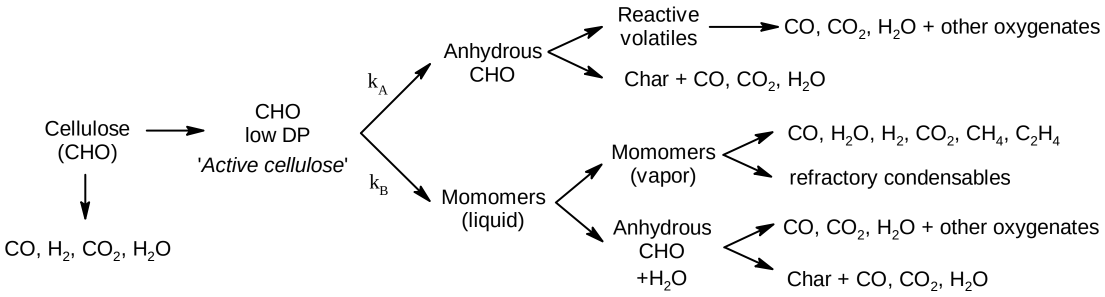


Figure 2.4 - Scheme of Cellulose Pyrolysis – Competing Pyrolytic Decomposition Routes

The first route involves dehydration of cellulose to yield an ‘anhydrocellulose’ (or ‘active cellulose’), and the second results in the depolymerisation of cellulose to yield primarily levoglucosan, with minor amounts of other anhydromonosaccacharides. The $k_A$ route in Fig. 2 is promoted at low temperatures and low heating rates, while the $k_B$ route becomes the major decomposition pathway at higher temperatures and high heating rates.

Thermal decomposition of hemicellulose is usually analogous to cellulose, and the major groups are categorised by Alén et al. (1996): (1) Light volatiles, (2) Anhydroglucopyranose, (3) Other anhydro-glucoses, (4) Other anhydrohexoses, (5) Levoglucosenone, (6) Furans and (7) Other products. The thermal stability is much lower than that of cellulose. This is due to the lack of crystallinity and short side chains, which crack easily, resulting in depolymerisation and intramolecular dehydration reactions (Alén et al., 1996, Wu et al., 2009).

Alén et al. (1996) reported that thermal decomposition of lignin could be divided into 8 major groups, namely; (1) Light volatiles; (2) Catechols; (3) Vanillins; (4) Others guaiacol; (5) Propyl guaiacols; (6) Others phenols; (7) Aromatic hydrocarbons; and (8) Others. Groups 3, 4 and 5 are largely predominant from 400 to 800 °C, while group 1 becomes dominant after 800 °C. The decomposition occurs over a wide temperature range, and breakdown is thought to be the result of side chain cracking and condensation reactions (Wu et al., 2009). Figure 2.5 shows a fragment of the lignin polymer structure with b-O-4 ether bond (Roberts et al., 2011).

Figure 2.5 - Fragment of Lignin Polymer Structure with β-O-4 Ether Bond

Thermochemical properties associated with biomass are important factors to consider, particularly when an element of selectivity is required in the pyrolysis liquid product. For example, work conducted by Broido and Kilzer (1963) showed that metal impurities of around 0.1% could significantly alter pyrolysis and combustion characteristics. Hydroxyacetaldehyde is a compound found in pyrolysis liquids, the concentration of this compound is known to alter according to metal content within the biomass. This was investigated by the addition of ash to the biomass prior to pyrolysis, where it was found that hydroxyacetaldehyde concentration increased (Piskorz et al., 1986). More recently, Nowakowski and Jones (2008) investigated the influence of catalysts on thermal breakdown, finding that metal content in biomass favoured production of hydroxyacetaldehye (heterolytic mechanism), whereas washed biomass (removal of majority of the metals) favoured production of levoglucosan (homolytic mechanism). In addition hydroxyacetaldehyde concentration within pyrolysis liquids is also thought to be related to ketene formation. Kang et al. (1976) investigated how ketene formation occurred as a result of dehydration of hydroxyacetaldehyde at around 200°C, and found that subsequent rehydration would result in the formation of acetic acid. Levoglucosan is another important compound found within pyrolysis liquids in high yields, and as mentioned earlier it can be selectively tailored to produce varying concentrations as a result of metal content. Levoglucosan is thought to be an intermediate for the formation of hydroxyacetaldehyde (Shafizadeh and Lai, 1972), although the formation of hydroxyacetaldehyde is not solely dependent on levoglucosan. Richards (1987) suggests hydroxyacetaldehyde could form directly from cellulose and proposed a mechanism for this process.

Fuentes et al. (2008) showed that volatile and fixed carbon content are partially effected by alkali metal content within willow SCR. This was achieved by demineralisation using an acid treatment and further impregnation of metals. The most notable thermogravimetric outcome was that potassium, iron and phosporus increased the fixed carbon content. Potassium and phosphorus were found to strongly catalyse degradation and subsequently lower the main degradation peak temperature. The impact of phosphorus was also studied by Di Blasi et al. (2008) who found that phosphorus decreased pyrolysis liquid yields and increased char yield. Py-GC-MS results from impregnated phosphorus in willow conducted by Fuentes et al. (2008) suggest that the chromatogram product spectrum showed fewer compounds compared to potassium impregnated willow. Potassium influence supports the heterolytic depolymerisation mechanism (Nowakowski and Jones, 2008) and fragmentation to low molecular weight products as a result of the breakdown of levoglucosan. Phosphorus influences the production of two major products, levoglucosenone and furfural.

Further research into the pyrolysis product distribution is very important because it is an essential step required for improving the product quality and optimising the processing facilities. The mechanisms of pyrolytic decomposition of biomass are still not well understood, due to both the overwhelmingly complex biomass chemistry and the capability limits of analytical instrumentation (Radlein et al., 1991; Westerhof et al., 2009). In addition, pyrolysis products are known to have low thermal stability, and this can cause further analysis issues, due to premature chemical changes in the usual high temperature environment of many analytical procedures. The mechanisms involved in chemical changes and chemical production during pyrolysis are also extremely difficult to determine. For this reason, the focus of the research in chapter 5 will be to examine how changes in pyrolysis product composition can be achieved by modification of pyrolysis temperature and heating rates using analytical equipment.

## 2.3 CROP HARVEST AND STORAGE

The aim of this section is to investigate the influence of harvest time, storage duration and storage location on the thermochemical properties of a potential fast pyrolysis feedstock, Miscanthus x giganteus. This review informs the experimental work that is reported in Chapter 6. The continuous supply of biomass for the renewable energy sector is mainly dictated by seasonal growth of the crop. Crops yields are highly dependent on the time of harvest. Ideally, the crop should be harvested when it reaches its maximum yield potential. In order to meet the continuous supply demands the crop would need to be stored or used in conjunction with other energy crops with different harvest times. It is therefore assumed that harvested biomass will be stored for several months before utilisation by energy converters. This not only achieves the continuous supply but it also allows for further in-storage-drying of the crop that is considered a necessity to achieve a moisture content of <15 wt.% (Styles et al., 2008). A storage period of 9.5 months was assumed by Styles at al. (2008) and estimated the cost between 48 and 110 €/ha/y.

Miscanthus x giganteus, an Asian C4 perennial grass, has been identified as a promising lignocellulosic crop for thermal and chemical energy conversion throughout Europe. Miscanthus has a high yielding potential of 6.9 – 24.1 t/ha/y on dry basis (Lewandowski et al. 2000; Price et al., 2004), and requires low fertiliser and pesticide inputs (Lewandowski et al., 2003). The growth of the crop starts in late spring and stops in late autumn, when the crop senesces and remobilises nutrients from the aerial biomass to the rhizome and soil. The remobilisation throughout the winter period provides a reservoir for nutrients for new shoot growth in the following season.

The implications of harvest time on crop yield and quality of miscanthus have been addressed by a number of researchers (Lewandowski et al., 2003; Brand et al., 2010; Hodgson et al., 2010; Le Ngoc Huyen et al., 2010; Ogden et al., 2010; Yates and Riche, 2007). A large majority of the studies have indicated that delaying harvest from autumn, when the crop senesces, until late spring can reduce dry matter yield by up to 65 wt.% according to Yates and Riche (2007), or 35 wt.% according to Lewandowski et al. (2003). The loss in yield is surpassed by the improvement of the biomass quality for thermal conversion. Lewandowski et al. (2003), and Lewandowski and Heinz (2003) found that by delaying the harvest from December to February concentrations of ash, nitrogen, potassium and chlorine were significantly reduced. Himken et al. (1997) also reported a decline in nitrogen and potassium during the winter months. However, the organic compositional changes of the crop during the winter months may be detrimental to some energy conversion techniques. Delaying the crop harvest leads to a significant increase in the cell wall fraction of the whole aerial biomass (Le Ngoc Huyen et al., 2010), which may reduce the accessibility of sugars for fermentation. Hodgson et al. (2010) reported that deferring the harvest significantly altered cell wall composition, resulting in an increase in lignin and cellulose over the winter period. From an environmental point of view, Santamarta et al. (2011) postulated that harvesting miscanthus early would deprive the soil of the annual input of leaves and the rhizomes from several months' accumulation of necessary nutrients for plant cycles.

The storage of potentially high moisture content biomass for long periods of time will have an impact on the fuel properties of the biomass. Brand et al. (2010) reported that for woody biomass, moisture content will decrease over a storage period with losses linked to storage piles, particle size and initial moisture content. This decrease has a significant effect on the fuel quality of the biomass due to the increase in calorific value associated with the decrease of biomass water content. However, ash content remained constant throughout the storage trial and the authors considered that this was because they found no major change in the chemical composition of the biomass while being stored. For arable straws, Santamarta et al. (2011) demonstrated that up to 20 months of on-farm-storage of canola straw bales (oil-seed rape) significantly changed the moisture and carbon-nitrogen ratio of the biomass.

Jirjis (2005) investigated the influence of storage duration with respect to particle size (chip and chunk), storage pile height and sample zone on the fuel properties of willow short rotation coppice. It was reported that the storage pile height influenced the rate of temperature rise. The temperature rise was fastest for the larger pile, reaching 65°C in about eight days. The smaller pile reached the same temperature after approximately two weeks. The temperature within the pile returned to normal after two months for the smaller pile and after three months for the larger pile. The temperature rise was much slower for the piles created using larger particle sizes (chunks). Jarjis et al. (2005) suggests that this is due to the increased air flow through the pile. The moisture content within the pile was seen to decrease with pile temperature and length of storage. The pile temperature was reported to influence moisture redistribution, resulting in sample zones with different moisture contents. Fungal activity was found to rapidly increase during the first few months. This was most evident in the piles created using small particle sizes (chips), because these offer a higher surface area and better thermal insulation. The average energy content was found to increase slightly in storage piles containing the larger particle fraction.

Mckervey et al. (2008) and Lotjonen et al. (2009) also investigated the impact of storage for high energy grasses. Mckervey et al (2008) looked at a variety of storage methods (airtight, covered, natural and ventilation) for miscanthus, and found that moisture content was most reduced when covered or ventilated during the 6 month storage period. Lotjonen et al. (2009) investigated other high energy grasses, such as reed canary grass, willow and popular, and identified a number of problems related to outdoor storage. Their investigation found that outdoor storage in bulk piles leads to fermentation and a loss of <5% dry matter per month. Suggested solutions were to storage under cover, adjust the pile dimensions and use special fabrics that let water out but not in.

## 2.4 FINDINGS AND RESEARCH GAPS

Findings and research gaps from the literature review in Chapters 1 and 2 are as follows:

I. A more accurate comparison of these feedstocks, wheat straw, switch grass, miscanthus, willow SRC and beech wood, is more beneficial to better compare and assess their potential for use as renewable fuels and chemicals. According to the literature review few studies have:
    a. Investigated the key light and medium volatile decomposition products found in these feedstocks using analytical equipment;
    b. Compared the yields and products of these feedstocks using the same processing equipment and processing parameters. The reported product yields vary considerably between studies, and this is thought to be mainly related to differences in the reactor type, experimental setup, processing capacity and the feedstock source. It is therefore necessary that the investigation of these feedstocks is replicated in order to produce a large enough body of studies in the field, which will allow for trends in the yields and products of the feedstocks to be identified.

Results will contribute to the existing knowledge of crop pyrolysis yields and products, and will provide a better comparison between the different feedstocks and their potential for upgrading. This will also provide a better understanding of the possible industrial implications of fast pyrolysis as a conversion technology for energy and chemical products.

II. A fundamental investigation into the influence of pyrolysis temperature and heating rate on product distribution is required to gain a deeper insight into the thermal degradation of biomass. According to the literature review few studies, particularly for the hardwood willow SRC, have:

   a. Investigated and quantified key light and medium volatile decomposition products using different pyrolysis temperatures and heating rates (using analytical equipment) and derived and compared bio-oil from the fast and slow pyrolysis process;
   b. Investigated the impact of staged pyrolysis or sequential pyrolysis on product distribution.

This is of particular importance to further develop our understanding of selective pyrolysis to help achieve better product distribution within the main pyrolysis product, the bio-oil. This is very important because it is an essential step required to improve product quality and optimise processing facilities.

III. An investigation into the variation of fuel properties associated with harvest time, storage duration and storage location for Miscanthus x giganteus. Changes in fuel quality of woody crops and arable straws during storage are relatively well reported, but there is very little information on the fate of dedicated energy crop properties during winter storage. According to the literature few studies have:
   a. Investigated the consequences of bale-storage and storage location on the feedstock thermal chemical properties;
   b. Investigated the key light and medium volatile decomposition products found in these feedstocks using analytical equipment;
   c. Compared fast pyrolysis processing yields from different harvests using the same processing equipment and processing parameters.

Such an investigation will help to further understand and maximise the potential fuel properties obtained from Miscanthus. In order to meet the continuous supply demands miscanthus will need to be stored or used in conjunction with other energy crops with different harvest times, therefore a better understanding is paramount. This will be highly beneficial to feedstock producers and thermal conversion operators.

Therefore, the main objective of the studies reported in the present thesis are to; characterise a diverse range of feedstocks and assess their fast pyrolysis product potential for fuels and chemicals, develop a better relationship between biomass properties, pyrolysis conditions and pyrolysis product properties and investigate the influence of harvest time and storage duration on fast pyrolysis product properties. This is could be achieved by

- Characterising and conducting laboratory-scale fast pyrolysis processing on feedstocks, available to this project, and by comparing their products and yields;

- Investigating how light and medium volatile decomposition products vary, using a step sequence, with different pyrolysis temperatures and heating rates using analytical equipment, and by comparing fast and slow pyrolysis products and yields generated using laboratory scale equipment;
- Characterising and comparing feedstocks from different harvests, storage durations and storage locations, in terms of their fuel and chemical properties.

# 3 EXPERIMENTATION METHODOLOGY

## 3.1 INTRODUCTION

This chapter describes and details the methodology used to obtain the feedstocks investigated and undertake experimental work that is reported in Chapters 4, 5 and 6. The first section of this chapter details the methodology behind the off-site cultivation, growth, harvesting, storage and pre-processing of the project crops. The second section describes and explains the pre-requisite feedstock requirements needed to carry out experimental work. The third section details and explains how the characterisation and thermal degradation studies have been carried out. This includes a description of the sample preparation and experimental conditions used for the characterisation, and a general description is given of the instruments and their underlying principles. Additionally, the equipment limitations and sources of error are noted, as well as their potential influence on the findings from the experiments. The fourth section describes the processing reactors used (0.15 kg slow pyrolysis reactor, 0.3 kg/h fast pyrolysis reactor and 1 kg/h fast pyrolysis reactor), and the methodology behind the determination of the mass balance. The last section details the methodology behind the characterisation of the pyrolysis products generated.

## 3.2 FEEDSTOCKS INVESTIGATED

In this section the methodology adopted for the off-site cultivation, growth, harvesting, storage and pre-processing are detailed. -The compositional content, harvest yields and associated production costs of these crops; wheat straw, switch grass, miscanthus, willow SRC and beech wood are mentioned in Chapter 1 – Project crops. The perennial grasses and straw have been provided by Rothamsted Research Institute in Harpenden, UK. Rothamsted Research contributes toward Theme 1 of the SUPERGEN project, which is the resources theme. The perennial grasses, miscanthus and switch grass, have been grown at the Woburn experimental farm in Bedfordshire, UK (52 01° N, 00 36° W, ca. 90 m AOD). They have been grown on sandy soil that is known to be low yielding and therefore less desirable for food production. Miscanthus is of particular interest because the points of harvest, duration of storage and location of storage have been varied. The wheat straw has been grown at Rothamsted Experimental Farm in the south east of England. The hardwoods, willow SRC and beech wood, were purchased from external suppliers; these details are supplied below.

### 3.2.1 Miscanthus

Miscanthus (*Miscanthus x giganteus*) was established in 2003 from recently harvested rhizome pieces. Approximately 3 rammets/m$^2$ were planted and the resulting plants have been harvested in the spring, annually, using standard farming machinery. From 2005 until 2007, the crop was part of a large agronomic experiment and in 2008 the whole ground devoted to the experiment received 100 kg N/ha fertiliser “Nitram” (ammonium nitrate) and 50 kg K/ha (potassium in the form of muriate of potash) to unify the yield across the field. The experiment did not receive any fertiliser or pesticides in 2009. The harvest timing and storage reported in this work commenced at this site in 2009.

The experimental farming ground comprised of 15 plots, each 600 $m^2$, in a fully randomised plot design with 3 replicates for each treatment. There were 4 harvest date treatments with 2 nitrogen rates applied at the earliest harvest date. Material from 3 plots was utilised, each plot from a different harvest date treatment (early Oct 2009, conventional May 2010 and late Jun 2010). Because the harvest of the “late harvest” was very late (June 2010), new growth was visible on the standing crop. The plots were harvested in favourable weather conditions using a conditioning mower. The conditioning mower was passed over the cut material three times to improve the condition of the crop for baling. When the crop was harvested on the early harvest dates, the cut material remained on the field for 8 days before bailing to enable natural drying of the crop in the field. For the remaining harvest dates, the crop was immediately baled after harvest using a round baler which was used for all treatments. The bales were then weighed using crane scales and stacked in a pyramid formation in the field, which is shown in Figure 3.1. Wheat bales were used at the base and the top of the stack and the treatment bales were placed in the middle of the stack. This reduces the storage variability in the treatment bales due to the location of the bale in the stack.

The crop was sampled at all three treatment dates just prior to baling and is referred to as the “at harvest” sample. After the storage period, the bales were opened and crop samples were taken from the sample zones. The shoulder and outside sample zones enter approximately 10 cm into the bale (outer 10 cm diameter of the bale). Prior to further analysis, all crop samples were weighed and dried at 80$^{o}$C for 36 h in a recirculating oven. The crop was then hammer milled to pass through a 1 mm sieve before being supplied to our laboratory. For further characterisation the sample was further milled down to obtain a representative fraction between 0.125 and 0.250 mm.

### 3.2.2 Switch Grass

Switch grass (*Panicum virgatum*) was sown in 2001 using standard farming machinery and was harvested annually. In the 2003 growing season, switch grass did not receive additional fertiliser. In 2004 samples were taken in late winter after the crop had fully senesced. The crop material was immediately removed from the field and placed in a re-circulating oven at 80$^{o}$C for 36 h. The dried material was then hammer milled to pass through a 1 mm sieve and stored at room temperature in an air tight container awaiting future analysis.

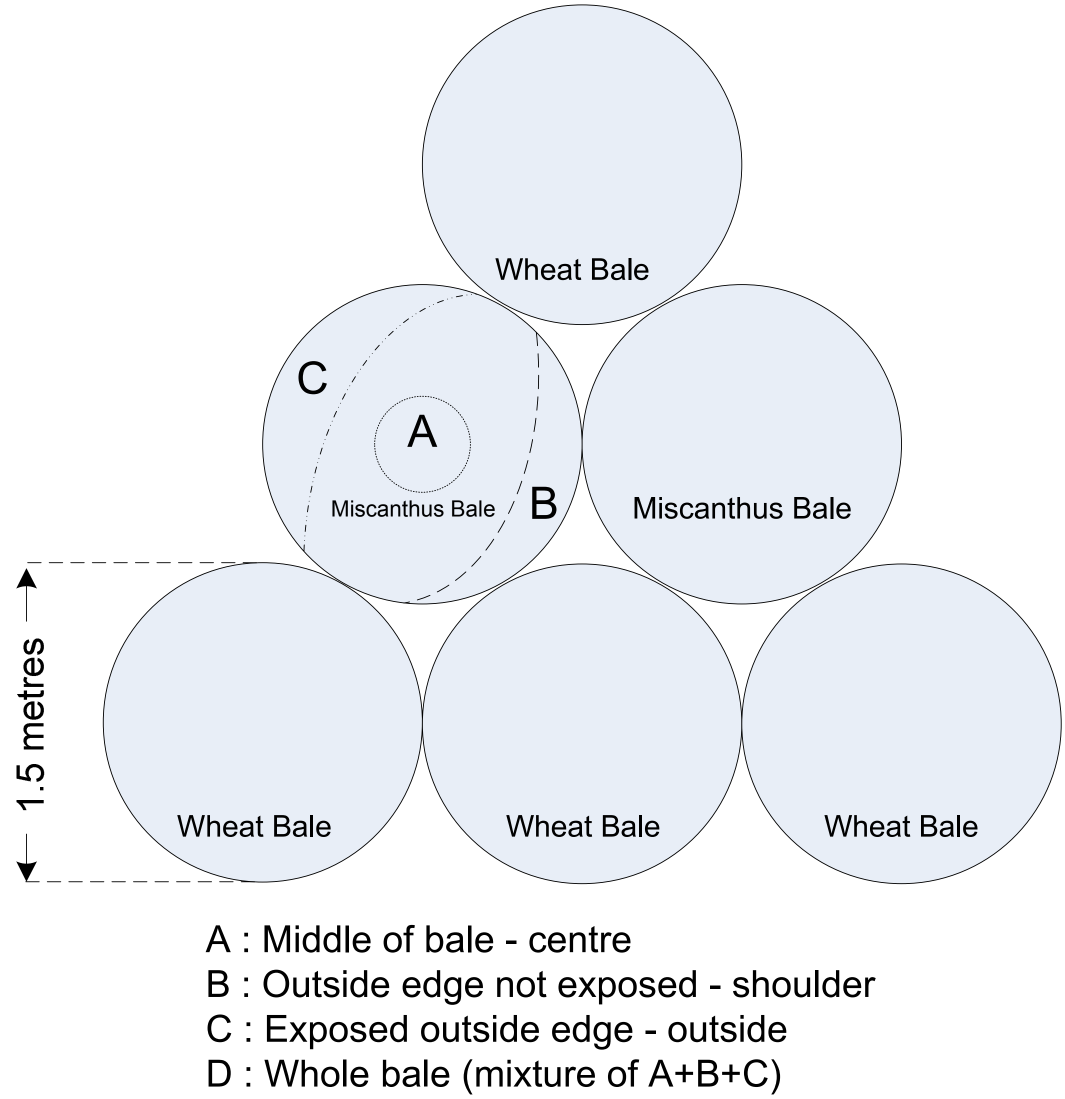


Figure 3.1 - The Storage of Miscanthus in a Pyramic Formation

### 3.2.3 Wheat Straw:

The agricultural straw, wheat straw (*Triticum aestivum),* was collected from commercially produced crops at the Rothamsted experimental farm in the south east of England in 2008. The crop was harvested in August and the remaining straw was collected and baled. Straw samples were again immediately dried at 80°C for 36 h in a re-circulating oven and hammer milled to pass through a 1 mm sieve.

### 3.2.4 Willow SRC and Beech Wood:

Willow SRC (Salix viminalis) was oven dried at 80°C for 36 h and obtained from Coppice Resources Ltd, Redford (UK). Beech wood (Fagus sylvatica) was purchased from J. Rettenmaier & Söhne GmbH + Co. KG D-73494 Rosenberg (Germany). The samples arrived pre-milled < 2 mm.

## 3.3 FEEDSTOCK PREPARATION FOR CHARACTERISATION, THERMAL DEGRADATION STUDIES AND PROCESSING BY PYROLYSIS

This section explains the pre-requisite feedstock properties that are necessary, after receiving the crop from the suppliers, before undergoing the characterisation, the analytical studies or the laboratory processing. Before the feedstock can be characterised, analytically investigated or processed, a suitable particle size and moisture content is required. There are three main reasons for this:

I. To obtain a representative sample;
II. To reduce possible inconsistencies, to an almost negligible effect, from the particle size, shape, regularity and surface area;
III. To generate suitable particle sizes and moisture contents for analytical studies and pyrolysis processing.

It is of high importance to obtain a representative sample, particularly for undertaking analytical studies that are limited to small sample volumes. This is because the milled feedstock will contain an assortment of different plant sections, i.e. leaves, stems and branches. The composition content of the different plant sections varies considerably when a comparison is made between the content of cellulose, hemicellulose and lignin (Hodgson et al. 2011). Therefore, thorough mixing to obtain a representative sample is essential. A biomass splitter has been used to obtain a representative sample, but only when preparing small volumes, and this is due to the low capacity limit of the splitter. The overall compositional content of the feedstocks investigated here are detailed in Chapter 1 within the project crops section.

Particle size, shape, regularity and surface area all contribute to the thermochemical properties of the feedstock (Bridgeman et al., 2007). A narrow particle size range has been used to reduce the implications of size, shape, regularity and surface area on the thermal chemical properties of the feedstock. Pyrolysis processing is limited to a specific range of feedstock moisture contents and particle sizes. A moisture content between 5 and 10 wt.% was obtained before use. This is mainly due to feeding related issues and to optimum organic liquid yield production, as previously mentioned in Chapter 2 and by He et al. (2009). The following particle size fractions were prepared for the characterisation and processing for all feedstocks: 150 - 250 µm for analytical work and 0.25 - 1.00 mm for pyrolysis processing. Findings from the reported literature in Chapter 2 show that the particle size range selected for pyrolysis processing is suitable to obtain optimal fast pyrolysis liquid yields (Tsai et al., 2007; Heo et al., 2010). A lower particle size has been used for analytical studies because of the small sample size requirements of the equipment.

According to the study conducted by Bridgeman et al. (2007), differences in the thermal chemical properties were found when comparing different particle size fractions from the same feedstock. Their results showed that for sample analysis using small particle sizes (<90 um), that the most evident differences were found in the content of ash and alkali metals, moisture, carbon, nitrogen, yield of volatiles, ratio of cell wall components (cellulose, hemicellulose and lignin) and pyrolysis decomposition products, when compared to sample analysis using larger particle sizes (90 – 600 um).

Consequently, when preparing the different particle size fractions (150 - 250 µm for analytical work and 0.25 - 1.00 mm for pyrolysis processing), it is important to acknowledge, in light of findings by Bridgeman et al. (2007), that the biomass composition from the different fractions may not be a true representation of the original biomass. Therefore the elimination of sample materials <150 µm and >250 µm from sample analysis carried out for the analytical work, will result in differences, when compared to the particle size used for the pyrolysis processing, and this should be taken into account.

## 3.4 FEEDSTOCKS CHARACTERISATION AND THERMAL DEGRADATION STUDIES

This section details and explains the experimental methodology used to characterise and investigate the thermal degradation and pyrolysis products of these feedstocks. To characterise, or classify, the feedstock in terms of its thermal chemical properties, a number of tests have been undertaken. This has been achieved by using a range of analytical equipment available at Aston University and off-site (SUPERGEN Project partners). The sample preparation and experimental conditions used for the characterisation are detailed, and a general description is given of the instruments and their principles. Additionally, the equipment limitations and sources of error are noted. For the investigation into the thermal degradation of these feedstocks, the methodology and experimental conditions used for the staged pyrolysis work are also shown. This includes the procedure used to carry out the quantification of light and medium volatile decompositions products by Py-GC-MS, using compounds purchased from Sigma Aldrich.

### 3.4.1 Ultimate Analysis and Proximate Analysis

Ultimate and proximate analysis is used mainly to classify coal fuel properties and can be used for biomass. Ultimate analysis, reported in wt. % on dry basis, is a partial representation of the elemental content within the feedstock (C, H, N, O and S). The elemental analysis for carbon, hydrogen and nitrogen were carried out by an external laboratory, using a Carlo-Erba 1108 elemental analyser EA1108. Carbon, hydrogen and nitrogen were analysed in duplicate and average values are reported. Proximate analysis reported in wt. %, shows the volatile, fixed carbon and ash content on dry basis. The proximate analysis was determined using thermogravimetric analysis.

### 3.4.2 Inorganic Analysis

Metals and other inorganic compounds were determined by digestion, and this was carried out by our external SUPERGEN partner. A Perkin Elmer Optima 7300DV Induced Coupled Plasma Emission Spectrometer was used, and the digestion procedure used is stated below. Analysis was conducted in triplicate and average values are reported.

1. Drying of the biomass material at 80$^{o}$C for 4 h and then cooling in a desiccator.
2. The biomass material (0.25 g) was then added to a digestion tube with 5 ml of nitric or perchloric acid and mixed at room temperature for 2 h.
3. The sample was then heated overnight and HCL (5 ml, 25%) was added the following day and further heated at 80$^{o}$C.
4. After cooling the sample was analysed by ICP.

For inorganics found in high abundance, such as K, Na, Ca and P, an excellent level of accuracy is obtained (>95%). For low abundant inorganics, accuracy is significantly reduced and results can be erroneous. Our SUPERGEN partner has made every effort to conform to the Joint Code of Practice (JCoPR) and actively participates in the European Quality Assurance programmes.

### 3.4.3 Thermogravimetric Analysis

The thermal properties of the feedstocks were investigated by thermogravimetric analysis, and the thermal data obtained here, was used for the proximate analysis mentioned above. The Perkin-Elmer Pyris 1 thermogravimetric analyser (TGA) and a Carbolite AAF 1100 Muffle Oven have been used.

#### *3.4.3.1 Perkin-Elmer Pyris 1 Analyser*

A quick, simple and reliable analytical method to investigate thermal decomposition is by thermogravimetric analysis. The application of thermogravimetric analysis (TGA), using the Perkin-Elmer Pyris 1 Analyser, to investigate thermal properties is extremely useful to determine how thermal properties of potential feedstocks vary with temperature. The understanding of feedstocks thermal behaviour is of great importance because the process parameters have a direct impact on the final chemical composition, quality and quantity, of the products. This technique has been employed by a large number of researchers to investigate the general and specific thermal characteristics of a range of organic materials, including biomass (Nowakowski et al., 2008; Antal and Varhegyi, 1995; Coats and Redfern, 1964; Deng et al., 2008; Kumar et al., 2008; Gronli et al., 1999; Park et al., 2009). This technique however, does not give any indication of the individual compounds produced during different temperature regions on the thermogravimetric profile. Pyrolysis - gas chromatography - mass spectrometry (Py-GC-MS) can be used in conjunction to TGA to gain a deeper insight into the decomposition products; this is discussed later in this chapter. Some of the specific details mentioned in this section are taken from the Perkin Elmer user manual (PerkinElmer et al., 2008 - 2010). TGA analysis is by no means representative of fast pyrolysis conditions or the product yields attainable, and is only used here as a rapid screening technique to compare the thermal properties of different feedstock at lower heating rates. This is due to the limitation of the equipment used and this is mentioned later.

##### 3.4.3.1.1 Instrument and Principles

The TGA is a vertically designed system equipped with a highly sensitive balance and a rapid response furnace. Figure 3.2 below depicts a sample pan setup situated within the equipment. The principle of the TGA is to measure weight change as a function of temperature, and this can be achieved by using isothermal or non-isothermal heating rates. Therefore, the thermal stability of the sample and the fraction of the volatile matter can be monitored. The atmosphere of operation and the desired heating programme can be adjusted to the desired operating conditions. Data acquisition produces a computerised TGA profile that is representatives of the sample being studied.

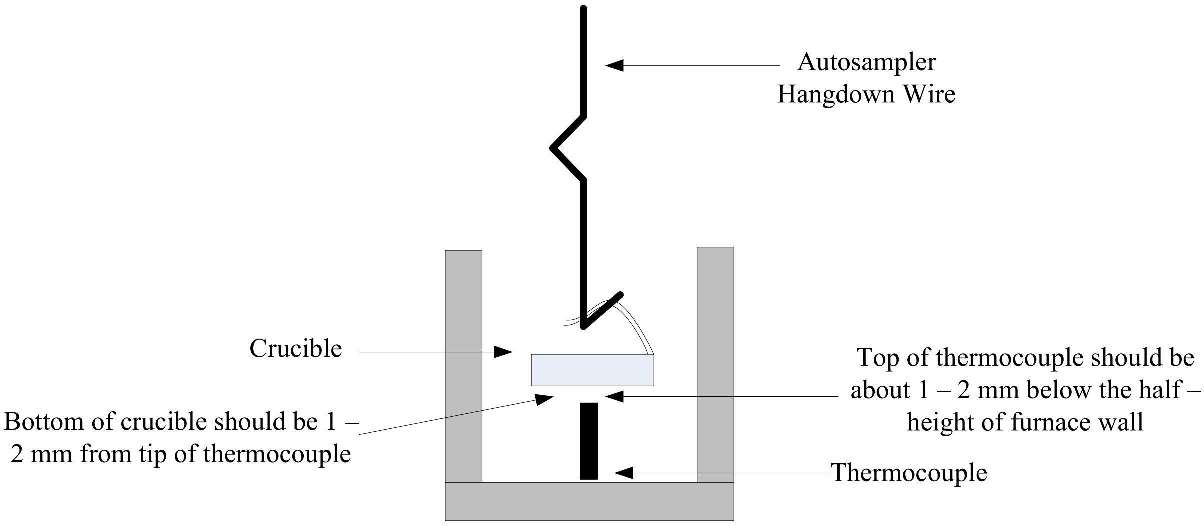


Figure 3.2 – TGA Sample Pan Setup [Adapted from (PerkinElmer, 2008 - 2010)]

The profile can be mathematically manipulated to determine the derivative(s) of the profile, commonly referred to as the differential thermogravimetric (DTG) profile, and to smooth the acquisition data to eliminate any external noise. From the DTG profile (wt. %/min. vs. temperature) the temperature at which the rate of maximum decomposition occurs can be determined.

#### 3.4.3.1.2 Methodology

For all the crops a sample of 3.0 ±0.1 mg was pyrolysed to the maximum temperature of 900$^{o}$C at a heating rate of 25$^{o}$C/min., with a nitrogen purge at a flow rate of 30 ml/min. and hold time of 15 min. The combustion (air atmosphere) study employed exactly the same temperature programme. The ash content was investigated in an air atmosphere at a maximum temperature of 575$^{o}$C, with a hold time of 15 min. at a heating rate of 5$^{o}$C/min. at a purge rate of 30 ml/min.

#### 3.4.3.1.3 Error Analysis and Limitations

The equipment is capable of a balance accuracy of ±0.02% of the initial sample mass. This can amount to significantly higher error margins when samples contain lower end weight values. The furnace is capable of temperature precision to ±2°C and scanning rates can be tailored between 0.1°C/min. and 200°C/min..

Thermal decomposition of biomass is subjected to heat and mass transfer issues which can significantly affect the results; a number of precautions are needed to ensure reliable results are obtained. Some of these precautions include the selection of the appropriate particle size, a suitable purge gas flow rate to eliminate secondary reactions, acknowledgement of the buoyancy effects, and the positioning of the thermocouple relative to the material of study (Biagini et al., 2008).

#### *3.4.3.2 Carbolite AAF 1100 Muffle Oven*

##### 3.4.3.2.1 Methodology

The ash content was determined by using approximately 2.0 g biomass at 575°C for 6 h. Samples were allowed to cool for approximately one hour inside a desiccator prior to weight measurements. This was repeated in triplicate. The heating programme followed a step sequence to prevent losses of material during the combustion process.

##### 3.4.3.2.2 Error Analysis and Limitations

A programmed temperature sequence was used to minimise losses during the combustion process. Weight measurements are accurate to four decimal places. A desiccator was used to minimise the effects of atmospheric humidity on sample weight.

### 3.4.4 Higher and Lower Heating Value

The higher heating value ($HHV_{dry}$) was calculated using Equation 1 proposed by Channiwala and Parikh (2002), and the lower heating value ($LHV_{dry}$) was calculated using Equation 2 proposed by ECN in 2005.

Equation 1

$HHV_{dry}$ (MJ/kg): $0.3491 \cdot C + 1.1783 \cdot H + 0.1005 \cdot S – 0.1034 \cdot O – 0.0151 \cdot N – 0.0211 \cdot ash$

Equation 2

$LHV_{dry}$ (MJ/kg): $HHV_{dry} - 2.442 \times 8.936 \times (H/100)$

where: C, H, N, O, S and ash values are expressed in terms of wt.% on dry basis

The difference between the higher and lower heating value is that the higher heating value takes into account the latent heat of vaporisation, whereas the lower heating value does not. Therefore, for the lower heating value, the energy necessary to vaporise the water is not accounted for as heat. Alternative terms commonly used to refer to the higher heating value are as follows: gross calorific value (GCV), upper heating value and higher calorific value (HCV). Alternative terms commonly used to refer to the lower heating value are as follows: net calorific value (NCV) and lower calorific value (LCV).

### 3.4.5 PY-GC-MS

The pyrolysis thermal decomposition products can be studied using Py-GC-MS. This is a technique that can be used as a rapid screening technology to investigate potential bioenergy feedstocks. Heating rates and process temperature can be tailored to be representative of potential industrial processing conditions. The advantage of this is that this will help to initially investigate the potential pyrolysis products and their relative abundance within the feedstock. This technique has been employed by a large number of researchers (Fahmi et al., 2007b; Lu et al., 2011b; Lu et al., 2011a; Dong et al., 2012). Additionally, the variation in light and medium volatile decomposition products, product distribution, can be investigated by variation of pyrolysis temperature and the heating rate. The methodology behind this is detailed in this section (staged pyrolysis).

#### *3.4.5.1 Instrument and Principles*

**CDS 5200 Pyrolyser (CDS Analytical):** According to the CDS analytical user manual, the principle function of the pyroprobe is to generate volatiles by thermal decomposition in an inert atmosphere, usually helium. The pyroprobe 5200 is a state of the art pyrolyser, fitted with a platinum filament capable of programmed pyrolysis temperatures up to 1400°C at 1°C increments, at heating rates from 0.01°C/min. to 20000°C/min.. The pyroprobe 5200 can be used for a sequence setup of up to eight temperature programme methods per sample, each with their own GC start capability. Pyrolysis gases can either be transferred directly to the GC inlet via a heated transfer line set at 350°C, or transferred to a trap (Tenax 2) connected to the valve end. This can be later desorbed when placed online with the GC.

**Varian GC-450 Chromatograph:** With reference to Varian (Varian et al., 2009a), the GC-450 is a gas chromatography used for separating and analysing compounds based on their volatility. A sample can be either injected, via the injection port, in a gaseous or liquid state. Typically, injection ports consist of a vaporisation chamber surrounded by a glass liner within a heated block, and have a carrier gas inlet, a split outlet, a septum purge outlet, and an entry to the start of the column. The vaporisation chamber is set to 275°C, and the Electronic Flow Control (EFC) system monitors and controls the digital flow control for the carrier gas (helium 15ml/min.), the digital pressure control and the split ratio (1:20). The column used is a Varian factorFOUR® stationary phase capillary column, 14% cyanopropylphenyl, 86% dimethylpolysiloxane VF-5ms: 30 m, 0.25 mm id., 0.25 µm df. This is a highly inert capillary column with a low bleed specification. Over time the stationary phase breaks down and leaves the column, and this is seen in the background signal generated by the column. Temperature is directly proportional to the rate of sample movement through the column; therefore the oven temperature is critical to the separation of the sample. This is because interaction within the column is reduced at high temperatures. For the experiments reported in this thesis the gas chromatograph oven was held at 45°C for 2.5 min. and then ramped at 5°C/min. to 250°C, with a final dwell time of 7.5 min. This temperature programme ensures adequate separation for early eluting compounds, and also reduces the time for late eluting compounds because of the non-isothermal heating rate.

**Varian 220-MS Mass Spectrometer:** The 220-MS is an ion trap mass spectrometer. Figure 3.3 below, depicts the mass spectrometer setup in coordination with the GC and data systems (Varian et al., 2009b). Compounds from the GC enter the ion trap via a transfer line. The ion trap assembly consist of a trap oven, a filament assembly, an electron gate and an electron multiplier. The filament assembly is responsible for the production of electrons and is situated within the trap oven. Once the compound undergoes electron ionisation it is detected by the electron multiplier and this produces a digital amplified signal proportional to the detected ions (Varian et al., 2009b). The data is then processed using Varian software [Varian MS workstation – MS data review – version 6.9.2] in conjunction with the NIST05 MS library.

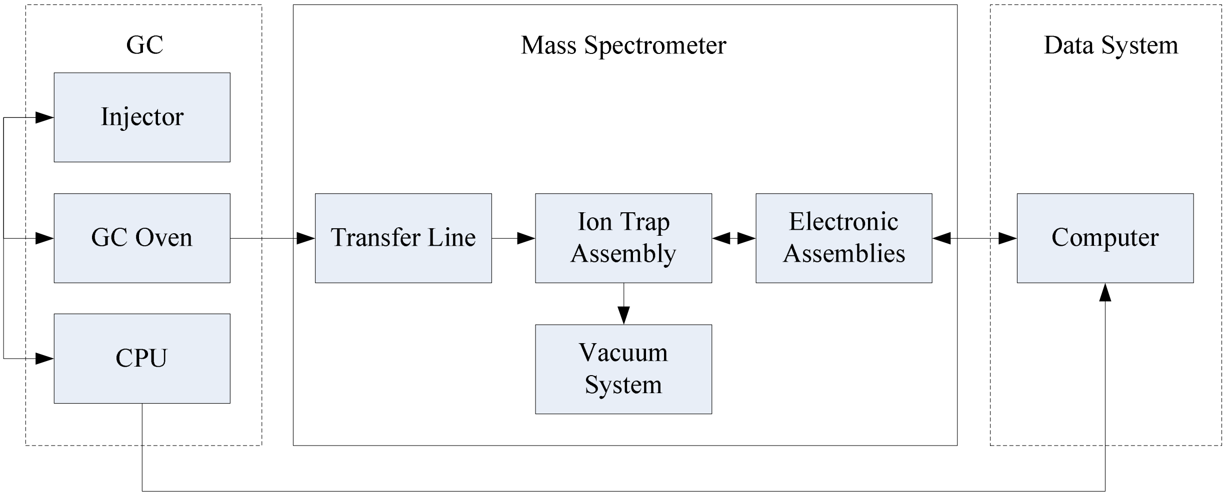


Figure 3.3 – GC/MS System Setup [adapted from (Varian et al., 2009b)]

### *3.4.5.2 Methodology*

#### 3.4.5.2.1 Standard Characterisation

Analytical pyrolysis was investigated using a heating rate of 20°C/ms in order to simulate fast pyrolysis heating rates. A single sample of approximately 2 - 3 mg was used for the pyrolysis experiment which had a final pyrolysis temperature of 520°C. Py–GC–MS analysis was performed on each sample using a CDS 5200 pyrolyser coupled with a Varian GC-450 chromatograph and an MS-220 mass spectrometer. The column used and the oven temperature programme are detail above. The devolalised components are transferred via a heated transfer line, maintained at 310°C, onto the GC column via the injector port, PTV 1070 type, which is held at 275°C. The mass spectra were obtained for the molecular mass range m/z = 45 to 300. Proposed assignments of the main peaks were made using mass spectra detection software, the NIST 98 and 05 MS libraries, and from literature assignments (Faix et al., 1990; Faix et al., 1991).

#### 3.4.5.2.2 Staged Pyrolysis

Analytical staged pyrolysis was investigated, between 320-520°C, using two different heating rates: 25°C/min. (to represent slow pyrolysis) and 1500°C/min. (to represent fast pyrolysis). A single sample of approximately 3 mg was used for the 8 stages of the pyrolysis experiment with the following pyrolysis temperature steps: 320, 350, 370, 390, 405, 420, 435 and 520°C. Py–GC–MS equipment and operating parameters are the same as above.

#### 3.4.5.2.3 Quantification of Compounds (Py-GC-MS)

This is the procedure used to carry out quantification of the light and medium volatile decomposition products by Py-GC-MS, using compounds purchased from Sigma Aldrich. The GC column was calibrated using thirteen different compounds purchased from Sigma Aldrich, UK. The compounds used for the calibration include: furan-2-carbaldehyde (furfural); 2-furanmethanol (furfuryl alcohol); phenol; 2-methoxyphenol (guaiacol); 2-methoxy-4-methylphenol (creosol); benzene-1,2-diol (catechol); 3-methoxycatechol (p-cresol), 1,2,4-trimethoxybenzene, 2-methoxy-4-vinylphenol; 4-allyl-2-methoxyphenol (eugenol), 4-hydroxy-3-methoxybenzaldehyde (vanillin), 1,6-anhydro-β-D-glucopyranose (levoglucosan) and 4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde). The stock solution was prepared using 0.5 ±0.1 mg (Sartorius ME36S microbalance) of each compound, dissolved in GC-grade ethanol (Sigma-Aldrich, UK), in a 50 ml volumetric flask. The stock solution (10 000 µg/ml) was then diluted into five different concentrations (500, 800, 1200, 2000, and 4000 µg/ml) using GC-grade ethanol. 1 µl of each of the five calibration solutions was then analysed separately. The pyroprobe, which is set up to a final temperature of 280°C at a heating rate of 100°C/min., was used to evaporate each calibration solution. Evaporated compounds were then transferred to the GC column via a heated transfer line, maintained at 310°C. The calibration curve was derived using the peak areas from each concentration versus the mass of the compound per 1 µl of solution. The calibration curve linearity (r2) ranged between 0.9434 – 0.9983 for all compounds quantified. The same GC-MS parameters (oven temperature programme and MS detector scan range) were applied for the compound quantification for the analytical pyrolysis experiments. The chromatograms obtained and used for the calibration and accuracy of line fitment can be found in Appendix B (10.2 Quantification Chromatograms).

#### *3.4.5.3 Error Analysis and Limitations*

##### 3.4.5.3.1 Sample size and preparation

Due to the use of small sample sizes, it is expected that issues related to attaining a representative results could be problematic. This is because of the difficulties in obtaining a representative sample on such a small scale. For this reason analysis was repeated. It was found that in the case of solid sample preparation for Py-GC-MS analysis, that the gloves used for the preparation have the potential to contaminate the sample. Precautions should be taken to minimise contact with the sample tube.

##### 3.4.5.3.2 Equipment

GC column bleed could potentially lead to higher levels of background noise, this can be minimised by the use of a low bleed column. Contaminates in the GC column could potentially result in inaccurate results. This was minimised by routinely cleaning the GC column to remove possible contaminates from previous experimental work.

##### 3.4.5.3.3 Data processing

In some cases difficulties arise in the determination of mass spectra fragmentation due to poor matches with the NIST05 MS library; as a result these could not be identified.

## 3.5 PROCESSING OF FEEDSTOCKS

This section describes the pyrolysis units that have been used (0.15 kg slow pyrolysis reactor, 0.3 kg/h fast pyrolysis reactor, and 1 kg/h fast pyrolysis reactor), and the methodology behind the determination of the mass balance. Additionally some of the variables and precautionary measures that have not been mentioned in Chapter 2 are discussed. The description of the pyrolysis unit focuses on the feeder, reactor setup and collection points. Also included are the specifications and flow diagrams of the pyrolysis units used.

### 3.5.1 Fast Pyrolysis Reactors

The feeder, the reactor setup and liquid collection points for the 1 kg/h and 0.3 kg/h continuously fed bubbling fluidised bed reactors, fast pyrolysis reactors, are illustrated in Figure 3.4 and Figure 3.5 respectively. Specification and further details can be found in Table 3.1. The 0.3 kg/h reactor was used to process the following feedstocks: the early, conventional and late harvested miscanthus. Processing results using this reactor are shown in Chapter 6. The 1 kg/h reactor was used to process the following feedstocks: wheat straw, switch grass, miscanthus, willow SRC and beech wood and processing results are presented in Chapter 4. The reason for the use of two reactors is the availability of equipment and the initial learning curve needed in the use the reactors.

#### *3.5.1.1 Feeder*

**1 kg/h Fast Pyrolysis Unit:** The feeder assembly consists of tubular a storage hopper (Figure 3.4: 1 – feed hopper), a nitrogen inlet valve, paddle shifter and a screw feeding mechanism. Once the biomass has been prepared, it is placed into the biomass hopper. The feed rate is then calibrated according to biomass type and quantity of feedstock available for processing. Some types of biomass can be very fibrous or have a high particle density, and this can influence the feeding rate. The feed rate can be altered to obtain a desired rate, by altering the paddle speed (helps to prevent bridging and blockages within the hopper), screw speed and entrainment flow. Problematic scenarios can result if the feeding rate is too high or low. Feeding rates that are too high are prone to blockages, were as low feeding rates can result in diluted pyrolysis vapours, and this leads to errors in the gas analysis.

**300g/h Fast Pyrolysis Unit:** The design and operation of the feeder (Figure 3.5: 1 – feed hopper) is similar to that used by the 1 kg/h fast pyrolysis reactor.

#### *3.5.1.2 Reactor Set-up*

**1 kg/h Fast Pyrolysis Unit:** The fast pyrolysis experiments were carried out using a continuous fed bubbling fluidised bed reactor (Figure 3.4: 2 – reactor). Inert quartz sand, with a particle size range between 710 and 855 µm, was used as the fluidising medium. In Chapter 2 it was found that quartz sand is a good heat transfer medium because it has a high solid density. The fluidising velocity is three times the minimum fluidising velocity, and this is sufficient to ensure good heat transfer by conduction and convection and removal of pyrolysis products from the reactor bed, while leaving the higher density quartz sand in the reactor bed.

The experiments were carried out at a reaction temperature between 500 and 520°C. Findings from Chapter 2 indicate a process temperature of between 480 and 520$^{o}$C is optimal to achieve high liquid yields (Tsai et al., 2007; Bridgwater, 2004; Bridgwater, 2007; Bridgwater, 2011). Typically, the reaction temperature is set 5 % higher than required to accommodate the nitrogen flow and endothermic reaction caused by the biomass thermal decomposition. Temperatures were measured and recorded using a Microlink 751 ADC Unit combined with Windmill data logging software. Pressure within the setup was monitored for safety and help aid the detection of possible blockages.

**300g/h Fast Pyrolysis Unit:** The fast pyrolysis experiments were carried out using a continuously fed bubbling fluidised bed reactor. Inert quartz sand with a particle size range between 355 and 500 µm was used due to the smaller reactor volume. Temperatures were measured and recorded using a digital temperature board and the operating parameters are similar to that described for the 1 kg/h reactor, except for the fluidising flow rate.

#### *3.5.1.3 Product Collection Points*

**1 kg/h Fast Pyrolysis Unit:** Two cyclones set up in series were used to separate the char particles from the condensable and non-condensable vapours (Figure 3.4: 3 – cyclone). The cyclones and transition pipes are heated to approximately 450$^{o}$C. This is of high importance to prevent condensation of pyrolysis vapours within the hot space zone which could result in subsequent blockages. The char pots (Figure 3.4: 4 – char pots) were thermally insulated, using adiabatic material, to reduce heat loss. Upon exit the vapours were condensed in a cooled quench column using ISOPAR™ as quenching media at 30°C. A wet ESP was used to separate the aerosols and this was flushed with isopar (Figure 3.4: 7 – ESP). The ISOPAR was recycled (skimmed from the top of the common tank) to the quench column and ESP.

The ESP was described in Chapter 2. Condensates were collected in a common tank (Figure 3.4: 6 – common tank) and this is the referred to as the main bio-oil. The remaining condensable light volatiles and vapours were condensed by a water cooled heat exchanger (10°C) and two dry ice cooled heat exchangers (-70°C) set up in series. It was found in Chapter 2 that rapid cooling is essential to condense vapours and prevent secondary reactions.

**300g/h Fast Pyrolysis Unit:** The setup is similar to the 1 kg/h pyrolysis unit (Figure 3.5).

#### *3.5.1.4 Mass Balance*

**1 kg/h Fast Pyrolysis Reactor:** Non-condensable gases passed through a cotton wool filter before they were metered with a diaphragm gas meter, and analyzed online using a Varian CP 4900 Micro GC for nitrogen, hydrogen, CO, CO2 and hydrocarbons up to C4. The mass balance of the product yields was determined gravimetrically on dry basis. The water content of the main liquid and secondary condensates was determined using the Karl Fisher volumetric titration. The water content of the feedstock and the products was used to calculate the reaction water found in the bio-oil.

The reaction water was calculated using the following equation:

- (Total liquid yield [g]/100 x overall bio-oil liquid water content [wt.%]) – (Biomass on dry basis [g]/100) x (Moisture content of biomass [wt.%])

The organic content was calculated using the following equation:

- (Total liquid [g]) – (biomass$^{a.r}$ [g]/ 100 x moisture of the biomass [wt.%]) - (reaction water [g])

The gas content in grams was calculated as follows:

- (101325 Pascal's) x (Vcomposition =(percentage composition from GC x total gas volume over the experiment/100) x (molecular weight of the gas, e.g. $H_2$ = 2) / 8.314 (gas constant) / 298 (room temperature).

A mass balances example is included in Appendix B (Section 10.1.1)

**300g/h Fast Pyrolysis Reactor:** The mass balance procedure is same as for the 1 kg/h pyrolysis unit. A mass balances example is included in Appendix B (Section 10.1.2)

### 3.5.2 Slow Pyrolysis Reactor

The reactor setup and liquid collection points for the 0.15 kg slow pyrolysis batch reactor are shown in Figure 3.6. The slow pyrolysis reactor was used to process willow SRC. This section is relevant to the experimental work reported in Chapter 5. This is because laboratory scale fast and slow pyrolysis products and yields are compared in this chapter.

#### *3.5.2.1 Reactor Set-up*

Slow pyrolysis experiments were carried out in a batch reactor. The vapours were purged from the batch reactor with nitrogen at a flow rate of 100 cm$^3$/min. and condensed at 10$^o$C by a water condenser, followed by two dry ice condensers at -70$^o$C. Temperatures were measured and recorded using a Microlink 751 ADC Unit combined with Windmill data logging software. The reactor specification can be found in Table 3.1.

#### *3.5.2.2 Collection Points*

The condensable gases were condensed in a cascade of one water condenser at 10°C and two dry ice condensers at -70°C. The remaining char was collected from the reactor.

#### *3.5.2.3 Mass Balance*

The mass balance follows the same outline as that mention for the 1 kg/h pyrolysis unit. Further details can be found in Appendix A – Detailed Methodology (Mass Balance Calculation). A mass balances example is included in Appendix B (Section 10.1.3)

## 3.6 PRODUCT CHARACTERISATION

This section details the equipment and methodology behind pyrolysis product characterisation.

### 3.6.1 Liquid Analysis

The recommended methodology for the bio-oil analysis shown in Chapter 2 was used for the below tests.

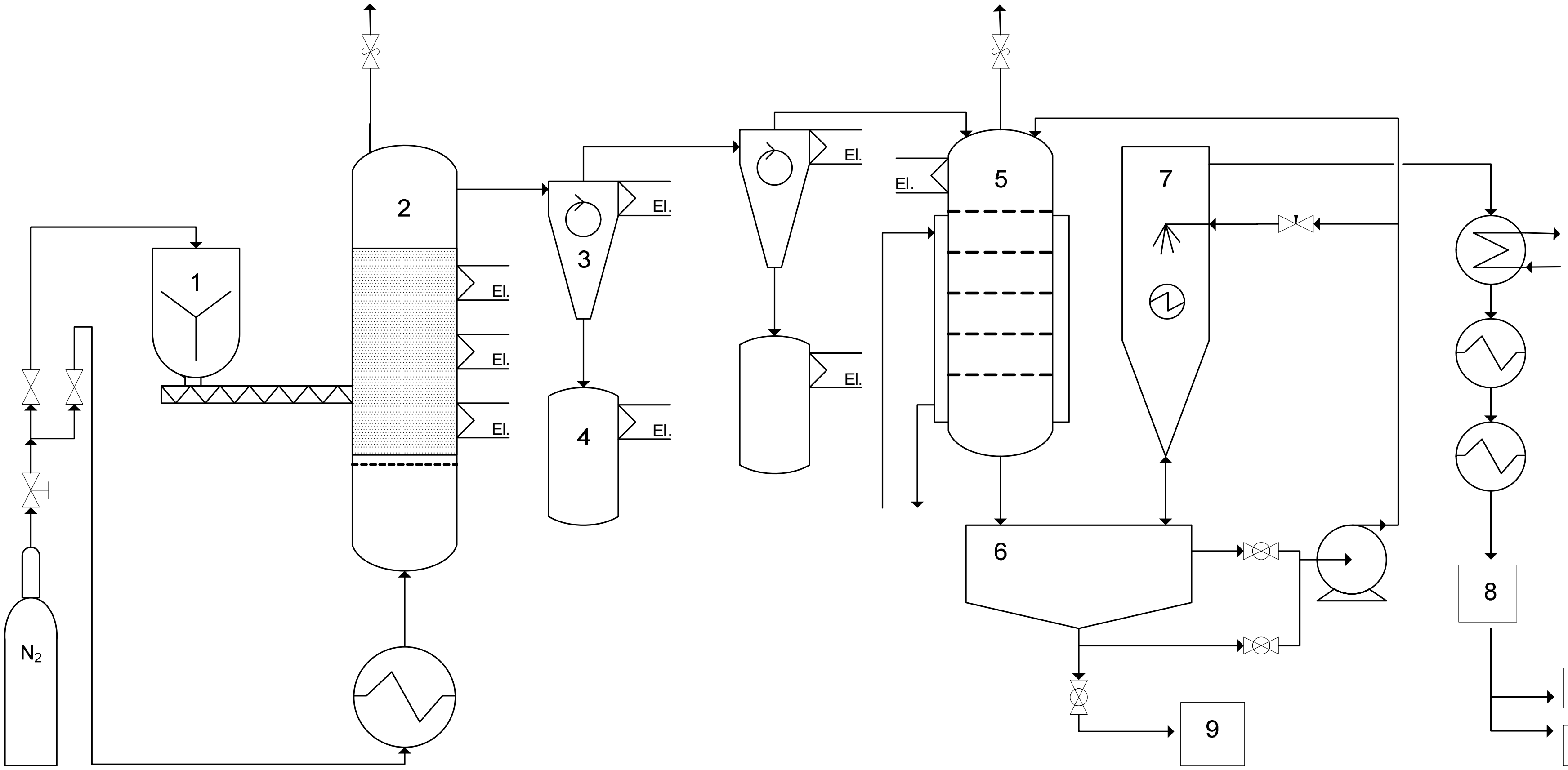


Figure 3.4 - Flow diagram of the 1 kg/h fast pyrolysis unit

(1 – feed hopper, 2 – reactor, 3 – cyclone, 4 – char pot, 5 – quench column, 6 – common tank, 7 – ESP, 8 - gas counter, 9 - liquid out, 10 - GC, 11 - gas out).

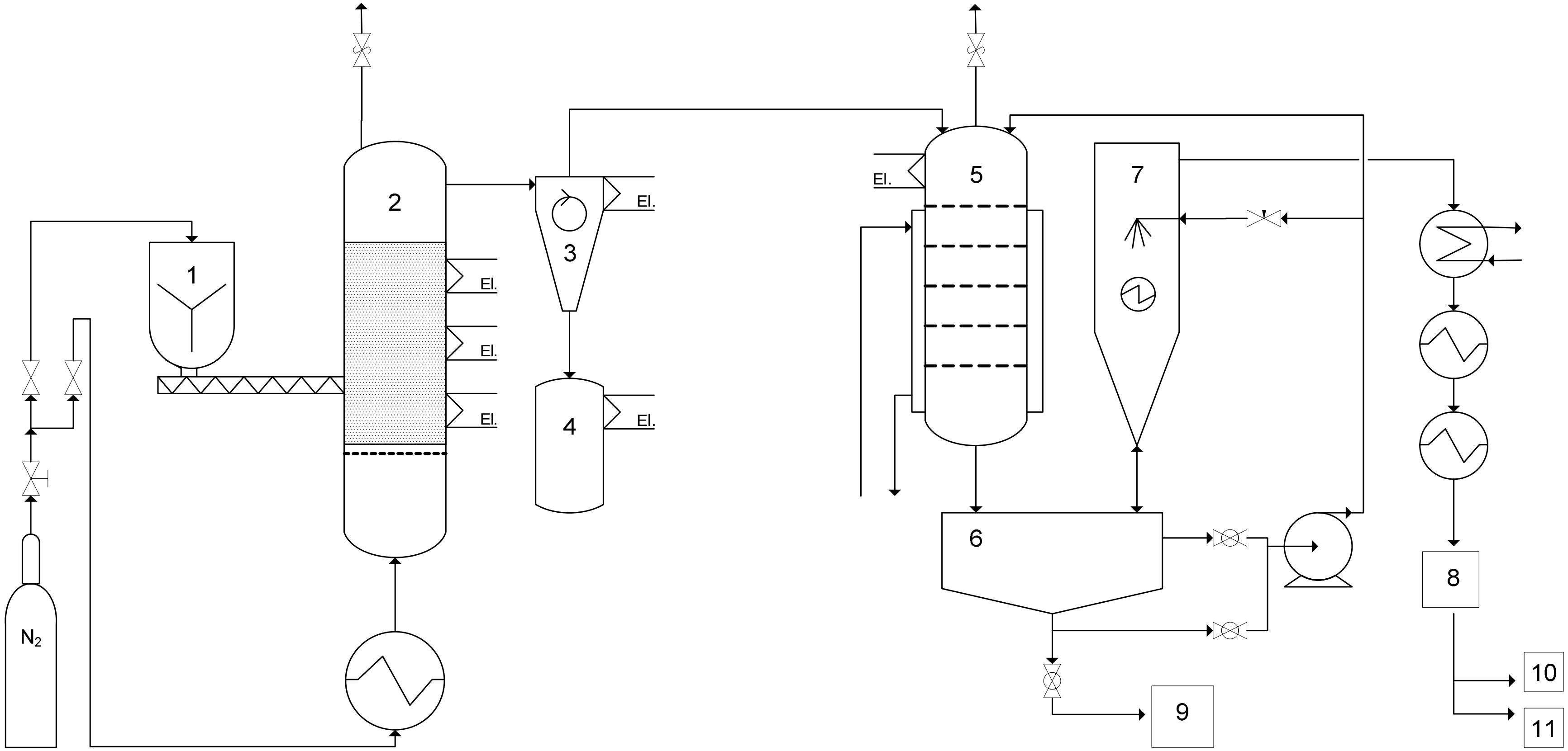


Figure 3.5 - Flow diagram of the 0.3 kg/h fast pyrolysis unit

(1 – feed hopper, 2 – reactor, 3 – cyclone, 4 – char pot, 5 – quench column, 6 – common tank, 7 – ESP, 8 - gas counter, 9 - liquid out, 10 - GC, 11 - gas out

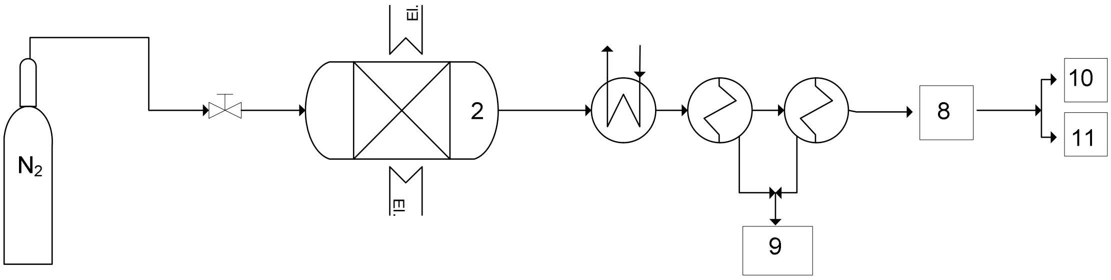


Figure 3.6 - Flow diagrams of the 0.15 kg slow pyrolysis unit

(1 – feed hopper, 2 – reactor, 3 – cyclone, 4 – char pot, 5 – quench column, 6 – common tank, 7 – ESP, 8 - gas counter, 9 - liquid out, 10 - GC, 11 - gas out).

#### *3.6.1.1 Ultimate Analysis*

The elemental analysis for carbon, hydrogen and nitrogen were carried out by an external laboratory using a Carlo-Erba 1108 elemental analyser EA1108. Carbon, hydrogen and nitrogen were analysed in duplicate and average values were taken. Values obtained for carbon, hydrogen and nitrogen were used to determine the higher and lower heating values.

#### *3.6.1.2 Water Content*

The water content of the main liquid and secondary condensates was determined using the Karl Fisher volumetric titration. The water content of the feedstock and the products was used to calculate the reaction water found in the bio-oil. Karl Fisher Titrator – Mettler Toledo – V20 Volumetric KF Titrator (Titrant – HYDRANAL – Composite 5K (34816) / Solvent – HYDRANAL – Working medium k (348170)).

#### *3.6.1.3 Higher and Lower Heating Value*

The higher and lower heating values of the bio-oils, on wet basis (as-received), were calculated using Equation 3 and Equation 4 (ECN, 2005).

Equation 3

$HHV_{a.r}$ (MJ/kg): $HHV_{dry} \times (1-H_2O/100)$

Equation 4

$LHV_{a.r}$ (MJ/kg): $LHV_{dry} \times (1-H_2O/100) – 2.442 \times (H_2O/100)$

where: $H_2O$ in wt.%, on dry basis

Table 3.1 – Specifications and Details of the Pyrolysis Units Used

| | Slow Pyrolysis | Fast Pyrolysis | |
|---|---|---|---|
| | 0.15 kg batch reactor* | 0.3 kg/h fluidised bed reactor | 1 kg/h fluidised bed reactor |
| **Feeder** | | | |
| Tubular storage hopper | n/a | yes | K Tron K2M-T20 Volumetric |
| Entrain tube aperture size Ø [mm] | n/a | 14 | 13 |
| Cooled entrain tube | n/a | water jacket | water jacket |
| Feeder agitator | n/a | yes | yes |
| Feed screw(s) type | n/a | Augur screw [12mm] | Augur screw [12mm] |
| $N_2$ entrainment flow | 100cm$^3$/min.[1bar at 20$^o$C] | 2 to 6 | 18 l/min.[1bar at 20$^o$C] |
| **Stainless steel reactor** | | | |
| Length [cm] | 41.5 | 26.5 | 42.24 |
| Internal diameter Ø [cm] | 4.27 | 4.1 | 7.29 |
| Fluidising medium - inert quartz sand particle size[µm] | n/a | 355 - 500 | 710 - 855 |
| Fluidising medium used [kg] | n/a | 0.16 | 1 |
| Perforated distribution plate [µm] | No | 100 inconel | 500 |
| $N_2$ fluidising [l/min.] | n/a | ? | 45 [1bar at 20$^o$C] |
| Pre-heated single pass $N_2$ fluidising [$^c$o] | No | 500 - 600 | 550 - 600 |
| **Other** | | | |
| Cyclone(s) | No | 2 | 2 |
| Char pot(s) | No | 2 | 2 |
| Quench column [isopar] | No | yes | yes |
| ESP [15000 - 20000 V] | No | yes | yes |
| Water condenser - double type 'Davies' | 1 | 1 | 1 |
| Dry ice condenser - cold finger type [acetone + dry ice] | 2 | 2 | 2 |
| Cotton wool filter | Yes | yes | yes |
| Gas meter | Yes | yes | yes |
| GC online gas analysis | Yes | yes | yes |

#### *3.6.1.4 pH*

The pH was determined using a pH meter. PB – 11 SARTORIUS

#### *3.6.1.5 GC-MS Analysis of Bio-oil*

The chemical content of the bio-oil was investigated using GC-MS. The equipment used is shown below. The PerkinElmer Turbo Mass Gold GC-MS system, the Varian GC-450 chromatograph and the MS-220 mass spectrometer were used to analyse the chemical composition of the bio-oil. GC samples were prepared by mixing GC grade ethanol with bio-oil at a volume ratio of 5:1. For each system setup 1 µl of GC sample was injected onto the GC column, helium was used as the carrier gas, and the mass spectra were obtained for a molecular mass range (m/z) of 45 to 300.

**Experimental Chapter 5:** A PerkinElmer TurboMass Gold GC-MS/FID system was used for the analysis of the fast and slow pyrolysis bio-oil samples. GC samples were prepared by mixing bio-oil with GC grade 2-propanol (1:5 v/v). 1 µl of GC sample was injected onto the GC column via an injection port kept at 280$^{o}$C, with 1:25 split ratio. Separation was carried out on a PerkinElmer Elite-1701 column (crossbond: 14% cyanopropylphenyl and 85% dimethyl polysiloxane; 60 m, 0.25 mm i.d.,0.25 mm df). GC oven programme was as follows: held constant at 45$^{o}$C for 5 min., then ramped at 5$^{o}$C/min. to 250$^{o}$C and held at 250$^{o}$C for 5 min.. Helium was used as carrier gas with a constant flow of 2 ml/min.. Column splitter was used to enable simultaneous detection by MS and FID detectors. Mass spectra were obtained using 70 eV ionisation energy in the molecular mass range of m/z = 35 to 300. Proposed assignments of the main peaks were made from mass spectra detection using (NIST98 MS library) and from literature assignments (Faix et al., 1990; Faix et al., 1991). The FID make-up gas was a mixture of hydrogen (45 ml/min.) and air (450 ml/min.). Detector temperature was 250$^{o}$C. Peak area under the FID chromatograms were used for quantification of bio-oil compounds.

**Experimental Chapter 4 and 5:** The PerkinElmer Turbo Mass Gold GC-MS system was used for the analyses of bio-oil generated from miscanthus and willow SRC. The injection port was kept at 280$^{o}$C and a 1:25 split ratio was used. The separation was carried out using a PerkinElmer Elite-1701 column (crossbond: 14% cyanopropylphenyl and 85% dimethyl polysiloxane; 60 m, 0.25 mm i.d., 0.25 mm df). The GC oven was held at 45$^{o}$C for 5 min., then heated at 5$^{o}$C/min. to 250$^{o}$C and held at this temperature for 5 min.. Proposed peak assignments were made from mass spectra detection, using the NIST98 MS library and from assignments in the literature (Faix et al., 1990; Faix et al., 1991).

**Experimental Chapter 4:** The Varian 450-GC gas chromatograph and 220-MS mass spectrometer were used for then analyses of bio-oil generated from wheat straw, beech wood and switch grass.

The GC-MS operating parameters are the same as those mentioned previously (Chapter 3 – Py-GC-MS).

### 3.6.2 Solid Analysis

#### *3.6.2.1 Ultimate Analysis*

The elemental analysis for carbon, hydrogen and nitrogen were carried out by an external laboratory using a Carlo-Erba 1108 elemental analyser, EA1108. Carbon, hydrogen and nitrogen were analysed in duplicate and average values were taken.

#### *3.6.2.2 Higher and Lower Heating Value*

The higher and lower heating values were calculated the same way as for the biomass.

#### *3.6.2.3 Thermogravimetric Analysis*

The ash content was investigated in an air atmosphere using the same TGA programme, using the Pyris 1 analyser, mentioned in the biomass characterisation section (Chapter 3).

### 3.6.3 Gas Analysis

The non-condensable gases were metered and analysed by a Varian CP 4900 Micro GC for nitrogen, hydrogen, CO, CO2 and hydrocarbons up to C4.

# 4 A COMPARATIVE STUDY OF STRAW, PERENNIAL GRASSES AND HARDWOODS IN TERMS OF FAST PYROLYSIS PRODUCTS

## 4.1 INTRODUCTION

This chapter investigates fast pyrolysis processing of straw, perennial grasses and hardwoods, available to the project, and compares and assesses their potential for use as fuels and chemicals.

The following was undertaken:

I. Analytical characterisation and comparison of pyrolysis products;
II. Semi- quantification by Py-GC-MS of potential key light and medium volatile decomposition products, under simulated fast pyrolysis heating rates;
III. Laboratory-scale fast pyrolysis processing using a continuously fed bubbling fluidised bed reactor, and a comparison of products and yields.

Feedstocks investigated included wheat straw (Triticum aestivum), switch grass (Panicum virgatum), miscanthus (Miscanthus x giganteus), willow short rotation coppice (Salix viminalis) and beech wood (Fagus sylvatica). The experimental work is divided into two sections; analytical, with and without close-coupled analysis, and laboratory scale processing using a continuously fed bubbling fluidised bed reactor with a capacity of up to 1 kg/h, with decoupled liquid and char analysis. Py-GC-MS has been used to semi- quantify and simulate fast pyrolysis heating rates, in order to study potential key light and medium volatile decomposition products found in these feedstocks.

## 4.2 RESULTS AND DISCUSSION

### 4.2.1 Elemental Analysis and Calorific Values

Comparisons of the ultimate, proximate and inorganic analyses, as well as the higher and lower heating values of the feedstocks investigated are shown in Table 4.1. The complexity and relative ratio of the major constituents varies with the plant species, and it is well known that biomass is constructed from oxygen rich organic polymeric material (as discussed in Chapter 1). Ultimate analysis and calorific values are of typical findings, and are representative of current literature values (Bridgeman et al., 2008; Lemus et al., 2002; Mani et al., 2010; Nowakowski et al., 2007).

From the ultimate analysis the hardwoods were seen to have a higher content of carbon and lower of oxygen. As a result, the calculated higher and lower heating values were found to be higher for the woody feedstocks. Results from the proximate analysis, show that higher amounts of volatile matter are obtained from beech wood (85.89 wt.%) and switch grass (83.23 wt.%). Ash content values were similar for the straw and perennial grasses, and lowest for the hardwood, beech wood (0.96 wt.%) and willow (2.96 wt.%).

The inorganic content in willow SRC is anticipated to be higher than that of beech wood, because of the different plant growth periods. Switch grass also contained low levels of inorganics, but the ash content was higher. This may be attributed to the high levels of silica found in the perennial grasses (Pimentel, 2008). Willow SRC contained the highest levels of calcium, magnesium, phosphorus and sulphur, and miscanthus had the highest level of potassium (1.20 %). The addition of fertiliser and the time of harvest have a noticeable impact on the feedstock inorganic levels (Yates and Riche, 2007). Wheat straw is grown commercially for its grain, and the fertiliser treatment is expected to be higher than that of perennial grasses and hardwoods. Switch grass did not receive any further fertiliser treatment after initial setup, and was harvested after the crop senesced. The time of harvest has been reported to influence inorganic content, particularly potassium, in the standing crop (Yates and Riche, 2007). This could be due to the natural weathering and leaching, of more mobile elements such as potassium, from the standing crop though the winter period. Miscanthus received additional fertiliser treatment and was harvested early, prior to the crop senescing. This is the probable cause for the high potassium content seen in miscanthus. Dust and soil adhesion to the crop sample could possibly further increase the inorganic content.

Table 4.1 - Proximate, Ultimate and Inorganic Analysis of the Straw, Perennial Grasses and Hardwoods

| | Wheat straw | Switch grass | Miscanthus | Willow SRC | Beech wood |
|---|---|---|---|---|---|
| **Ultimate analysis %$^{(d.b)}$** | | | | | |
| C | 44.93 | 46.21 | 46.95 | 48.48 | 53.04 |
| H | 5.71 | 5.80 | 5.85 | 5.74 | 5.42 |
| N | 0.63 | 0.40 | 0.92 | 1.87 | - |
| O* | 48.73 | 47.59 | 46.28 | 43.91 | 41.63 |
| **Proximate analysis %** | | | | | |
| Moisture | 4.56 | 4.61 | 4.55 | 5.71 | 4.24 |
| Volatile matter $^{(d.b)}$ | 79.92 | 83.23 | 75.62 | 81.19 | 85.89 |
| Fixed carbon $^{(d.b)}$ | 15.18 | 11.04 | 19.92 | 15.85 | 13.15 |
| Ash $^{(d.b)}$ | 4.89 | 5.73 | 4.46 | 2.96 | 0.96 |
| **Heating Value (MJ/kg)** | | | | | |
| HHV $^{(d.b)}$ | 17.25 | 17.90 | 18.38 | 19.06 | 20.55 |
| LHV $^{(d.b)}$ | 16.00 | 16.63 | 17.10 | 17.81 | 19.37 |
| **Inorganic analysis %$^{(d.b)}$** | | | | | |
| Al | 0.01 | 0.02 | - | 0.03 | - |
| Ca | 0.51 | 0.50 | 0.18 | 1.15 | 0.27 |
| Fe | 0.02 | 0.01 | - | 0.02 | - |
| K | 0.57 | 0.09 | 1.20 | 0.59 | 0.14 |
| Mg | 0.07 | 0.06 | 0.15 | 0.16 | 0.04 |
| Mn | 0.01 | - | - | 0.01 | 0.01 |
| Na | 0.01 | 0.02 | - | 0.01 | 0.01 |
| Ni | - | - | - | - | - |
| P | 0.04 | 0.05 | 0.07 | 0.19 | 0.01 |
| Pb | - | - | - | - | - |
| S | 0.09 | 0.06 | 0.04 | 0.14 | 0.02 |
| Zn | - | - | - | 0.02 | - |

* - by difference

$^{d.b}$ - dry basis

\- - not detected

### 4.2.2 Thermal Decomposition Studies (TGA)

The differential thermogravimetric pyrolysis and combustion profiles can be found in Figure 4.1 and Figure 4.2 respectively. The differential thermogravimetric profile (DTG), the first derivative of the TGA profile, reports the percentage weight loss per minute as a function of temperature (previously mentioned in Chapter 3). The shape of the DTG profile is correlated to the compositional content of the crop (Deng et al., 2008; Park et al., 2009). This is largely reflective of the cellulose, hemicellulose, lignin and inorganic content. From the DTG pyrolysis profile, shown in Figure 4.1, it can be seen that the maximum rate of thermal degradation occurs between 339 and 392$^{o}$C for all feedstocks. The hardwoods are found to have lower maximum thermal decomposition rates and these are seen to occur at higher temperatures. This is partly related to the higher lignin content, which constitutes a major part of the overall structure of hardwoods. Miscanthus has a maximum decomposition rate at the lowest temperature when compared to the other feedstocks.

The catalytic impact of potassium is thought to be major contributor to the occurrence of the maximum decomposition rate (Fuentes et al., 2008). The shoulder-like features on the DTG curves can be seen for both beech wood and switch grass, and is probably representative of the hemicellulose content. Based on data shown in Table 1.1, the ratio of hemicellulose to cellulose in switch grass was found to be the highest, and its shoulder-like feature is most prominent. Varhegyi et al. (1989) showed that the thermal decomposition of hemicellulose takes place at a lower temperature when compared to cellulose. Yang et al. (2007) reported that the thermal decomposition of lignin occurs over a broad temperature range, and partially contributes to the cellulose and hemicellulose regions.

The DTG combustion profile shown in Figure 4.2 shows two distinct decomposition regions. The first decomposition region occurs below 400$^{o}$C, and this is representative of the initial volatile combustion. The temperature of the maximum rate of decomposition is seen to be highest for switch grass, and lowest for miscanthus. The catalytic impact of potassium is assumed to be responsible for the differences seen between the perennial grasses. The second decomposition region, after 400$^{o}$C, is reflective of the char burnout. The hardwoods were found to have distinct broad regions and this is appears to be related to the lignin content. Ghetti et al. (1996) showed that the first region of decomposition is associated with the combustion of hemicellulose and cellulose, and the second with the combustion of lignin. This is because lignin is more aromatic than cellulose and hemicellulose, and therefore requires more energy to break the bonds.

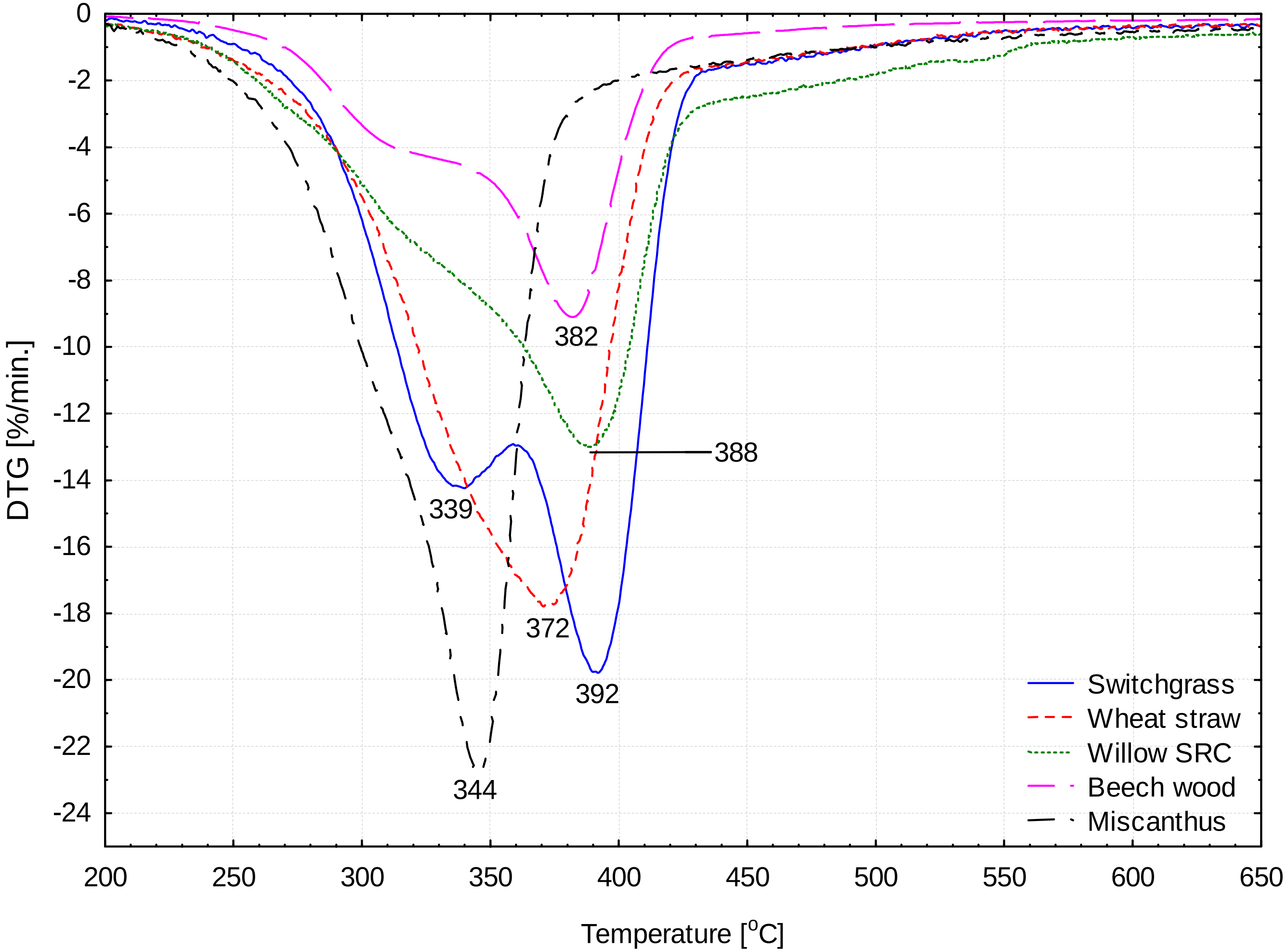


Figure 4.1 - Differential thermogravimetric pyrolysis profiles of the Straw, Perennial Grasses and Hardwoods

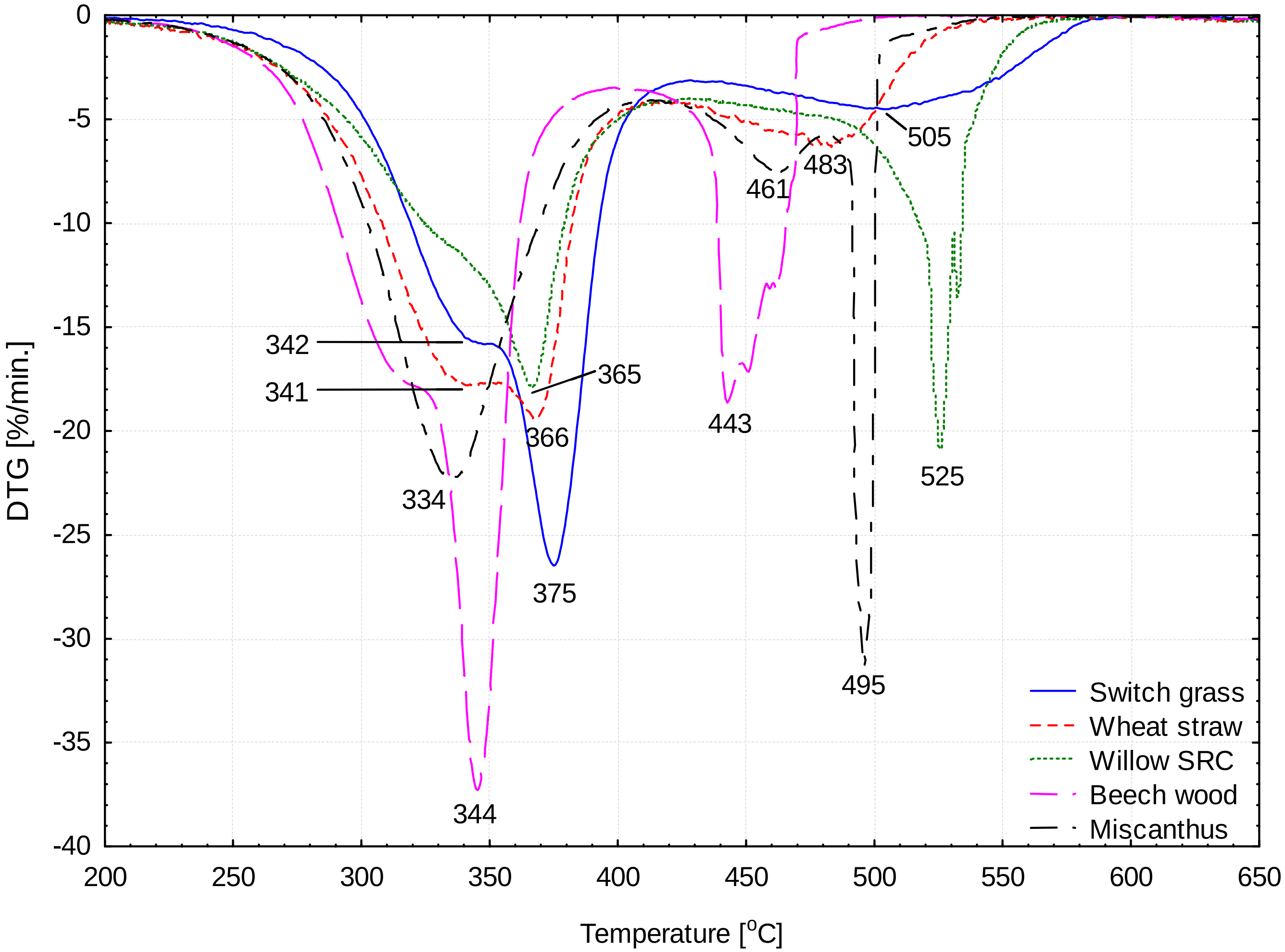


Figure 4.2 - Differential thermogravimetric combustion profiles of the Straw, Perennial Grasses and Hardwoods

### 4.2.3 Analytical Pyrolysis (Py-GC-MS)

The pyrolysis–gas chromatography–mass spectrometry results for the straw, perennial grasses and hardwoods are shown in Figure 4.3 to Figure 4.7 (chromatograms). Data obtained, but not shown in the chromatograms, was used to semi-quantify the 27 highest yielding identifiable cellulose, hemicellulose and lignin biomass key products. This takes into the consideration the GC peak areas (relative peak areas), and this is shown in Figure 4.8 and 4.9 and Table 4.2 shows additional information regarding the peak assignments.

From Figure 4.8, notable differences were seen in the content of 1,2-cyclopentanedione (cellulose marker), butanedioic acid, dimethyl ester (hemicelluloses decomposition products) and catechol lignin decomposition product) for switch grass. The other feedstocks, produced similar yields for the remaining compounds identified and no further major difference was seen, except for beech wood which had the highest content of acetic acid. From Figure 4.9, larger differences were seen between the different feedstocks. Switch grass was found to produce the highest yields of 2-methoxy-4-vinylphenol (guaiacyl lignin decomposition product) and levoglucosan an intermediate pyrolytic decomposition product of cellulose. Beech wood was seen to produce a high content of 2,6-dimethoxy-phenol (syringyl lignin decomposition product), 1,4:3,6-dianhydro-α-D-glucopyranose (a cellulose decomposition product), 2-methoxy-6-(2-propenyl)-phenol (guaiacyl lignin decomposition product) and 2,6-dimethoxy-4-(2-propenyl)-phenol (syringyl lignin decomposition product). Willow SRC was seen to have highest level of 1,2,4-trimethoxybenzene (guaiacyl lignin decomposition product), and miscanthus was found to have similar levels to switch grass for the lignin decomposition product 3-methyl-benzaldehyde. Nowakowski et al. (2007) investigated the impact of catalysts on thermal breakdown (previously mentioned in Chapter 2), to find that inorganic content in biomass favoured production of hydroxyacetaldehye (heterolytic mechanism of cellulose pyrolyitic decomposition), whereas washed biomass (removal of majority of the metals) favoured production of levoglucosan (homolytic mechanism of cellulose pyrolyitic decomposition). This may be a cause for the reduced levoglucosan yield found in wheat straw and miscanthus. Key products, such as 3-methyl-1,2-cyclopentanedione (cellulose) and 2-methoxyphenol (guaiacyl lignin marker) in Figure 4.8 were found to be highest in wheat straw.

### 4.2.4 Laboratory Scale Fast Pyrolysis Experiments

The fast pyrolysis process conditions and mass balances are shown in Table 4.3 and Table 4.4 respectively. Losses in the mass balance are thought to be caused by errors in weight measurement, water content analysis, liquid holdup within the quench system and gas analysis errors caused by heavily diluted pyrolysis gases, with content of nitrogen above 97%. A graphical representation of the data in Table 4.4 can be found in Figure 4.10. This clearly shows the differences in pyrolysis yields between feedstocks. The organic liquid yield was highest for beech wood and lowest for wheat straw. From the preliminary thermogravimetric data presented in Table 4.1, beech wood had the highest weight percentage of volatile matter and lowest of char. Switch grass was found to produce high organic liquid yields irrespective of the ash content. This is thought to be related to the lower level of potassium within switch grass. The other perennial grass, miscanthus, produced a similar organic liquid yields to willow SRC. When compared to willow SRC, wheat straw had lower calcium levels and similar potassium levels. The reduced organic liquid yield in wheat straw is caused by the higher production of non-condensable gases and reaction water. The gas analysis shows that the yields of non-condensable gases such as carbon dioxide, methane, ethane, propene, propane and n-butane are highest for wheat straw. A possible cause for the high non-condensable gases is thought to be related to the potassium content.

The standard errors computed for the mean values (Table 4.4) of the three Willow SRS experiments indicate that although in general there are only small to negligible errors associated to the measurements (e.g., S.E. = .001 for n-Butane content), there are remarkable exceptions to this trend, such as the case of CH4, with S.E. = 2.57. In order to further investigate this and reach conclusions regarding the extent to which the measurement error is large enough to render the results unreliable bivariate correlation coefficients were computed for all repeated runs of the experiments. The findings for Willow SRC indicate that the results of each run correlate exceptionally highly and significantly to each other (first and second run: $r = .99$, $p <.001$; first and third run: $r = .97$, $p <.001$; second and third run: $r = .97$, $p <.001$). This means that there is as much as 97-99% of shared variance in the results between the different runs, indicating that in essence the difference in the results is very small and there is only 1-3% variance in the findings that is not shared. Similar results were obtained for the remainder feedstocks where two runs were conducted for each (Beach Wood: $r = .99$, $p <.001$; Wheat Straw: $r = .95$, $p <.05$; Switchgrass: $r = .99$, $p <.001$; Miscanthus: $r = .99$, $p <.001$).

A number of similarities and differences can be seen when comparing obtained with reported results presented in Table 2.2 (Chapter 2). A large number of authors did not report on the reaction water generated. Similar values of char content were found for the feedstock investigated, except for miscanthus. The low char yield reported by Hodgson et al. (2010), is thought to be linked to the reduced reactor capacity and amount of feedstock used. Char content results presented by Fahmi et al. (2008) for wheat straw, switch grass and willow SRC, using a smaller capacity reactor, were found to be very similar. The char yield of beech wood was found to be the lowest and results are similar to those presented by Wang et al. (2005). The ash content of the feedstock significantly contributes to the overall char yield. The overall bio-oil yield was reported in to be highest for beech wood and this corresponds well with the finding. The organic content, reported by Fahmi et al. (2008), for switch grass and willow SRC produced similar results to that found here; wheat straw was found to have a value approximately 10% lower.

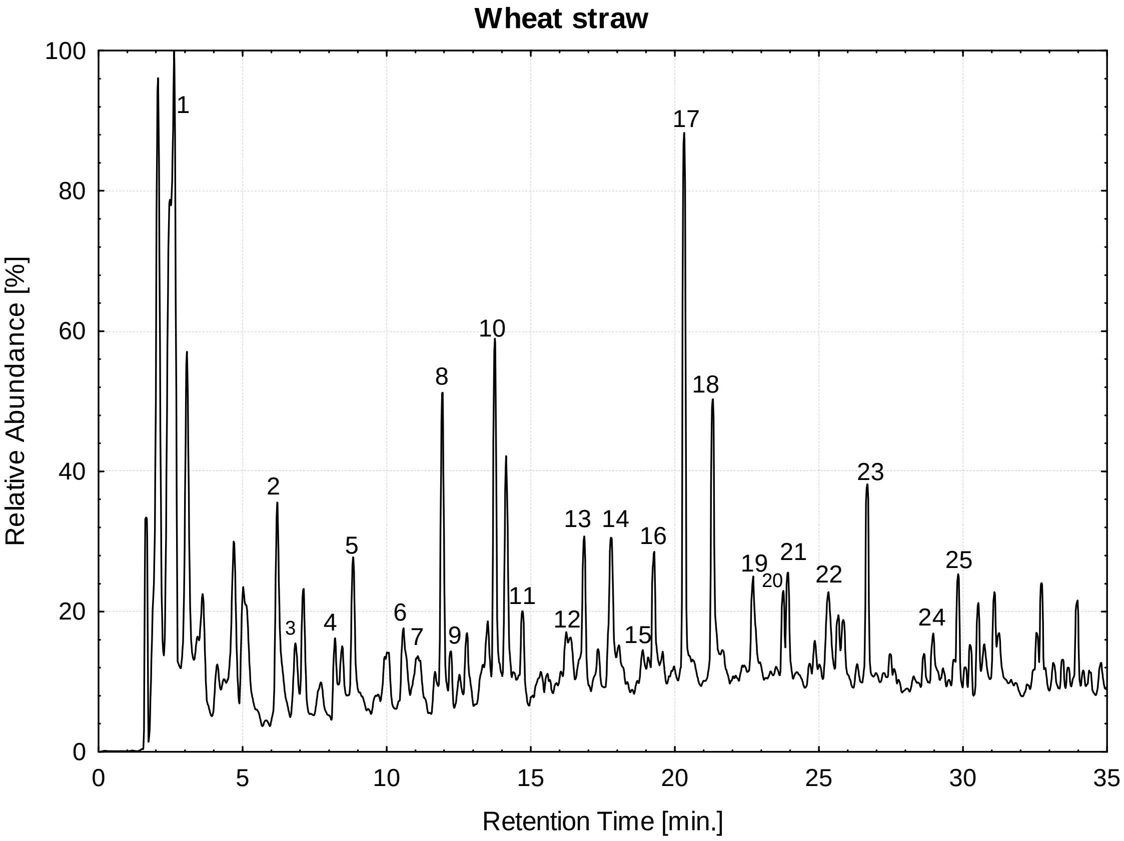


Figure 4.3 - PY-GC-MS Chromatogram for Wheat Straw:

1) Acetic Acid; 2) Furfural; 3) 2-Furanmethanol; 4) 2(5H)-Furanone; 5) 1,2-Cyclopentanedione; 6) Phenol; 7) Butanedioic Acid; 8) 3-Methyl-1,2-Cyclopentanedione; 9) 2-Methylphenol; 10) Guaiacol; 11) 3-Ethyl-2-Hydroxy-2-Cyclopentene-1-One; 12) 2-Methoxy-4-Methylphenol; 13) Catechol; 14) 3-Methyl-Benzaldehyde; 15) 3-Methoxycatechol; 16) 4-Ethyl-2-Methyl-Phenol; 17) 2-Methoxy-4-Vinylphenol; 18) 2,6-Dimethoxy-Phenol; 19) Vanillin; 20) 1,2,4-Trimethoxybenzene; 21) 2-Methoxy-6-(2-Propenyl)-Phenol; 22) Levoglucosan; 23) 3'5'-Dimethoxyacetophenone; 24) Syringaldehyde; 25) 2,6-Dimethoxy-4-(2-Propenyl)-Phenol.

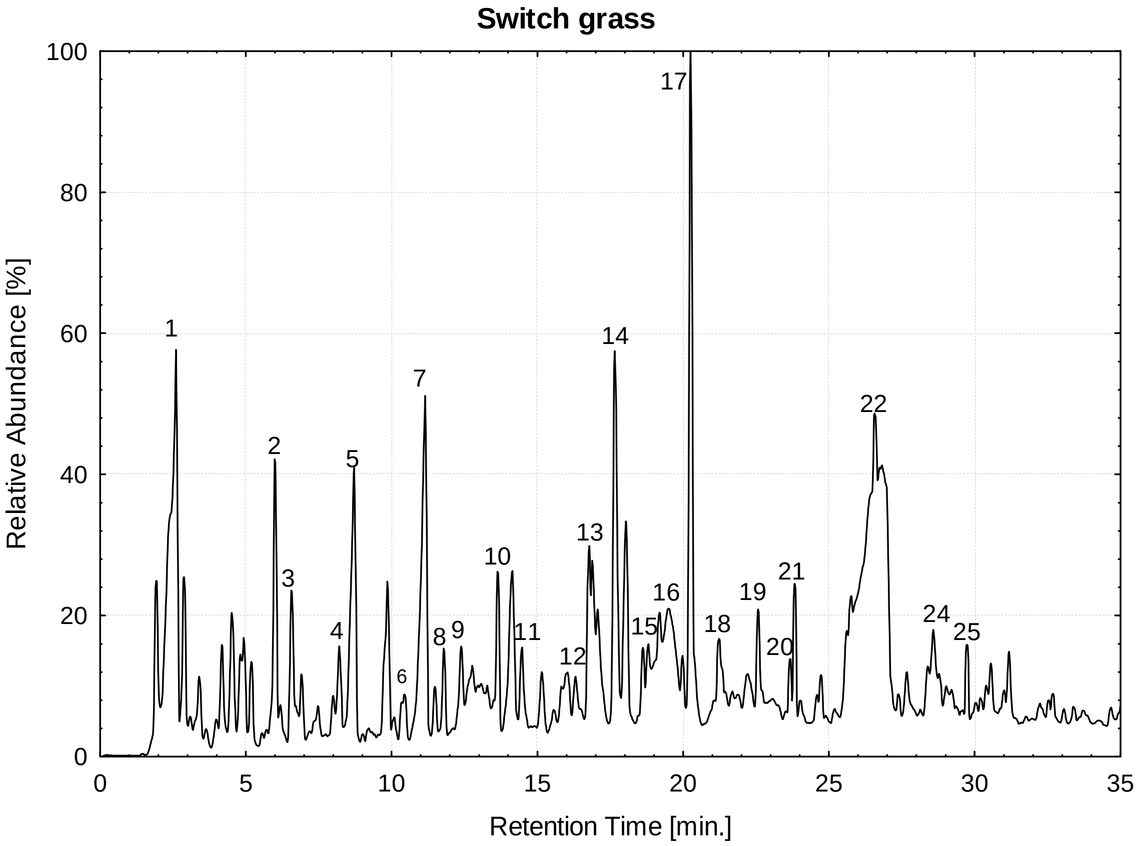


Figure 4.4 - PY-GC-MS Chromatogram for Switch Grass:

1) Acetic Acid; 2) Furfural; 3) 2-Furanmethanol; 4) 2(5H)-Furanone; 5) 1,2-Cyclopentanedione; 6) Phenol; 7) Butanedioic Acid; 8) 3-Methyl-1,2-Cyclopentanedione; 9) 2-Methylphenol; 10) Guaiacol; 11) 3-Ethyl-2-Hydroxy-2-Cyclopentene-1-One; 12) 2-Methoxy-4-Methylphenol; 13) Catechol; 14) 3-Methyl-Benzaldehyde; 15) 3-Methoxycatechol; 16) 4-Ethyl-2-Methyl-Phenol; 17) 2-Methoxy-4-Vinylphenol; 18) 2,6-Dimethoxy-Phenol; 19) Vanillin; 20) 1,2,4-Trimethoxybenzene; 21) 2-Methoxy-6-(2-Propenyl)-Phenol; 22) Levoglucosan; 23) 3'5'-Dimethoxyacetophenone; 24) Syringaldehyde; 25) 2,6-Dimethoxy-4-(2-Propenyl)-Phenol.

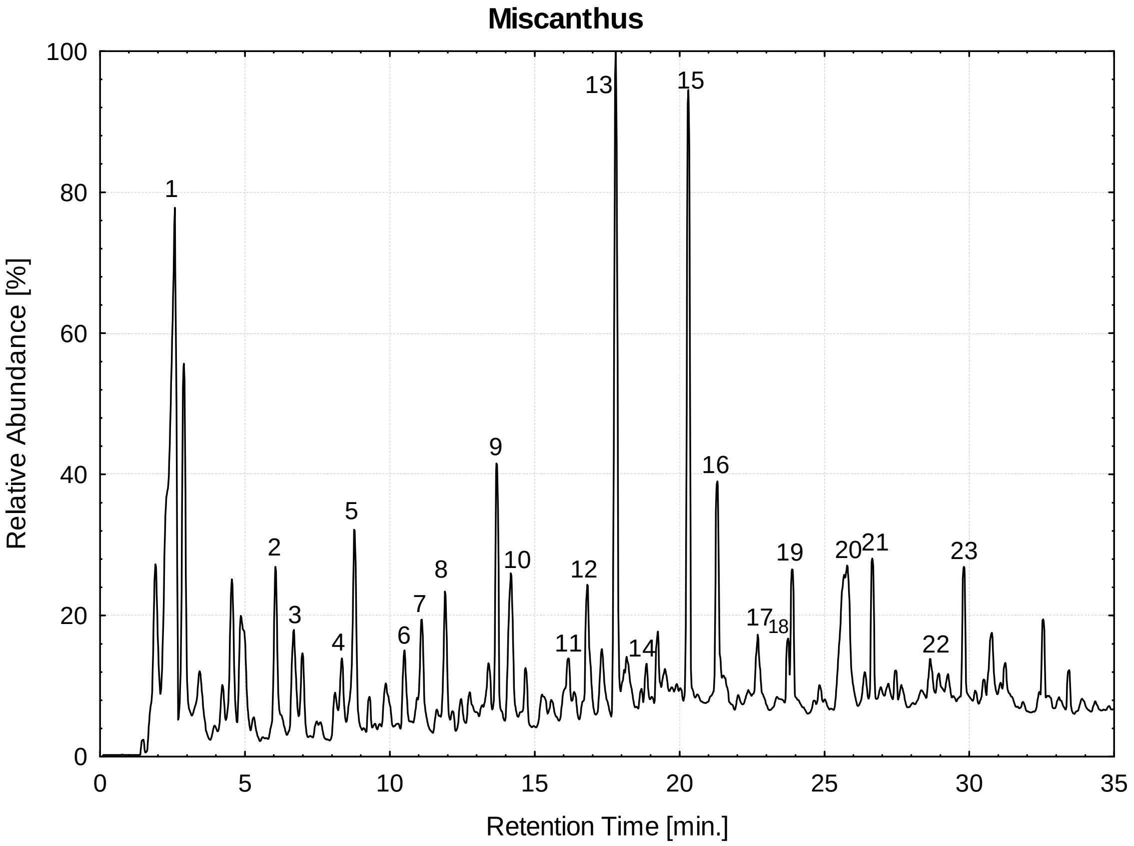


Figure 4.5 - PY-GC-MS Chromatogram for Miscanthus:

1) acetic acid; 2) furfural; 3) 2-furanmethanol; 4) 2-methyl,2-cyclopenten-1-one; 5) cyclopentanedione; 6) phenol; 7) 3,4-dihydroxy-3-cyclobutene-1,2-dione; 8) 2-hydroxy-3-methyl-2-cyclopenten-1-one; 9) guaiacol; 10) tetrahydro-2-furnanmethanol; 11) 2-methoxy-4-methylphenol;12) catechol; 13) 3-methyl-benzaldehyde;14) 3-methoxycatechol; 15) 3-methoxy-4-vinylphenol; 16) 2,6-dimethoxy-phenol; 17) vanillin; 18) 1,2,4-trimethoxybenzene; 19) 2-methoxy-6-(2-propenyl)-phenol; 20) levoglucosan; 21) 3'5'-dimethoxyacetophenone; 22) syringaldehyde; 23) 2,6-dimethoxy-4-(2-propenyl)-phenol.

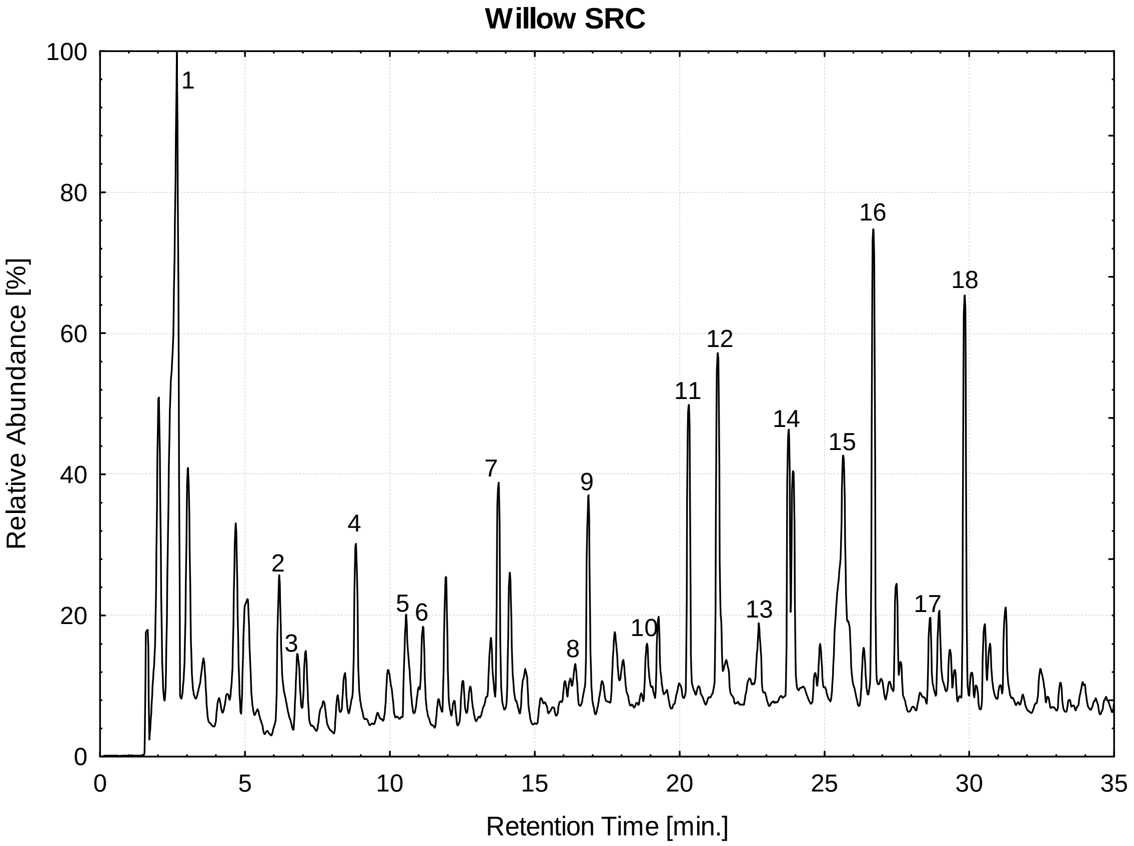


Figure 4.6 - PY-GC-MS Chromatogram for Willow SRC:

1) Acetic Acid; 2) Furfural; 3) 2-Furanmethanol; 4) 1,2-Cyclopentanedione; 5) Phenol; 6) 3,4-Dihydroxy-3'-Cyclobutene-1,2-Diol; 7) Guaiacol; 8) 2-Methoxy-4-Methylphenol; 9) Catechol; 10) 3-Methoxycatechol; 11) 2-Methoxy-4-Vinylphenol; 12) 2,6-Dimethoxy-Phenol; 13) Vanillin; 14) 1,4:3,6- Dianhydro-α-D-Glucopyranose; 15) Levoglucosan; 16) 3'5'-Dimethoxyacetophenone; 17) Syringaldehyde;18) 2,6-Dimethoxy-4-(2-Propenyl)-Phenol.

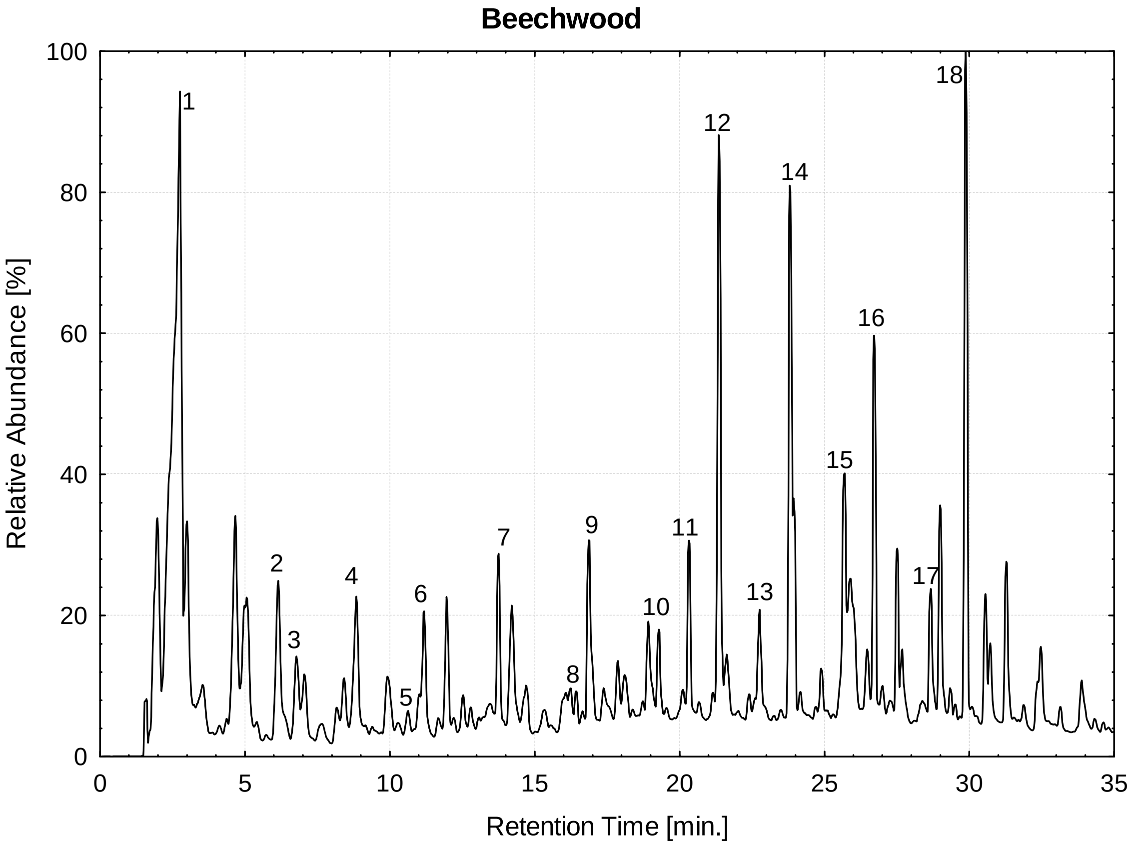


Figure 4.7 - PY-GC-MS Chromatogram for Beech Wood:

1) Acetic Acid; 2) Furfural; 3) 2-Furanmethanol; 4) 1,2-Cyclopentanedione; 5) Phenol; 6) 3,4-Dihydroxy-3'-Cyclobutene-1,2-Diol; 7) Guaiacol; 8) 2-Methoxy-4-Methylphenol; 9) Catechol; 10) 3-Methoxycatechol; 11) 2-Methoxy-4-Vinylphenol; 12) 2,6-Dimethoxy-Phenol; 13) Vanillin; 14) 1,4:3,6- Dianhydro-�-D-Glucopyranose; 15) Levoglucosan; 16) 3'5'-Dimethoxyacetophenone; 17) Syringaldehyde;18) 2,6-Dimethoxy-4-(2-Propenyl)-Phenol.

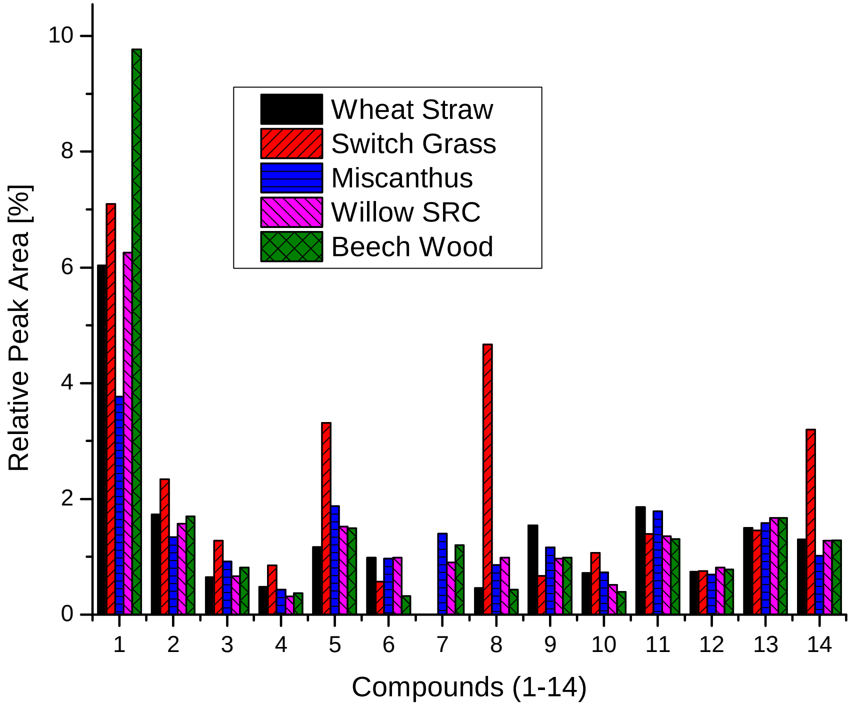


Figure 4.8 - Relative Peak area comparison of key pyrolysis products from wheat straw, switch grass, miscanthus, willow SRC and beech wood (for additional information see Table 4.2).

1) Acetic Acid; 2) Furfural; 3) 2-Furanmethanol; 4) 2(5H)-Furanone; 5) 1,2-Cyclopentanedione; 6) Phenol; 7) 3,4-dihydroxy-3-cyclobutene-1,2-dione; 8) Butanedioic Acid; 9) 3-Methyl-1 ,2-Cyclopentanedione; 10) 2-Methylphenol; 11) Guaiacol; 12) 3-Ethyl-2-Hydroxy-2-Cyclopentene-1-One; 13) 2-Methoxy-4-Methylphenol; 14) Catechol.

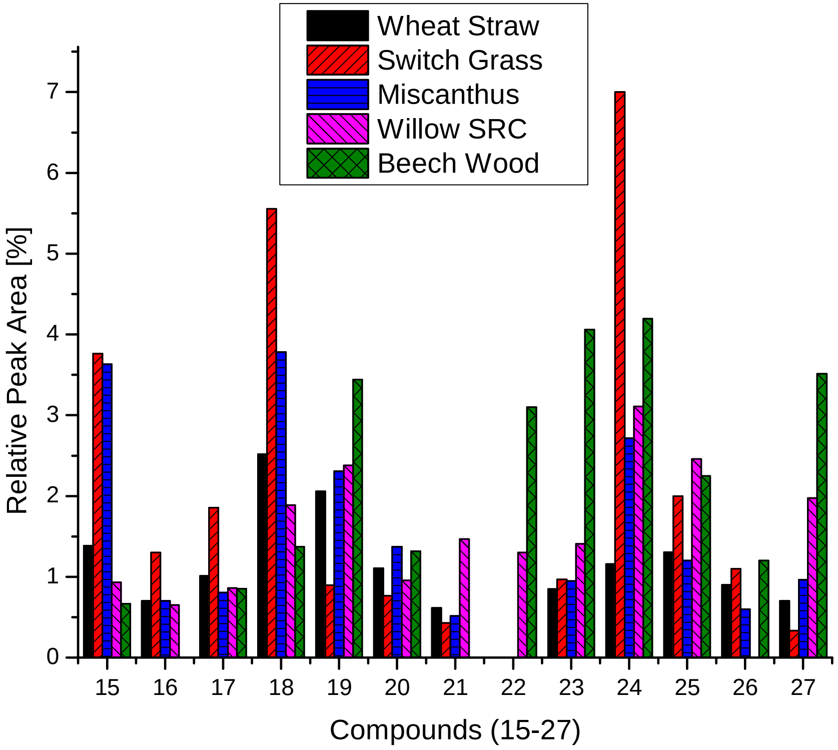
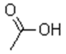
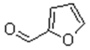
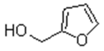
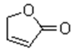
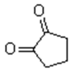
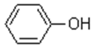
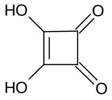
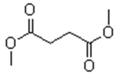
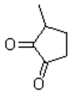
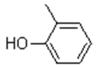
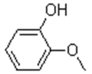
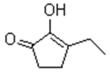
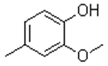
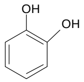
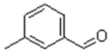


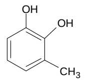
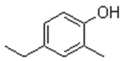
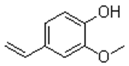
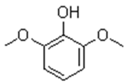
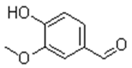
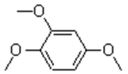
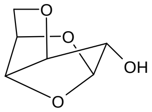
Figure 4.9 - Relative Peak area comparison of key pyrolysis products from wheat straw, switch grass, miscanthus, willow SRC and beech wood (for additional information see Table 4.2).

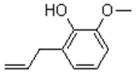
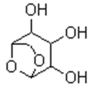
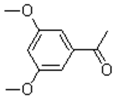
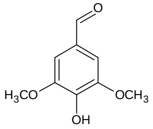
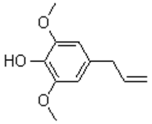
15) 3-Methyl-Benzaldehyde; 16) 3-Methoxycatechol; 17) 4-Ethyl-2-Methyl-Phenol; 18) 2-Methoxy-4-Vinylphenol; 19) 2,6-Dimethoxy-Phenol; 20) Vanillin; 21) 1,2,4-Trimethoxybenzene; 22) 1,4:3,6- Dianhydro-α-D-Glucopyranose; 23) 2-Methoxy-6-(2-Propenyl)-Phenol; 24) Levoglucosan; 25) 3'5'-Dimethoxyacetophenone; 26) Syringaldehyde; 27) 2,6-Dimethoxy-4-(2-Propenyl)-Phenol.

Table 4.2 - Key Compound Assignment for Py–GC–MS of the Straw, Perennial Grasses and Hardwoods

| ~Retention time (min.) | Compound | Structure | Formula | Type of key marker | Molecular weight (g/mol) | Base peak (100%) | Peak index mass (relative intensities) | Library match accuracy (%) |
|---|---|---|---|---|---|---|---|---|
| 2.36 | Acetic acid |  | $C_2H_4O_2$ | C, H | 60.05 | 43 | 45 (90.3), 60 (74.7), 15 (17.0), 42 (13.0), 29 (8.4), 14 (4.8), 28 (4.0), 41 (3.5), 18 (2.7) | 92.5 - 96.2 |
| 6.04 | Furfural [R] |  | $C_5H_4O_2$ | C | 96.08 | 96 | 95 (88.5), 39 (56.1), 29 (14.2), 38 (14.2), 37 (8.4), 97 (5.9), 40 (5.8), 67 (5.7), 42 (4.6) | R |
| 6.63 | 2-Furanmethanol [R] |  | $C_5H_6O_2$ | C | 98.10 | 98 | 41 (68.0), 81 (57.0), 97 (52.4), 39 (51.0), 53 (46.9), 42 (39.3), 69 (32.6), 70 (30.1), 27 (23.2) | R |
| 8.20 | 2(5H)-furanone |  | $C_4H_4O_2$ | C | 84.07 | 55 | 84 (69.0), 27 (56.9), 26 (33.7), 54 (19.8), 39 (13.8), 28 (8.1), 38 (6.9), 37 (5.6) | 91.4 - 95.0 |
| 8.80 | 1,2-Cyclopentanedione |  | $C_5H_6O_2$ | C | 98.10 | 98 | 55 (45.2), 42 (20.9), 41 (203), 69 (16.1), 43 (14.2), 27 (13.6), 39 (12.8), 70 (8.2), 99 (5.7) | 89.3 - 93.7 |
| 10.57 | Phenol [R] |  | $C_6H_6O$ | C, L | 94.11 | 94 | 66 (38.7), 65 (26.6), 39 (24.3), 40 (11.4), 38 (9.2), 55 (7.9), 63 (7.1), 95 (6.8), 50 (6.3) | R |
| 11.05 | 3,4-dihydroxy-3-cyclobutene-1,2-dione |  | $C_4H_2O_4$ | C, H | 114.06 | 114 | 115 (4.5), | 87.2 – 90.8 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 11.15 | Butanedioic acid, dimethyl ester |  | $C_6H_{10}O_4$ | C, H | 146.14 | 115 | 55 (43.7), 59 (35.1), 114 (23.3), 87 (12.6), 27 (5.4), 116 (5.0), 56 (4.9), 15 (4.8), 57 (4.3) | 86.2 – 89.3 |
| 11.90 | 3-Methyl-1,2-cyclopentanedione |  | $C_6H_8O_2$ | C | 112.13 | 112 | 55 (49.0), 69 (47.2), 41 (36.2), 56 (27.3), 83 (25.7), 43 (25.7), 83 (25.7), 39 (20.6), 27 (16.9), 42 (12.8) | 90.4 - 96.8 |
| 12.80 | 2-Methlyphenol |  | $C_7H_8O$ | GL | 108.14 | 108 | 107 (67.3), 79 (25.3), 77 (22.0), 90 (20.7), 39 (10.8), 80 (10.2), 51 (9.6), 89 (8.3), 109 (7.9) | 95.1 - 97.6 |
| 13.71 | 2-Methoxyphenol [R] |  | $C_7H_8O_2$ | GL | 124.14 | 109 | 124 (87.0), 81 (60.7), 53 (13.4), 27 (10.1), 52 (9.2), 51 (8.3), 125 (6.8), 110 (6.8) | R |
| 14.74 | 3-ethyl-2-hydroxy-2-Cyclopentene-1-one |  | $C_7H_{10}O_2$ | C | 126.15 | 126 | 55 (38.3), 83 (38.5), 69 (32.0), 43 (27.0), 84 (20.7), 41 (20.4), 27 (19.7), 39 (19.6), 97 (17.5) | 91.7 – 95.4 |
| 16.78 | 2-Methoxy-4-methyl-phenol [R] |  | $C_8H_{10}O_2$ | GL | 138.16 | 138 | 123 (86.9), 95 (36.5), 67 (19.6), 55 (18.3), 77 (17.0), 39 (16.2), 41 (11.7), 51 (11.4), 139 (8.8) | R |
| 16.95 | Catechol [R] |  | $C_6H_6O_2$ | L | 110.10 | 110 | 64 (32.6) | R |
| 17.80 | 3-Methyl-benzaldehyde |  | $C_8H_8O$ | L | 120.15 | 91 | 119 (93.2), 120 (86.3), 65 (25.3), 39 (15.2), 92 (11.4), 63 (11.3), 51 (8.5), 121 (7.8), 89 (7.6) | 91.0 - 98.3 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 18.85 | 3-Methoxycatechol R |  | C7H8O3 | L | 140.14 | 140 | 125 (89.8), 97 (69.9), 51 (31.7) | R |
| 19.28 | 4-Ethyl-2-methyl-phenol |  | $C_9H_{12}O$ | L | 136.19 | 121 | 136 (26.5), 77 (15.2), 39 (13.5), 91 (12.9), 122 (12.5), 107 (12.2), 27 (12.0), 51 (9.7), 108 (7.0) | 92.4 - 96.6 |
| 20.25 | 2-Methoxy-4-vinylphenol R |  | $C_9H_{10}O_2$ | GL | 150.17 | 135 | 150 (97.3), 107 (67.3), 77 (66.6), 51 (28.5), 79 (23.5), 15 (22.8), 39 (21.0), 53 (20.7), 78 (17.3) | R |
| 21.23 | 2,6-Dimethoxy-phenol |  | $C_8H_{10}O_3$ | SL | 154.16 | 154 | 139 (44.8), 111 (20.4), 93 (17.6), 96 (16.8), 65 (13.2), 39 (11.4), 155 (9.0), 51 (9.0), 68 (7.5) | 91.9 - 95.2 |
| 22.74 | Vanillin R |  | $C_8H_8O_3$ | GL | 152.15 | 152 | 151 (94.3), 81 (30.9), 109 (22.1), 123 (17.1), 51 (16.1), 52 (15.0), 53 (10.6), 65 (10.2), 39 (10.1) | R |
| 23.70 | 1,2,4-Trimethoxybenzene R |  | $C_9H_{12}O_3$ | GL | 168.19 | 168 | 153 (86.9), 125 (48.9), 110 (16.2), 69 (14.5), 52 (12.0), 169 (10.5), 51 (10.2), 79 (10.1), 154 (8.4) | R |
| 23.96 | 1,4:3,6-Dianhydro-α-D-Glucopyranose |  | $C_6H_8O_4$ | C | 144.13 | 69 | 29 (38.4), 57 (37.8) | 89.4 – 93.9 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 23.92 | 2-Methoxy-4-(2-propenyl)-phenol [R] |  | $C_{10}H_{12}O_2$ | GL | 164.20 | 164 | 131 (27.9), 103 (27.6), 77 (26.8), 121 (26.4), 149 (25.4), 91 (15.9), 39 (11.4), 104 (11.2), 65 (11.2) | R |
| 25.43 | 1,6-Anhydro-β-D-glucopyranose (levoglucosan) [R] |  | $C_6H_{10}O_5$ | C | 162.14 | 60 | 57 (44.1), 73 (35.8), 29 (19.9), 56 (15.0), 70 (14.1), 43 (12.6 ), 42 (11.8), 31 (10.9), 55 (8.8) | R |
| 26.8 | 3'5'-Dimethoxyacetophenone |  | $C_{10}H_{12}O_3$ | L | 180.20 | 165 | 180 (64.2), 137 (40.5), 122 (33.4), 43 (19.7), 77 (19.2), 107 (15.1), 63 (14.4), 79 (9.7), 166 (9.4) | 89.1- 94.0 |
| 28.85 | Syringaldehyde [R] |  | $C_9H_{10}O_4$ | SL | 182.17 | 182 | 183 (10.0), 184 (1.2) | R |
| 29.77 | 2,6-Dimethoxy-4-(2-propenyl)-phenol |  | $C_{11}H_{14}O_3$ | SL | 194.23 | 194 | 91 (36.8 ), 119 (24.4), 39 (21.6), 77 (18.4), 131 (16.9), 65 (14.2), 179 (13.6), 79 (13.7), 53 (13.6) | 91.8 – 94.7 |

C: Cellulose; H: Hemicellulose; L : Lignin; GL: Guaiacyl lignin, SL: Syringyl lignin, [R]: Reference compound used to verify identified compound.

Table 4.3 - Fast Pyrolysis Processing Conditions using the 1 kg/h Reactor

| | Wheat straw $^{No.1}$ | Wheat straw $^{No.2}$ | Switch grass $^{No.1}$ | Switch grass $^{No.2}$ | Miscanthus $^{No.1}$ | Miscanthus $^{No.2}$ |
|---|---|---|---|---|---|---|
| Average feeding rate (g/h) | 403.18 | 410.53 | 499.83 | 482.07 | 468.57 | 446.00 |
| Feedstock particle size (mm) | 0.25-1.00 | 0.25-1.00 | 0.25-1.00 | 0.25-1.01 | 0.25-1.00 | 0.25-1.00 |
| Average pyrolysis temperature ($^{o}$C) | 525 | 502 | 510 | 515 | 505 | 510 |
| Run time (min.) | 107 | 95 | 121 | 116 | 210 | 120 |
| Biomass moisture content (%) | 4.60 | 5.20 | 6.20 | 7.4 | 8.71 | 8.32 |
| Biomass used ($^{w.b}$) (g) | 719.00 | 650.00 | 1008.00 | 932.00 | 1640.00 | 892.00 |
| Hot vapour residence time (s) | < 1.5 | < 1.5 | < 1.5 | < 1.5 | < 1.5 | < 1.5 |

| | Beech wood $^{No.1}$ | Beech wood* $^{No.2}$ | Willow SRC $^{No.1}$ | Willow SRC* $^{No.2}$ | Willow SRC* $^{No.3}$ |
|---|---|---|---|---|---|
| Average feeding rate (g/h) | 484.86 | 932.89 | 418.50 | 910.37 | 996.71 |
| Feedstock particle size (mm) | 0.25-1.00 | 0.25-2.00 | 0.25-1.00 | 0.25-2.00 | 0.25-2.00 |
| Average pyrolysis temperature ($^{o}$C) | 512 | 510 | 500 | 512 | 506 |
| Run time (min.) | 203 | 475 | 120 | 275 | 220 |
| Biomass moisture content (%) | 10.42 | 10.88 | 6.50 | 12.67 | 11.67 |
| Biomass used ($^{w.b}$) (g) | 2551.00 | 7385.37 | 837.00 | 4172.55 | 3657.94 |
| Hot vapour residence time (s) | < 1.5 | < 1.5 | < 1.5 | < 1.5 | < 1.5 |

*Data provided by the Bioenergy Research Group (the feedstock is identical, harvest time and source, to the one's used here), $^{w.b}$ - wet basis

Table 4.4 - The Fast Pyrolysis Mass Balance (wt.% on dry basis) using the 1 kg/h Reactor

| | Beech wood $^{No.1}$ | Beech wood*$^{No.2}$ | Mean | Willow SRC $^{No.1}$ | Willow SRC* $^{No.2}$ | Willow SRC* $^{No.3}$ | Mean | SD | SE |
|---|---|---|---|---|---|---|---|---|---|
| **Char total** | 14.43 | 17.21 | 15.82 | 19.28 | 19.98 | 20.18 | 19.81 | 0.39 | 0.22 |
| **Bio-oil total** | 63.17 | 61.37 | 62.27 | 51.34 | 58.68 | 60.81 | 56.94 | 4.06 | 2.34 |
| Organics | 55.47 | 50.05 | 52.76 | 40.51 | 48.64 | 43.98 | 44.38 | 3.33 | 1.92 |
| Reaction water | 7.70 | 11.32 | 9.51 | 10.83 | 10.04 | 16.83 | 12.57 | 3.03 | 1.75 |
| **Gas total** | 13.03 | 17.57 | 15.30 | 19.89 | 17.94 | 17.02 | 18.28 | 1.20 | 0.69 |
| $H_2$ | 0.64 | 0.04 | 0.34 | 0.78 | 0.05 | 0.03 | 0.29 | 0.35 | 0.20 |
| CO | 6.09 | 6.89 | 6.49 | 9.22 | 5.70 | 5.39 | 6.77 | 1.74 | 1.00 |
| $CH_4$ | 0.14 | 0.79 | 0.47 | 1.45 | 0.67 | 10.50 | 4.20 | 4.46 | 2.58 |
| $CO_2$ | 5.81 | 9.30 | 7.55 | 7.71 | 11.00 | 0.60 | 6.44 | 4.34 | 2.51 |
| Ethene | 0.14 | 0.15 | 0.14 | 0.32 | 0.13 | 0.13 | 0.19 | 0.09 | 0.05 |
| Ethane | 0.10 | 0.15 | 0.13 | 0.16 | 0.16 | 0.11 | 0.14 | 0.02 | 0.01 |
| Propene | 0.08 | 0.06 | 0.07 | 0.19 | 0.06 | 0.16 | 0.14 | 0.06 | 0.03 |
| Propane | 0.02 | 0.18 | 0.10 | 0.04 | 0.15 | 0.08 | 0.09 | 0.05 | 0.03 |
| n-Butane | 0.01 | 0.01 | 0.01 | 0.02 | 0.02 | 0.02 | 0.02 | 0.00 | 0.00 |
| **Closure** | 90.63 | 96.15 | 93.39 | 90.51 | 96.60 | 98.01 | 95.04 | 3.25 | 1.88 |

*Data provided by the Bioenergy Research Group (the feedstock is identical, harvest time and source, to the one's used here)

Table 4.4 – Conti. The Fast Pyrolysis Mass Balance (wt.% on dry basis) using the 1 kg/h Reactor

| | Wheat straw $^{\text{No.1}}$ | Wheat straw $^{\text{No.2}}$ | Mean | Switch grass $^{\text{No.1}}$ | Switch grass $^{\text{No.2}}$ | Mean | Miscanthus $^{\text{No.1}}$ | Miscanthus $^{\text{No.2}}$ | Mean |
|---|---|---|---|---|---|---|---|---|---|
| **Char total** | 28.05 | 25.12 | 26.59 | 20.03 | 21.86 | 20.95 | 31.37 | 28.96 | 30.17 |
| **Bio-oil total** | 34.97 | 38.01 | 36.49 | 57.90 | 54.59 | 56.25 | 46.61 | 46.09 | 46.35 |
| Organics | 21.39 | 25.15 | 23.27 | 45.36 | 40.73 | 43.05 | 40.53 | 34.86 | 37.70 |
| Reaction water | 13.58 | 12.86 | 13.22 | 12.54 | 13.86 | 13.20 | 6.08 | 11.23 | 8.66 |
| **Gas total** | 26.99 | 25.59 | 26.29 | 16.57 | 13.25 | 14.91 | 9.13 | 11.46 | 10.30 |
| $H_2$ | 0.85 | 0.82 | 0.84 | 0.59 | 0.88 | 0.74 | 0.76 | 0.88 | 0.82 |
| CO | 8.44 | 7.1 | 7.77 | 5.90 | 4.70 | 5.30 | 4.36 | 4.90 | 4.63 |
| $CH_4$ | 1.95 | 1.65 | 1.80 | 1.20 | 0.92 | 1.06 | 0.78 | 1.10 | 0.94 |
| $CO_2$ | 11.11 | 11.99 | 11.55 | 5.88 | 4.21 | 5.05 | 2.76 | 3.50 | 3.13 |
| Ethene | 0.73 | 0.64 | 0.69 | 0.62 | 0.41 | 0.52 | 0.23 | 0.19 | 0.21 |
| Ethane | 0.80 | 0.7 | 0.75 | 0.58 | 0.30 | 0.44 | 0.15 | 0.14 | 0.15 |
| Propene | 1.48 | 1.23 | 1.36 | 0.53 | 0.58 | 0.56 | 0.07 | 0.50 | 0.29 |
| Propane | 0.92 | 0.84 | 0.88 | 0.68 | 0.76 | 0.72 | 0.01 | 0.01 | 0.01 |
| n-Butane | 0.71 | 0.62 | 0.67 | 0.59 | 0.49 | 0.54 | 0.01 | 0.01 | 0.01 |
| **Closure** | 90.01 | 88.72 | 89.37 | 94.50 | 89.70 | 92.10 | 87.11 | 86.51 | 86.81 |

*Data provided by the Bioenergy Research Group (the feedstock is identical, harvest time and source, to the one's used here)

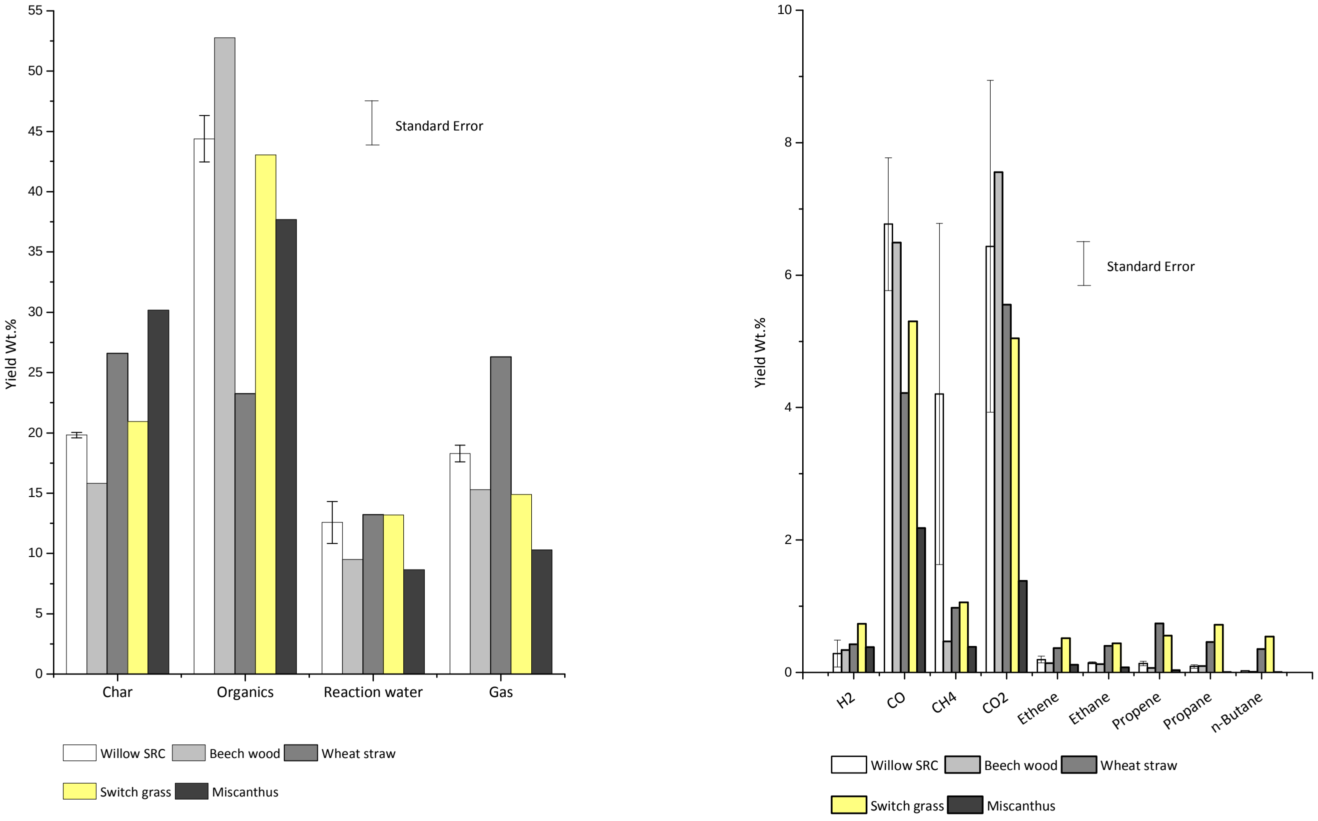


Figure 4.10 - Mass Balance and Gas Analysis for Wheat Straw, Switchgrass, Willow SRC, Miscanthus and Beech Wood (wt.% on dry basis)

### 4.2.5 Product Characterisation

The properties of the bio-oils produced are shown in Table 4.5. The straw and perennial grasses were found to have the highest bio-oil water content. The moisture content of the feedstock is the amount of water contained in the feedstock. The thermal conversion of the feedstock, via fast pyrolysis, produces a bio-oil product with a water content that not only contains the moisture content of the feedstock, but the reaction water generated by thermal degradation reactions that occur during the fast pyrolysis of the feedstock. Therefore pre-drying of the feedstock will impact the bio-oil water content. He et al. (2009) reported that the bio-oil water content generally increases by increasing the initial feedstock moisture content. The basic elemental analysis for the bio-oils and chars produced are shown in Table 4.5.

The H:C and O:C atomic ratios for the feedstocks, bio-oils and chars are shown in Figure 4.11. Three main clusters can be seen on the Van Krevelen diagram, and these are representative of the feedstocks, bio-oils and chars. Thermal conversion by fast pyrolysis has reduced the pyrolysis product O:C atomic ratio from 0.65 – 0.85 to 0.15 – 0.55, thus producing a more carbonaceous bio-oil and char product. The char H:C atomic ratio (0.40 – 0.70) was found to be very low when compared to the feedstocks and the bio-oils produced (1.70 – 1.10). The lower H:C and O:C atomic ratios in the chars are indicative of increased carbon-carbon bonds (McKendry, 2002). This is clearly evident when comparing the higher and lower heating values. The bio-oil higher heating values, on dry basis, range from 18.81 to 22.34 MJ/kg and in most cases, except for miscanthus and beech wood, they are found to be higher than the chars; this is because of the high ash content in the chars. Switch grass bio-oil has the highest higher heating value of 22.34 MJ/kg, on as received basis.

The bio-oil obtained from wheat straw was phase separated, and the bottom layer was used for all analytical investigations. The bottom layer of the wheat straw bio-oil was seen to have a high viscosity. Oasmaa et al. (2002) investigated bio-oil phase separation and reported that feedstocks rich in extractives, e.g. forestry and agricultural residues, generally produce phase separation bio-oils. The bottom layer is reported to exist in the form of a micro-emulsion, and this is stabilised by acids within that layer. The micro-emulsion can be destabilised by the addition of water. This is because water addition reduces the interaction between the acid and the micro-emulsion, ultimately resulting in a change in solubility and subsequent precipitation. The pH of wheat straw derived bio-oil was found to be the least acidic (pH 4.10). The higher pH value may be partly responsible for the phase separation seen in wheat straw. The main bio-oil generated was compared by GC-MS and the results are presented in Figure 4.12 and Figure 4.13. It can be observed that the bio-oils are mainly composed of oxygenated organic compounds such as: light organic acids, furans, ketones and aldehydes, phenols and anhydrosugars.

The fast pyrolysis chars were analysed by thermogravimetric analysis and this is shown in Figure 4.14. The maximum thermal degradation occurred between 380 – 443$^{o}$C. The ash content within the char is shown in Table 4.5. The char ash content is typically higher than the initial feedstock because the non-volatile inorganics will mainly remain within the char particle. Beech wood char was seen to have the highest higher heating value of 26.90 MJ/kg, and this is due to the low ash content found in the char. Results from this chapter are further discussed in Chapters 7 and 8.

Table 4.5 - Bio-oil and Char Product Analysis

| | Wheat straw** | Switch grass | Miscanthus | Willow SRC | Beech wood |
|---|---|---|---|---|---|
| **Bio-oil** | | | | | |
| Water content (wt.%) | 22.10 | 21.60 | 22.00 | 15.00 | 12.80 |
| pH | 4.10 | 3.39 | 3.78 | 3.42 | 2.86 |
| Homogeneity | Phase-separated | Single phase | Single phase | Single phase | Single phase |
| Elemental composition (wt.% d.b) | | | | | |
| Carbon | 60.33 | 63.15 | 54.90 | 62.94 | 54.24 |
| Hydrogen | 8.61 | 7.97 | 7.40 | 5.86 | 6.90 |
| Nitrogen | 1.05 | 0.73 | 1.63 | 0.11 | 0.00 |
| Oxygen* | 30.01 | 28.15 | 36.07 | 31.09 | 38.86 |
| Heating values (MJ/kg) | | | | | |
| HHV (a.r) | 22.01 | 22.34 | 18.81 | 21.79 | 20.07 |
| LHV (a.r) | 20.00 | 20.44 | 17.02 | 20.34 | 18.44 |
| **Char** | | | | | |
| Elemental composition (wt.% d.b) | | | | | |
| Carbon | 60.45 | 56.47 | 62.31 | 61.97 | 73.45 |
| Hydrogen | 2.67 | 2.76 | 3.00 | 3.37 | 3.21 |
| Nitrogen | 0.63 | 0.69 | 1.12 | 0.88 | 0.17 |
| Oxygen* | 36.26 | 40.09 | 33.58 | 33.79 | 23.17 |
| Ash (wt.% d.b) | 14.00 | 24.85 | 18.40 | 16.14 | 5.31 |
| Heating values (MJ/kg) | | | | | |
| HHV (d.b) | 20.19 | 18.28 | 21.41 | 21.75 | 26.90 |
| LHV (d.b) | 19.61 | 17.68 | 20.76 | 21.02 | 26.20 |

a.r – as received (wet basis); d.b. - dry basis; * - by difference; ** - analysis of bottom phase of bio-oil

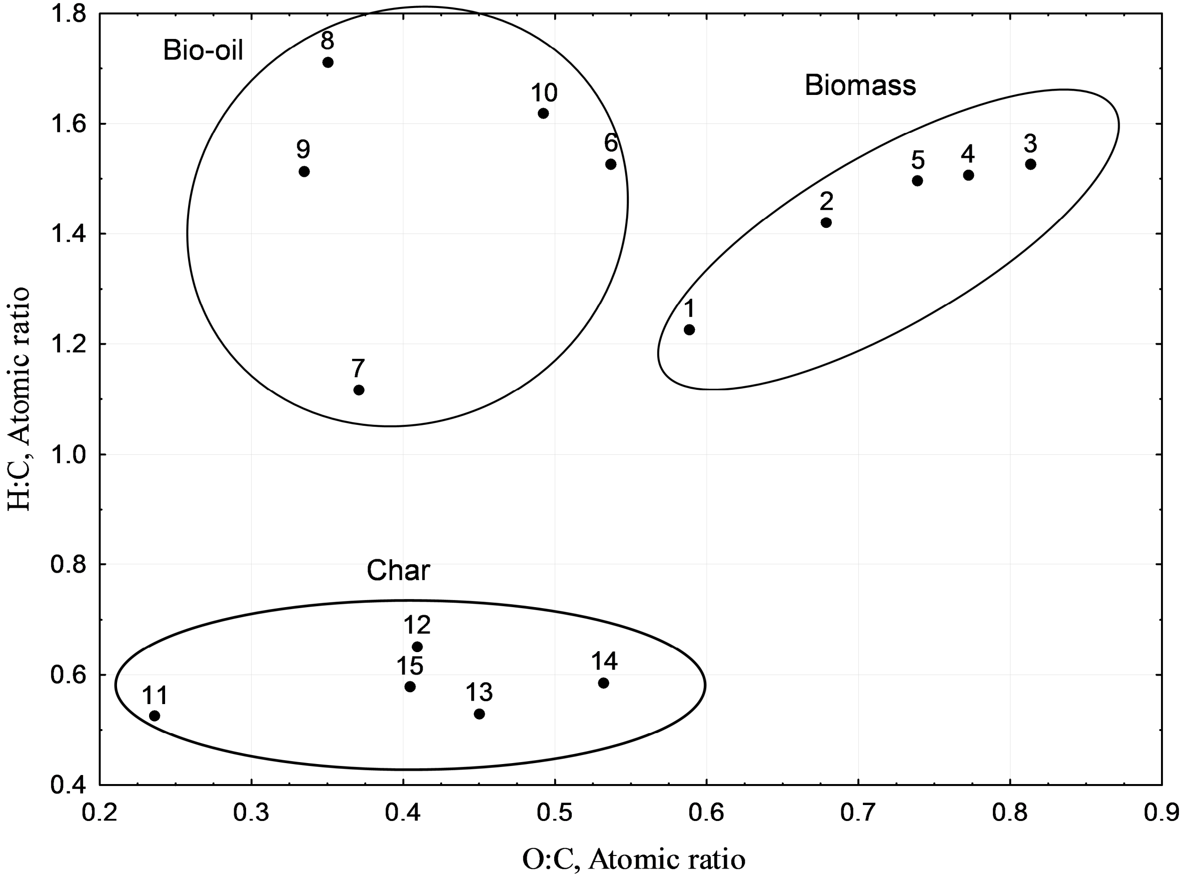


Figure 4.11 -. H:C and O:C Atomic Ratios of Biomass, Fast Pyrolysis Char and Fast pyrolysis Bio-oil (wt.% on dry basis)

*(Biomass – beech wood 1; willow SRC 2; wheat straw 3; switch grass 4; miscanthus 5); (Bio-oil – beech wood 6; willow SRC 7; wheat straw 8; switch grass 9; miscanthus 10); (Char– beech wood 11; willow SRC 12; wheat straw 13; switch grass 14; miscanthus 15)*

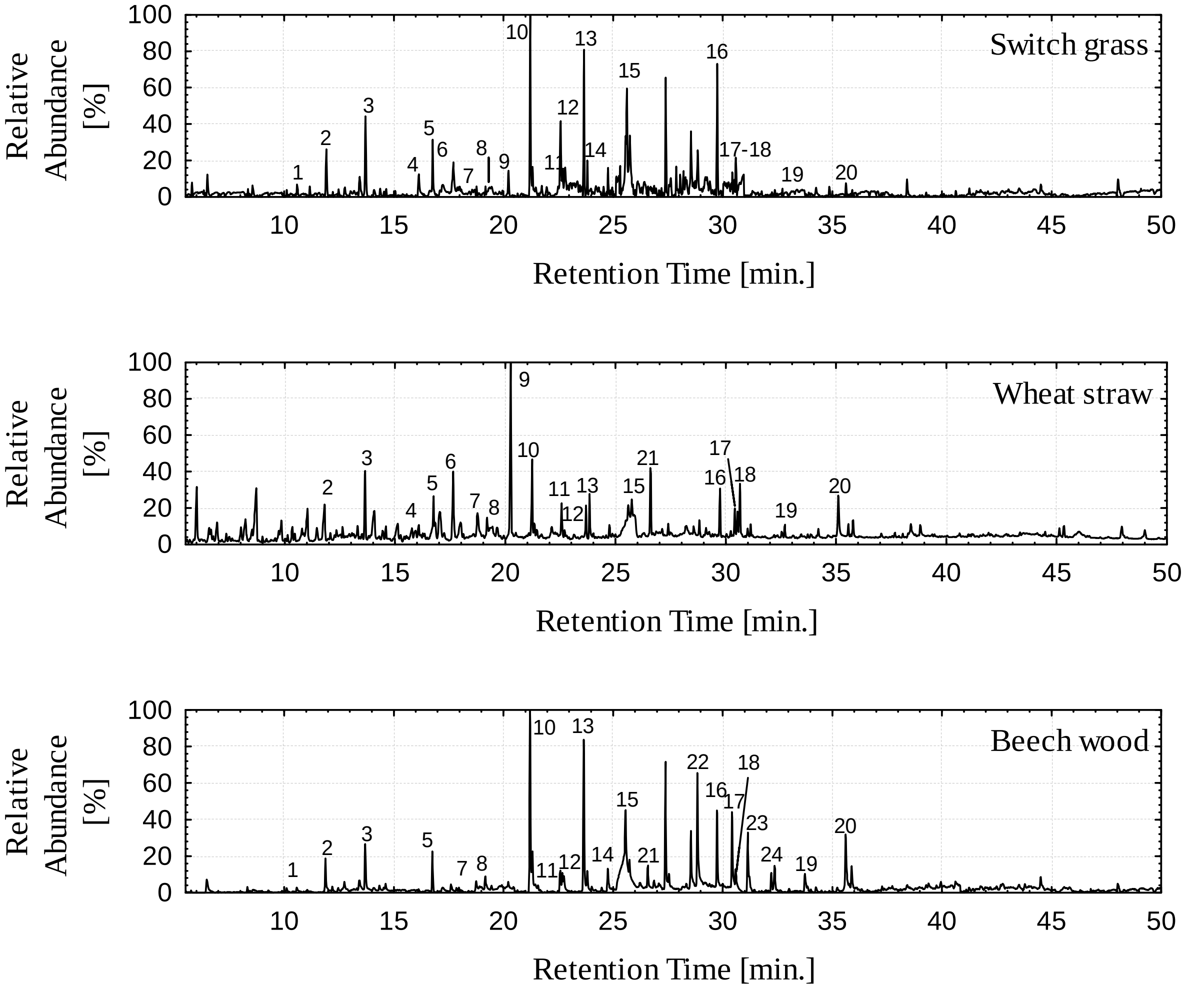


Figure 4.12 - Bio-oil Chromatograms for Switch Grass, Wheat Straw and Beechwood.

Peak assignments: 1) Phenol; 2) 3-Methyl-1,2,Cyclopentanedione; 3) 2-Methoxyphenol; 4) 1,4-Benzenedimethanol; 5) 2-Methoxy-4-Methyl-Phenol; 6) 2-Methyl, Benzaldehyde; 7) 3-Methoxy-1,2-Benzenediol; 8) 4-Ethyl-2-Methoxy-Phenol; 9) 2-Methoxy-4-Vinylphenol; 10) 2,6-Dimethoxy-Phenol; 11) Isovanillin; 12) Vanillin; 13) 1,2,4-Trimethoxybenzene; 14) 2-Methoxy-4-Propenyl-Phenol; 15) 2,5-Dimethoxybenzoic Acid; 16) 2,6-Dimethoxy-4-(2-Propenyl)-Phenol; 17) 2,4,5-Trimethoxy-Benzaldehyde; 18) 4-Hydroxy-2-Methoxycinnamaldehyde; 19) 2,3,4-Trimethoxybenzoic Acid; 20) Asarone; 21) 3',5'-Dimethoxyacetophenone; 22) 4-Hydroxy-3,5-Dimethoxy-Benzaldehyde; 23) Desaspidinol; 24) 1,2,5-Dimethoxybenzylacetate;

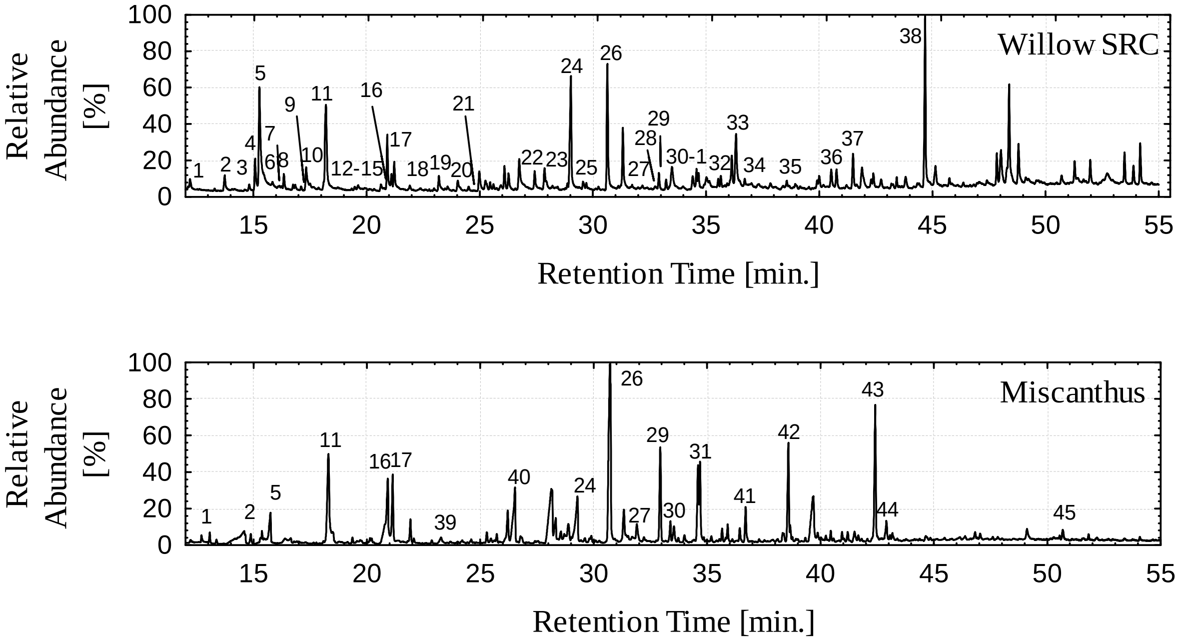


Figure 4.13 - Bio-oil Chromatograms for Willow SRC and Miscanthus

Peak assignments: 1) 3-Hydroxy-2-Butanone; 2) Furfural; 3) 1,4-Dimethyl-Pyrazole; 4) 1,3-Cyclohexanediol; 5) 2-Methyl-Furan; 6) Hexanoic Acid; 7) 1-(Acetyloxy)-2-Propanone; 8) 2-Methyl-2-Cyclopenten-1-One; 9) 2-Methyl-Propanoic Acid; 10) 2-Ethyl-3-Methyl-2-Pentanol; 11) 2-Butenoic Acid; 12) 4-Hydroxy-Butanoic Acid; 13) 2- And/Or 3-Methyl-2-Cyclopenten-1-One; 14) Cyclopentanone; 15) 3,4-Dimethyl-2-Pentene; 16) 4-Methyl-2-Pentene; 17) 3-Penten-2-ol; 18) 2-Methoxy-Phenol Or/And 19) 2-Methyl-Phenol; 20) 2-(2-Propenyl)-Furan; 21) Maltol; 22) 4-Ethyl-2-Methoxy-Phenol; 23) 2,3- And/Or 3,4-Anhydrogalactosan; 24) 1-(2-Hydroxy-Methylphenyl)-Ethanone; 25) Eugenol; 26) Phenol; 27) 2-Methoxy-4-(1-Propenyl)-Phenol; 28) 1,2,4-Trimethoxybenzene; 29) Vanillin; 30) 1,2,3-Trimethoxy-5-Methyl-Benzene; 31) 1-(4-Hydroxy-3-Methoxyphenyl)-Ethanone; 32) 2-Methoxy-4-Propenyl-Phenol; 33) 2,6-Dimethoxy-4-(2-Propenyl)-Phenol; 34) 2,5-Dimethoxy-Ethylbenzene; 35) 4-Hydroxy-3,5-Dimethoxy-Benzaldehyde; 36) 1-(4-Hydroxy-3,5-Dimethoxyphenyl)-Ethanone; 37) 1-(2,4,6-Trihydroxyphenyl)-2-Pentanone; 38) 2,6-Dimethoxyphenol; 39) 2,5-Diethoxytetahydrofuran; 40) 4-Hydroxy-Butanoic Acid; 41) 2,3-Dimethylphenol; 42) 3,5-Dimethylphenol; 43) 2- Or/And 3- Or/And 4 Methylbenzaldehyde; 44) 1,2-Benzenediol; 45) 2-Methyl-1,3-Benzenediol; Menquinol;

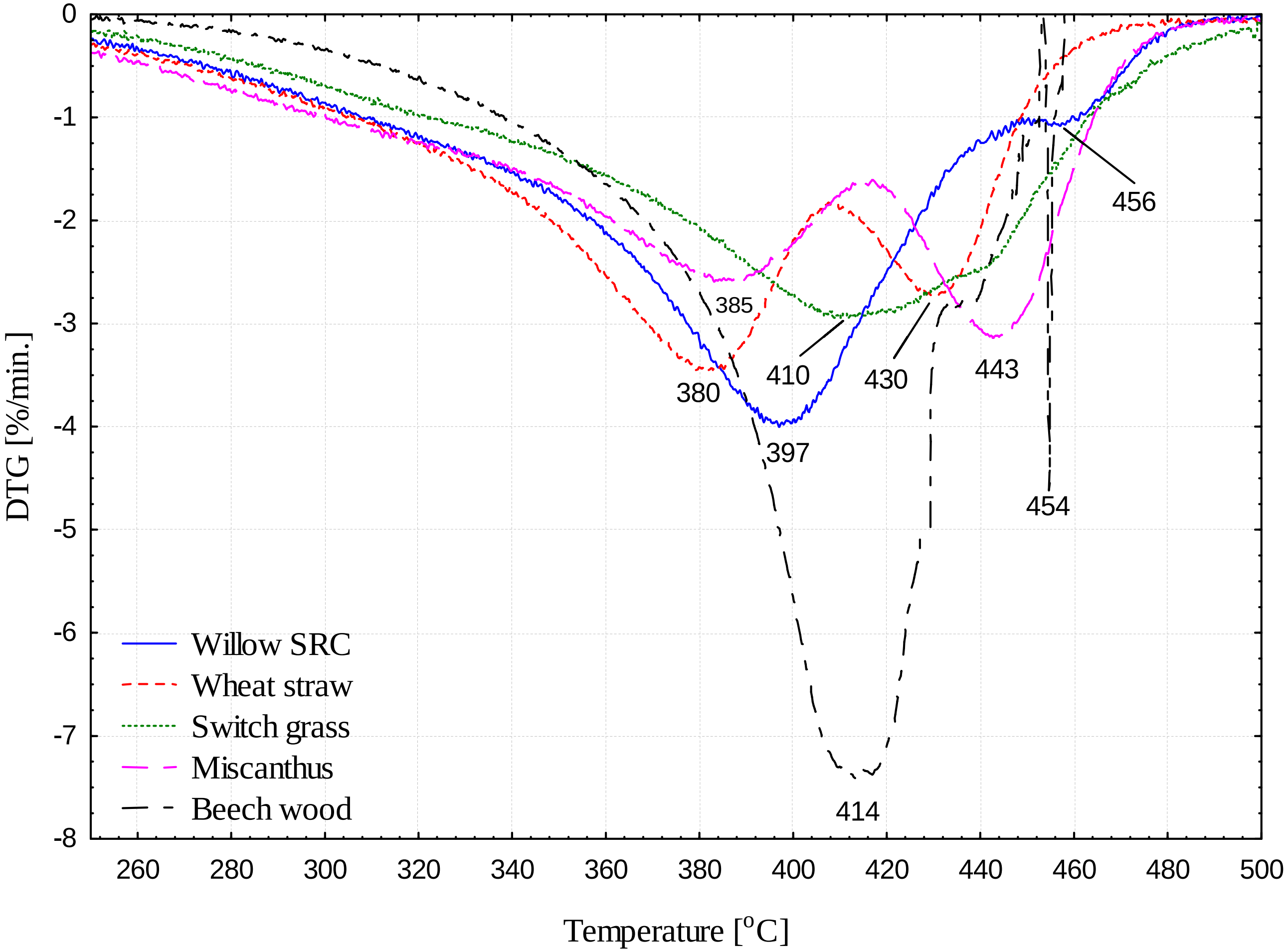


Figure 4.14 - Differential Thermogravimetric Combustion Profiles of Fast Pyrolysis Char

# 5 SEQUENTIAL PYROLYSIS OF WILLOW SRC AT LOW AND HIGH HEATING RATES – IMPLICATIONS FOR SELECTIVE PYROLYSIS

## 5.1 INTRODUCTION

This chapter investigates sequential pyrolysis and its implications for selective pyrolysis, and compares fast and slow pyrolysis products and yields using the hardwood willow SRC.

The following was undertaken:

I. An analytical investigation into how light and medium volatile decomposition products vary, using a step sequence, with different pyrolysis temperatures and heating rates;

II. Comparison of fast and slow pyrolysis products and yields generated using larger scale laboratory equipment.

Sequential pyrolysis was carried out using two different heating rates, 25 and 1500 $^{o}$C/min., over eight different pyrolysis temperatures in a step sequence, ranging from 320 to 520 $^{o}$C by Py–GC–MS. Fast pyrolysis has been carried out using a 1 kg/h continuously fed bubbling fluidized bed reactor and slow pyrolysis using a 0.15 kg batch reactor. The chemical composition of the bio-oil has been analysed by GC with mass (MS) and flame ionisation (FID) detection.

## 5.2 RESULTS AND DISCUSSION

### 5.2.1 Basic Characterisation

Ultimate, proximate and inorganics analyses were carried out for willow SRC and are shown in Table 5.1.

Table 5.1 - Proximate Analysis, Ultimate Analysis, Inorganic Analysis and the Higher Heating Value of Willow SRC

| Ultimate analysis %$^{(d.b)}$ | | Inorganic analysis$^{(d.b)}$ | ppm |
|---|---|---|---|
| C | 48.48 | Al | 277 |
| H | 5.74 | As | - |
| N | 1.87 | Ca | 11546 |
| O* | 43.91 | Cd | - |
| | | Co | - |
| Proximate analysis % | | Cr | - |
| Moisture | 5.71 | Cu | 11 |
| Volatile matter$^{(d.b)}$ | 78.59 | Fe | 240 |
| Fixed carbon$^{(d.b)}$ | 16.04 | K | 5883 |
| Ash$^{(d.b)}$ | 5.38 | Mg | 1590 |
| | | Mn | 118 |
| Higher heating value$^{(d.b)}$ | | Mo | - |
| (MJ/kg) | 19.12 | Na | 118 |
| | | Ni | - |
| | | P | 1884 |
| | | Pb | - |
| | | S | 1423 |
| | | Se | - |
| | | Ti | 5 |
| | | Zn | 202 |

- Not detected
* Oxygen by difference
d.b - Dry bases

Proximate and ultimate results are typical for biomass material, oxygen content is very high and this is consistent with willow biomass polymeric constituents. Higher heating value was calculated using the equation proposed by Channiwala and Parikh (2002) (see Table 5.1). Oxygen content is known to be correlated to the calorific value, and this is apparent because high oxygen content was detected and a low calorific value has been obtained. Thermogravimetric analysis in a nitrogen atmosphere was carried out and this is shown in Figure 5.1. The maximum rate of weight loss occurs at 388°C, at a rate of 13 %/min. (mentioned in Chapter 4). A partial shoulder-like feature can be seen prior to the maximum rate of weight loss, and this is thought to be indicative of the hemicellulose content

(Vamvuka et al., 2003). Ash content is representative of inorganic content and it has been found that calcium is the most abundant inorganic within willow SRC. The main inorganics found are shown in Table 5.1; these include calcium, potassium, phosphorous and magnesium.

### 5.2.2 Sequential Pyrolysis

Analytical sequential pyrolysis (Py-GC-MS) was used to investigate product distribution, as a function of heating rate (25 & 1500$^{o}$C/min.) and pyrolysis temperature (320, 350, 370, 390, 405, 420, 435 & 520$^{o}$C), in a stepped sequence, using single willow samples for each heating rate. At the low heating rate (25$^{o}$C/min.), the willow sample was initially heating from room temperature (25$^{o}$C) to a final temperature of 320$^{o}$C at a heating rate of 25$^{o}$C/min, and held at the final temperature for 60 s. The devolatilised components are then transferred onto the Tenax 2 trap, and desorbed once the GC is ready. The total hot reaction time for this initial step (from 25$^{o}$C to 320$^{o}$C at 25$^{o}$C/min. with a hold time of 60 s) is 12 min. and 48 s. The devolatilised components were not collected after this point and the sample is allowed to cool to room temperature (under inert conditions throughout). Once the sample reaches room temperature and the equipment is ready, the next stage will commence and the sample will be heating to 350$^{o}$C with the same hold time as before. The total hot reaction time will now be longer (to 350$^{o}$C at 25$^{o}$C/min. with a hold time of 60 s = 14 min.). This is repeated with the same initial sample until the final pyrolysis temperature of 520$^{o}$C is reached. For the high heating rate (1500$^{o}$C/min.), the hot reaction time is significantly lower (from 25$^{o}$C to 320$^{o}$C at 1500$^{o}$C/min. with a hold time of 60 s = 112 s). The procedure is identical to the lower heating rate scenario, but the total hot reaction times are much lower. Figure 5.1 shows the TGA profile and the main pyrolysis temperatures of interest (A-H).

Table 5.2 presents thirteen chemical compounds and their weight percentage (on dry ash free basis), at eight different pyrolysis temperatures, using two different heating rates (25 and 1500$^{o}$C/min.); representative of slow and fast pyrolysis. Of the sixteen chromatograms obtained, only six have been selected to show the most interesting differences. These can be found in the Figure 5.2, Figure 5.3 and Figure 5.4 at pyrolysis temperatures of 370, 405 and 520$^{o}$C (shown in Figure 5.1 as C, E and H respectively). Two heating rates are shown in each figure to emphasise the difference in product distribution. Comparison of Figure 5.2, Figure 5.3 and Figure 5.4 reveals some interesting findings. Firstly, the chromatograms are different at their corresponding temperatures, and therefore product distribution is a function of temperature. This makes it possible, in principle, to carry out selective pyrolysis to acquire desired products, which is reported by Wu et al. (2009). Secondly, the chromatograms are different due to the use of different heating rates, and this adds to the ability to carry out selective pyrolysis as mentioned above. A direct comparison of the two heating rates at different pyrolysis temperatures can be seen in Figure 5.5, this is a graphical representation of the data in Table 5.2. The general pattern of devolatisation at different pyrolysis temperatures follows previous work in the literature (Alén et al., 1996; Wu et al., 2009). Figure 5.6 shows the overall yield, on dry ash free (daf), between the two heating rates investigated, for each sequential pyrolysis experiment. For higher heating rates, yield increases were seen in the content of levoglucosan and furfural. Furfural, a furan derivative that is relatively similar in structure to 2-furanmethanol, is a pyrolytic decomposition product of levoglucosan. This was observed by Paine et al. (2008), and is shown in Figure 5.7. An inverse relationship between the yield of furfural and 2-furanmethanol can be seen when comparing the two heating rates (Figure 5.6).

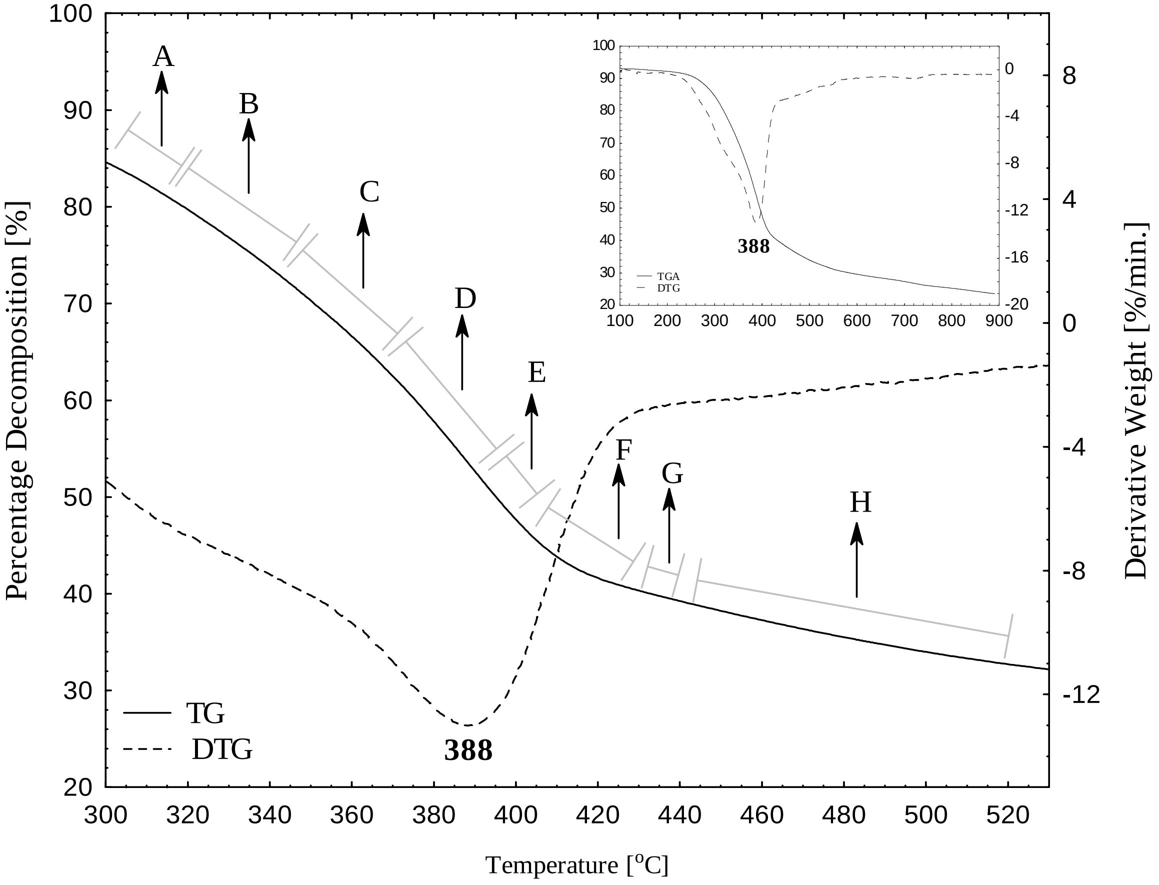


Figure 5.1 - Chemical Decomposition Products Investigated (A-H) of Willow SRC

(A-H are indicative of pyrolysis temperatures regions)

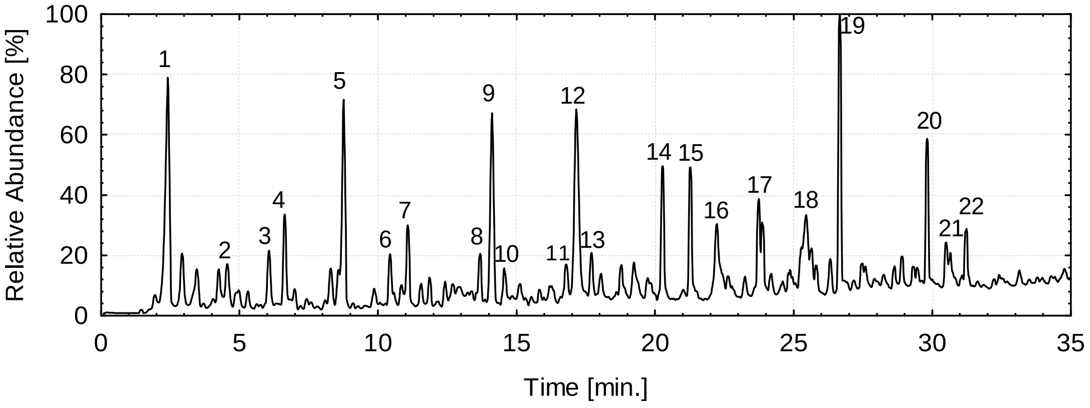
Table 5.2 - Yields of Quantified Compounds at Two Heating Rates (25 and 1500 $^{o}$C/min.)

| | [wt%$^{daf}$, heating rate - 25$^{o}$C/min.] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 320$^{o}$C | 350$^{o}$C | 370$^{o}$C | 390$^{o}$C | 405$^{o}$C | 420$^{o}$C | 435$^{o}$C | 520$^{o}$C | Total 320 - 520$^{o}$C |
| Furfural | 0.044 | 0.143 | 0.082 | 0.105 | 0.033 | - | - | - | 0.407 |
| 2-Furanmethanol | 0.042 | 0.103 | 0.134 | 0.240 | 0.048 | 0.030 | - | - | 0.596 |
| Phenol | 0.015 | 0.044 | 0.036 | 0.035 | 0.056 | 0.017 | 0.011 | 0.012 | 0.227 |
| Guaiacol | 0.013 | 0.019 | 0.027 | 0.042 | 0.051 | 0.014 | 0.012 | - | 0.179 |
| 2-Methoxy-4-methylphenol | - | - | 0.012 | 0.027 | 0.034 | 0.007 | - | - | 0.081 |
| Catechol | 0.111 | 0.238 | 0.198 | 0.215 | 0.187 | 0.089 | 0.080 | 0.068 | 1.186 |
| 3-Methoxycatechol | 0.019 | 0.020 | 0.029 | 0.055 | 0.065 | 0.018 | 0.017 | 0.017 | 0.240 |
| 1,2,4-Trimethoxybenzene | - | - | 0.023 | 0.029 | 0.024 | - | - | - | 0.076 |
| 2-Methoxy-4-vinylphenol | 0.019 | 0.059 | 0.087 | 0.082 | 0.035 | - | - | - | 0.282 |
| Eugenol | - | 0.038 | 0.027 | 0.016 | - | - | - | - | 0.081 |
| Vanillin | 0.013 | 0.018 | 0.017 | - | - | - | - | - | 0.048 |
| Levoglucosan | - | 0.062 | 0.088 | 0.274 | 0.112 | - | - | - | 0.536 |
| Syringaldehyde | - | 0.025 | 0.021 | 0.015 | - | - | - | - | 0.061 |
| | | | | | | | | | **4.000** |

| | [wt%$^{daf}$, heating rate - 1500$^{o}$C/min.] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 320$^{o}$C | 350$^{o}$C | 370$^{o}$C | 390$^{o}$C | 405$^{o}$C | 420$^{o}$C | 435$^{o}$C | 520$^{o}$C | Total 320 - 520$^{o}$C |
| Furfural | 0.039 | 0.191 | 0.126 | 0.162 | - | - | - | - | 0.518 |
| 2-Furanmethanol | 0.037 | 0.077 | 0.102 | 0.181 | 0.150 | - | - | - | 0.547 |
| Phenol | 0.016 | 0.041 | 0.043 | 0.037 | 0.058 | 0.018 | 0.014 | 0.016 | 0.242 |
| Guaiacol | 0.015 | 0.026 | 0.032 | 0.045 | 0.076 | 0.020 | 0.015 | - | 0.229 |
| 2-Methoxy-4-methylphenol | - | 0.010 | 0.015 | 0.027 | 0.053 | 0.011 | 0.009 | 0.010 | 0.134 |
| Catechol | - | 0.041 | 0.052 | 0.080 | 0.105 | - | - | - | 0.278 |
| 3-Methoxycatechol | - | - | 0.024 | 0.040 | 0.086 | 0.020 | - | - | 0.170 |
| 1,2,4-Trimethoxybenzene | - | - | 0.018 | 0.029 | 0.040 | 0.012 | 0.011 | - | 0.110 |
| 2-Methoxy-4-vinylphenol | 0.016 | 0.045 | 0.071 | 0.094 | 0.076 | 0.014 | 0.012 | - | 0.329 |
| Eugenol | 0.011 | 0.031 | 0.032 | 0.026 | 0.016 | 0.009 | - | - | 0.126 |
| Vanillin | 0.012 | 0.017 | 0.019 | 0.022 | - | - | - | - | 0.070 |
| Levoglucosan | - | 0.047 | 0.071 | 0.123 | 0.385 | - | - | - | 0.626 |
| Syringaldehyde | - | 0.027 | 0.026 | 0.020 | 0.016 | - | - | - | 0.090 |
| | | | | | | | | | **3.470** |

- Not detected; daf – dry ash free

**(A) 25 °C/min.**



**(B) 1500 °C/min.**

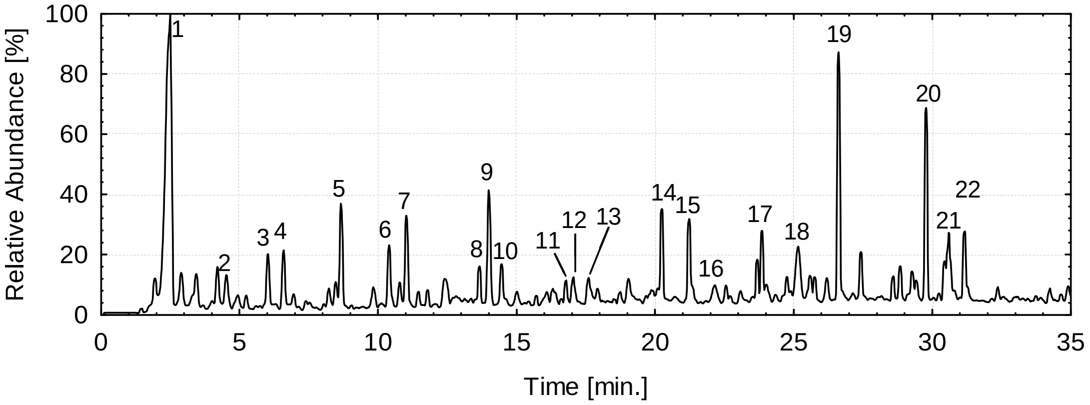
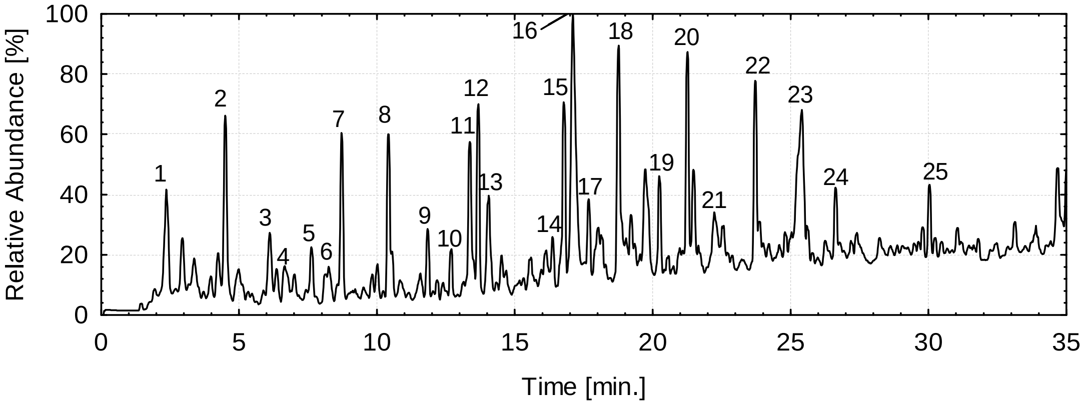


Figure 5.2 - Chromatograms for Stage Pyrolysis of Willow SRC at 370°C using Two Heating Rates: 25°C/min. (A) and 1500°C/min. (B)

*Peak assignments*: 1) Acetic acid; 2) Toluene; 3) Furfural or/and 3-Furaldehyde; 4) 2-Furanmethanol or/and 3-Furanmethanol; 5) 1,2-Cyclopentanedione; 6) Phenol; 7) 3,4-Dihydroxy-3'-cyclobutene-1,2-diol; 8) 2-Methoxyphenol; 9) Cyclopropylcarbinol; 10) 5-(Hydroxyl)-2-furancarboxaldehyde; 11) 2-Methoxy-4-methyl-phenol; 12) 1,2-Benzenediol; 13) 1,2,4-Trimethoxybenzene; 14) 2-Methoxy-4-vinylphenol; 15) 2,6-Dimethoxy-phenol; 16) 4-Ethylcatechol or/and 4-Ethyl-1,3-benzenediol; 17) 1,4:3,6- Dianhydro-α-D-glucopyranose; 18) 1,6-Anhydro-β-D-glucopyranose (levoglucosan); 19) 3'5'-Dimethoxyacetophenone; 20) 2,6-Dimethoxy-4-(2-propenyl)-phenol; 21) 4-Hydroxyl-2-methoxycinnamaldehyde; 22) Desaspidinol

**(A) 25 °C/min.**



**(B) 1500 °C/min.**

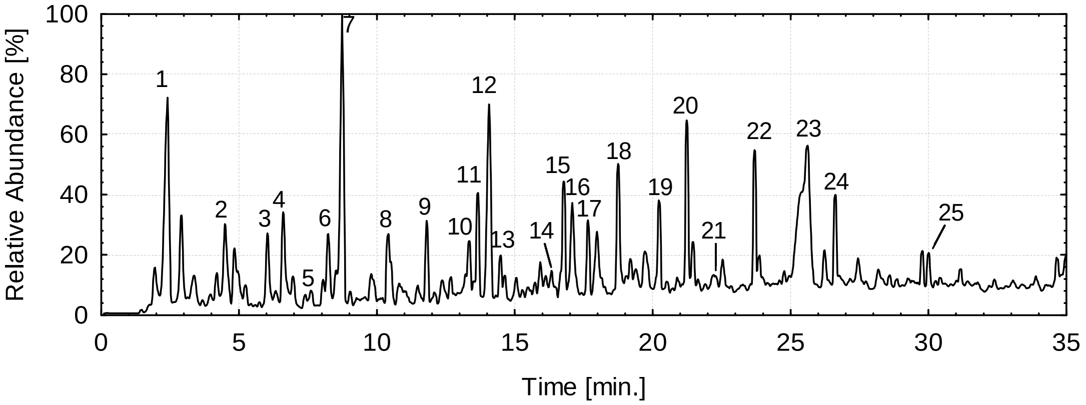


Figure 5.3 - Chromatograms for Stage Pyrolysis of Willow SRC at 405°C using Two Heating Rates: 25°C/min. (A) and 1500°C/min. (B)

*Peak assignments*: 1) Acetic acid; 2) Toluene; 3) Furfural or/and 3-Furaldehyde; 4) 2-Furanmethanol and/or 3-Furanmethanol; 5) Cyclohexanone; 6) 2(5H)-Furanone; 7) 1,2-Cyclopentanedione and/or 1,3-Cyclopentanedione; 8) Phenol; 9) 3-Methyl-1,2-cyclopentanedione; 10) 2-Methylphenol; 11) 2-Methoxyphenol; 12) Cyclopropylcarbinol; 13) 5-(Hydroxyl)-2-furancarboxaldehyde; 14) 3-Ethylphenol or/and 4-Ethylphenol; 15) 2-Methoxy-4-methyl-phenol; 16) 1,2-Benzenediol and/or Resorcinol; 17) 1,2,4-Trimethoxybenzene; 18) 3-Methoxy-1,2-dibenzenediol; 19) 2-Methoxy-4-vinylphenol; 20) 2,6-Dimethoxy-phenol; 21) 4-Ethylcatechol or/and 4-Ethyl-1,3-benzenediol; 22) 1,4:3,6- Dianhydro-α-D-glucopyranose; 23) 1,6-Anhydro-β-D-glucopyranose (levoglucosan); 24) 3',5'-Dimethoxyacetophenone; 25) 2,6-Dimethoxy-4-(2-propenyl)-phenol.

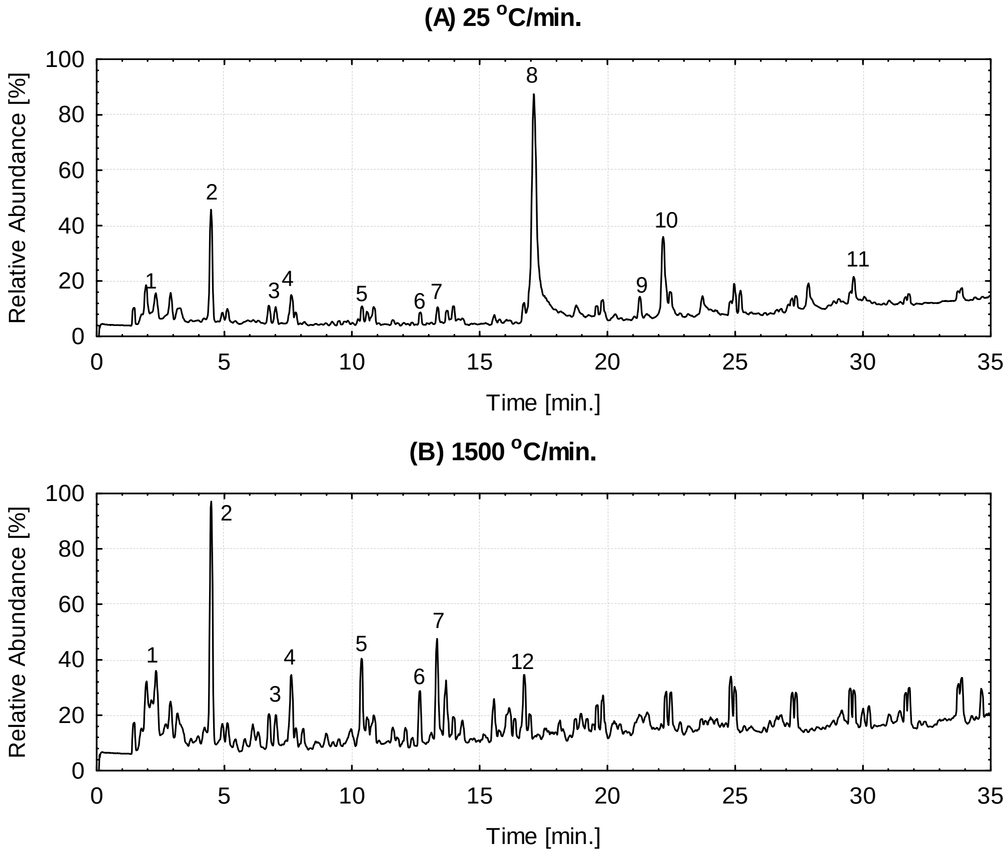


Figure 5.4 - Chromatograms for Stage Pyrolysis of Willow SRC at 520°C using Two Heating Rates: 25°C/min. (A) and 1500°C/min. (B)

*Peak assignments*: 1) Acetic acid; 2) Toluene; 3) p-Xylene; 4) o-Xylene; 5) Phenol; 6) 2-Methylphenol; 7) 2-Methoxyphenol; 8) 1, 2-Benzenediol or/and Resorcinol; 9) 2,6-Dimethoxy-phenol; 10) 4-Ethylcatechol or/and 4-Ethyl-1,3-benzenediol; 11) 2,6-Dimethoxy-4-(2-propenyl)-phenol; 12) 2-Methoxy-4-methyl-phenol.

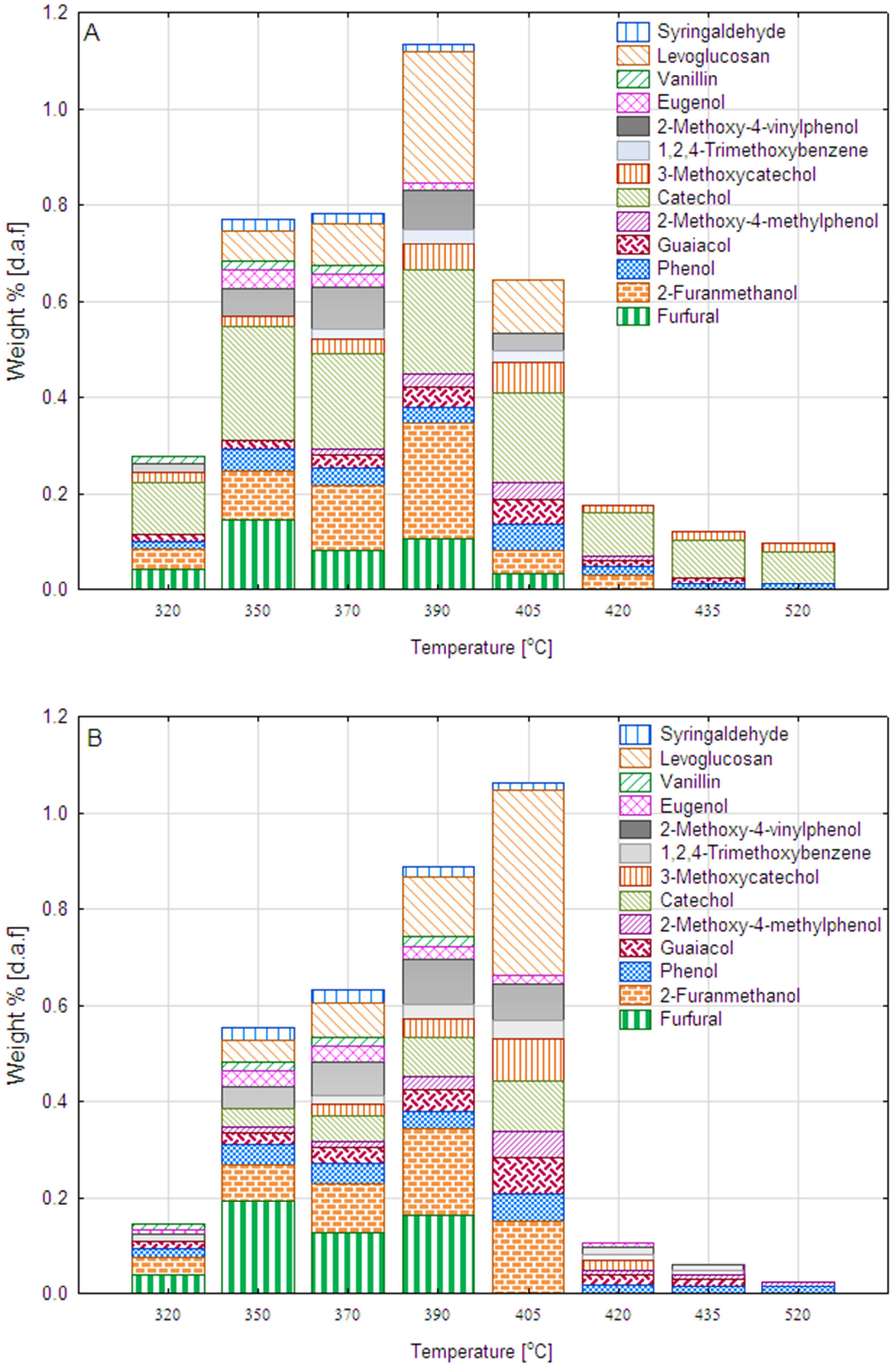


**Figure 9**.

Figure 5.5 - Comparison of Compound Peak Areas Between 320 and 520°C at Two Heating Rates: 25°C/min. (A) and 1500°C/min. (B)

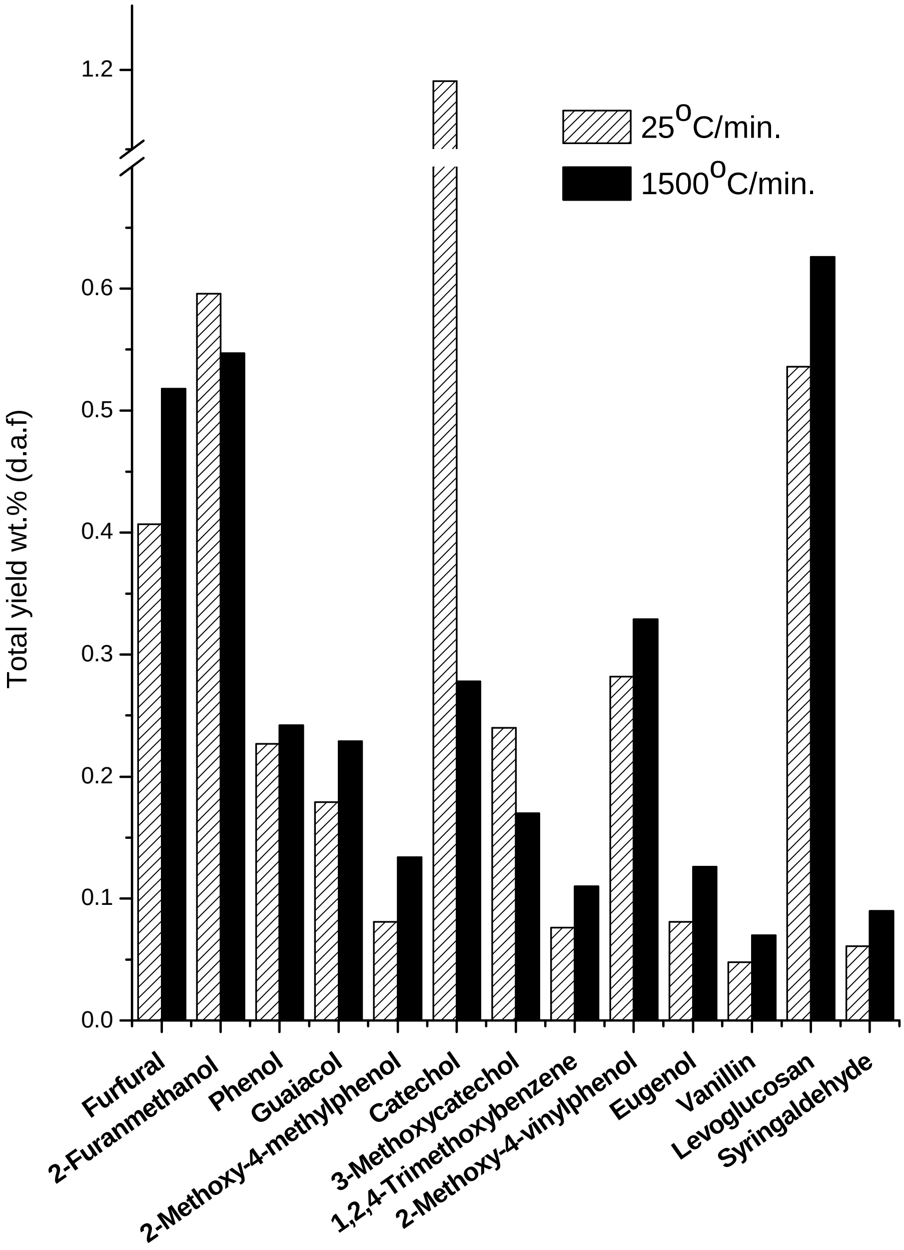


Figure 5.6 - Total Yield of Quantified Compounds at Two Heating Rates (25°C/min. and 1500°C/min) for each Sequential Pyrolysis Experiment (320 – 520°C)

Figure 5.7 - Proposed Pathway of the Formation of Furfural (Paine et al., 2008)

Kilzer and Broido were able to propose a mechanism to support their claim, which was consistent with the energy release observed in char formation (Broido and Kilzer, 1963). They reported this to be a result of cross linking reactions by etherification and subsequent rearrangement, to produce water and a 5-hydroxymethylfurfural moiety. They also cited data to indicate that cross linking reactions for char formation are optimal at around 220°C, and that higher temperatures around 400°C resulted in significantly lower levels of char residue. Later work conducted by Weinstein and Broido (1970) found that the crystalline region of cellulose and the mechanism of char formation are favourable to the plausibility of this mechanism. Lower heating rates promote further char formation. The elevated levels of hydroxymethylfurfural may contribute to the content of furfural and 2-furanmethanol. Char formation is believed to be associated with increased levels of free radicals. Shafizadeh (1972), reported that low temperature pyrolysis of cellulose results in a decline in the degree of polymerisation, an increase in the level of free radicals, elimination of water, and the formation and evolution of carbonyl, carboxyl, hydroperoxide and aldehyde groups. Proton addition can result in the formation of 2-furanmenthanol from furfural, and this may be more favourable at lower heating rates. A possible formation pathway, at low heating rates, for furfural and 2-furanmethanol can be seen in Figure 5.8 (Moldoveanu, 2010). The pathway produces an intermediate product known as hydroxymethylfurfural. The short residence times and reduced proton addition, seen at high heating rates, may favour an alternative decomposition pathway, that leads to the formation of furfural. A pathway for the formation of furfural (Moldoveanu, 2010), at high heating rates, is shown in Figure 5.9. This pathway does not produce a hydroxymethylfurfural intermediate. Subsequent proton addition, to the final furfural product in Figure 5.9, could result in the formation of 2-furanmethanol.

In contrast to cellulose and hemicellulose, lignin decomposition occurs at higher temperatures and produces a range of phenolic compounds. The difference in overall yield wt.% (daf), between low and high heating rates, can be seen in Figure 5.6. For high heating rates, yield increases were seen for 2-methoxy-4-methylphenol, eugenol, vanillin, 1,2,4-trimethoxybenzene, syringaldehyde and guaiacol.

Figure 5.10 shows the primary and secondary pyrolytic decomposition products from lignin (Moldoveanu, 2010). Guaiacol is thought to be a key intermediate for the production of catechol, p-cresol and phenol. Guaiacol can be formed either directly from lignin, or from other primary lignin decomposition products, e.g. eugenol and syringaldehyde. The numbers of secondary reactions are higher for lower heating rates because of the longer residence times. Longer residence times increase the number of decarboxylation, disproportionation and decarbonylation reactions. Therefore, at lower heating rates the content of primary decomposition products, such as guaiacol, eugenol and syringaldehyde, are expected to be low. This is evident when comparing the overall yield wt.% (daf) for these compounds in Figure 5.6. When comparing heating rate, minor differences were found in the content of phenol. It is possible that at higher heating rates the decomposition pathway to produce phenol could proceed through the pathway labelled k1 on Figure 5.10.

### 5.2.3 Laboratory Scale Pyrolysis

Fast and slow pyrolysis laboratory scale process conditions are shown in Table 5.3. Fast pyrolysis results have been taken from chapter 6. The product yields and gas composition are given in Table 5.4. A mass balance closure of 91% was achieved for fast pyrolysis and 98% for slow pyrolysis.

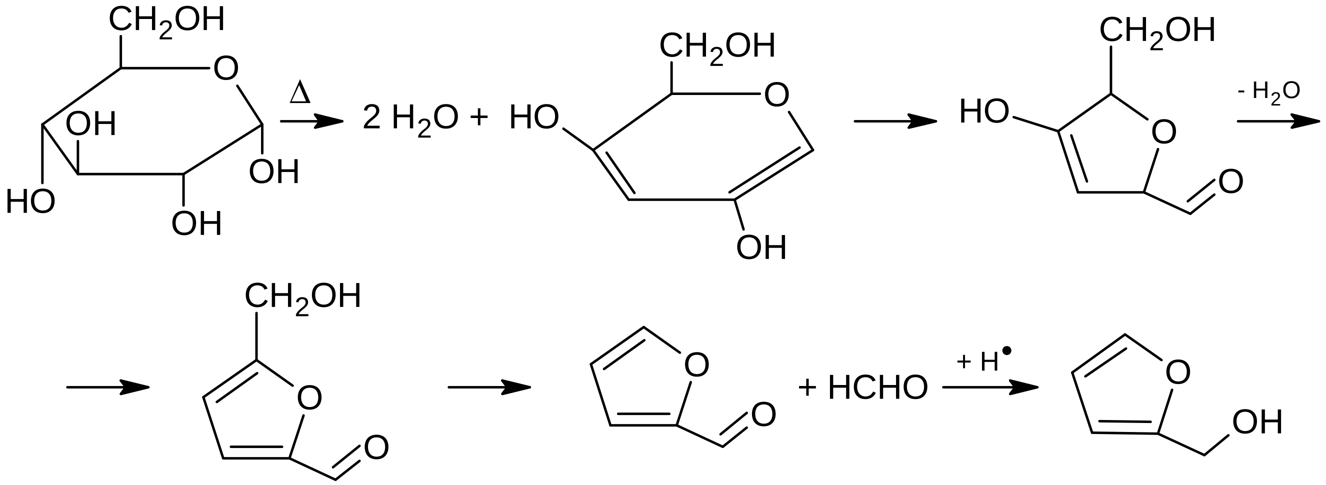


Figure 5.8 - Proposed Pathway of the Formation of 2-furanmethanol during the Pyrolytic Decomposition of Levoglucosan at Low Heating Rate (adapted from Moldoveanu, 2010)

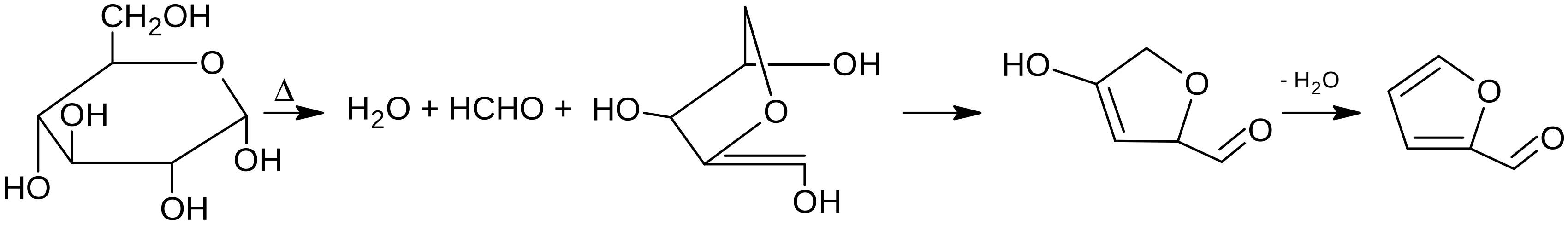


Figure 5.9 – Proposed Pathway of the Formation of Furfural during the Pyrolytic Decomposition of Levoglucosan at Higher Heating Rate (adapted from Moldoveanu, 2010)

Table 5.3 - Fast and Slow Pyrolysis of Willow SRC

| Operating conditions | Fast pyrolysis | Slow pyrolysis | |
|---|---|---|---|
| Average feeding rate (g/h) | 418.50 | * | g/h |
| Biomass particle size (mm) | 0.25-1.00 | 0.25-1.00 | mm |
| Average pyrolysis temperature ($^{o}$C) | 500 | 500 | $^{o}$C |
| Run time (min.) | 120 | 120 | min. |
| Biomass moisture content (%) | 6.50 | 13.58 | % |
| Biomass used on dry basis (g) | 837.01 | 57.68 | g |
| Hot vapour residence time (s) | < 1.5 | > 107 | s |
| Quench liquid temperature ($^{o}$C) | 30 | n/a | $^{o}$C |

* Batch reactor fixed amount

Acceptable mass balance closures were obtained in both cases. The lower figure for fast pyrolysis is typical of closures on this unit due to liquid hold up and high nitrogen content in the gas leading to gas analysis errors. The very high char yield in slow pyrolysis is due to the relatively low temperature in non-oxidising carbonisation and relatively short reaction time for a finely ground biomass sample with the possibility for adsorption and cracking of liquid precursors on the product char.

The main bio-oil generated was compared by GC-MS/FID and the results are found in Table 5.5. The chemical analysis of the liquids show a high level of accountability with over 70% of the peak area in both cases having chemical assignments. The analyses show high yields of acetic acid and methyl acetate from fast pyrolysis as well as significant yields of phenol and 2,6-dimethoxyphenol. Notable in the slow pyrolysis organic fraction is high yields of methyl acetate, 3-hydroxy-2-butane, furfural and cyclopenentes, a final decomposition product of cellulose pyrolysis. Results from this chapter are further discussed in Chapters 7 and 8.

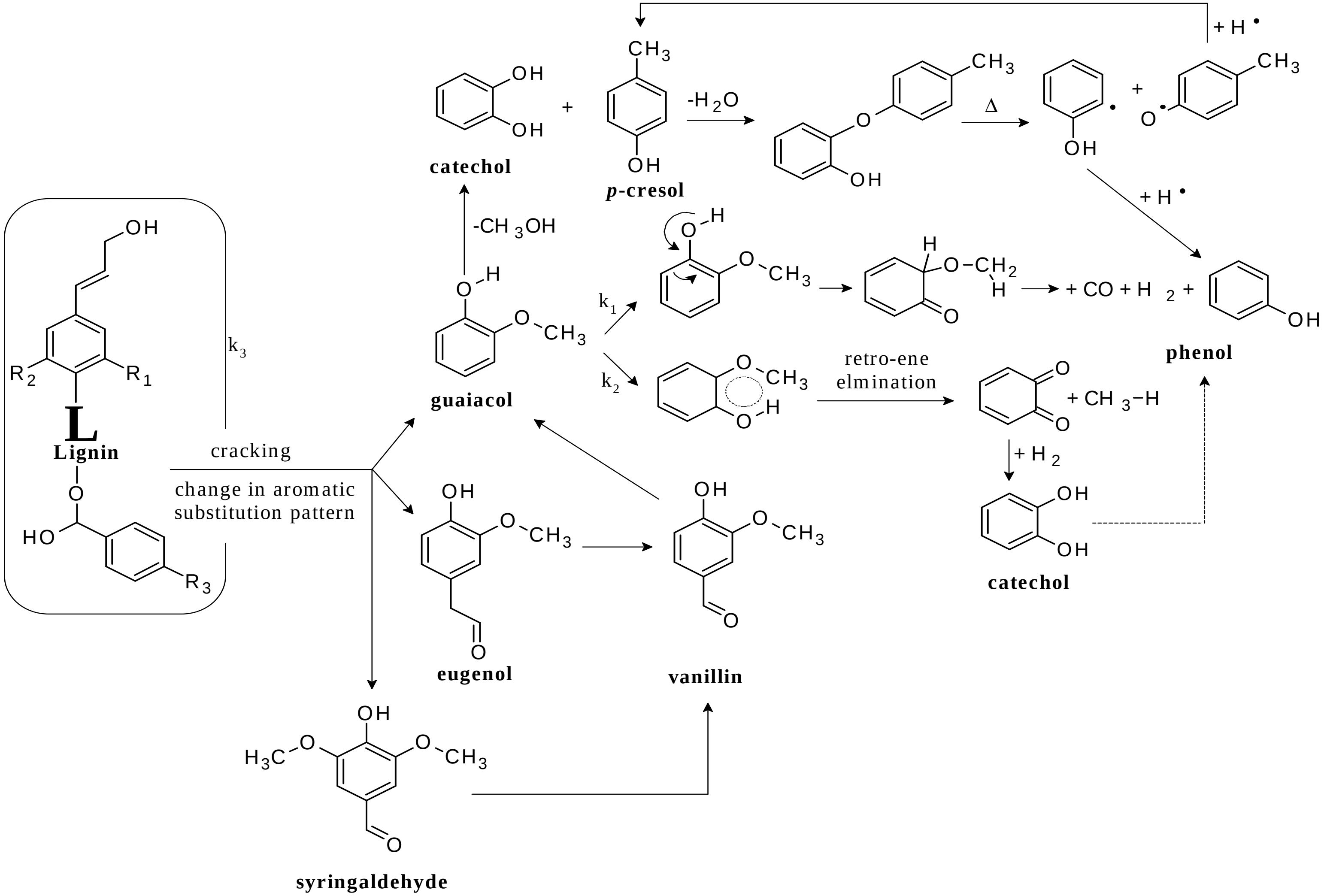


Figure 5.10 - Products from the Pyrolytic Decomposition of Lignin (adapted from Moldoveanu, 2010)

Table 5.4 - Mass balance for Fast and Slow Pyrolysis of Willow SRC (wt.% on dry basis)

| | Fast pyrolysis | | Slow pyrolysis | |
|---|---|---|---|---|
| Mass balance | | | | |
| | g | % | g | % |
| Biomass | 837.01 | | 57.68 | |
| **Char total** | 161.37 | **19.28** | 34.54 | **59.89** |
| **Bio-oil total** | 429.74 | **51.34** | 16.10 | **27.91** |
| Organics | 339.11 | 40.51 | 7.81 | 13.55 |
| Reaction water | 90.63 | 10.83 | 8.28 | 14.36 |
| **Gas total** | 168.67 | **19.89** | 5.92 | **10.26** |
| $H_2$ | 0.40 | 0.78 | 0.02 | 0.50 |
| CO | 65.65 | 9.22 | 1.57 | 3.26 |
| $CH_4$ | 5.88 | 1.45 | 0.31 | 1.11 |
| $CO_2$ | 86.22 | 7.71 | 3.63 | 4.79 |
| Ethene | 2.231 | 0.32 | 0.06 | 0.13 |
| Ethane | 0.33 | 0.16 | 0.09 | 0.18 |
| Propene | 3.35 | 0.19 | 0.08 | 0.11 |
| Propane | 1.82 | 0.04 | 0.08 | 0.11 |
| n-Butane | 2.78 | 0.02 | 0.07 | 0.07 |
| **Closure** | | **90.51** | | **98.06** |

Table 5.5 - Comparison of Laboratory Scale Fast and Slow Pyrolysis Bio-oil

| Retention time (min.) | Compound name | Fast pyrolysis | Slow pyrolysis |
|---|---|---|---|
| | | Peak area % | Peak area % |
| 6.67 | Acetic acid, anhydride with formic acid | - | 5.00 |
| 10.8 | Acetic acid | 20.42 | 5.10 |
| 11.6 | Acetic acid, methyl ester | 14.70 | 15.90 |
| 12.12 | 3-Hydroxy-2-butanone | 0.18 | - |
| 12.2 | 3-Hydroxy-2-butane | - | 8.03 |
| 13.46 | Furfural | 2.06 | 7.23 |
| 14.48 | 1,4-Dimethyl-pyrazole | 2.50 | - |
| 14.75 | 1,3-Cyclohexanediol | 1.90 | - |
| 15.05 | 2-Methyl-furan | 1.56 | - |
| 15.58 | Hexanoic acid | 0.61 | - |
| 16.22 | 1-(Acetyloxy)-2-propanone | 1.16 | - |
| 16.6 | 2-Furnamethanol | - | 2.95 |
| 16.61 | 2-Methyl-2-cyclopenten-1-one | 0.26 | - |
| 16.95 | 2-Methyl-propanoic acid | 0.43 | - |
| 17.42 | 2-Ethyl-3-methyl-2-pentanol | 0.05 | - |
| 17.73 | 2-Butenoic acid | 0.17 | - |
| 18.99 | 2-Hydroxy-2-cyclopenten-1-one | - | 4.00 |
| 19.2 | 4-Hydroxy-butanoic acid | 1.13 | - |
| 19.4 | 2- and/or 3-Methyl-2-cyclopenten-1-one | 0.70 | - |

|  |  |  |  |
|---|---|---|---|
| 19.48 | Dihydro-4-methyl-2(3H)-furanone and/or 2,4-dimethyl-cyclopentanone | - | 1.13 |
| 19.74 | Cyclopentanone | 1.95 | - |
| 19.9 | 3,4-Dimethyl-2-pentene | 0.43 | - |
| 20.86 | 4-Methyl-2-pentene | 0.64 | - |
| 21.6 | Phenol | 7.10 | 0.46 |
| 21.86 | 2-Hydroxy-3-methyl-2-cyclopenten-1-one | - | 3.89 |
| 22.48 | 2-Methoxy-phenol or/and menquinol | 1.54 | 0.63 |
| 22.99 | 2-Methyl-phenol | 0.27 | - |
| 23.16 | 2-(2-Propenyl)-furan | 0.33 | - |
| 23.9 | 3-Ethyl-2-hydroxy-2-cyclopenten-1-one and/or 3,4-dimethyl-2-hydroxy-cyclopenten-2-en-1-one | - | 1.21 |
| 24.39 | Maltol | 0.29 | 0.66 |
| 27.5 | 4-Ethly-2-methoxy-phenol | 0.30 | - |
| 28.33 | 2,3- and/or 3,4-Anhydrogalactosan | 0.70 | 0.57 |
| 28.73 | 1,4:3,6-Dianhydro-α-D-glucopyranose | - | 0.42 |
| 28.9 | 1-(2-Hydroxy-methylphenyl)-ethanone | 0.35 | - |
| 28.91 | 2-Methoxy-4-vinylphenol | - | 0.28 |
| 29.54 | Eugenol | 0.38 | - |
| 30.46 | 2,6-Dimethoxyphenol | 4.91 | 4.31 |
| 32.16 | 2-Methoxy-4-(1-propenyl)-phenol | 0.28 | 0.54 |
| 32.541 | 1,2,4-Trimethoxybenzene | 1.73 | 1.83 |
| 32.76 | Vanillin | 1.45 | 0.27 |
| 34.17 | 1,2,3-Trimethoxy-5-methyl-benzene | 0.41 | 0.98 |
| 34.64 | 1-(4-Hydroxy-3-methoxyphenyl)-ethanone | 0.87 | 0.23 |
| 35.58 | 2-Methoxy-4-propenyl-phenol | 0.23 | - |
| 35.89 | 2,6-Dimethoxy-4-(2-propenyl)-phenol | 0.37 | 0.52 |
| 35.9 | 2,5-Dimethoxy-ethylbenzene | 1.09 | 0.25 |
| 36.98 | 2,5-dimethoxy-4-ethylbenzaldehyde | - | 0.25 |
| 38.26 | 2,4,6-Trimethoxystyrene | - | 1.15 |
| 38.92 | 4-Hydroxy-3,5-dimethoxy-benzaldehyde | 1.20 | 0.70 |
| 40.33 | 1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone | 1.15 | 0.46 |
| 41.06 | 1-(2,4,6-Trihydroxyphenyl)-2-pentanone | 0.70 | 1.43 |
|  | Total (%) | 76.50 | 70.38 |

- Not detected

# 6 THE INFLUENCE OF HARVEST AND STORAGE ON THE FUEL PROPERTIES OF MISCANTHUS X GIGANTEUS

## 6.1 INTRODUCTION

This chapter investigates the fuel and chemical property variation associated with the time of crop harvest, duration of storage and location of storage.

The following was undertaken:

I. Analytical characterisation and comparison of pyrolysis products of samples from different harvests times, storage durations and storage locations;

II. Laboratory scale fast pyrolysis processing of samples from different harvest times, and a comparison of fast pyrolysis products and yields.

The perennial grass Miscanthus x giganteus was harvested at three different times as follows: early (September 2009), conventional (April 2010) and late (June 2010). Once harvested the crop was baled and stored. The thermochemical properties were investigated using a range of analytical equipment including thermogravimetric analysis (TGA) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). Fast pyrolysis processing was undertaken using a continuous fed fluidised bed reactor with a capacity of 300g/h.

## 6.2 RESULTS AND DISCUSSION

### 6.2.1 Harvest and Storage Results

The yield of *Miscanthus* at harvest is shown in Table. 6.1. In contrast to the late harvest, the early harvest was found to produce yields 18.2% higher. The moisture content of the conventional harvest was found to be the highest, and this is shown in Table 6.2. Moisture content is expected to be higher for the early harvest and lower for the late harvest. Weather conditions may be responsible for the high moisture content of the conventional harvest. The moisture content for the "after storage" samples were typically below 18% except for the early harvest shoulder sample (64.28%). This is believed to be as a result of direct contact between bales, causing moisture to accumulate within the shoulder region.

### 6.2.2 Elemental and Thermogravimetric Analysis

The elemental analysis for all samples is shown in Table 6.3. The H:C and O:C atomic ratios for all samples are shown on the Van Krevelen diagram in Figure 6.1. It can be clearly seen that by delaying the harvest time the O:C atomic ratio is reduced, and a more carbonaceous feedstock is produced. The H:C atomic ratio was found to mainly cluster between 1.47 and 1.51, and the O:C atomic ratio between 0.73 and 0.77. Coal typically has an atomic H:C ratio of 0.45 and O:C ratio of 0.05. Nitrogen and inorganic content (Ca, K, P and Mg) were found to decrease with delay of harvest. No clear trend could be seen for after storage bale sample zones. Inorganics content could transfer from the wheat bales placed above. The rate of transfer would be partly related to the rainfall over the storage duration. The shoulder region should be more susceptible because of close contact between bales and moist conditions.

Thermogravimetric analysis for all samples can be found in Table 6.4. Moisture content was found to decrease with increasing delay of harvest and no clear trend was seen with respect to after storage sample zones. Char, ash and fixed carbon content were highest during the early harvest, volatiles were found to increase with delay of harvest. The after storage late harvest centre sample was found to have a volatile content of 86.07% on dry basis, this is 9.65% higher than that attained from the early harvest centre sample (76.42%). The centre sample is thought to be representative of 85% of the bale, this is based on the shoulder and outside sample accommodating the outer 10 cm diameter of the bale. The temperature of the maximum rate of decomposition was found to be lowest for the late harvest samples (peak temperature $T_p$ between 303 and 315$^{o}$C). The higher and lower heating values for all samples can be found in Table 6.5. In general the heating values were found to increase with delay of harvest. The late harvest centre sample had the highest overall after storage heating value of 18.7 MJ/kg. For the early and conventional harvest the higher values were

Table 6.1 - Weather conditions, Harvest Times, Harvest Yields and Storage Durations for Miscanthus

| Year | 2009 | | | | | | 2010 | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Month | Jul | Aug | Sep | Oct | Nov | Dec | Jan | Feb | Mar | Apr | May | Jun | Jul | Aug |
| **Weather Conditions*** | | | | | | | | | | | | | | |
| Precipitation (mm) | 63 | 98 | 14 | 23 | 109 | 65 | 45 | 80 | 35 | 20 | 56 | 38 | 17 | 152 |
| Average temperature ($^{o}$C) | 17 | 18 | 15 | 12 | 9 | 3 | 1 | 3 | 6 | 9 | 11 | 15 | 18 | 16 |
| Average humidity (%) | 75 | 75 | 77 | 87 | 88 | 91 | 90 | 91 | 82 | 70 | 71 | 71 | 67 | 77 |
| **Harvest Time and Yields**** | | | | | | | | | | | | | | |
| Early harvest | ▨ | ▨ | ▨ | 9.45 t/ha | | | | | | | | | | |
| Conventional harvest | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | 8.86 t/ha | | | |
| Late harvest | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | 7.73 t/ha | | |
| **Storage Duration** | | | | | | | | | | | | | | |
| Early harvest | | | | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ |
| Conventional harvest | | | | | | | | | | | ▨ | ▨ | ▨ | ▨ |
| Late harvest | | | | | | | | | | | | ▨ | ▨ | ▨ |

*Woburn Experimental Farm [Meteorological data obtained from Met Office]

**dry weight “at harvest”

found to increase when comparing the “at harvest” with after storage “centre sample”. No differences were seen in the higher heating values between the late harvest “at harvest” and the after storage “centre sample”. The percentage content and standard deviation for all results from proximate and elemental analysis can be found in Table 6.6.

Table 6.2 - The Moisture Content of Miscanthus (After Harvest) Prior to Oven Drying

| | Moisture (wt.%) | | | | |
|---|---|---|---|---|---|
| | | After Storage | | | |
| Harvest | At Harvest | Centre | Shoulder | Outside | Whole Bale |
| Early | 22.57 | 15.44 | 64.28 | 5.89 | 16.18 |
| Conventional | 40.14 | 17.22 | 14.75 | 11.03 | 17.77 |
| Late | 9.77 | 13.94 | 12.64 | 10.21 | 11.56 |

### 6.2.3 Analytical Pyrolysis (Py-GC-MS)

Influence of harvest time on the pyrolytic decomposition products obtained from the “at harvest” and “after storage centre” samples can be found in Table 6.7. The pyrolysis products have been divided into the following categories: organic acids, alcohols, ketones, furans and phenols. A total is shown for each category. This is a sum of the relative peak area of each chemical compound within that category. Figure 6.2 shows the relative variation (ratio between selected key chemical categories and this is normalised to 100%) of this total for “at harvest” and “after storage centre” samples. It was found that the harvest time influenced mainly the alcohol content when comparing the early harvest (9.87%) with the conventional (22.64%) and late (21.07%) harvests. For the after storage samples the acid content was found to decrease with storage.

### 6.2.4 Fast Pyrolysis Processing

The 300 g/h fast pyrolysis continuous bubbling fluidised bed reactor was used to generate bio-oil from the early, conventional and late harvest. The typical sample mass of 120 grams was used for each fast pyrolysis experiment. The operating parameters and feedstock properties can be found in Table 6.8. The fast pyrolysis product yields and gas composition are shown in Table 6.9. Acceptable mass balance closures (>89%) were obtained for the early, conventional and late harvests. Losses in the mass balance are thought to be caused by errors in weight measurement, water content analysis, liquid holdup within the quench system and gas analysis errors caused by heavily diluted pyrolysis gases, with content of nitrogen above 97%.

The char content was found to be the same for all three harvest times, yielding around 34%. The late harvest had the highest overall bio-oil yield of 51.21% with the highest organic and reaction water content of 36.54% and 14.67%, respectively. Reaction water was found to be lowest in the early harvest (7.55%). Of the non-condensable gases investigated, methane and hydrogen were highest in the early and conventional harvest. The conventional harvest had the highest carbon monoxide yield and the early harvest had the highest carbon dioxide yield. The C2-C4 gas content was found to be very low in all three harvest samples and no clear differences could be seen.

The standard deviation and standard error were calculated from mean values obtained from the early harvest fast pyrolysis processing (Table 6.9). The standard deviation was found to be highest, showing the largest scatter from the mean, for the bio-oil and gas product yields. A high standard error was found for the same products and this is due to the interrelation between the standard deviation and standard error. A small standard error indicates that the calculated mean is relatively close to the true mean of the sample set. Causes for these errors are discussed in the discussion in Chapter 7.

Table 6.3 - Elemental Analysis of the Miscanthus At Harvest and Storage Samples

| | | daf (wt.%) | | | | (wt.%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Harvest | C | H | N | O* | Ca | K | Mg | Na | P | S |
| | **Early** | | | | | | | | | | |
| 1 | At harvest | 44.86 | 5.58 | 0.88 | 48.68 | 0.18 | 1.20 | 0.15 | - | 0.07 | 0.04 |
| 2 | Outside of bale | 43.42 | 5.13 | 1.46 | 49.99 | 0.29 | 1.64 | 0.16 | - | 0.10 | 0.06 |
| 3 | Shoulder of bale | 46.01 | 5.77 | 0.97 | 47.25 | 0.11 | 0.96 | 0.09 | - | 0.05 | 0.05 |
| 4 | Whole bale | 43.83 | 5.63 | 1.03 | 49.51 | 0.07 | 0.87 | 0.07 | 0.01 | 0.05 | 0.04 |
| 5 | Centre of bale | 43.15 | 5.55 | 0.98 | 50.32 | 0.11 | 1.05 | 0.07 | - | 0.06 | 0.04 |
| | **Conventional** | | | | | | | | | | |
| 6 | At Harvest | 46.58 | 5.80 | 0.36 | 47.26 | 0.09 | 0.71 | 0.08 | 0.01 | 0.03 | 0.03 |
| 7 | Outside of bale | 47.44 | 5.82 | 0.45 | 46.29 | 0.28 | 1.57 | 0.18 | - | 0.11 | 0.07 |
| 8 | Shoulder of bale | 46.20 | 5.76 | 0.52 | 47.52 | 0.12 | 0.54 | 0.08 | 0.01 | 0.03 | 0.03 |
| 9 | Whole bale | 44.51 | 5.53 | 0.33 | 49.63 | 0.06 | 0.60 | 0.06 | 0.01 | 0.04 | 0.03 |
| 10 | Centre of bale | 46.78 | 5.87 | 0.51 | 46.84 | 0.23 | 1.30 | 0.16 | - | 0.07 | 0.05 |
| | **Late** | | | | | | | | | | |
| 11 | At harvest | 47.48 | 5.86 | 0.27 | 46.39 | 0.07 | 0.66 | 0.09 | 0.01 | 0.02 | 0.03 |
| 12 | Outside of bale | 46.77 | 5.72 | 0.40 | 47.11 | 0.12 | 1.05 | 0.12 | - | 0.09 | 0.05 |
| 13 | Shoulder of bale | 46.90 | 5.82 | 0.49 | 46.79 | 0.28 | 1.37 | 0.21 | - | 0.08 | 0.06 |
| 14 | Whole bale | 47.12 | 5.86 | 0.22 | 46.80 | 0.11 | 0.71 | 0.09 | 0.01 | 0.04 | 0.03 |
| 15 | Centre of bale | 47.37 | 5.94 | 0.44 | 46.25 | 0.11 | 0.59 | 0.08 | 0.01 | 0.03 | 0.04 |

$^{daf}$ dry ash free; * by difference

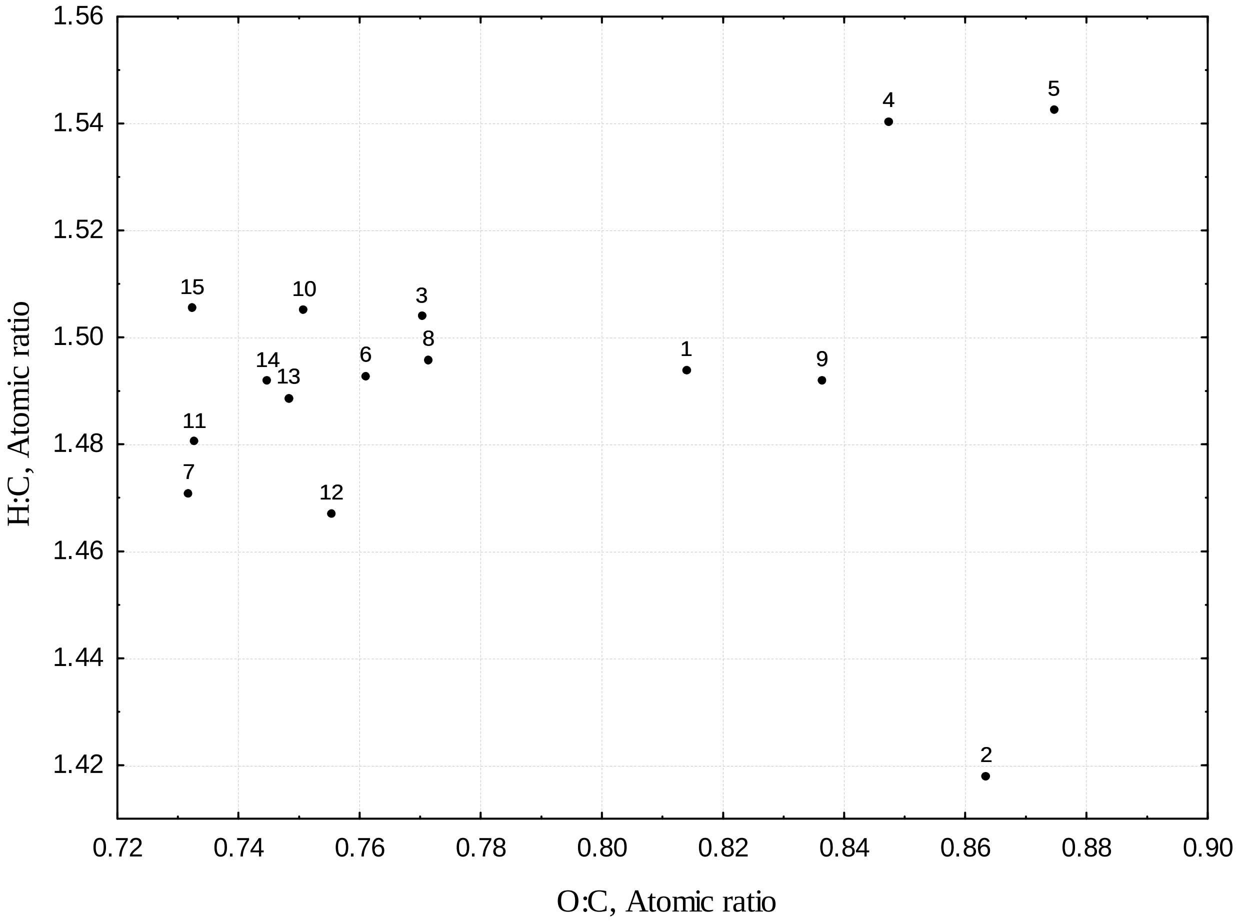


Figure 6.1 - H:C and O:C Atomic Ratios

Miscanthus sample numbers 1-15 (see Table 6.4 for number identification)

Table 6.4 - Thermogravimetric analysis of the Miscanthus At Harvest and Storage Samples

| | | TGA Pyrolysis Experiment | | | | | TGA Ashing Experiment | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Moisture | Volatiles $^{(d.b)}$ | Char $^{(d.b)}$ | $T_p$ | max. (*dx*/*dt*) | Ash $^{(d.b)}$ | Fixed Carbon $^{(d.b)}$ | $T_p$ | max. (*dx*/*dt*) |
| | | wt.% | | | °C | %/min. | wt.% | | °C | %/min. |
| Sample No. | **Early Harvest** | | | | | | | | | |
| 1 | At harvest | 6.05 | 76.68 | 23.32 | 321.70 | 3.93 | 4.25 | 19.07 | 384.10 | 2.07 |
| 2 | Outside of bale | 7.36 | 79.31 | 20.69 | 320.20 | 2.75 | 8.60 | 12.09 | 414.50 | 1.29 |
| 3 | Shoulder of bale | 6.35 | 84.30 | 15.70 | 328.40 | 3.60 | 3.61 | 12.09 | 394.60 | 1.93 |
| 4 | Whole bale | 6.48 | 87.16 | 12.84 | 314.20 | 4.39 | 5.64 | 7.20 | 378.10 | 1.88 |
| 5 | Centre of bale | 6.18 | 76.42 | 23.58 | 319.80 | 4.18 | 6.23 | 17.35 | 380.80 | 2.05 |
| | **Conventional Harvest** | | | | | | | | | |
| 6 | At harvest | 4.87 | 84.18 | 15.82 | 326.50 | 3.93 | 2.12 | 13.69 | 415.20 | 4.46 |
| 7 | Outside of bale | 5.13 | 81.81 | 18.19 | 321.90 | 4.49 | 1.05 | 17.14 | 433.10 | 4.17 |
| 8 | Shoulder of bale | 5.46 | 81.00 | 19.00 | 333.10 | 3.69 | 3.52 | 15.48 | 409.70 | 3.85 |
| 9 | Whole bale | 6.22 | 85.76 | 14.24 | 321.90 | 4.32 | 2.82 | 11.42 | 428.80 | 3.89 |
| 10 | Centre of bale | 5.44 | 79.3 | 20.70 | 328.10 | 4.45 | 2.49 | 18.21 | 434.30 | 4.64 |
| | **Late Harvest** | | | | | | | | | |
| 11 | At harvest | 5.27 | 90.90 | 9.10 | 313.00 | 2.28 | 1.87 | 7.23 | 277.90 | 2.33 |
| 12 | Outside of bale | 5.00 | 85.13 | 14.87 | 303.40 | 2.43 | 2.58 | 12.29 | 273.50 | 2.48 |
| 13 | Shoulder of bale | 5.10 | 86.93 | 13.07 | 306.30 | 2.35 | 2.36 | 10.71 | 274.80 | 2.51 |
| 14 | Whole bale | 5.62 | 81.93 | 18.07 | 305.40 | 2.57 | 2.66 | 15.41 | 273.80 | 2.52 |
| 15 | Centre of bale | 5.30 | 86.07 | 13.93 | 315.10 | 2.30 | 2.02 | 11.92 | 277.40 | 2.34 |

d.b - dry basis; Tp - Temperature at maximum (dx/dt)

Table 6.5 - Higher (HHV) and Lower (LHV) Heating Values of the Miscanthus At Harvest and Storage Samples

|  |  |  | HHV | LHV |
|---|---|---|---|---|
| Plot | Sample No. | Location | (MJ/kg) |  |
| **Early Harvest** | 1 | At harvest | 16.9 | 15.6 |
|  | 2 | Outside | 15.5 | 14.4 |
|  | 3 | Shoulder | 17.7 | 16.4 |
|  | 4 | Whole bale | 16.4 | 15.1 |
|  | 5 | Centre | 16.1 | 14.8 |
| **Conventional Harvest** | 6 | At harvest | 17.9 | 16.7 |
|  | 7 | Outside | 18.3 | 17.0 |
|  | 8 | Shoulder | 17.6 | 16.4 |
|  | 9 | Whole bale | 16.6 | 15.4 |
|  | 10 | Centre | 18.1 | 16.8 |
| **Late Harvest** | 11 | At harvest | 18.7 | 17.4 |
|  | 12 | Outside | 18.1 | 16.9 |
|  | 13 | Shoulder | 18.3 | 17.1 |
|  | 14 | Whole bale | 18.5 | 17.2 |
|  | 15 | Centre | 18.7 | 17.4 |

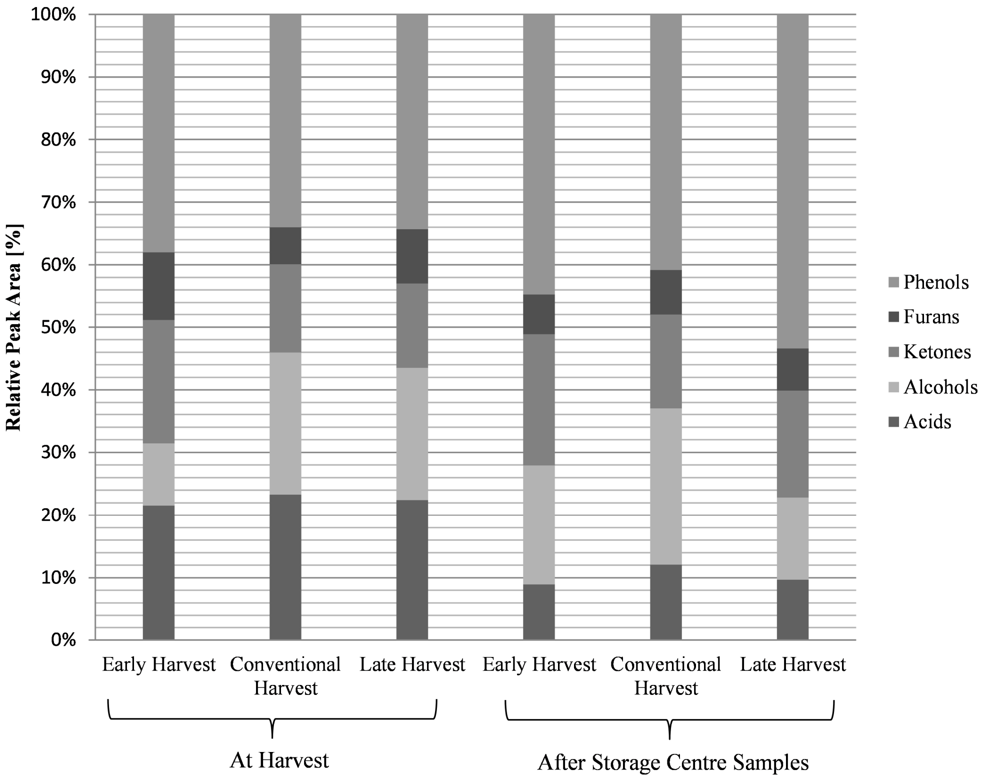


Figure 6.2 - Relative Peak Area Comparison Between “At Harvest” and “After Storage Centre” Samples

### 6.2.5 Liquid Analysis (GC-MS)

The bio-oil produced was analysed by gas chromatography with mass spectrometry detection (GC-MS). The chromatograms and a relative peak area comparison can be seen for each harvest in Figure 6.3, Figure 6.4 Figure 6.5 and Figure 6.6 respectively. Major differences were found when comparing the chemical content of the early with the late harvest. The early harvest was found to have high levels of 4-hydroxy-butanoic acid and phenol content while the late harvest was seen to have high levels of methylbenzaldehyde, 1,2-benzenediol and levoglucosan. Nowakowski et al. (2007) investigated the impact of catalysts on the thermal breakdown of biomass, finding that inorganic content in biomass favoured production of hydroxyacetaldehye (heterolytic mechanism of cellulose pyrolytic decomposition), whereas washed biomass (removal of majority of the metals) favoured production of levoglucosan (homolytic mechanism of cellulose pyrolytic decomposition). This may be an indication why levoglucosan content is found to increase with delayed harvest. The conventional harvest did not show major differences in the content of 3-methyl-1,2-cyclopentanedione and 2-methoxy-phenol. Results from this chapter are further discussed in Chapters 7 and 8.

Table 6.6 - Percentage content variation and the standard deviation for all samples.

| | Mean | Minimum | Maximum | |
|---|---|---|---|---|
| | | (wt. %) | | Std. dev. |
| **Proximate Analysis** | | | | |
| Volatiles$^{(d.b)}$ | 83.66 | 76.42 | 90.90 | 4.11 |
| Fixed Carbon $^{(d.b)}$ | 13.15 | 7.23 | 19.07 | 3.66 |
| Ash $^{(d.b)}$ | 4.83 | 1.05 | 8.60 | 1.99 |
| **Ultimate Analysis** | | | | |
| $C^{daf}$ | 45.90 | 43.15 | 47.48 | 1.53 |
| $O^{daf}$* | 47.78 | 46.25 | 50.32 | 1.44 |
| $N^{daf}$ | 0.62 | 0.22 | 1.45 | 0.35 |
| $H^{daf}$ | 5.71 | 5.13 | 5.94 | 0.2 |
| **Inorganics** | | | | |
| K | 0.99 | 0.54 | 1.64 | 0.36 |
| N | 0.62 | 0.22 | 1.45 | 0.35 |
| H | 5.71 | 5.13 | 5.94 | 0.20 |
| Ca | 0.15 | 0.06 | 0.29 | 0.08 |
| Mg | 0.11 | 0.06 | 0.21 | 0.05 |
| P | 0.06 | 0.02 | 0.11 | 0.03 |
| S | 0.04 | 0.03 | 0.07 | 0.01 |

d.b dry basis; $^{daf}$ dry ash, * oxygen by difference free

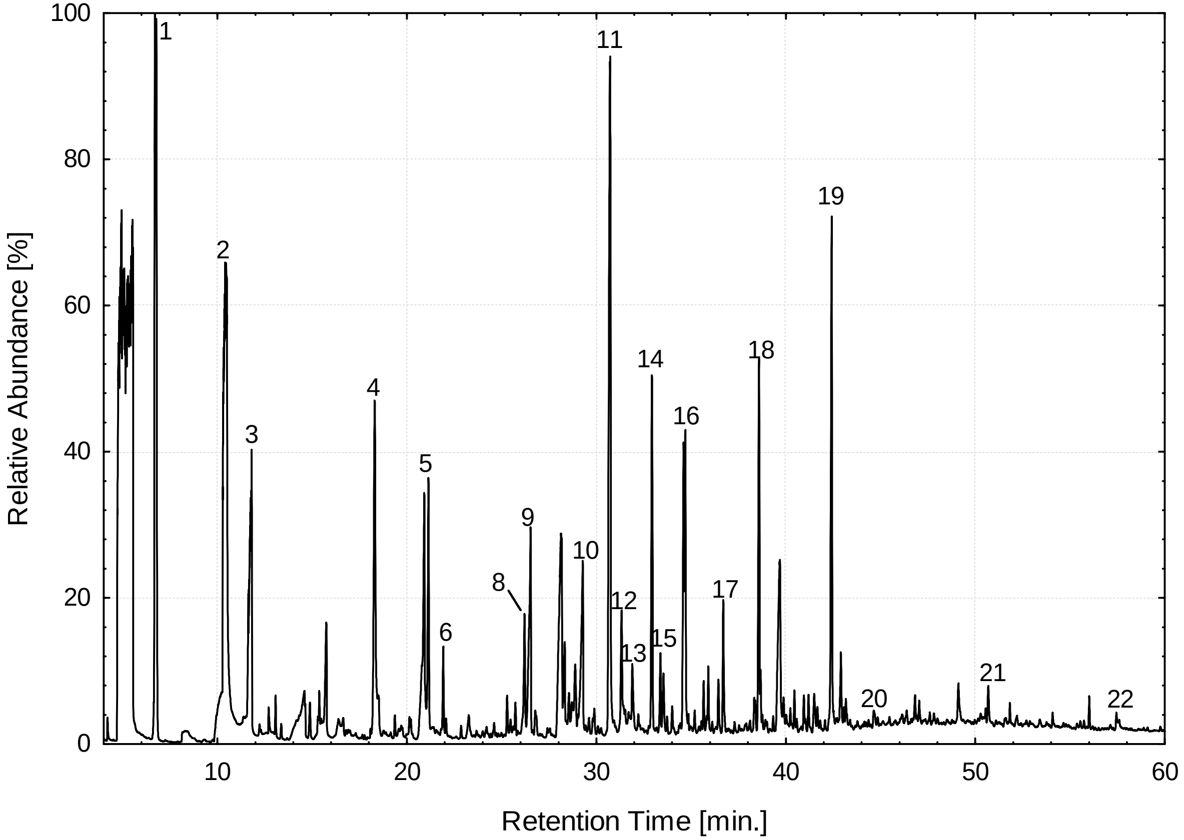


Figure 6.3 - Fast Pyrolysis Bio-oil Liquid Analysis – Miscanthus Early Harvest

1) Acetic acid, anhydride with formic acid; 2) Acetic acid; 3) Acetic acid, methyl ester; 4) Furfural; 5) 1-(Acetyloxy)-2-propanone; 6) 1-(2-Furanyl)-ethanone; 7) 2,5 Diethoxytetrahydro-furan; 8) 2-Methyl-2-cyclopenten-1-one; 9) 4-Hydroxy-butanoic acid; 10) 3-Methyl-1,2-cyclopentanedione; 11) Phenol; 12) 2-Methoxy-phenol or/and menquinol; 13) 1-Ethyl-cyclohexene; 14) 2-Methyl-phenol; 15) 3-Ethyl-2-hydroxy-2-cyclopentene-1-one; 16) 4-Methyl-phenol; 17) 2,3-Dimethyl-phenol; 18) 3,5-Dimethyl-phenol; 19) 2- or/and 3- or/and 4-Methylbenzaldehyde; 20) 1,2-Benzenediol; 21) 2-Methyl-1,3-benzenediol; 22) Levoglucosan.

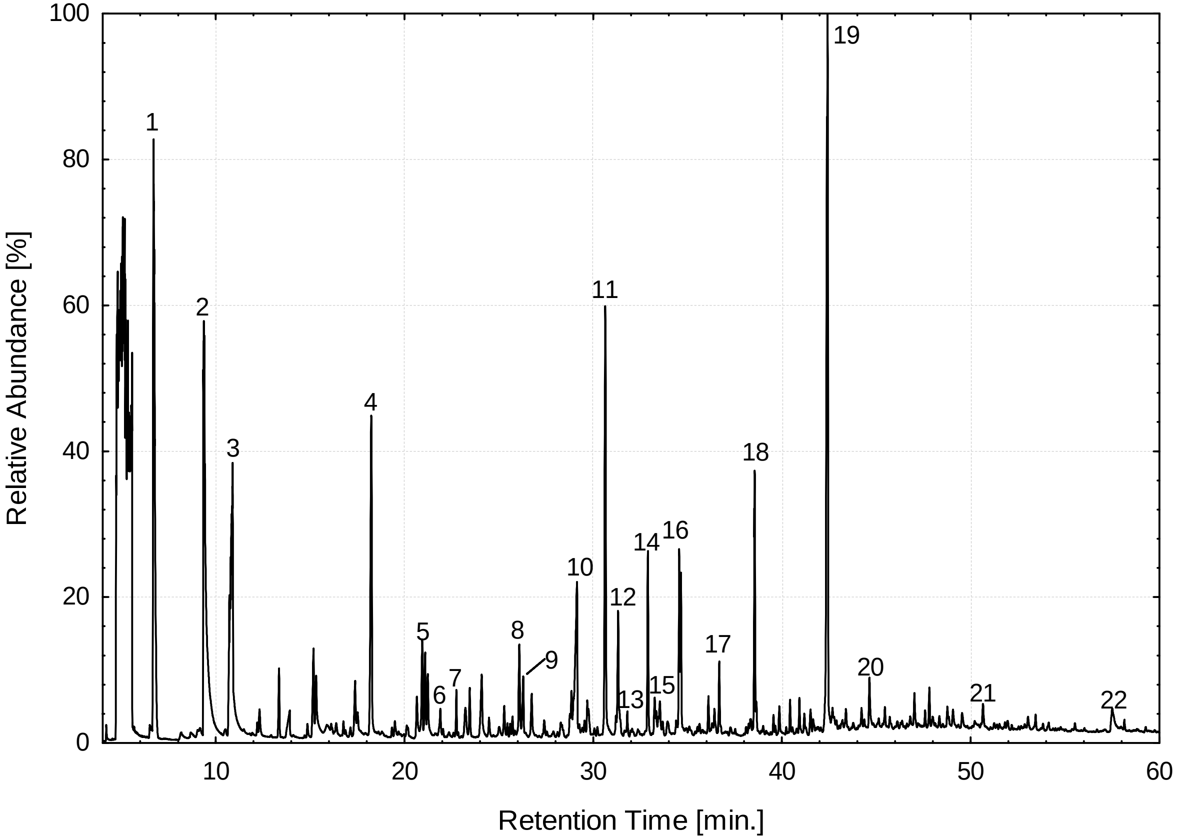
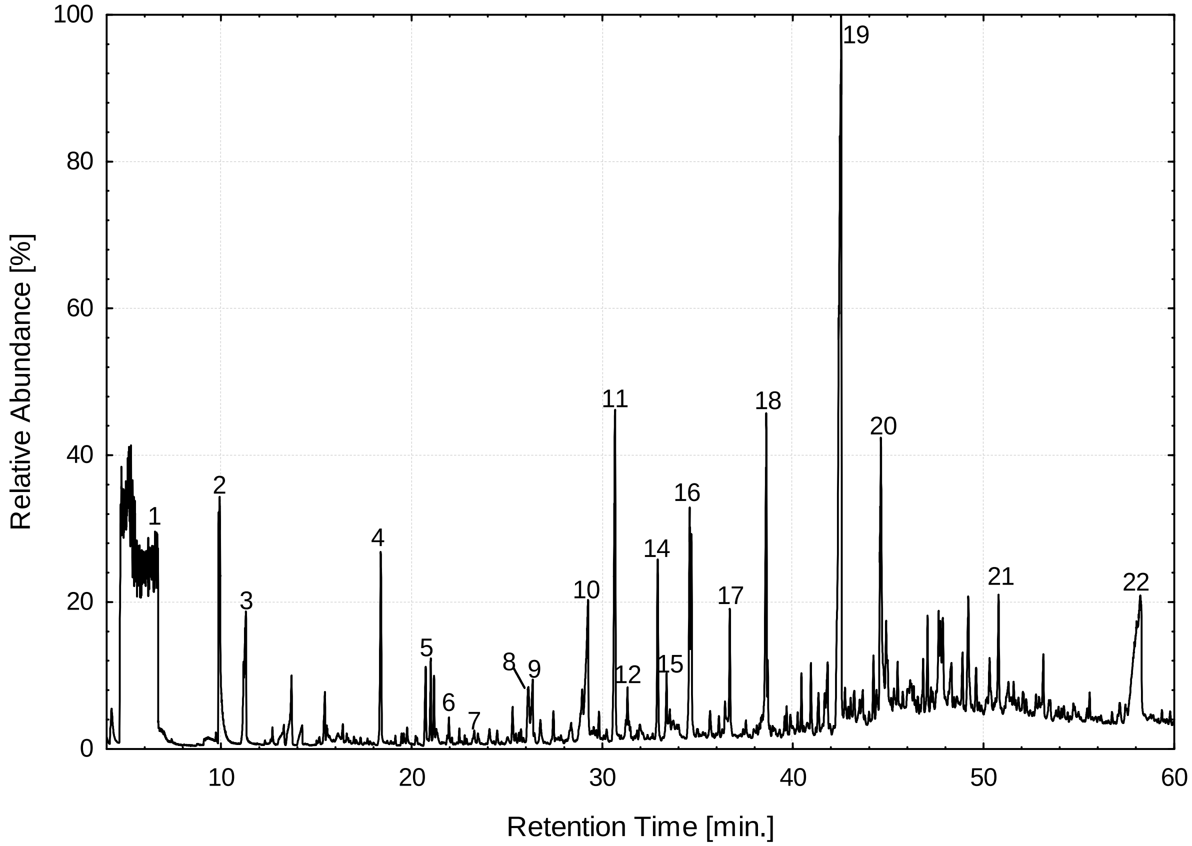


Figure 6.4 - Fast Pyrolysis Bio-oil Analysis – Miscanthus Conventional Harvest

(peak numbers identification see Figure 6.3 caption)



Late Harvest

Figure 6.5 - Fast Pyrolysis Bio-oil Analysis – Miscanthus Late Harvest

(peak numbers identification see Figure 6.3 caption)

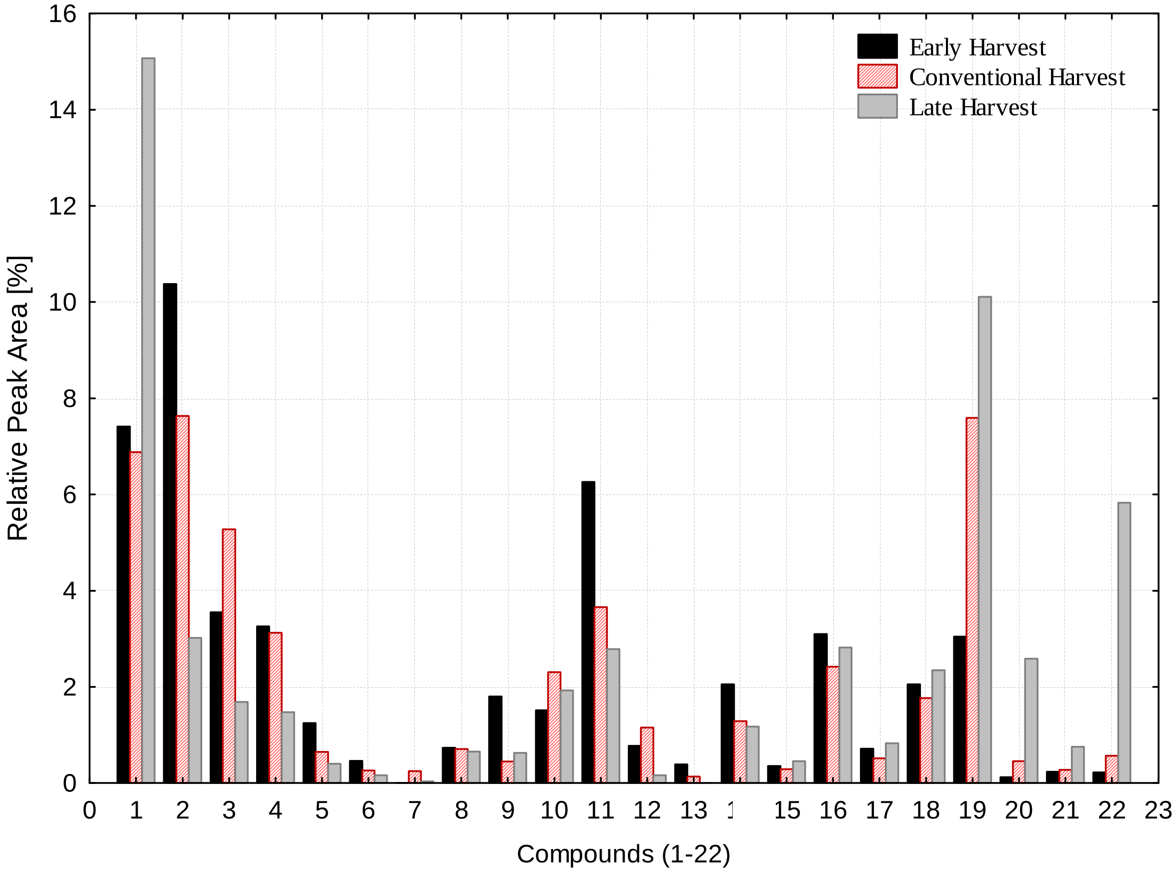


Figure 6.6 - Bio-oil Analysis for the Miscanthus Early, Conventional and Late Harvests

1) Acetic acid, anhydride with formic acid; 2) Acetic acid; 3) Acetic acid, methyl ester; 4) Furfural;5) 1-(Acetyloxy)-2-propanone; 6) 1-(2-Furanyl)-ethanone;7) 2,5 Diethoxytetrahydro-furan;8) 2-Methyl-2-cyclopenten-1-one; 9) 4-Hydroxy-butanoic acid; 10) 3-Methyl-1,2-cyclopentanedione; 11) Phenol; 12) 2-Methoxy-phenol or/and menquinol; 13) 1-Ethyl-cyclohexene; 14) 2-Methyl-phenol; 15) 3-Ethyl-2-hydroxy-2-cyclopentene-1-one; 16) 4-Methyl-phenol; 17) 2,3-Dimethyl-phenol; 18) 3,5-Dimethyl-phenol; 19) 2- or/and 3- or/and 4-Methylbenzaldehyde; 20) 1,2-Benzenediol;21) 2-Methyl-1,3-benzenediol; 22) Levoglucosan.

Table 6.7 - Py-GC-MS Relative Peak Area Comparison of the Miscanthus At Harvest and Storage Samples

| | Relative peak area (%) | | | | | |
|---|---|---|---|---|---|---|
| | At harvest | | | After storage centre samples | | |
| | Early harvest | Conventional harvest | Late harvest | Early harvest | Conventional harvest | Late harvest |
| ***Acids*** | | | | | | |
| Acetic acid | 7.33 | 7.03 | 8.63 | 1.81 | 2.80 | 3.16 |
| Acetic acid, anhydride with formic acid | 2.85 | 1.80 | 2.31 | 1.32 | 3.05 | 1.85 |
| 2-Methyl-2-pentenoic acid | 0.44 | n.d. | n.d. | 0.12 | 0.15 | 0.32 |
| **Total** | **10.62** | **8.83** | **10.94** | **3.25** | **6.00** | **5.33** |
| ***Alcohols*** | | | | | | |
| 1,2-Benzenedimethanol | 4.01 | 7.77 | 9.42 | 6.04 | 11.79 | 6.50 |
| Desaspidinol | 0.85 | 0.80 | 0.86 | 0.83 | 0.57 | 0.70 |
| **Total** | **4.86** | **8.57** | **10.28** | **6.87** | **12.36** | **7.20** |
| ***Ketones*** | | | | | | |
| 2,3-Pentanedione | 1.42 | 0.31 | 0.34 | 0.29 | 0.44 | 0.37 |
| 2-Methly-2-cyclopenten-1-one | 0.44 | 0.36 | 0.49 | 0.25 | 0.33 | 0.30 |
| Cyclopentanone | 0.68 | 0.19 | 0.22 | 0.85 | 0.05 | 0.19 |
| 1,3-Cyclopentanedione | 1.84 | 2.44 | 2.96 | 1.88 | 3.25 | 3.65 |
| 3-Methyl,2-cyclopenten-1-one | 0.75 | 0.17 | 0.21 | 0.13 | 0.16 | 0.14 |
| 3,4-Dihydroxy-3-cyclobutene-1,2-dione | 1.12 | 0.67 | 1.40 | 0.66 | 1.57 | 1.57 |
| 2-Hydroxy-3-methyl-2-cyclopenten-1-one | 1.08 | 0.09 | 0.03 | 1.29 | 0.06 | 1.39 |
| 2,3-Dimethyl-2-cyclopenten-1-one | 0.23 | 0.08 | n.d. | 0.11 | 0.10 | 0.02 |
| 1-(4-Hydroxy-3-methoxyphenyl)-ethanone | 0.42 | 0.16 | 0.13 | 0.74 | 0.44 | 0.52 |
| 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone | 1.72 | 0.88 | 0.81 | 1.37 | 1.02 | 1.20 |
| **Total** | **9.70** | **5.35** | **6.59** | **7.57** | **7.42** | **9.35** |

| | | | | | | |
|---|---|---|---|---|---|---|
| ***Furans*** | | | | | | |
| Furfural [R] | 1.58 | 1.59 | 2.30 | 1.22 | 2.14 | 2.12 |
| 2-Furanmethanol [R] | 1.05 | 0.37 | 1.15 | 0.62 | 0.96 | 1.18 |
| 2,3-Dihydro-2,5-dimethyl-furan | 0.71 | 0.04 | 0.57 | 0.14 | 0.05 | 0.22 |
| Tetrahydro-2-furanmethanol | 1.63 | n.d. | n.d. | 0.17 | 0.15 | 0.18 |
| 3-Methyl-2,4(3H,5H)-furandione | 0.38 | 0.23 | 0.21 | 0.18 | 0.26 | 0.01 |
| **Total** | **5.35** | **2.23** | **4.23** | **2.33** | **3.56** | **3.71** |
| ***Phenols*** | | | | | | |
| 4-Ethylphenol | 1.00 | 0.07 | 0.06 | 0.90 | 0.85 | 0.88 |
| 2/3 - Methylphenol | 0.58 | 0.53 | 0.15 | 0.46 | 0.13 | 0.06 |
| 4-Methylphenol | 0.75 | 2.31 | 2.61 | 2.87 | 3.51 | 4.39 |
| 2-Methoxyphenol [R] | 1.86 | 0.48 | 0.46 | 0.26 | 0.59 | 0.22 |
| Phenol [R] | 0.74 | 0.53 | 0.35 | 0.97 | 0.70 | 1.03 |
| 2-Methoxy-4-methylphenol [R] | 1.63 | 0.35 | 0.28 | 0.24 | 0.11 | n.d. |
| 1,2-Benzenediol [R] | 1.14 | n.d. | n.d. | 0.21 | n.d. | n.d. |
| 3-Methoxy-1,2-benzenediol [R] | 0.57 | 0.07 | 0.47 | 0.18 | 0.22 | 0.17 |
| 4-Ethyl-2-methoxyphenol | 0.78 | 0.38 | 0.70 | 0.93 | 0.37 | 0.97 |
| 2-Methoxy-4-vinylphenol [R] | 3.80 | 4.22 | 5.21 | 5.57 | 8.35 | 8.97 |
| 2,6-Dimethoxyphenol | 2.24 | 2.81 | 3.44 | 2.76 | 5.00 | 6.01 |
| 2-Methoxy-6-(2-propenyl)-phenol | 1.31 | 0.44 | 0.40 | 0.30 | 0.18 | 2.33 |
| 4-(3-Hydroxy-1-propenyl)-2-methoxy-phenol | 1.04 | 0.45 | 0.29 | 0.32 | 0.12 | 0.63 |
| 2,6-Dimethoxy-4-(2-propenyl)-phenol | 1.27 | 0.24 | 2.33 | 0.21 | 0.10 | 3.65 |
| **Total** | **18.71** | **12.88** | **16.75** | **16.18** | **20.23** | **29.31** |

n.d. –not detected, R: Reference compound used to verify identified compound.

Table 6.8 - Fast Pyrolysis Processing Conditions using the 0.3 kg/h Reactor

| | Harvest time | | | | | | |
|---|---|---|---|---|---|---|---|
| | Early | | | Conventional | | Late | |
| Biomass particle size (mm) | 0.25-1.00 | 0.25-1.00 | 0.25-1.00 | 0.25-1.00 | 0.25-1.00 | 0.25-1.00 | 0.25-1.00 |
| Average pyrolysis temperature ($^{o}C$) | 483 | 495 | 505 | 504 | 498 | 477 | 480 |
| Run time (min.) | 60 | 50 | 45 | 50 | 46 | 42 | 35 |
| Biomass moisture content (%) | 9.22 | 9.22 | 10.23 | 5.82 | 5.82 | 4.8 | 4.8 |
| Hot vapour residence time (s) | < 1.5 | < 1.5 | < 1.5 | < 1.5 | < 1.5 | < 1.5 | < 1.5 |

Table 6.9 - Fast Pyrolysis Product Yields for the Three Miscanthus Harvest Times (wt.% on dry basis) using the 0.3 kg/h Reactor

| | **Harvest time** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Early (wt.%) | | | | | | Conventional (wt.%) | | | Late (wt.%) | | |
| | | | | mean | SD | SE | | | mean | | | mean |
| **Char** | **34.27** | **33.56** | **31.25** | **33.03** | **1.29** | **0.74** | **34.04** | **30.78** | **32.41** | **34.01** | **33.68** | **33.85** |
| **Bio-oil** | **41.22** | **39.78** | **37.25** | **39.42** | **1.64** | **0.95** | **46.05** | **44.26** | **45.16** | **51.21** | **48.52** | **49.87** |
| Organics | 33.67 | 31.41 | 30.42 | 31.83 | 1.36 | 0.79 | 33.13 | 34.75 | **33.94** | 36.54 | 36.99 | **36.77** |
| Reaction $H_2O$ | 7.55 | 8.37 | 6.83 | 7.58 | 0.63 | 0.36 | 12.92 | 9.51 | **11.22** | 14.67 | 11.53 | **13.10** |
| **Gas** | **13.87** | **15.23** | **18.23** | **15.78** | **1.82** | **1.05** | **18.03** | **16.23** | **17.13** | **6.39** | **7.56** | **6.98** |
| $H_2$ | 2.44 | 2.50 | 2.60 | 2.51 | 0.07 | 0.04 | 1.88 | 1.62 | 1.75 | 1.12 | 1.29 | 1.21 |
| CO | 4.40 | 5.15 | 7.26 | 5.60 | 1.21 | 0.70 | 8.84 | 7.95 | 8.40 | 2.85 | 2.96 | 2.91 |
| $CO_2$ | 4.80 | 4.98 | 5.64 | 5.14 | 0.36 | 0.21 | 4.55 | 4.17 | 4.36 | 0.95 | 0.84 | 0.90 |
| Methane | 1.49 | 1.68 | 1.78 | 1.65 | 0.12 | 0.07 | 2.26 | 2.10 | 2.18 | 1.14 | 2.10 | 1.62 |
| Ethene | 0.26 | 0.30 | 0.26 | 0.27 | 0.02 | 0.01 | 0.22 | 0.19 | 0.21 | 0.06 | 0.09 | 0.08 |
| Ethane | 0.29 | 0.21 | 0.25 | 0.25 | 0.03 | 0.02 | 0.12 | 0.10 | 0.11 | 0.20 | 0.24 | 0.22 |
| Propene | 0.14 | 0.20 | 0.25 | 0.20 | 0.04 | 0.03 | 0.11 | 0.08 | 0.10 | 0.05 | 0.02 | 0.04 |
| Propane | 0.04 | 0.20 | 0.18 | 0.14 | 0.07 | 0.04 | 0.02 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 |
| n-Butane | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.03 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 |
| **Total** | **89.36** | **88.57** | **86.73** | **88.22** | **1.10** | **0.64** | **98.12** | **91.27** | **94.70** | **91.61** | **89.76** | **90.69** |

Table 6.10 - Dry yields at Harvest and Potential Fast Pyrolysis Yields for Miscanthus

| | "At harvest" (dry t/ha) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Early | | | | | | Conventional | | | Late | | |
| | | | | Mean | SD | SE | | | Mean | | | Mean |
| Crop yield | 9.45 | 9.45 | 9.45 | | | | 8.86 | 8.86 | | 7.73 | 7.73 | |
| Bio-oil (organics and reaction water) | 3.90 | 3.76 | 3.52 | 3.72 | 0.16 | 0.09 | 4.08 | 3.92 | 4.00 | 3.96 | 3.75 | 3.85 |
| Organics | 3.18 | 2.97 | 2.87 | 3.01 | 0.13 | 0.07 | 2.94 | 3.08 | 3.01 | 2.82 | 2.86 | 2.84 |
| Reaction Water | 0.71 | 0.79 | 0.65 | 0.72 | 0.06 | 0.03 | 1.14 | 0.84 | 0.99 | 1.13 | 0.89 | 1.01 |
| Char | 3.24 | 3.17 | 2.95 | 3.12 | 0.12 | 0.07 | 3.02 | 2.73 | 2.87 | 2.63 | 2.60 | 2.62 |
| Gases | 1.31 | 1.44 | 1.72 | 1.49 | 0.17 | 0.10 | 1.60 | 1.44 | 1.52 | 0.49 | 0.58 | 0.54 |

# 7 GENERAL DISCUSSION AND LIMITATIONS

The aim of this chapter is to discuss the experimental findings, their implications and to acknowledge the limitations of the experimental work carried out. To address this fully, the thesis objectives are reiterated, together with the initial research gaps found in the literature review, reported in Chapter 2. The underlying purpose of all experiments undertaken in this work is to investigate the impact of the fast pyrolysis process for different feedstocks, the implications of selective pyrolysis, crop harvest time and storage on the thermal decomposition products and their properties, and to develop, where possible, a better understanding of the process in order to optimise the products derived from various types of biomass.

## 7.1 DISCUSSION AND IMPLICATIONS OF FINDINGS

This section summarises the reasoning behind each of the objectives of the reported research, discusses how the findings address each objective and what their implications are.

**[I]. Characterise and conduct laboratory-scale fast pyrolysis processing on feedstocks available for this work, and compare their products and yields;**

From the feedstocks available to the project (wheat straw, switch grass, miscanthus, willow SRC and beech wood), it was found from the literature review that a more accurate comparison of these feedstocks is required to better assess and compare their potential for use as renewable fuels and chemicals. It was found that few studies had investigated the key light and medium volatile decomposition products found in these feedstocks or had compared the fast pyrolysis yields and products using the same laboratory processing equipment and operating parameters. It was expected that this type of investigation would contribute to existing knowledge of crop pyrolysis yields and products, and provide a better comparison between the different feedstocks and their potential for further upgrading. It would also better the understanding of the possible industrial implications of fast pyrolysis of these feedstocks as a conversion technology for energy and chemical products. Based on these observations the following experimental work was undertaken:

1. Analytical characterisation and comparison of pyrolysis products;
2. Semi- quantification by Py-GC-MS of potential key light and medium volatile decomposition products, under simulated fast pyrolysis heating rates;
3. Laboratory-scale fast pyrolysis processing using a continuously fed bubbling fluidised bed reactor (with a capacity of 1 kg/h), and a comparison of products and yields.

### Response to Objectives [I]:

Biomass characterisation was carried out to compare straws, perennial grasses and hardwoods commonly found in the UK. Straw is well suited for renewable energy use because of its low cost and high abundance (DEFRA, 2010; Scarlat et al., 2010). Nevertheless there are a number of draw-backs associated with use of straws in comparison to perennial grasses and the hardwood willow SRC. The main drawback appears to be associated with harvest time. This is because, unlike the perennial grasses or the hardwood willow SRC, harvest time cannot be varied because of the need to recover seeds or grain for the crop's primary use.

From the ultimate and calorific analysis, it was found that hardwoods have a higher calorific value (HHV of willow SRC: 19.06 MJ/kg; beech wood: 20.55 MJ/kg), and this is due to their higher carbon and lower ash content. The ash content reduces the calorific value because of its non-combustible nature. The volatile matter, investigated using thermogravimetric analysis, was seen to be highest on dry basis for beech wood (85.89 wt.%) and switch grass (83.23 wt.%) and lowest for miscanthus (75.62 wt.%). The high volatile content is related to the reduced char content found in switch grass and beech wood. Char content is a combination of fixed carbon and ash. Fixed carbon is the solid combustible material remaining after the removal of ash, moisture and volatiles. The fixed carbon content was calculated (by difference) to be highest in miscanthus (19.92 wt.%) and lowest for switch grass (11.04 wt.%) and beech wood (13.15 wt.%). The high fixed carbon content found in miscanthus should produce a char with a high calorific value; when comparing fast pyrolysis chars obtained from wheat straw and switch grass. The inorganic content found in these feedstocks varied considerably. Willow SRC had a higher inorganic content in comparison to beech wood, and this can be explained by its shorter growth periods and higher fertiliser inputs. Switch grass was found to contain low levels of inorganics overall, but ash content was found to be similar to those observed in miscanthus and wheat straw. This is thought to be a consequence of the high silica content, not investigated here, found in the perennial grass switch grass (Pimentel, 2008). Miscanthus was found to have the highest potassium content (1.20 wt.%), this is related to the time of harvest and fertiliser treatment to the crop. Yates and Riche (2007) investigated the impact of harvest time, and their reported findings indicate that the early harvest of the crop has a noticeable impact on the inorganic content. Miscanthus used here was harvested early, prior to the crop senescing, and this is a possible cause for the high potassium content found in this feedstock. The impact of harvest time is discussed later in this chapter. Additionally, dust and soil adhesion to the crop during harvesting, storage and relocation could alter the inorganic content further, because of inorganics present in the soil.

From thermogravimetric studies, it was found that the compositional content of the crop (cellulose, hemicellulose, lignin and inorganics) influence the shape and temperature of the main decomposition region (rate of maximum decomposition) on the decomposition profile. The main decomposition region (for the pyrolysis profiles) for all crops investigated was found to fall between 339 and 392°C. The rate of decomposition was seen to be lowest for the hard woods (willow SRC: 13 %/min.; beech wood: 9 %/min.) and highest for the perennial grasses (miscanthus: 23 %/min.; switch grass: 20 %/min.). The rate of decomposition is reflective of the thermal reactivity of the crop, and the catalytic impact of potassium (investigated by Fluentes et al. (2008)), and is thought to be a major contributor to the maximum decomposition rate, and its respective temperature. This is a probable cause for the high decomposition rate and temperature of occurrence observed in miscanthus. A shoulder like feature was seen for switch grass, and this is thought to represent the hemicellulose content in the crop. Switch grass was reported to have the highest ratio of hemicellulose to cellulose (Chapter 1 – Table 1.1 pg.18) and this is the probable cause for this observation. The temperature of the maximum rate of decomposition was found to occur at higher temperatures for the hardwoods; this is thought to be related to the higher lignin content reported in hardwoods (Chapter 1 – Table 1.1). Yang et al. (2007) reported that lignin decomposes over a broad temperature range and decomposes at higher temperatures than cellulose and hemicellulose. This is because lignin is more aromatic and therefore requires more energy to break the bonds (Ghetti et al., 1996). From the combustion profiles, it was observed that the hard woods have broad second decomposition region at higher temperatures, and this is thought to be reflective of their higher lignin content.

Py-GC-MS semi- quantification results show, for the 27 highest yielding identifiable cellulose, hemicellulose and lignin biomass key products, that the perennial grass switch grass had the highest content of furfural, 2-furanmethanol, 1,2,-cyclopenanedione and levoglucosan which are all decomposition products of cellulose. Miscanthus was found to have a low content of levoglucosan and this is thought to be an impact of the high potassium content found in this crop (Nowakowski et al., 2007). Levoglucosan is an intermediate decomposition product of cellulose; the high content of cellulose in miscanthus (Chapter 1 – Table 1.1) should result in the production of higher levoglucosan content when compared with that produced by the hard woods. Switch grass was seen to have a high content of 2-methoxy-4-vinylphenol (a guaiacyl lignin decomposition product), catechol (lignin decomposition product) and butanedioic acid (cellulose or hemicellulose decomposition product). Miscanthus was found to have similar yields of 3-methyl-benzaldehyde, a decomposition product of lignin, to that of switch grass. Beech and willow SRC were found to have a high content of the guaiacyl lignin decomposition products 2-methoxy-6-(2-propenyl)-phenol and 1,2,4-trimethoxybenzene respectively. Beech wood was seen to produce a high content of syringyl lignin decomposition products 2,6-dimethoxy-phenol and 2,6-dimethoxy-4-(2-propenyl)-phenol, and the cellulose decomposition product 1,4:3,6-dianhydro-α-D-glucopyranose. As expected, lignin decomposition products were found to be more prominent in the hard woods because of their higher lignin content.

Good mass balance closures above 87 wt.% on dry basis were achieved for all fast pyrolysis runs carried out on these feedstocks. The standard error between experimental runs, for willow SRC, was in most cases negligible but there were exceptions to this trend, particularly when comparing gas analysis results (methane gas SE: 2.57). As a result of this finding, bivariate correlation coefficients were calculated to assess the shared variance between each experimental run. It was found that shared variance between the runs was as high as 97% and similar results were found when comparing results from other feedstock. Therefore, results from these experimental runs are comparable and do give an accurate representation of yields achievable, taking into account losses in the mass balance. As previously discussed in Chapters 4 and 6, loses in the mass balance for bio-oil yield is likely to be caused by errors in the weight measurement, the liquid holdup in the quench column and the water content determination. The amount bio-oil held in the quench column is difficult to determine, but signs of this hold up are indicated when flushing the systems during cleaning. The water content determination of the bio-oil is undertaken using small sample volumes and may not be representative of the total bio-oil produced. Water determination of the biomass prior to processing is also undertaken with a small sample size and this may not be representative of the total biomass prior to processing. This has the potential to lead to high errors because yields shown on this table are reported on dry basis. Gas analysis errors are expected to be caused by the heavily diluted pyrolysis gases (nitrogen content of above 97%). Gas analysis readings are taken at specific time intervals and not analysed as single gas at the end of the experiment. Carbon monoxide and dioxide are found to have the highest standard error. Causes for this may be related to escaping gases not captured for gas analysis (in between intervals of the gas analysis) and variation in the ash content within the biomass. Ash content has been found in proceeding chapters to influence the volatile content and this may be a consequence of catalytic activity caused by the inorganics found in the biomass. Overall the standard error for the total yields (mass balance closure) was relatively low and this is evident of good mass balance closures. The accumulative total of errors in this mass balance accounts for the losses found in the total mass balance closure.

The organic liquid yield was highest for beech wood and lowest for wheat straw. From the preliminary thermogravimetric work, results show that the volatile content is highest for beech wood (85.89 wt%) and lowest for miscanthus (75.62 wt.%) and wheat straw (79.92 wt.%). The volatile content is part representative of the potential bio-oil yield. The main reason for the part representation of the potential bio-oil yield is because the volatile content does not directly translate to bio-oil yield. This is because not all volatile matter will be condensable; non-condensable gases will be produced and the extent will be reflective of the crop properties and the process conditions. The low yield of bio-oil produced by wheat straw is related to the higher production of char, reaction water and non-condensable gases. From thermogravimetric data, the char yields were expected to be highest for wheat straw and miscanthus and this is observed in these findings. When comparing fast pyrolysis processing results with those reported in the literature (Chapter 2 – Table 2.2 pg.37) a number of differences and similarities can be found. Char content values were similar for all feedstock investigated except for miscanthus; may be due the reduced reactor capacity used by Hodgson et al. (2010). The variation in yield may be because the reactor capacity does not fully represent the respective yields attainable (because of the reduced feedstock used), differences in the feedstock (source of feedstock and harvest time) or experimental error. Fahmi et al. (2008) reported similar char yields for switch grass, wheat straw and willow SRC to those found the experiments reported here. The reactor capacity used by Fahmi et al. (2008) is similar to that used by Hodgson et al. (2010). Char yield was found to be lowest for the hard woods, beech wood and willow SRC, and this is part related to the lower ash content found in these feedstocks; this should also be reflected in a higher calorific value of the char for the hard woods.

It was found from the bio-oil characterisation that the bio-oil water content was highest for the straw (22.10 wt.%) and perennial grasses (switch grass: 21.60 wt.%; miscanthus: 22.00 wt.%), and lowest for the hardwoods, beech wood (12.80 wt.%) and willow SRC (15.00 wt.%). The thermal conversion of the feedstock, via fast pyrolysis, produces a bio-oil product with a water content that not only contains the moisture content of the feedstock, but the reaction water generated by thermal degradation reactions that occur during the fast pyrolysis of the feedstock. The water content is representative of the initial biomass moisture content and reaction water generated during the thermal conversion process (He et al., 2009).

All bio-oils produced were found to be homogenous except for wheat straw which produced a phase separated bio-oil. According to Oasmaa et al. (2002), feedstocks rich in extractives, such as agricultural residues, are commonly found to phase separate. From the literature review in Chapter 2, it was found that destabilisation of the micro-emulsion within the bio-oil can result in phase separation (Oasmaa et al., 2002). Addition of water can cause this to occur. The higher pH value found in wheat straw may be partly responsible for the destabilisation of the micro-emulsion, hence phase separation

The elemental composition (C, H and N content wt.% on dry basis) of the bio-oil and char were investigated and results show that the thermal conversion by fast pyrolysis has reduced the O:C atomic ratio, from 0.65 – 0.85 to 0.15 – 0.55, thus producing a more carbonaceous product (bio-oil and char). The char H:C atomic ratio was found to be reduced when compared with the feedstock and bio-oil product (char: 0.40 – 0.70; bio-oil: 1.10 – 1.80; feedstock: 1.20 – 1.60). According to McKendry (2002) the lower O:C and H:C atomic ratios are indicative of increased carbon-carbon bonds in the char, and this will be representative of the fixed carbon in the char. Beech wood char was found to have the lowest atomic ratios and the low ash content is thought to be a main contributor to this. Beech wood had the lowest ash content in the char (5.31 wt.% d.b) and switch grass the highest (24.85 wt.% d.b). The ash content is typically higher than that of the initial biomass because non-volatile inorganics will remain within the particle. The bio-oil higher heating value was highest for switch grass (22.34 MJ/kg), and the char higher heating value was highest for beech wood (26.90 MJ/kg). Willow SRC was found to produce a bio-oil and char product with similar high heating values (bio-oil: 21.79; char: 21.75 MJ/kg). GC-MS of the bio-oil shows that the bio-oil is mainly composed of oxygenated compounds such as: furans, ketones, organic acids, phenols and anhydrosugars.

**Implications of Findings [I]:**

Based on the results from the characterisation of straw, perennial grasses and hardwoods in Chapter 4, the hardwoods had the most attractive properties for fast pyrolysis processing. This is because of their low ash and high carbon content. The perennial grass switch grass was found to be more attractive than miscanthus or wheat straw for fast pyrolysis processing. This is because the switch grass produced higher volatile yields and contained low levels of potassium. The volatile content found is related to the expected yields attainable from fast pyrolysis processing, and the potassium content has a catalytic effect on the breakdown (Fuentes et al., 2008). This catalytic effect can influence fast pyrolysis product yields and also alter the product distribution.

As previously mentioned in Chapter 3, the thermal properties of the different feedstock are influenced by the particle size (Bridgemen et al., 2007). Pyrolysis processing and analytical studies were carried out using particle sizes between 0.25 and 1.00 mm and 150 and 250 µm, respectively. For pyrolysis processing this particle size range is important in order to achieve optimal pyrolysis product yields (Tsai et al., 2007; Heo et al., 2010). The analytical work was not carried out using this particle size due to the very small sample requirements. Differences found in the work conducted by Bridgeman et al. (2007) were between particles size below 90 µm and larger particles between 90 – 600 µm. These differences were mainly in the content of inorganics, moisture, carbon, nitrogen cellulose and volatiles. Work carried out in this thesis excluded particle sizes below 150 µm to avoid issues mentioned by Bridgemen et al. (2007). Their findings from larger particle sizes (90 – 600 µm) accommodates a majority of the sample particle sizes used in this work; hence differences when comparing results from analytical and processing are minor, when compared to the fractions below 90 µm. Particle size issues are applicable to work carried out in Chapters 4, 5 and 6, and their significance is difficult to accurately comment on, as this requires further research.

According to Oasmaa et al. (2005), who investigated the end-user specification requirements for fast pyrolysis liquids, the main bio-oil requirements is a water content of <27 wt.%, solid content <0.01 wt.%, inorganics <0.01 wt.%, homogeneity – single-phase and max. 100 % increase in viscosity at 80°C over 24 h. The values for calorific content, pH, viscosity, flash point and lubrication requirements were not detailed. From the fast pyrolysis processing, perennial grasses and hardwoods generate high bio-oil liquid yields that were found to be homogeneous. Wheat straw was found to be phase separated and this could be problematic for its use, if not separated (Lu et al., 2009). This is because there will be a large variation in the fuel characteristics when being used. The water content was found to be lower than that required for all bio-oils obtained. The high bio-oil and char heating value and low water content found in willow SRC, makes this crop an attractive energy feedstock for fast pyrolysis processing, if associated production costs and harvest yields can be maintained at current reported values (SAC, 2008). This bio-oil could be further upgraded by blending the bio-oil with other traditional fossil fuels or by further upstream processes, e.g. catalyst addition. The bio-oil from switch grass has the highest potential for upgrading to produce high value chemicals. A fractionation process could be implemented to separate these chemicals but it is expected that this would be troublesome, due to the complex nature of bio-oil.

The estimated production costs for switch grass, miscanthus and willow SRC are similar but harvest yields are higher per hectare for miscanthus (Christian et al., 2008). Miscanthus had the lowest bio-oil calorific value, this is expected to be higher than that of a representative sample of the bio-oil derived from wheat straw (the bottom layer of the bio-oil was only analysed because of the phase separation that occurred). The point of the harvest is highly influential on the feedstock properties (Lewandowski et al., 2003). Further harvest delay to miscanthus should improve the bio-oil properties. The harvest delay has been investigated in Chapter 6 and the implications are addressed later here. Since the same reactor configuration and operating parameters have been used, the results presented here for these feedstocks are thought to be more directly comparable.

**[II]. Investigate how light and medium volatile decomposition products vary with different pyrolysis temperatures and heating rates using analytical equipment, and compare fast and slow pyrolysis products and yields;**

From the literature review it was found that a fundamental investigation into the influence of pyrolysis temperature and heating rate on product distribution is required to gain a deeper insight into the thermal degradation of biomass. According to the literature review, few studies had investigated and quantified key light and medium volatile decomposition products using different pyrolysis temperatures and heating rates (using analytical equipment), and derived and compared bio-oil from fast and slow pyrolysis processes, or investigated the impact of staged pyrolysis or sequential pyrolysis on product distribution (especially for the hardwood willow SRC). This is of particular importance to further develop our understanding of selective pyrolysis to help achieve better product distribution within the main pyrolysis product, the bio-oil. This is very important because it is an essential step required to improve product quality and optimise processing facilities. In order to achieve this, the following experimental work was undertaken:

1. An analytical investigation into how light and medium volatile decomposition products vary, using a step sequence, with different pyrolysis temperatures and heating rates;
2. Comparison of fast and slow pyrolysis products and yields generated using larger scale laboratory equipment.

**Response to Objective [II]:**

Analytical sequential pyrolysis using different heating rates was shown to influence product quantity and product distribution. A single biomass sample was used in a step sequence to investigate what impact different pyrolysis temperatures (previously investigated by Wu et al. (2009)) and heating rates had on the product distribution. The advantage of this process is the ability to target better production distribution of the generated light and medium volatile decomposition products. These volatile products part represent the potential bio-oil chemical composition. The thermal pre-treatment by sequential pyrolysis could be further tailored by the variation of the heating rate. This would further alter the production distribution and add to the possibilities of selective pyrolysis.

A number of interesting relations were found between compounds at different heating rates over a range of different pyrolysis temperatures. From the analytical sequential pyrolysis an inverse relationship was seen between the total yield of furfural (at high heating rates) and 2-furanmethanol (at low heating rates). The total yield of 1,2-dihydroxybenzene (catechol) was found to be significantly higher at low heating rates. The intermediates of catechol, 2-methoxy-4-(2-propenyl)-phenol (eugenol); 2-methoxyphenol (guaiacol); 4-Hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde) and 4-hydroxy-3-methoxybenzaldehyde (vanillin), were found to be highest at high heating rates.

When comparing slow and fast pyrolysis using laboratory scale processing equipment, it was also found that the pyrolysis bio-oil chemical composition and the proportions of pyrolysis product yields alter. The GC-MS/FID analysis of fast and slow pyrolysis bio-oils reveals significant differences. The analyses shows high yields of acetic acid and methyl acetate from fast pyrolysis, as well as significant yields of phenol and 2,6-dimethoxyphenol. Notable in the slow pyrolysis organic fraction are high yields of methyl acetate, 3-hydroxy-2-butane, furfural and cyclopenentes, which is a final decomposition product of cellulose pyrolysis.

As previously mentioned in this chapter, the impact of particle size is an important consideration and this may obscure results when comparing those obtained from analytical and processing equipment.

**Implications of Findings [II]:**

Based on the results reported in Chapter 5, it was found that heating rate and pyrolysis temperature have a significant influence on the thermal decomposition products and their yields. Because of the complex nature of bio-oil and its plethora of chemical compounds, the focus was on developing the fundamental understanding of how product distribution could be tailored. From the analytical investigation, results show that the volatile product distribution can be tailored to help achieve a better final product, and this final preferred product is end-user specific. The implication of this work is that this study has further developed our understanding of the thermal decomposition nature of biomass and also built on current literature findings to provide further evidence. The mechanisms to account for the decomposition nature of some of these products have been shown.

**III. Characterise and compare feedstocks from different harvests, storage durations and storage locations, in terms of their fuel and chemical properties.**

From the literature review it was found that the changes in fuel quality of woody crops and arable straws during storage are relatively well reported, but there is very little information on the fate of dedicated energy crop properties during winter storage, especially for miscanthus. According to the literature few studies had investigated the consequences of bale-storage and storage location on the feedstock thermal chemical properties, investigated the key light and medium volatile decomposition products found in these feedstocks using analytical equipment, or compared fast pyrolysis processing yields from different harvests using the same processing equipment and operating parameters. It is thought that this type of investigation will help to further understand and maximise the potential fuel properties obtained from miscanthus. In order to meet the continuous supply demands, miscanthus will need to be stored or used in conjunction with other energy crops with different harvest times; therefore a better understanding is paramount.

1. Analytical characterisation and comparison of pyrolysis products of samples from different harvest times, storage durations and storage locations;

2. Laboratory scale fast pyrolysis processing of samples from different harvest times, and comparison of fast pyrolysis products and yields.

**Response to Objective [III]:**

Influence of Harvest Time:

The higher heating value is found to generally increase with harvest time. This was most evident when comparing the "at harvest" samples (early harvest 16.9 MJ/kg; conventional harvest 17.9 MJ/kg; late harvest 18.7 MJ/kg). This is because the O:C ratio is reduced making the feedstock material more carbonaceous. A reduction in inorganic content was also found with harvest time, this is because during the winter period the crop leaches and dies back. Thermogravimetric analysis further confirms a reduction in the inorganic content because ash yields are reduced from 4.25 % at the early harvest to 1.87 % at the late harvest. A large reduction of 11.84 % is seen in fixed carbon content between the early and late harvest. Volatile content is seen to increase by 14.22 % between the early and late harvest time, for the "at harvest" samples.

The dry yield (t/ha) of biomass was found to decrease by as much as 18.2 % between the early and late harvest. As a consequence the potential dry tonne per hectare of organics and char are found to be highest in the early harvest. By comparing the mean values obtained, the bio-oil organic yield is reduced by 5.65 % (0.17 t/ha) between the early and the late harvest; the char yield was also reduced by 16.02 % (0.50 t/ha). Reaction water within the bio-oil was found to increase by 28.71 % (0.29 t/ha) between the early and late harvests. The highest gas yields were observed for the conventional harvest (1.52 t/ha). Based on the result obtained from the fast pyrolysis runs carried out in Chapter 6, causes for losses in the mass balance are similar, discussed earlier in the chapter, to those found for experimental work carried out in Chapter 4, using the 1kg/h reactor. The standard error found in these results, for most pyrolysis products, is much lower. The standard error was found to be lower for organics, reaction water and gases but higher for char when comparing results obtained using the 1kg.h reactor. This is primarily due to the amount of feedstock processed, processing scale and the ability to carry out weight measurements every component of the pyrolysis system.

Influence of Storage**:**

The duration of storage was not equal between the early, conventional and late harvest. This is because the experiment was set up over one year to investigate continuous supply possibilities. The moisture content of the bales zones after the storage show varied results. Findings from thermogravimetric analysis show that the volatile content of the centre sample decreases with storage time when compared to the "at harvest sample" for each harvest time. Similarly, char and ash content are found to increase with storage. The ash content is thought to increase within the centre samples because of possible redistribution of inorganics caused by rainfall on the bale. Ash content increases in the shoulder and outside samples zones are thought to be due to dust and soil adhesion while positioned in the fields.

**Implications of Findings [III]:**

Findings show that the point of harvest, length of storage and storage location influence the fuel properties of the feedstock. To meet the continuous supply demands of the future, crops will need to be stored or used in conjunction with other crops with different harvest times. The use of other crops in conjunction could be somewhat problematic, because the thermal chemical properties of the pyrolysis products may differ, thus interfering with their end-user application. The results show that crop yields are influenced by the point of harvest and this has implications on the thermal chemical properties, yields and cost effectiveness associated with the process. The loss of crop yield (late harvest) is surpassed by better feedstock fuel properties. The harvest of the crop early to maximise yields is problematic because poorer fuel properties are obtained, and this could cause soil fertility issues, because the soil will be deprived of its annual input of leaves (Santamarta et al., 2011).

The storage of biomass is beneficial to the fuel properties of the feedstock, this is because it allows for further in-storage-drying. It should be noted that there are cost implications associated with storage (Styles et al., 2008), and that poor weather conditions could further enhance the moisture content, thus reducing the potential benefits to the fuel properties. The high moisture content could further promote fungal activity and this may result in rotting of the feedstock, and reduce the fuel properties further. The bale storage technique is thought to be beneficial because the centre region is representative of 85% of the bale area, is part shielded from weather conditions and is subjected to high temperatures during storage which could further help to dry the feedstock.

Overall, the late harvest of the crop produces the best feedstock fuel properties (high HHV, low moisture content, high volatile content and low ash content) for further processing by fast pyrolysis, and storage of the feedstock reduces the moisture content. From a general chemical content prospective (based on Py-GC-MS results), an increase in harvest time increases the alcohol content and storage duration decreases the acid content. The impact of particle size used is important to consider when comparing results between analytical and processing, as previously mentioned in this chapter.

## 7.2 LIMITATIONS OF THE EXPERIMENTAL WORK

From work carried out in Chapter 4 “A comparative study of straw, perennial grasses and hardwoods in terms of fast pyrolysis products”, the main limitations appear to be associated with the need for further experiment repetitions in order to produce statistically significant results. Due to the nature of biomass sample composition and characteristics tend to vary, and this can lead to non-generalisable results from experiments with small sample sizes. Using a larger sample (i.e., repeating the same experiment and analysis on many samples of the same biomass) would make it possible to conduct statistical analysis of the results that would account for the variations between the samples and produce more generalisable results, which would be more useful for informing large-scale industry pyrolysis parameters and techniques for optimal yields. GC-MS compound identification can be difficult because of the large amount of compounds identified, and the determination of compound is subject to interpretation. The accuracy of the match is also critical to ensuring that the compound found is identical to that of the library. Library matches below 86% were excluded from this work, because it is believed that the match may be erroneous. The heating rate employed to study the light and medium decomposition products, using Py-GC-MS, is only representative of the estimated heating rate achieved when using large scale processing equipment. The thermal chemical properties of the feedstocks are highly influenced by the point of harvest and this is problematic to this comparison.

Analytical analysis and laboratory processing reported in Chapter 5 “Sequential pyrolysis of willow SRC at low and high heating rates – implications for selective pyrolysis”, faced similar problems to those mentioned in Chapter 4. For the analytical investigation, the use of small biomass sample sizes is thought to be problematic because of the difficulty in attaining a representative sample, as mentioned above. The shown pathways are speculative, and this could be subject to errors. The shown decomposition routes (Chapter 5 Figure 5.10) are based on the total yields of the sequential pyrolysis experiments. Between the different sequential pyrolysis temperatures the sample was cooled and this may have a small impact on the product distribution. This is because during the cooling process further decomposition could occur and this will not contribute to the product yields. Additionally, the study of thermal decomposition products by analytical Py-GC-MS is not fully representative of the content of the bio-oil.

Work reported in Chapter 6 used a smaller reactor size (0.3 kg/h) and this may influence the respective pyrolysis yields, when comparing to large scale processes. The potential dry tonne per hectare is based on these results and this is thought to only be a guide of the respective yields possible. The harvest of miscanthus was not evenly distributed throughout the year and the storage durations of the bales were different. As a result of this, accurate comparison is somewhat difficult.

New growth was visible on the standing crop, for the late harvest (June 2010), and it is expected that this would influence the characterisation results when comparing a crop with no new growth.  This is a limitation of such a study.

# 8 CONCLUSION AND RECOMMENDATIONS

The aim of this chapter is to summarise the overall conclusions, and to make recommendations for future work on the basis of the findings reported in this thesis. Both conclusions and recommendations are organised around the three themes that the thesis deals with, as these are stated in the research objectives that guided the experimental studies conducted.

## 8.1 CONCLUSIONS

**[I]. Characterise and conduct laboratory-scale fast pyrolysis processing on feedstocks available for this project, and compare their products and yields;**

- Based on the analytical characterisation work carried out, the hard woods were found to be the most attractive for fast pyrolysis processing. This is because of their high calorific value and low ash content. From the thermogravimetric analysis the volatile content was highest in beech wood and switch grass, and the compositional content of the crop will influence the decomposition profile. High inorganic content, especially potassium, reduces the peak temperature of the main decomposition region and increase the rate of decompostion, and this is most evident when comparing the inorganic content of miscanthus with the hard woods. The reported high ratio of hemicellulose to cellulose in switch grass influenced the decomposition profile and produced the largest shoulder like feature, seen on the DTG curve. From the Py-GC-MS analysis, switch grass has the highest yields of most light and medium decomposition products derived from cellulose and hemicellulose. Lignin decomposition products are most prominent in the hardwoods and this corresponds well with their reported high lignin content.

- Pyrolysis processing results for the feedstock investigated are comparable and give an accurate indication of the yields achievable. Experimental runs carried out using willow SRC correlate exceptionally highly and have a shared variance greater than 97%. Similar findings were obtained for the other feedstock investigated were only two experimental runs have been carried out. The error evaluation has accounted for the gap in the mass balance closure. The standard error is highest for the bio-oil total (organics and reaction water) and for the non-condensable gases; the standard error for char was lowest. From these results it is reasonable conclude that beach wood generated the highest yield of organics and wheat straw the lowest. Organics yields for willow SRC, switch grass and miscanthus are similar if the error ranges are taken into account, hence no conclusive organic yield difference can be seen between willow SRC and switch grass and miscanthus. This is similarly applicable to the yield of reaction water between all feedstock, when taking into account the standard error, thus no conclusive difference can be seen when a comparison is made. Clear difference in the total gas yield can be seen for wheat straw, generating the highest yield, and miscanthus the lowest yield; no difference was seen between the total gas yield of beach wood and switch grass. A high standard error was seen between individual gases, methane and carbon dioxide, and no clear distinction, when comparing yields, can be seen. Switch grass and miscanthus were found to produce the highest yields of ethane, ethane, propene, propane and n-butane, when taking into account the standard error. A clear distinction can be seen in the char yield, the lowest standard error of all pyrolysis products, miscanthus produced the highest and beach wood the lowest. From these results it was found that the perennial grasses and hardwoods generate high bio-oil liquid yields that are homogeneous. The estimated production cost to produce switch grass, miscanthus and willow SRC are similar but harvest yields are higher per hectare for miscanthus. The high bio-oil and char heating value and low water content in willow SRC, makes this crop an attractive energy feedstock for fast pyrolysis processing, if the associated production costs and harvest yields can be maintained at current reported values.

**[II]. Investigate how light and medium volatile decomposition products vary with different pyrolysis temperatures and heating rates using analytical equipment, and compare fast and slow pyrolysis products and yields.**

- Analytical sequential pyrolysis (Py-GC-MS) using two different heating rates was seen to influence product quantity and distribution. This shows that a combination of a specific pyrolysis temperature and heating rate will increase the possibilities for targeting more desirable chemicals. A number of interesting correlations were found between compounds at different heating rates over a range of different pyrolysis temperatures. Decomposition pathways have been shown to account for the decomposition nature of willow SRC.
- The catechol content was found to be significantly higher at lower heating rates, and this was approximately three times higher than that obtained at higher heating rates. A derivative of catechol, 3-methoxycatechol also known as p-cresol, was also found to have a higher content at lower heating rates. Although the overall weight percentage is higher than that obtained at higher heating rates, the absolute amount found in the bio-oil derived by slow pyrolysis will be lower. This is because bio-oil yield obtained by fast pyrolysis is typically a lot higher. For example, the slow pyrolysis route to produce catechol may be more preferred because it is the most dominant compound, when compared to catechol yields using fast pyrolysis, but this may not translate to the highest yield obtainable.

- Although there is a difference in the total hot reaction time between the two heating rates, there is also a difference in the rate of heat transfer to the sample. The experiment design is setup to reach a set pyrolysis temperature and maintain that temperature for an equal amount of time. As a consequence, the longer hot reaction time for the lower heating rate will result in further exposure of the sample towards high temperatures and this will result in further decomposition. At a higher heating rate the sample will be subjected to very fast increases in temperature over very short periods of time, this will have an impact on the structural breakdown and extent of decomposition. It is possible that this could potentially result in incomplete pyrolysis, due to the shorter hot reaction time.

**[III]. Characterise and compare feedstocks from different harvests, storage durations and storage locations, in terms of their fuel and chemical properties.**

- Crop yields are influenced by the point of harvest and this has implications on the thermal chemical properties, yields and cost effectiveness associated with the farming system and thermal conversion process. The storage of biomass is beneficial to the fuel properties of the feedstock, this is because it allows for further in-storage-drying. Crop yields were highest for the early harvest and lowest for the late harvest. Harvest time is most influential on the thermochemical properties of the raw biomass. Overall, the late harvest of the crop produces the best feedstock fuel properties (high HHV, low moisture content, high volatile content and low ash content) for further processing by fast pyrolysis. The loss of crop yield (late harvest) is surpassed by better feedstock fuel properties.

- The thermogravimetric analysis show that the volatile content of the centre sample decreases with storage time when compared to the “at harvest sample” for each harvest time. Char, ash and fixed carbon content were highest during the early harvest, volatiles were found to increase with delay of harvest. It can be clearly seen that by delaying the harvest time the O:C atomic ratio is reduced and a more carbonaceous feedstock is produced.

- From the PY-GC-MS analysis, the harvest time was observed to influence mainly the alcohol content when comparing the early harvest with the conventional and late harvests; this was found to increase with harvest delay. The acid content of the crop was observed to reduce with storage time.

- From the fast pyrolysis results (using the 0.3 kg/h reactor), the potential organic liquid yield based on findings reported here, was found to vary between 2.82 and 3.01 dry t/ha with a standard error of 0.07. The bio-oil organic yield is reduced by 5.65 % (0.17 t/ha) between the early and the late harvest. Char yield was also reduced by 16.02 % (0.50 t/ha). Reaction water within the bio-oil was found to increase by 28.71 % (0.29 t/ha) between the early and late harvests. The standard error found in these results, organics, reaction water, char and gases, are a lot lower than those found for the pyrolysis processing carried out using the 1kg/h reactor. This is due to the reduced feedstock processed, scale and ability to carry out weight measurements on all components of the pyrolysis processing unit. The GC-MS analysis of the bio-oil shows that levoglucosan, methylbenzaldehyde, 2-methyl-1,3-benzenediol and 1,2-benzenediol all increase as a consequence of harvest delay. Levoglucosan and methylbenzaldehyde levels are found to increase by 5.61% and 7.07%, respectively between the early and late harvest.

In line with the European Commission projection's (66% renewable energy by 2020 from biomass), a number of challenges are faced; limited availability of biomass, competition for high value land and crops, scale – not commercially attractive due to the distributed nature of biomass and biomass properties – further research and refinement of biomass and its processing facilities is required. Agriculturally derived biomass (including energy grasses) offer promising prospects for renewable energy use and findings from this work clearly distinguish these differences. The point of harvest and duration of storage is also of critical importance if demands for the future are to be met (13.5 Mt to 43 Mt in 2030). The impact of harvest time and storage has been addressed in this work and results show that biomass properties vary significantly, especially when comparing crops harvested at different times of the year. Solutions to accommodate this variation in properties need to be further investigated if a more consistent pyrolysis product is required. Findings from this research help to develop a better understanding of biomass properties, the thermal conversion process and the pyrolysis products derived. Further refinement into processing facilities is still required if further success is to be achieved in the future.

## 8.2 RECOMMENDATIONS FOR FUTURE RESEARCH

**[I]. Characterise and conduct laboratory-scale fast pyrolysis processing on feedstocks available for this project, and compare their products and yields;**

- The most important factor when considering the industrial implications of fast pyrolysis feedstocks appears to be related to the lignin and inorganic content. Lignin is the source of high molecular weight polyphenols, which interfere with refining techniques for extraction and purification of chemical specialities. The inorganics have a catalytic effect on the thermal degradation processes, through cracking vapours and reducing organic yields. This is most evident when comparing the perennial grasses relative compounds yields with the straws. Findings suggest that the straws could be pre-treated to minimise inorganic content and thereby increase chemical yields.

- Pre-treatment by torrefaction could promote the fuel properties and this should be considered, but there is further cost implications associated with this. Nevertheless, these may be offset by the reduced cost implications of feedstock milling.

- It is recommended that for analytical work using small sample sizes (i.e. TGA, Py-GC-MS and liquid GC-MS) that a large number of repetitions should be carried out to improve the accuracy of the results. This is because it is difficult to obtain a representative sample when using small sample sizes. Additionally, by using larger sample sizes in the future it will become possible to conduct statistical analysis that would take into account any error attributable to sample composition. This will result in more generalisable findings that could be directly used to inform industrial-scale pyrolysis processing.

- The implication of feedstock mixing (e.g. mixing willows SRC and with wheat straw) on the fast pyrolysis products should be investigated. This would be beneficial particularly when using feedstocks for fast pyrolysis that are low in cost with poor fuel properties.

**[II]. Investigate how light and medium volatile decomposition products vary with different pyrolysis temperatures and heating rates using analytical equipment, and compare fast and slow pyrolysis products and yields.**

- Further optimisation of the process and bio-oil product is an essential step to further develop this technology. This could be further achieved by investigating additional key light and medium volatile products and the impact of catalysts as this would help to provide a better insight into the thermal degradation process.

- Different heating rates could also be investigated, nearer to the expected fast pyrolysis heating rates. This could then be upgraded from the micro-reactor setup used here, to a laboratory scale reactor. The setup will require a well calibrated heating system to ensure accurate results.

**[III]. Characterise and compare feedstocks from different harvests, storage durations and storage locations, in terms of their fuel and chemical properties.**

- The harvest window difference between the conventional and late harvest in the study reported here was only about 1-2 months. Although the present research shows that harvest time and storage duration are suitable methods for tailoring feedstock yields, a more detailed map of their influences can be obtained by future studies that collect samples from more frequent (e.g., monthly, if possible) harvest times and storage durations, that are spread throughout a full year.

- The reported study looked at various storage times; some additional insights can be gained by future studies that conduct fast pyrolysis processing on the after-storage samples, to further investigate what influence the storage time has on the bio-oil quality.

- GC-MS analysis of the bio-oil is only representative of part of the bio-oil, and high molecular weight compounds are excluded from the analysis due to the equipment capacity. HPLC could be used to investigate higher molecular weight compounds and this would further improve analysis capability.

- Fractionation and catalyst addition to the bio-oil should be further investigated to further improve the bio-oil fuel properties.

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# 10 APPENDIX A

## 10.1 THERMOGRAVIMETRIC ANALYSIS

### 10.1.1 Perkin-Elmer Pyris 1 Analyser Temperature Programs:

#### *10.1.1.1 Detailed temperature program for pyrolysis and combustion studies.*

1. Hold for 5.0 min. at 50.00°C
2. Heat from 50.00 to 105.00°C at 5.00°C/min
3. Hold for 15.0 min. at 105.00°C
4. Heat from 105.00 – 900.00°C at β°C/min
5. Hold for 15.0 min. at 900.00°C
6. Cool from 900.00°C to 50.00 at 25°C/min

β°C/min

Pyrolysis studies: 25°C/min

Combustion studies: 25°C/min

Pyrolysis kinetic studies: 5, 8 and 10°C/min

#### *10.1.1.2 Detailed temperature program for ashing studies.*

1. Hold for 5.0 min. at 50.00°C
2. Heat from 50.00 to 105.00°C at 5.00°C/min
3. Hold for 15.0 min. at 105.00°C
4. Heat from 105.00 – 575.00°C at 5°C/min
5. Hold for 15.0 min. at 575.00°C
6. Cool from 575.00°C to 50.00 at 10°C/min

### 10.1.2 Carbolite AAF 1100 Muffle Oven

- Detailed temperature program for ashing studies.

1. Heat from 20.00°C to 200°C
2. Hold at 200.00°C for 10.0 min.
3. Heat from 200.00°C to 350°C
4. Hold at 350.00°C for 10.0 min.
5. Heat for 350.00°C to 575.00°C
6. Hold at 575.00°C for 6.o hrs.
7. Cool to 20.00°C

# 11 APPENDIX B

## 11.1 EXAMPLE MASS BALANCES

### 11.1.1 1 kg/h Fast Pyrolysis Reactor

| | | |
|---|---|---|
| Biomass name | Wheat Straw | |
| Experimental date | 3.12.10 | |
| Moisture | 4.6 | % |
| Gas flow rate | - | $cm^3$/min |
| Approx. heating rate | - | $^oC$/min |
| Run time | 107 | mins |
| Start time | 13:14 | am |
| Finish time | 15:00 | pm |
| Gas meter (151.80-147.14) | 4.66 | $m^3$ |
| Main bio-oil $H_2O$ content | 22.14 | % |
| WTC bio-oil $H_2O$ content | 92.33 | % |
| DIC bio-oil $H_2O$ content | 82.83 | % |
| Biomass experimental use | 718.89 | g |

| | | Grams (g) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Before | After | Diff. | | Char | Liquid | Gas |
| | Reactor | | | | | | | |
| 1 | Silica sand | 1000.18 | 1046.04 | 45.86 | | 45.86 | | |
| 2 | Cyclone char | | | | | | | |
| 3 | Char pot 1 | | | | | | | |
| 4 | Char pot 2 | | | | | | | |
| 5 | 2+3+4 | | | 146.50 | | 146.50 | | |
| | Glassware | | | | | | | |
| 1 | Main bio-oil | | | 173.92 | | | 173.92 | |
| 2 | Cotton filter + 3 screws | 2132.65 | 2142.88 | 10.23 | | | 10.23 | |
| 3 | Condenser 2 | 911.14 | 911.73 | 0.59 | | | 0.59 | |
| 4 | Condenser 3 | 954.82 | 955.82 | 1.00 | | | 1.00 | |
| 5 | Round bottom flask | 98.71 | 153.94 | 55.23 | | | 55.23 | |
| 6 | Round bottom flask | 95.35 | 112.39 | 17.04 | | | 17.04 | |
| 7 | Round bottom flask | 112.02 | 121.53 | 9.51 | | | 9.51 | |
| 8 | Y pipe | 75.84 | 76.00 | 0.16 | | | 0.16 | |
| 9 | Elongated condenser | 45.30 | 45.43 | 0.13 | | | 0.13 | |
| 10 | Condenser | 42.23 | 42.28 | 0.05 | | | 0.05 | |
| 11 | Flexi rubber connector | 135.13 | 135.17 | 0.04 | | | 0.04 | |
| 12 | Condensate EP to WTC | | | 5.50 | | | 5.00 | |

| | Char | Liquid | Gas |
|---|---|---|---|
| Total | 192.36 | 272.9 | 185.0819 |
| % | 26.75792 | 37.9613 | 25.74551 |
| Closure (%) | 90.46 | | |

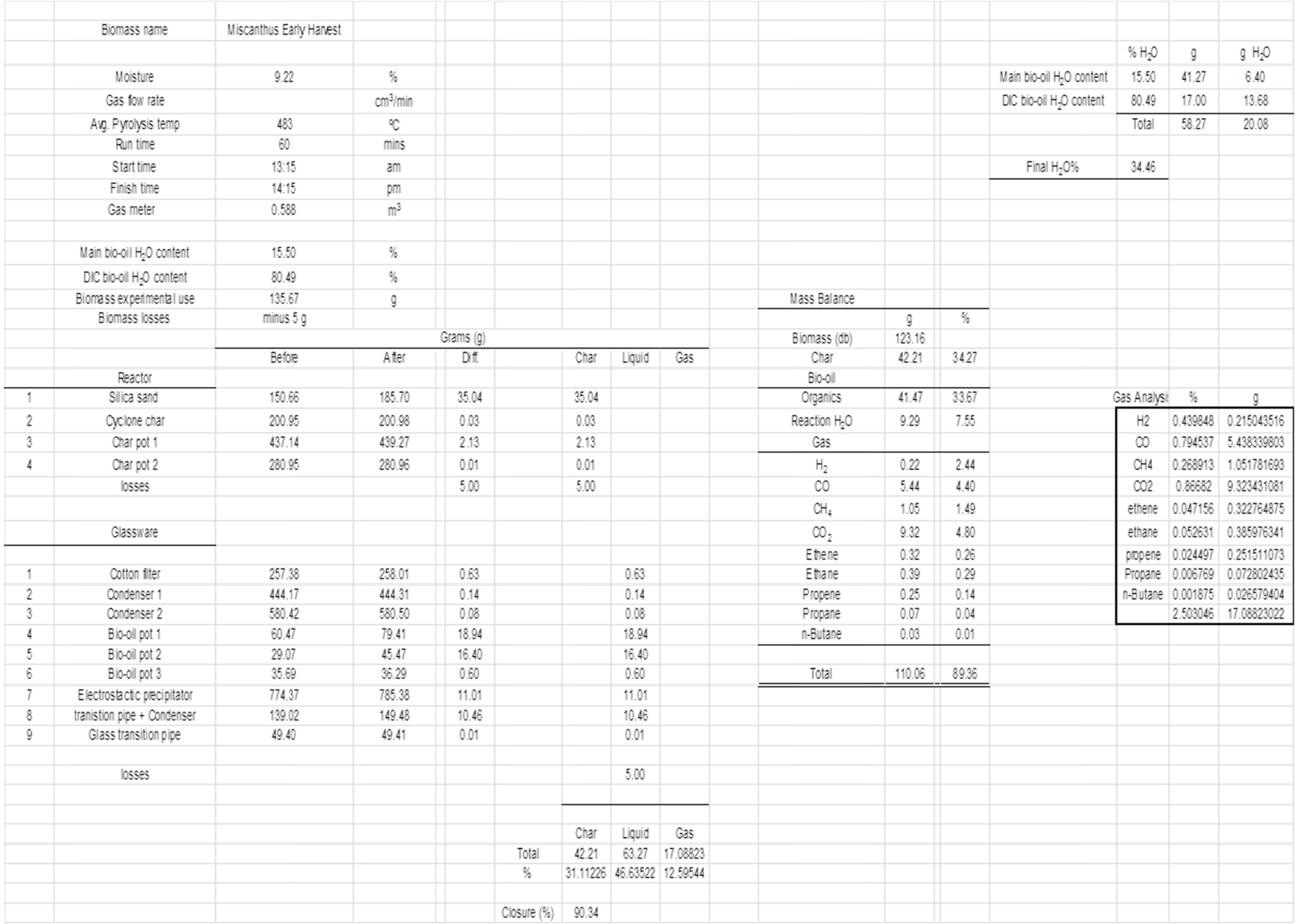
| | % $H_2O$ | g | g $H_2O$ |
|---|---|---|---|
| Main bio-oil $H_2O$ content | 22.14 | 173.92 | 38.50 |
| WTC bio-oil $H_2O$ content | 92.33 | 60.61 | 55.96 |
| DIC bio-oil $H_2O$ content | 82.83 | 38.37 | 31.78 |
| | Total | 272.90 | 126.24 |
| Final $H_2O$% | 46.26 | | |

Mass Balance

| | g | % |
|---|---|---|
| Biomass (db) | 685.82 | |
| Char | 192.36 | 28.05 |
| Bio-oil | | |
| Organics | 146.66 | 21.39 |
| Reaction $H_2O$ | 93.17 | 13.58 |
| Gas | | |
| $H_2$ | 0.32 | 0.83 |
| CO | 46.20 | 8.44 |
| $CH_4$ | 6.11 | 1.95 |
| $CO_2$ | 95.54 | 11.11 |
| Ethene | 3.98 | 0.73 |
| Ethane | 4.72 | 0.80 |
| Propene | 12.18 | 1.48 |
| Propane | 7.94 | 0.92 |
| n-Butane | 8.10 | 0.71 |
| Total | 617.27 | 90.00 |

| Gas Analysis | % | g |
|---|---|---|
| H2 | 0.083788 | 0.324649 |
| CO | 0.851736 | 46.20252 |
| CH4 | 0.19699 | 6.106141 |
| CO2 | 1.1208053 | 95.54005 |
| ethene | 0.0733525 | 3.979018 |
| ethane | 0.0811526 | 4.716568 |
| propene | 0.1496375 | 12.17566 |
| Propane | 0.0931438 | 7.939792 |
| n-Butane | 0.0720645 | 8.097521 |
| | 2.7226703 | 185.0819 |

### 11.1.2 0.3 kg/h Fast Pyrolysis Reactor



| | | |
|---|---|---|
| Biomass name | Miscanthus Early Harvest | |
| Moisture | 9.22 | % |
| Gas flow rate | | $cm^3/min$ |
| Avg. Pyrolysis temp | 483 | °C |
| Run time | 60 | mins |
| Start time | 13:15 | am |
| Finish time | 14:15 | pm |
| Gas meter | 0.588 | $m^3$ |
| Main bio-oil $H_2O$ content | 15.50 | % |
| DIC bio-oil $H_2O$ content | 80.49 | % |
| Biomass experimental use | 135.67 | g |
| Biomass losses | minus 5 g | |

| | | Grams (g) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Before | After | Diff. | Char | Liquid | Gas |
| | Reactor | | | | | | |
| 1 | Silica sand | 150.66 | 185.70 | 35.04 | 35.04 | | |
| 2 | Cyclone char | 200.95 | 200.98 | 0.03 | 0.03 | | |
| 3 | Char pot 1 | 437.14 | 439.27 | 2.13 | 2.13 | | |
| 4 | Char pot 2 | 280.95 | 280.96 | 0.01 | 0.01 | | |
| | losses | | | 5.00 | 5.00 | | |
| | Glassware | | | | | | |
| 1 | Cotton filter | 257.38 | 258.01 | 0.63 | | 0.63 | |
| 2 | Condenser 1 | 444.17 | 444.31 | 0.14 | | 0.14 | |
| 3 | Condenser 2 | 580.42 | 580.50 | 0.08 | | 0.08 | |
| 4 | Bio-oil pot 1 | 60.47 | 79.41 | 18.94 | | 18.94 | |
| 5 | Bio-oil pot 2 | 29.07 | 45.47 | 16.40 | | 16.40 | |
| 6 | Bio-oil pot 3 | 35.69 | 36.29 | 0.60 | | 0.60 | |
| 7 | Electrostactic precipitator | 774.37 | 785.38 | 11.01 | | 11.01 | |
| 8 | tranistion pipe + Condenser | 139.02 | 149.48 | 10.46 | | 10.46 | |
| 9 | Glass transition pipe | 49.40 | 49.41 | 0.01 | | 0.01 | |
| | losses | | | | | 5.00 | |

| | Char | Liquid | Gas |
|---|---|---|---|
| Total | 42.21 | 63.27 | 17.08823 |
| % | 31.11226 | 46.63522 | 12.59544 |
| Closure (%) | 90.34 | | |

| Mass Balance | g | % |
|---|---|---|
| Biomass (db) | 123.16 | |
| Char | 42.21 | 34.27 |
| Bio-oil | | |
| Organics | 41.47 | 33.67 |
| Reaction $H_2O$ | 9.29 | 7.55 |
| Gas | | |
| $H_2$ | 0.22 | 2.44 |
| CO | 5.44 | 4.40 |
| $CH_4$ | 1.05 | 1.49 |
| $CO_2$ | 9.32 | 4.80 |
| Ethene | 0.32 | 0.26 |
| Ethane | 0.39 | 0.29 |
| Propene | 0.25 | 0.14 |
| Propane | 0.07 | 0.04 |
| n-Butane | 0.03 | 0.01 |
| Total | 110.06 | 89.36 |

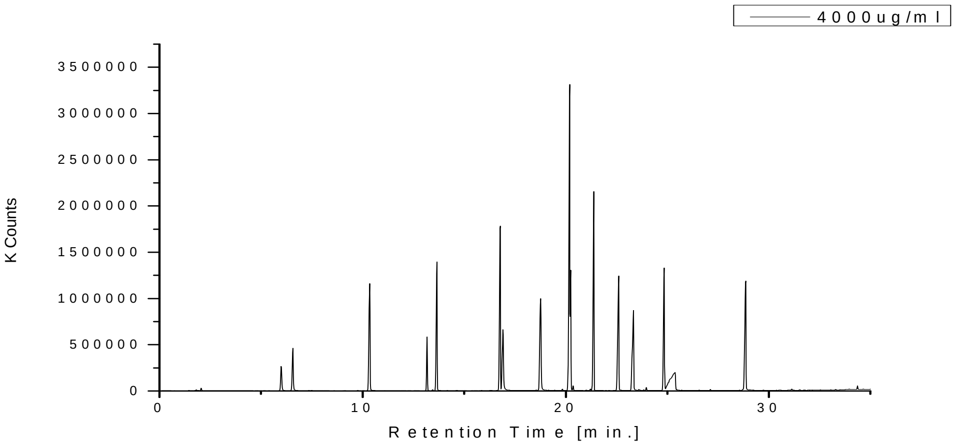
| | % $H_2O$ | g | g $H_2O$ |
|---|---|---|---|
| Main bio-oil $H_2O$ content | 15.50 | 41.27 | 6.40 |
| DIC bio-oil $H_2O$ content | 80.49 | 17.00 | 13.68 |
| | Total | 58.27 | 20.08 |
| Final $H_2O$% | 34.46 | | |

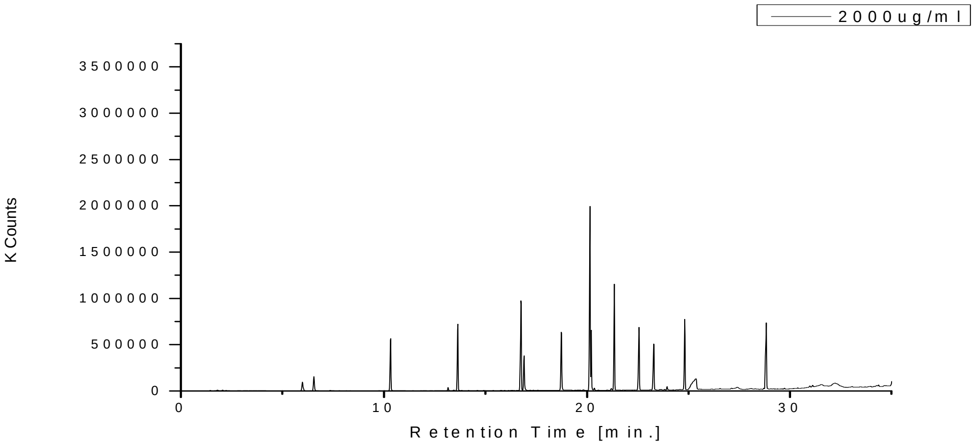
| Gas Analysi | % | g |
|---|---|---|
| H2 | 0.439848 | 0.215043516 |
| CO | 0.794537 | 5.438339803 |
| CH4 | 0.268913 | 1.051781693 |
| CO2 | 0.86682 | 9.323431081 |
| ethene | 0.047156 | 0.322764875 |
| ethane | 0.052631 | 0.385976341 |
| propene | 0.024497 | 0.251511073 |
| Propane | 0.006769 | 0.072802435 |
| n-Butane | 0.001875 | 0.026579404 |
| | 2.503046 | 17.08823022 |

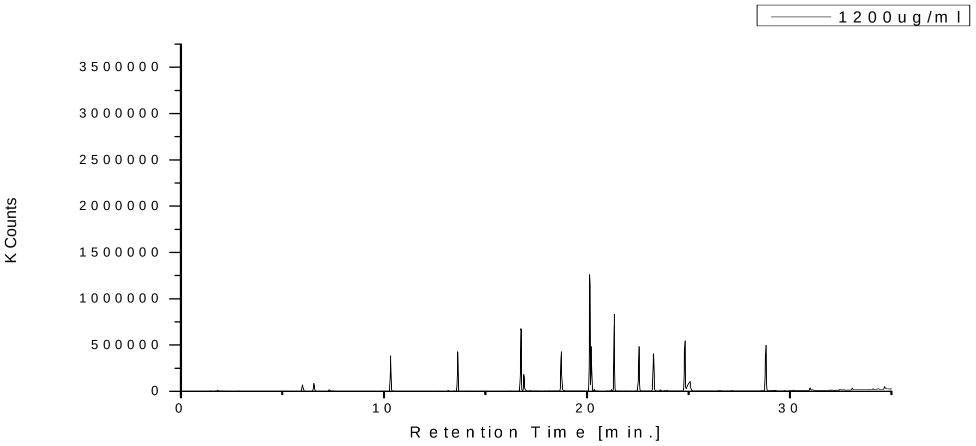
### 11.1.3 0.15 kg Slow Pyrolysis Reactor

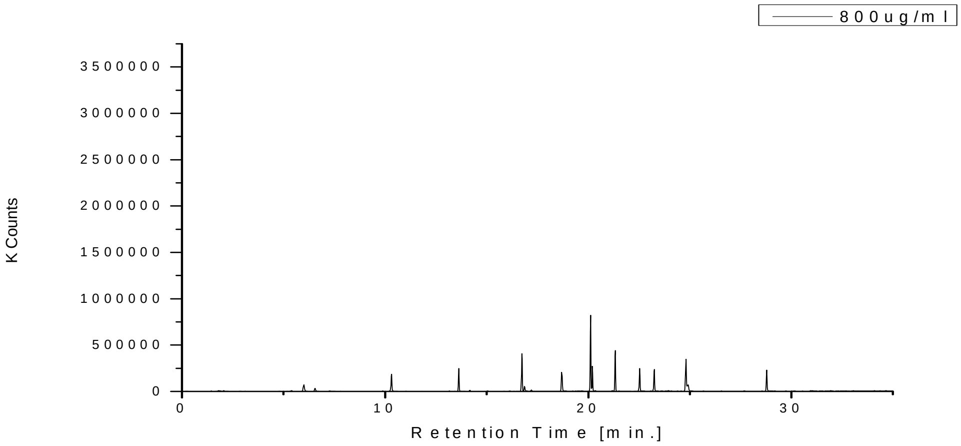
| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Name | Willow SRC | | | | | | | | | |
| | Experimental date | 25.01.11 | | | | | | | | | |
| | Moisture | 13.58 | % | | | | | | | | |
| | Gas flow rate | 100 | $cm^3$/min | | | | | | | | 9.063292 |
| | Approx. heating rate | 15 | °C/min | | | | | | | | |
| | Run time | 145 | mins | | | | | | | | |
| | Start time | 13.03 | am | | | | | 17.3453 | | | |
| | Finish time | 15.28 | pm | | | | | | | | |
| | Gas meter (58.218-58.184) | 0.034 | $m^3$ | | | | | | 9.06 | | |
| | Bio-oil $H_2O$ content | 68.94 | % | | | | | | 16.1 | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | Before | After | Diff. | Char | Liquid | Gas | | | | |
| | Reactor | g | g | g | g | g | | | Mass Balance on Dry Basis | | |
| 1 | Rear of reactor + rubber disc | 390.33 | | | | | | | | g | % |
| 2 | Front of reactor | 483.45 | 483.85 | 0.40 | 0.40 | | | | Biomass | 57.68 | |
| 3 | Main section of reactor | 1703.29 | | | | | | | Char | 34.54 | 59.89 |
| 4 | total (1+2+3) | | | | | | | | Bio-oil | | |
| 5 | 1+3+(wire mesh) + biomass | 2211.11 | | | | | | | Organics | 7.81 | 13.55 |
| 6 | 1+3+(2xwire mesh) + biomass | 2220.60 | 2188.00 | | 34.14 | | | | Reaction $H_2O$ | 8.28 | 14.36 |
| | | | | | | | | | Gas | | |
| | Biomass | | | | | | | | $H_2$ | 0.02 | 0.50 |
| 1 | Experimental use | 66.74 | | | | | | | CO | 1.57 | 3.26 |
| 2 | Remaining material | | 34.14 | | | | | | $CH_4$ | 0.31 | 1.11 |
| | | | | | | | | | $CO_2$ | 3.63 | 4.79 |
| | Glassware | | | | | | | | Ethene | 0.06 | 0.13 |
| 1 | DIC | 449.69 | 450.49 | 0.80 | | 0.80 | | | Ethane | 0.09 | 0.18 |
| 2 | DIC | 454.14 | 454.38 | 0.24 | | 0.24 | | | Propene | 0.08 | 0.11 |
| 3 | Cotton filter P1 | | | | | | | | Propane | 0.08 | 0.11 |
| 4 | Cotton filter P2 | | | | | | | | n-Butane | 0.07 | 0.07 |
| 5 | Cotton Filter P1 + P2 | | | | | | | | | | |
| 6 | 3+4+(cotton) | 290.26 | 290.70 | 0.44 | | 0.44 | | | Total | 56.55 | 98.06 |
| 7 | Water condenser | 122.62 | 127.43 | 4.81 | | 4.81 | | | | | |
| 8 | Glass corner | 16.74 | 17.08 | 0.34 | | 0.34 | | | | 8.2853 | |
| 9 | Round bottom flask 1 x | 60.46 | 78.96 | 18.50 | | 18.50 | | | | | |
| 10 | Round bottom flask 2 | 60.31 | 60.34 | 0.03 | | 0.03 | | | | | |
| | | | | | | | | | | | |
| | Addition notes | | | | Char | Liquid | Gas | | 16.1 | | |
| | | | | Total. | 34.54 | 25.16 | 5.92 | | | | |
| | | | | %. | 51.75 | 37.70 | 8.87 | | | | |
| | | | | | | | | | | | |
| | | | | Closure (%) | 98.32 | | | | | | |

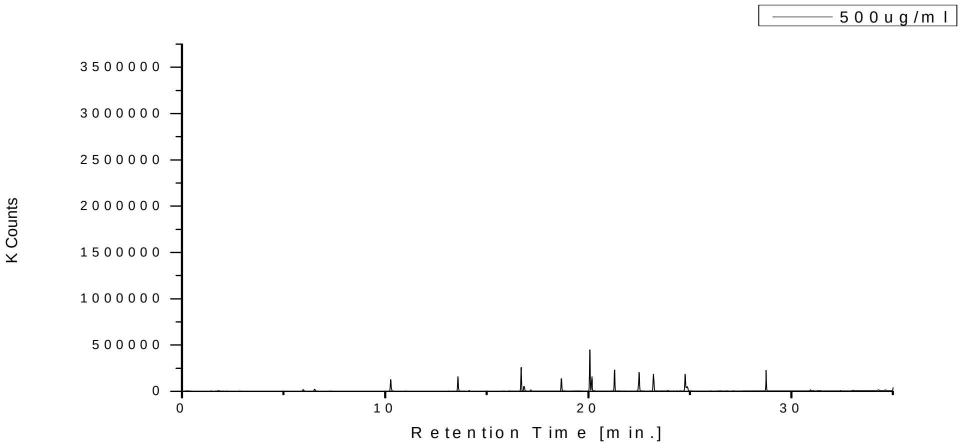
# 11.2 QUANTIFICATION CHROMATOGRAMS











The calibration curve linearity (r2) ranged between 0.9434 – 0.9983 for all compounds quantified. The calibration accuracy for each compound is shown below:

| | $r^2$ |
|---|---|
| Furfural | 0.9434 |
| 2-Furanmethanol | 0.9801 |
| Phenol | 0.9983 |
| Guaiacol | 0.9981 |
| 2-Methoxy-4-methylphenol | 0.9979 |
| Catechol | 0.9946 |
| 3-Methoxycatechol | 0.9949 |
| 1,2,4-Trimethoxybenzene | 0.9930 |
| 2-Methoxy-4-vinylphenol | 0.9818 |
| Eugenol | 0.9950 |
| Vanillin | 0.9926 |
| Levoglucosan | 0.9834 |
| Syringaldehyde | 0.9925 |

# 12 PUBLICATIONS

**Journals:**

Greenhalf, C.E., Nowakowski, A.B., Titiloye, J.O., Bridgwater, A.V., Yates, N. Riche, A., Shield, I., 2011.Thermochemical characterisation of straws and high yielding perennial grasses. Industrial Crops and Products. 2012, 36, 449-459.

Greenhalf, C.E., Nowakowski, D.J., Harms, A.B., Titiloye, J.O., & Bridgwater, A.V. Sequential pyrolysis of willow SRC at low and high heating rates – implications for selective pyrolysis. Fuel. 2012, 93, 692-702.

Greenhalf, C.E., Nowakowski, A.B., Bridgwater, A.V., Yates, N. Riche, A., Shield, I., The influence of harvest and storage on the properties of and fast pyrolysis products from Miscanthus x giganteus. Energy and Fuel. 2013, 56, 247-259.

Greenhalf, C.E., Nowakowski, D.J., Harms, A.B., Titiloye, J.O., & Bridgwater, A.V., A comparative study of straw, perennial grasses and hardwoods in terms of fast pyrolysis products. Fuel. 2013, 108, 216-230.

**Conferences:**

Greenhalf, C.E., Nowakowski, D.J., Titiloye, J.O., & Bridgwater, A.V. (2010). Thermochemical characterisation of willow short rotation coppice and bio-oil derived from fast pyrolysis. Bioten Conference, Birmingham, UK, 2010. ISBN: 978-1-872691-54-1