DOCTOR OF PHILOSOPHY

Ash control methods to limit biomass inorganic content and its effect on fast pyrolysis bio-oil stability

Scott Banks

2014

Aston University

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Summary

This research investigates specific ash control methods to limit inorganic content within biomass prior to fast pyrolysis and effect of specific ash components on fast pyrolysis processing, mass balance yields and bio-oil quality and stability.

Inorganic content in miscanthus was naturally reduced over the winter period from June (7.36 wt. %) to February (2.80 wt. %) due to a combination of senescence and natural leaching from rain water. September harvest produced similar mass balance yields, bio-oil quality and stability compared to February harvest (conventional harvest), but nitrogen content in above ground crop was to high (208 kg $ha.^{-1}$) to maintain sustainable crop production.

Deionised water, 1.00% HCl and 0.10% Triton X-100 washes were used to reduce inorganic content of miscanthus. Miscanthus washed with 0.10% Triton X-100 resulted in the highest total liquid yield (76.21 wt. %) and lowest char and reaction water yields (9.77 wt. % and 8.25 wt. % respectively). Concentrations of Triton X-100 were varied to study further effects on mass balance yields and bio-oil stability. All concentrations of Triton X-100 increased total liquid yield and decreased char and reaction water yields compared to untreated miscanthus. In terms of bio-oil stability 1.00% Triton X-100 produced the most stable bio-oil with lowest viscosity index (2.43) and lowest water content index (1.01).

Beech wood was impregnated with potassium and phosphorus resulting in lower liquid yields and increased char and gas yields due to their catalytic effect on fast pyrolysis product distribution. Increased potassium and phosphorus concentrations produced less stable bio-oils with viscosity and water content indexes increasing. Fast pyrolysis processing of phosphorus impregnated beech wood was problematic as the reactor bed material agglomerated into large clumps due to char formation within the reactor, affecting fluidisation and heat transfer.

Keywords: Fast pyrolysis, biomass ash, demineralisation, potassium and phosphorus impregnation, bio-oil quality and stability

Dedication

To my family and friends

Acknowledgments

Firstly, I would like to thank my supervisor Professor Anthony V. Bridgwater for his guidance, advice, knowledge and support throughout my PhD.

My thanks go to Dr Daniel J. Nowakowski for his advice, knowledge and encouragement throughout my PhD which has helped me achieve my targets and goals.

I would also like to thank my colleague Dr Michal Mos from the Institute of Biological, Environmental and Rural Sciences (IBERS) in Aberystwyth University for our research collaboration (SUPERGEN project), for providing agronomy on soil nutrients remobilisation and plant development.

Thanks also to Surila Darbar, Emma Wylde and Irene Watkinson for their support, as well as past and present researchers of the Aston University Bioenergy Research Group.

Finally I am thoroughly grateful and thankful to my parents Steve and Wendy, Brother Ryan and partner Charlotte for their endless support, patience and encouragement. They have been a constant reminder that there is a light at the end of the tunnel.

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Abbreviations

b.d.l	Below detection level
BERG	Bioenergy Research Group
d.a.f.	Dry ash free
d.b.	Dry basis
DTG	Differential thermogravimetric
ESP	Electrostatic precipitator
FB	Free board
FID	Flame ionisation detector
GC - MS	Gas chromatography – mass spectrometry
HCl	Hydrochloric acid
HHV	Higher heating value
IBERS	Institute of Biological Environmental and Rural Sciences
ICP	Induced coupled plasma
KF	Karl-Fischer
LHV	Lower heating value
n/d	Not determined
N/D	Not detected
PPE	Personal protective equipment
ppm	Parts per million
Py-GC-MS	Pyrolysis – gas chromatography – mass spectrometry
SPAD	Single photon avalanche diode
T_f	Temperature corresponding to 90 % of mass loss on a dry basis
T_o	Temperature corresponding to 1 % mass loss on a dry basis
T_p	Pyrolysis peak temperature
T_s	Temperature of shoulder – like feature
TGA	Thermogravimetric analysis
wt. %	Weight per cent
*	Calculated by difference
-	Not analysed
#	CHN results on a dry basis

1 Introduction

Renewable energy sources from biomass are a growing importance when considering trying to reduce the environmental concerns from fossil fuels. Certain processes have been developed to convert biomass into a product which has the potential to be used as a renewable fuel source. One of these approaches is fast pyrolysis which converts biomass, such as *Miscanthus x giganteus*, by rapidly heating in the absence of oxygen and then rapidly cooling the vapours. The products are bio-oil, gas and some char. The key product is bio-oil which is the renewable fuel source. The overall quality of the bio-oil has been tried to be improved; this can be achieved by using a catalyst or by reducing inorganic content in the initial biomass.

1.1 Context and background

Biomass contains small amounts of ash which consists of inorganic material. The inorganic content of biomass can vary from different types of biomass, and is generally a function of soil type and timing of the harvest. Ash is made up of a number of components including silica, potassium, calcium, sulphur, chlorine, sodium and others

A major part of ash has negative effects on the formation of a quality bio-oil, these being alkali metals. When fast pyrolysis occurs with alkali metal cations present it leads to catalytic cracking of the fast pyrolysis condensable vapours. Alkali metals lead to reduced organic liquids and increased yields of water, char and gas, resulting in a bio-oil which has a low calorific value and has an increased chance of phase separation. High alkali metal contents do not necessary mean high ash content, a majority of ash can be made up of silica which has no or little effect on the bio-oil quality and stability.

Alkali metals are essential for the healthy growth of crops. There are a few options for limiting the total ash content in harvested crops. One option is to take into account harvesting times as different harvest times affect the inorganic content of the biomass and consequently optimising harvest time may reduce ash components that adversely affect fast pyrolysis product distribution. Senescence has to be taken into account when different harvesting times are considered as it affects both the composition of the crop and the availability of nutrients for the next perennial growth cycle. A second option is to advance the idea of natural leaching of ash from biomass due to rain. Since natural rain leaching cannot be relied on to reduce the soluble alkali metal content of biomass it would be useful to reduce the alkali metal content by a separate controlled washing process. Many different advances have been attempted in the pre-treatment of biomass, the main being water washing.

The leading method in reducing the inorganic content of biomass is water washes. By taking into account fertiliser requirements and harvesting times it will also help to reduce the overall ash content significantly.

1.2 Objectives

The main objective of this PhD research is to investigate specific ash control methods to limit the inorganic content within biomass prior to fast pyrolysis and investigate the effect of specific ash components on fast pyrolysis processing, mass balance yields and bio-oil quality and stability. The aim is to limit the ash content of the fast pyrolysis feedstock prior to thermal conversion so that the maximum fast pyrolysis liquid yield can be achieved which also has desired characteristics such as being stable over a one year period (viscosity and water content). The overall objective was divided into three subtasks that are described in this section.

1.2.1 Subtask 1: Senescence

The aims of this research were to study the impact of miscanthus biomass harvested at different senescence stages on fast pyrolysis bio-oil quality as well as the impact of utilising biomass of different harvest time on nitrogen remobilisation. All samples are to be converted using fast pyrolysis and the resulting bio-oil analysed for composition and stability (Section 8). We discuss the potential impact of harvest time and plant development on biomass composition and subsequent conversion to bio-oil in the context of varying harvest times and maintaining a good energy balance of the crop.

1.2.2 Subtask 2: Demineralisation

The aims of this research were to study the impact different demineralisation experiments have on resulting fast pyrolysis mass balance yields and to see if there is any improvement in bio-oil stability. The initial aim was to determine the optimum washing conditions (temperature and duration) on pyrolysis profiles. Once determined the aim was to process demineralised miscanthus samples on a large scale so that fast pyrolysis mass balance yields and products could be directly compared. All samples are to be converted using fast pyrolysis and the resulting bio-oil analysed for composition and stability (Section 9).

1.2.3 Subtask 3: Impregnation

The aims of this research were to study the impact potassium and phosphorus had on fast pyrolysis mass balance yields, as well as the quality and stability of fast pyrolysis bio-oil. All samples were converted using fast pyrolysis and the resulting bio-oil analysed for composition and stability (Section 10). Also by impregnating specific elements into biomass feedstock samples it was tested if any fast pyrolysis processing problems occur due to these elements.

1.3 Structure of thesis

This thesis consists of twelve chapters and the structure is described below.

- Chapter one provides an introduction and objectives of the research project. This chapter also outlines the structure of the thesis.
- Chapter two focuses on theory and literature review of biomass, sources of ash, ash composition, ash control methods, fast pyrolysis processing and products, and effect of inorganics on fast pyrolysis.
- Chapter three describes the biomass and specific feedstock preparation procedures used in this work. Biomass characterisation techniques used in this work are described also.
- Chapter four presents and discusses results for the characterisation of senesced miscanthus.
- Chapter five presents and discusses results for the characterisation of demineralised miscanthus. Small scale, large scale and surfactant demineralisation experiments are performed.
- Chapter six presents and discusses results for the characterisation of beech wood, potassium impregnated beech wood and phosphorus impregnated beech wood.
- Chapter seven describes the fast pyrolysis of biomass using 1 kg $h.^{-1}$ fluidised bed reactor and accompanying liquid collection system. Mass balances were completed for each run and the procedure is explained in this chapter, including errors and losses. Product analysis techniques for fast pyrolysis liquid, solid and gaseous products are described. The procedure for accelerated storage experiment is described.
- Chapter eight presents and discusses results for fast pyrolysis of senesced miscanthus samples including mass balances, fast pyrolysis product characterisation and accelerated storage experiments. The possibilities of extending the miscanthus harvest window are discussed.
- Chapter nine presents and discusses results for fast pyrolysis of large scale demineralised and surfactant demineralised miscanthus samples including mass balances, fast pyrolysis product characterisation and accelerated storage experiments.
- Chapter ten presents and discusses results for fast pyrolysis of potassium and phosphorus impregnated beech wood samples including mass balances, fast pyrolysis product characterisation and accelerated storage experiments.
- Chapter eleven summarises all the results from the thesis.
- Chapter twelve provides an overall conclusion for the thesis.
- Chapter thirteen makes recommendations for future research.

2 Theory and literature review

This chapter presents the theory and reviews the literature to biomass, sources of ash, ash composition, ash control, fast pyrolysis processing, fast pyrolysis products and effect of inorganics on fast pyrolysis. Ash is of particular interest as it contains alkali metals which catalyse cracking reactions of fast pyrolysis vapours and have significant effect on fast pyrolysis product distribution and bio-oil stability.

2.1 Biomass

Biomass composition can vary significantly [1-3], especially the inorganic constituents [2, 3]. It is important to understand the thermal decomposition of biomass which is determined by its three main organic components; cellulose, hemicellulose and lignin (refer to Section 2.5.3, 2.5.4 and 2.5.5). The component content of softwoods and hardwoods and for comparison, beech wood and miscanthus are listed in Table 1. Biomass also contains extractives and alkali metals in the form of ash. Moisture, sulphur, phosphorus and nitrogen are also contained in biomass. This section reviews cellulose, hemicellulose, lignin, extractives and ash.

Table 1 Cellulose, hemicellulose and lignin content of biomass

Biomass	Cellulose	Hemicellulose	Lignin	Extractives / ash
		wt. % $^{d.b.}$		
Softwoods [4]	35 - 40	25 - 30	27 - 30	0 - 13
Hardwoods [4]	45 - 50	20 - 25	20 - 25	0 - 15
Beech wood [5]	45	32	22	1
Miscanthus [6]	38	24	24	14

The composition of biomass depends on a number of factors, such as:

- Biomass type, species or part of plant [2-11]
- Growing conditions [3, 8, 12] such as location [8, 11], season [10, 13, 14] and soil type [3, 9, 13]
- Fertiliser and pesticide use [2, 13]
- Distance from pollution [8, 10] and the sea such as roads and industrial buildings
- Harvesting time [2, 10, 14], harvesting technique, transport and storage [2, 9]
- Soil contamination (refer to Section 2.2)
- Blending of biomass types [9] (refer to Section 2.4.3)

2.1.1 Cellulose

Cellulose makes up the cell wall structure in biomass with a general formula of $(C_6H_{10}O_5)_n$ [15]. Some lignocellulosic materials can have more cellulose (dry wt. %) then wood. Cellulose is made up of units of anhydrogloscose in a giant straight chain molecule. Hydrogen bonds are formed between OH groups within each cellulose chain and the surrounding chains resulting in chains being parallel to each other and forming a crystalline super molecular structure [16]. Due to these hydrogen bonds the structure of cellulose is difficult to break down. The glucose bonds need to undergo hydrolysis whilst being catalysed by enzymes or acids [17]. The bonds can be broken by alkali metals at ambient temperatures in the presence of oxygen or at higher temperature when the presence of oxygen is not required. Cellulose exists in both crystalline and amorphous forms but this has no impact on fast pyrolysis.

2.1.2 Hemicellulose

Hemicellulose has a general formula of $(C_5H_8O_5)_n$ [15] and is also found in the cell walls of biomass, however, unlike cellulose which has a crystalline formation, hemicellulose is unstructured and provides little strength [18]. The hemicellulose structure can consist of many branched structures which differ depending on the type of biomass species. A mixture of polymerised monosaccharides make up hemicellulose such as glucose, mannose, galactose, xylose, arabinose and galacturonic acid residues [19]. Hemicellulose has a lower molecular weight than cellulose as the number of repeating saccharide monomers is only 150 compared to 5000 - 10,000 for cellulose [19]. The hemicellulose structure is easier to break down into its component sugars than cellulose as it is soluble in hot water and alkali, in addition it can be hydrolysed by acids and hence broken down into its component sugars [20].

2.1.3 Lignin

Lignin is the most complex chemical compound within lignocellulosic biomass. It is a highly branched polymer of phenylpropane [18]. Lignin is a highly branched mononuclear aromatic polymers in the cell walls of biomass and can often be found bound to cellulose fibres forming a lignocellulosic complex. This complex can be broken by treatment with strong acids (e.g. sulphuric acid) in which lignin is insoluble [15]. As the lignin bonds with cellulose to form a lignocellulosic complex it acts as a sort of glue which provides the overall support to plant and tree structures. The structure contains various functional groups including hydroxyl, methoxyl and carbonyl, which give it high polarity.

2.1.4 Extractives

Extractives give wood certain properties such as colour and natural resistance to fungi and insect attack [19]. Examples include fatty acids, waxes, tannin, sugars and wood resins which are largely found in the core of the biomass structure [21]. Organic solvents or hot water can be used to extract these extractives from biomass but hemicellulose can also be removed from the biomass as a result. [20].

2.1.5 Ash

Biomass contains small amounts of ash which consists of inorganic material such as silica, potassium, calcium, sulphur, sodium, magnesium and chlorine [19]. Research by Nowakowski et al. [22] shows that metal cations have the most significant effects on the formation of a quality bio-oil. When fast pyrolysis occurs with alkali metal cations present it leads to catalytic cracking of fast pyrolysis vapours. High alkali metal contents do not necessary mean high ash content, a majority of ash can be made up of silica which has no or little effect on the bio-oil quality. Ash yield on its own provides limited information when the composition and biomass origin are not considered. Ash content of biomass can occur naturally or due to contamination, these different sources are discussed in Section 2.2.

2.2 Sources of ash

Ash content of biomass can originate from a number of sources: natural or contamination as shown in Table 2. The sources of ash are discussed in this section and relate to herbaceous, agricultural and woody biomass.

Table 2 Source of ash (adapted from [23])

Natural	**Time of formation**	**Mechanism**
Formed in biomass	During plant growth	Photosynthesis, diffusion, adsorption, hydrolysis, precipitation
	After plant death	Evaporation, precipitation
Formed outside biomass	During plant growth and death	Pre-existing fine mineral particle fixed in pores, voids and cracks due to water and wind
Contamination	**Time of formation**	**Mechanism**
Formed in and outside biomass	During and after biomass harvesting	Natural or industrial components added to biomass due to harvesting, transport and further processing

2.2.1 Natural

Inorganic content such as alkali metals are essential for the healthy growth of crops. Inorganic content inside biomass is generated by plant growth (photosynthesis, diffusion, adsorption, hydrolysis and precipitation) (refer to Section 2.3) and after biomass death (storage) inorganic content can be increased by natural processes such as evaporation and precipitation [23]. As mentioned, precipitation can increase inorganic content of biomass as rain splashes soil onto the biomass stems. Soil contamination due to heavy rain is much greater for thinner shorter stemmed crops such as switchgrass. This is due to a number of reasons: rain can only splash mud a certain height, so therefore taller stemmed plants have a lower proportion of contamination. Thin stemmed plants have a greater surface area to volume ratio which results in a greater exchange rate between surface contamination and overall mass contamination [12]. Inorganic content can also form outside the biomass during plant growth and after biomass death (storage), pre-existing fine mineral grains can be introduced by water and wind on biomass surfaces and fixed in pores, voids and cracks [23].

2.2.2 Contamination

Inorganic content can be increased by harvesting, transport and storage [2, 9], as well as pollution [8, 10] from roads and industrial sites. The harvesting process of biomass can result in soil contamination [4, 23-25].

Harvesting technologies can be divided depending on processing technique between shredders and balers [25]. Of the two processing techniques shredders are preferred due to cheaper harvesting costs. As shredding is a single-pass recovery technique (collected, shredded and extracted from field in one visit) it ensures that the crop has limited contact with soil. Harvesting aims to maximise yields (reduce amount of crop left on field) but this can be directly linked to contamination. Depending on the harvesting machine setting can increase or decrease both crop yield and contamination [24]. The crop can be harvested lower to the ground maximising harvested crop yield, but doing so can increase soil contamination as a larger quantity of soil particles are entrained with the harvested crop. Acampora et al. [24] studied harvesting losses and product contamination with six commercial machines set at three pick-up heights: conventional (2 cm), 1 cm above ground and 3 cm above ground. The study found that harvesting losses were directly related to pick-up height setting. Raising the pick-up height to 3 cm above the ground reduced ash content by 1% compared to a pick-up height of 1 cm which collected soil and other inorganic materials [24]. The silica content of biomass during growth is relatively low for the majority of biomass types but if soil contamination occurs due to harvesting the silica content can be greatly increased [4].

Biomass must be stored so that it is kept in good condition (reduced fungal growth and microbial degradation) and protected from moisture. Ash content changes due to storage have been shown not to be significant [26-28]. During storage leaf material maybe dropped [27] resulting in a reduction of ash content at the expense of crop yield. The majority of leaf material is dropped over the winter period and during harvesting and following conventional harvesting by chipping or baling storage losses of leaf material will be low.

Soil can be contaminated with heavy metals e.g. Pb, Cu, Cr, Zn, Mn, Cd, As and Hg [29] as a result of agrochemicals, animal manure, mineral fertiliser, sewage sludge and pollution from local industries or traffic [29, 30]. Fossil fuel combustion is a major source of heavy metals notably Cd and Pb resulting in soil contamination via the atmosphere [31]. Heavy metals have been shown to be toxic to soil microorganisms [32] which can affect crop yields. High concentrations negatively affect plant photosynthesis, respiration and transpiration [33], leading to reduced growth. Only small quantities of heavy metals have been shown to be transferred from soil to plant tissue [34] which is important as they are highly toxic to plants. Certain crops such as switch grass can be used to remove heavy metals

from contaminated soil [35-38] so that the site can be used for crops which are affected by soil heavy metal content.

Fertiliser application (refer to Section 2.4.1) is used to supply crops with the required nutrients to achieve optimum crop yield as certain nutrients can become deficient in soil over time, this therefore increases the inorganic content of biomass. Fertiliser application is not a contamination but neither is it a natural source of ash, due to it being physically added to the crop it can be classed as contamination.

2.3 Ash composition

The chemical breakdown of biomass, by thermo-chemical, produces a solid residue. When produced by pyrolysis it is known as char, which contains fixed carbon and ash. Ash is formed from inorganic material found within and on the surface of biomass (refer to Section 2.2). The amount of inorganic material in biomass should be taken into account as part of the total composition. The inorganic content of biomass can vary from different types of biomass as shown in Table 3, and is generally a function of soil type [3, 9, 13] and timing of harvest [2, 10, 13, 14], other factors are mentioned in Section 2.1. Alkali metals are essential for the healthy growth of crops which leads to a better quality bio-oil after being processed. There are a number of options for limiting the total ash content in harvested crops (refer to Section 2.4).

Elemental concentrations can be recalculated from Table 3 so that the elements can be classified into major (> 1.00%), minor (0.10 - 1.00%) and trace (< 0.10%) amounts, dry basis. The major elements in biomass are normally C, H, N, O, Ca and K; minor elements are normally Si, P, Al, Mg, Fe, S, Cl and Na; trace elements are Ti plus other elements which are not discussed. This is not correct for all biomass types as certain elements can be major elements in one biomass and are minor elements in others. C, H, N, O and S are the organic forming elements in biomass, and the other elements mentioned above are the inorganic forming elements. Some organic elements also are contained in the inorganic matter of biomass and the same can occur for inorganic elements being contained in organic matter of biomass, therefore all elements above can be ash forming elements [23].

Table 3 Chemical ash composition of five varieties of biomass (normalised to 100%), wt. % (adapted from [23])

Biomass	SiO_2	CaO	K_2O	P_2O_5	Al_2O_3	MgO	Fe_2O_3	SO_3	Na_2O	TiO_2
Beech bark	12.40	68.20	2.60	2.30	0.12	11.50	1.10	0.80	0.90	0.10
Willow	6.10	46.09	23.40	13.01	1.96	4.03	0.74	3.00	1.61	0.06
Miscanthus	56.42	10.77	19.75	5.54	0.79	3.01	0.94	2.28	0.47	0.03
Switch grass	66.25	10.21	9.64	3.92	2.22	4.71	1.36	0.83	0.58	0.28
Wheat straw	50.35	8.21	24.89	3.54	1.54	2.74	0.88	4.24	3.52	0.09

2.3.1 Potassium

Potassium is involved in a large number of essential processes for plant growth including enzyme activation, protein synthesis, photosynthesis, regulation of osmotic pressure, vascular transport and cation-anion balance [39]. Plants with potassium deficiency can lead to a variety of inhibiting growth factors, such as wilting, lodging and increased susceptibility to frost and fungal damage [39]. Lodging is defined as the state of permanent displacement of stems from the upright position as a result of top heavy plants (excess growth) or weather conditions [40]. This indicates that there is a lower limit of potassium which is required (varying between plant species). By being able to identify the required quantity of potassium needed for optimum growth would reduce the final content when harvested.

Uptake of potassium in excess of the plants immediate growth requirements is known as 'Luxury Consumption' [41]. This characteristic can be seen with all nutrients which are supplied in abundance but more so with potassium [42-44]. This characteristic can be useful for young plants that store potassium for future usage, but in the case of feedstocks being harvested for use in a fast pyrolysis system it has a major negative effect due to increased inorganic content. When the whole plant is harvested any excess potassium that is absorbed remains in the plant, and leads to increased alkali metal concentrations.

2.3.2 Phosphorus

Phosphorus is essential for plant growth and its functions cannot be performed by any other nutrient [45]. Therefore an adequate supply of phosphorus is required for optimum growth. It is involved in key plant functions such as energy transfer, photosynthesis, transformation of sugars and starches and transfer of genetic characteristics from one generation to the next [45]. Plants with phosphorus deficiency have a reduced leaf number with a reduction in leaf expansion [46, 47]. A reduction in leaf expansion is a result of the rate of cell division and expansion slowing down therefore the leaf has a smaller surface area [47]. Root growth is also reduced due to phosphorus deficiency, limiting water and nutrient up take [48]. Phosphorus is taken up as the primary orthophosphate ion ($H_2PO_4^-$), but as soil pH increases the secondary orthophosphate ($HPO_4^=$) is taken up more readily [49].

2.3.3 Sodium

Sodium is not an essential element in plants and does not have any specific role in the metabolic activities. Sodium can substitute potassium in some cellular functions such as osmotic functions [50, 51], but in others it is toxic. It has never been shown that sodium can completely replace potassium, where the latter is deficient. When potassium is deficient, sodium is ineffective as a substitute even for sodium loving plants such as sugar beet. Sodium can help crops to withstand drought conditions which would otherwise produce severe negative effects [52].

Pardo et al. [53] found that sodium ions are very similar to potassium ions in plants, and that potassium ion transporters do not discriminate between either cation. This can result in accumulation of sodium ions in plant cells, and as sodium ions are toxic to cells it is not desirable.

2.3.4 Calcium and Magnesium

Calcium and magnesium have many roles in plants such as binding form, cell wall stabilisation, secretary processes, membrane stabilisation and regulation of osmotic pressure [54-56]. The number of roles identifies how important these chemicals are to plant growth and health, therefore have to be taken into account for fertiliser application when considering limiting their availability.

2.3.5 Other contaminants

Sulphur is used by all plant tissues for protein synthesis and is a structural component of amino acids, proteins, vitamins and enzymes and is essential to produce chlorophyll [55]. Soil tests for sulphur are not always reliable, because sulphur exists in several oxidation states in soil and only one of these is available to plants, sulphate (SO_4^{-2}) [57]. Sulphur deficiencies are identified as light green leaves. Rennenberg [58] found that the amount of sulphur in a plant at one time is determined by the availability of sulphate in the soil and the availability of volatile sulphur to the leaves (SO_4^2 and H_2S). This means that when trying to work out specific fertiliser needs for crops both soil conditions and atmosphere conditions have to be considered. Rennenberg also found that excess sulphur will be taken up by the plant at 2 to 3 times the required amount. Any more sulphur taken up by the plant will be deposited by the roots back into the soil.

Iron is used in plants for chlorophyll production and maintenance, almost all of plant iron is located in the chloroplasts which are responsible for photosynthesis [59]. Iron is absorbed by plants as Fe^{2+} [60]. As iron is an integral part of photosynthesis iron deficiency is recognised by yellowing of new plant leaves, as chlorophyll cannot be maintained.

Aluminium has no function in plants but can be toxic in high concentrations. Aluminium toxicity in soil can be recognised by inhibition of root growth [61]. Even though aluminium has no function it still can be absorbed by biomass or be incorporated in its composition due to soil contamination (refer to Section 2.2).

Titanium is not an essential element for plant growth but can be classed as 'beneficial'[62], so there is no deficiency [63]. It can help maintain osmotic pressure and compensate for toxic effects of other elements [62].

Silica has a number of beneficial effects to many species of plant. High silica content increases leaf resistance to fungal attack and insect pests [64]. It also increases leaf erectness reducing the chance of lodging (refer to Section 2.3.1) [64]. This means that if the silica uptake or silica plant content is reduced it would result in major harm to the plant, and its overall growth.

2.3.6 Importance of ash

Ash contains inorganics which are distributed throughout biomass. It has been recognised that these metals have a major impact on thermal processing such as fast pyrolysis. A number of studies have been performed [65-76] on the influence of inorganics on pyrolysis which have found that fast pyrolysis reactions were affected by alkali metals present in biomass ash (refer to Section 2.8).

2.4 Ash control

There are a number of methods that can be utilised for controlling ash content in biomass. Ash control can be used to limit biomass ash content during growth, harvesting and processing (sample preparation) or can be used to reduce the total biomass ash content after growth and harvesting such as washing. Each method for controlling ash content has its own advantages and disadvantages.

2.4.1 Fertiliser

Fertilisers are any organic or inorganic material of natural or synthetic origin that is added to soil to supply a single or multiple nutrients for plant growth (refer to Section 2.3). Plants can only absorb nutrients if they are easily dissolved chemicals. Fertilisers are applied to supply crops with the required nutrients to achieve optimum crop yield as certain nutrients can become deficient in soil over time. By looking at specific components in ash related to plant growth certain steps can be taken to try and limit the total inorganic content in harvested crops. Tiemann et al. [13] studied the effects of low and high fertiliser application (P, K, Ca, Mg and S) in both the dry and rainy season, results showed that high fertiliser application in the rainy season had the greatest effect on increasing biomass yield. Fertilisers could be applied to crops to achieve optimum crop yields but it has to be controlled so that 'Luxury Consumption' (refer to Section 2.3.1) can be limited thereby limiting inorganic content of the crop. Soils have to be studied to identify which nutrients are deficient to achieve optimum crop yields and are replaced with specific fertiliser application.

2.4.2 Harvesting

The type of biomass feedstock that is grown for fast pyrolysis can have a great effect on bio-oil quality due to ash content and proportion of biomass components. Leaf material generally contains a higher ash content than compared to stem material (leaf blade - 185 g $kg.^{-1}$, leaf sheath - 191 g $kg.^{-1}$ and stem - 140 g $kg.^{-1}$) [7, 77], therefore feedstocks that drop their leaves before harvesting or where the lower stem is left in the ground minimises the overall ash content of the crop.

Harvesting times and methods [2, 9, 10, 14] can have a considerable effect on the ash content of biomass depending on feedstock. Harvesting methods have to try and limit the amount of contact the crop has with the soil, as ash content can be increased drastically if this occurs (refer to Section 2.2). As mentioned in Section 2.2.1, soil contamination due to heavy rain can increase crop ash content. Dayton et al. [12] suggested that short thin stemmed plants should be harvested before the winter period, so that less heavy rains are experienced and reduced soil contamination occurs. But for tall thick stemmed plants it could be beneficial to harvest after the winter so that soluble ash content can

be reduced through natural rain leaching. Harvesting methods and storage can also affect ash content which has been discussed in Section 2.2.2.

Senescence has to be taken into account when different harvesting times are considered for varying feedstocks. Senescence is a complex, highly controlled stage of plant development with multiple effects that may contribute to, or improve a number of the characteristics that make certain crops suitable bioenergy crops such as miscanthus. Senescence involves the coordinated degradation of cellular components and molecules (proteins, lipids and carbohydrates) and the subsequent mobilisation of essential nutrients (such as nitrogenous compounds) to below ground storage organs. Consequently senescence affects both the composition of the crop that is harvested by lowering inorganic content and the availability of nutrients for the next perennial growth cycle. Senescence affects leaf turnover and canopy duration and thus affects the length of the growth season. Senescence is triggered by various abiotic and biotic environmental factors including light, drought, hormones and pests [78] that can also have an influence on biomass quality and yield [79]. Greater understanding of senescence may allow for the optimisation of the crop for both biomass yield and subsequent biofuel quality [80].

2.4.3 Biomass blending

Using the same concept of blending biomass with coal for power stations, different varieties of biomass could be blended to achieve desirable ash contents. For example if a 4% ash content biomass is blended with a 1% ash content biomass, the overall mixture of biomass will have an ash content that falls within these percentages. This could result in reduced washing requirements (refer to Section 2.4.8) as only a certain proportion of biomass would have to be washed and when dried could be blended with unwashed biomass to decrease the overall ash content. There are a number of biomass varieties that can be blended [23] such as woody biomass, herbaceous and agricultural biomass, aquatic biomass, animal and human waste and contaminated biomass (Table 4).

Table 4 Biomass varieties and examples

Biomass groups	Examples
Woody	Soft or hard, branches, foliage, bark, chips, pellets, sawdust, other
Herbaceous and agricultural	Grasses, straws, residues (fruits, shells, grains, seeds, bagasse, fodder), others
Aquatic	Algae, seaweed, kelp, others
Animal and human waste	Meat-bone meal, chicken litter, manures, others
Contaminated	Municipal solid waste, sewage sludge, paper pulp, waste paper, chip board, ply wood, others
Biomass mixtures	Blend from above varieties

2.4.4 Physical

Grinding of biomass can be used as a pre-treatment to open up the structure and overcome natural resistance to chemical, biological or thermal degradation [81]. It is very important that the biomass is not ground any more than required as there is a minimum particle size that can be processed in certain fast pyrolysis rigs (refer to Section 7.1) due to blockages. It has been shown that grinding of biomass to a suitable size fraction for fast pyrolysis results in reduced ash content for most crops [82, 83]; therefore to achieve a lower ash content feedstock particles smaller than 0.25 mm should be removed. Particles below 0.25 mm have shown to have higher ash content compared to larger particle fractions (refer to Appendix 1). Another physical pre-treatment is separation of plant constituents, leaves and stalk. Leaf material has a higher ash content than the stalk material [7, 77] refer to Section 2.4.2 for specific data. Leaf removal can be linked with time of harvest and senescence (refer to Section 2.4.2).

2.4.5 Chemical

In the bioethanol industry, milled biomass is soaked in dilute sulphuric acid and then heated up to around 160 ^{o}C to break down the hemicellulose to form its component sugars [84]. The pre-treated biomass is then neutralized and conditioned to remove compounds that have been released from the biomass such as acetic acid, or from the degradation of biomass, such as furfural [85]. Chemical pre-treatment helps to break down the structure of the biomass so that it is more easily processed.

2.4.6 Biological

In the bioethanol industry after the biomass has been chemically pre-treated the sugar solution is mixed with several bacteria that have been genetically engineered to ferment the sugars [86]. The bacteria convert the sugars to ethanol.

2.4.7 Thermal

Biomass torrefaction is a thermal pre-treatment in relatively low temperature range of 200 to 300 ^{o}C in the absence of oxygen (prevents conversion of carbon to carbon dioxide and loss of energy) causing the biomass to dry and part of the hemicellulose fraction to decompose and lose its fibrous structure [87-94]. Therefore the biomass is easier to grind and has an increased energy density. The biomass is also much easier to pelletise resulting in easier storage and transportation [95]. Torrefaction is a partial pyrolysis process but at lower temperatures, slower heating rates and much longer residence times.

2.4.8 Washing

Advancing the idea of natural leaching of ash from biomass due to rain can lead to some very useful results. Different approaches have been used to pre-treat biomass including with water [96-101]. To improve the efficiency of washing pre-treatments a suitable biomass size fraction is required (refer to Section 2.4.4); an increased surface area is required for efficient washing techniques.

Water washings remove the majority of soluble alkali metals and are more efficient when the wash is agitated. Water washes have been shown to be efficient in potassium, sodium and chlorine removal [96], also around 90% of alkali metals in biomass is present in water soluble form [102]. Alkali metal cations have been reduced in a higher quantity using this method than compared to alkali earth metals; this is expected due to the difference in solubility [103]. This research shows that removal of the majority of alkali metals is simple to achieve with water washing. As some of the ash content is due to soil contamination (refer to Section 2.2) a small proportion of phosphorus can be expected to be removed even though it tends to be insoluble [103]. This is beneficial to the pyrolysis process as phosphate compounds are known to promote char formation and are used for this purpose in fire

retardant materials [104, 105]. Water washing are more suited to high ash content biomass, as biomass with lower ash contents (woody biomass) have a higher concentration of alkali metals bound to the organic structure which limits the effect of water washing.

Tan et al. [97] has shown that metal ion content of biomass is decreased after hydrochloric acid (HCl) washing resulting in an increased release rate of volatiles during pyrolysis, an increased volatile release rate leads to increased bio-oil yields and a decrease in secondary reactions of volatiles. A decrease in mineral content after demineralisation with HCl was also observed by Mayer [98], but it was found to change the primary polymer structure decreasing hemicellulose content. A change in the primary polymer structure from strong acid washes was also found by Tan et al. [97]. Cellulose pyrolysis produces higher yields of bio-oil compared to hemicellulose and lignin, which produce char and gas in higher yields [106]. As mentioned above strong acid washes decrease the amount of hemicellulose and cellulose in biomass due to hydrolysis, therefore increasing the ratio of lignin. This leads to lower yields of bio-oil and increased char and gas yields. Weaker acid washes can either partially or fully hydrolyse hemicellulose but have little or no effect on cellulose content [99], but do not decrease metal ion content as much as a strong acid wash. Strong acid washes completely hydrolyse hemicellulose and cellulose increasing porosity of the biomass due to their removal, weak acids only partially hydrolyse hemicellulose therefore the porosity is not increased as much. Research by Park [100] found that strong acid treatment of biomass caused mass losses; washing with Nitric acid (HNO_{3-}) and HCl caused 17% and 15% mass losses respectively. Park also found that alkali treatments resulted in greater mass losses; washing with Sodium hydroxide (NaOH) and Ammonium hydroxide (NH_4OH) caused 47% and 35% mass losses respectively. This relates to research mentioned above as the degradation of hemicellulose and cellulose can result in mass loss. Work by Vamvuka [107] observed that carbonates, sulphates and alkali chloride minerals were dissolved when biomass was washed with HCl, when a weaker acid was used (Acetic acid - CH_3COOH) the carbonates and sulphates were only partially removed.

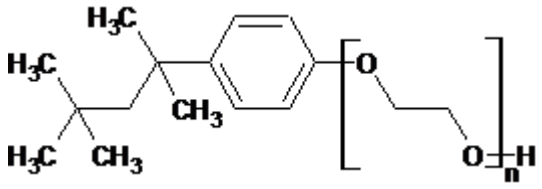
Davidsson et al. [101] showed that water washing and acid washes have a limited effect on alkali metal removal from biomass. They studied release of alkali compounds from untreated and washed biomass samples in a nitrogen atmosphere at two temperature ranges, one being 200 - 500 ^{o}C which can be associated to a pyrolysis process. By using a water wash alkali emission was reduced by 5 - 30%, acid washing reduced the alkali emission by 70% [101]. This research supports other research that was mentioned above. Complete alkali removal by water or acid washing was not possible; this was shown by inefficient removal of alkali bound to the organic structure of pure cellulose (ash content 0.07%).

Other compounds can be added to the washing solution to aid in ash reduction, such as surfactants. Surfactants are compounds that lower surface tension between two liquids or between a liquid and a solid. Surfactants are widely used in numerous commercial and industrial products, including detergents, emulsifiers, wetting agents and dispersants [108]. Coulson et al. [109] added a surfactant (wetting agent) to water to try and improve ash removal. It was found that the agent sped up the wetting of biomass permitting the water to pass quicker through the smaller diameter capillaries, these smaller capillaries may not have been washed without a surfactant present in the solution. Also swelling the capillaries by twice there original size allows water to wash the entirety of the biomass reducing the ash content considerably. As the capillaries were swelled it reduced the water retention, resulting in less water being held by the biomass. Triton X-100 (refer to Section 2.4.8.1) has been shown to increase cell permeability either alone [110], in combination [111] or with physical methods [112]. It is only possible for the permeability to be increased if the surfactant can penetrate the cell wall and reach the membrane, therefore the permeabilisation procedure depends on cell wall and cell membrane composition [113]. Galabova et al. [113] showed that the permeability depended on the concentration of Triton X-100 and not the volume of solution. This identifies that a more concentrated surfactant wash will have a greater effect on permeability than a high volume low concentration surfactant wash. As mentioned above experiments on permeability have been carried out using Triton X-100 and other disrupting agents in conjunction [111, 114] . A disadvantage of using surfactants, such as Triton X-100, is that they are non-selective and may allow for extraction of lipids as well as proteins [114]. The main reason for adding a surfactant to the washing solution is to aid in inorganic material removal from biomass, therefore anything else removed from the biomass is detrimental to the washing procedure. Surfactant added to a water wash is still a very useful technique as it helps to increase the efficiency of ash removal and should be considered when examining the economic merit due to less water being retained by biomass; therefore reducing drying requirements (refer to Section 2.5.6).

There are two main problems with washing, the first being that the biomass has to be dried so that the moisture content is below 10% (refer to Section 2.5.6), due to fast pyrolysis requirements. Secondly if the biomass is acid washed the acid has to be separated and recovered or disposed, which increases the operation costs of pre-treatment. Acid washed biomass has to be rewashed with deionised water to remove certain ions remaining from the acid, such as chlorine ions from a hydrochloric acid wash. If chlorine ions were to remain in pre-treated biomass it can lead to negative effects on bio-oil yields and quality, due to catalytic cracking of the pyrolysis vapours. This increases the water supply demand which can increase operation costs dramatically.

2.4.8.1 Triton X-100

Triton X-100 ($C_{14}H_{22}O(C_2H_4O)n$) is a nonionic surfactant, which has a hydrophilic polyethylene oxide chain and an aromatic hydrocarbon lipophilic group.



n = 9 - 10

Figure 1 Triton X-100 structure

Triton X-100 is a very stable liquid with a clear to slightly hazy colouring. Below are some of its properties**:**

- Specific gravity: 1.065 at 25 ^{o}C (Approximately 1.07 g ml.$^{-1}$)
- Approximate molecular weight: 625
- Viscosity: 240 cP at 25 ^{o}C
- pH: 6.0 to 8.0
- Cloud point: 65 ^{o}C

If the temperature of the surfactant solution is increased the hydrogen bonds gradually break causing the surfactant to come out of solution. This is commonly referred to as the cloud point. The cloud point for Triton X-100 is 65 °C, this identifies that any washing procedures involving Triton X-100 cannot be increased above 65 ^{o}C. Triton X-100 produces less foam when in a water solution due to being non-ionic; this is a positive as there will be no excess foam formed due to agitation of washing solution. Triton X-100 is biodegradable [115] and large amounts of the surfactant and biodegraded by-products are currently released into the environment. As Triton X-100 is biodegradable it can be used in a washing solution without having to be separated and recovered or disposed of after use, this saves on operation costs.

2.5 Fast pyrolysis

Fast pyrolysis converts biomass, such as *Miscanthus x giganteus*, by rapidly heating in the absence of oxygen, and then rapidly cooling the vapours [116]. The products are bio-oil, non-condensable gases and char. The key product is bio-oil which is the renewable fuel source. The overall quality of bio-oil has been tried to be improved; this can be achieved by using a catalyst (refer to Section 2.6.7) or by reducing certain compounds present in the initial biomass (refer to Section 2.4).

Bio-oil is known to be viscous, acidic, thermally unstable and contains a high amount of oxygenated compounds (refer to Section 2.7.1). Advances in current pyrolysis techniques are aimed at producing bio-oil of high quality so that it can replace or supplement the current fossil fuel usage.

There are two main types of pyrolysis: slow pyrolysis and fast pyrolysis. Details on each pyrolysis residence time, heating rate and operating temperature range can be found below in Table 5. By using different heating rates and vapour residence times has a major effect on the product composition. The typical product composition for fast pyrolysis is 75% liquid, 12% char and 13% gas, compared to slow pyrolysis which is 30% liquid, 35% char and 35% gas [117]. By comparing the results fast pyrolysis is the preferred technique for liquid products (bio-oil). Mohan et al. [19] found that there were four essential features of fast pyrolysis, firstly very high heating rates, secondly a controlled pyrolysis reaction temperature, thirdly short hot vapour residence times and finally the vapours and aerosols are rapidly cooled to form bio-oil.

Table 5 Types of pyrolysis technology [118]

Pyrolysis type	Residence time	Heating rate ($^{o}C\ s.^{-1}$)	Operating temperature (^{o}C)
Slow	5 - 30 minutes	0.10 - 1	400 - 600
Fast	1 - 2 seconds	10 - 200	400 - 600

Fast pyrolysis produces bio-oil by rapidly heating biomass up to a controlled temperature of between 400 and 600 ^{o}C. Bridgwater et al. [119] found that fast pyrolysis produces maximum yields at processing temperatures around 500 ^{o}C. The biomass feed has been pre-dried to contain less than 10 wt. % water. Less than 10 wt. % water content is a standardised value for most pyrolysis operations (refer to Section 2.5.6), high water content in biomass results in greater effects on the rapid heating and in the end the final bio-oil composition. The essential features of fast pyrolysis for producing liquids are very high heating and heat transfer rates which require a biomass feed of an appropriate particle size (refer to Section 3.2). The pyrolysis temperature should be carefully controlled as well as the vapour phase temperature between 400 and 450 ^{o}C (refer to Section 7.1). Fast pyrolysis has a short

vapour residence time typically less than 2 seconds. The residence time has to be kept as short as possible to prevent secondary reactions taking place which will convert the condensable fast pyrolysis vapours into permanent gases, water vapour and char. Typical liquid yields are around 75% [120].

2.5.1 Fast pyrolysis reactor types

The main part of the fast pyrolysis process is the reactor. Varying reactors can be used to meet specific fast pyrolysis requirements. There are several extensive reviews published supplying detailed descriptions of different fast pyrolysis reactor types [116, 117, 119].

There are a number of fast pyrolysis reactors that are used or have been developed [117]:

- bubbling fluidised bed reactor
- circulating fluidised bed reactor
- ablative reactor with rotating plate
- ablative reactor with rotating cone
- vacuum reactor

Fluidised bed reactors are currently used in commercial production of bio-oil and extensively used in academic research. They are the most popular choice of reactor due to their reliability and ease to operate. Also they are quite simple to scale up from lab to commercial plant scale.

Biomass used in a bubbling fluidised bed reactor has to be prepared to certain specifications. The particle size of biomass has to be between 0.25 - 3.00 mm and have been dried to below 10% moisture content. The heat transfer material inside the reactor can be silica sand which provides a constant temperature distribution within the fluidised bed. Silica sand is a very efficient heat transfer material due to its high solid density. The residence time of the solids and vapours is controlled by the fluidising gas flow rate. Char (solid) residence times are far greater than the pyrolysis vapour residence times.

Fluidised bed reactor advantages [116]:

- easily scalable from lab to commercial
- good reaction zone temperature control
- high heat transfer from bed material
- short hot vapour residence time of below 2 seconds
- no moving parts with reactor
- established and well researched reactor set up

The fluidisation velocity of the fluidised bed reactor has to be high enough that the fast pyrolysis char is entrained while the bed material remains in the reactor (refer to Section 7.1). Also the difference in density of the bed material and fast pyrolysis char has to be sufficient enough that only char is entrained and all the bed material stays within the reactor.

2.5.2 Distribution of fast pyrolysis products from certain biomass components

There are no standard decomposition processes of cellulose, hemicellulose and lignin available. The thermal decomposition of cellulose has been studied the most as it is the major component of wood and has a less complex structure than hemicellulose and lignin. The varying proportions of cellulose, hemicellulose and lignin in biomass influence the fast pyrolysis product distribution. The most important factors that affect fast pyrolysis product distribution are: biomass component composition, poor thermal conductivity of biomass, high reactivity of volatiles and the catalytic effect of char and alkali metals contained in ash [22, 71, 73, 121], as well as fast pyrolysis conditions (biomass particle size, pyrolysis temperature and hot vapour residence time).

Primary products of cellulose and hemicellulose decomposition are condensable vapours (liquid product) and gas. Lignin decomposes to liquid, solid (char) and gas products. Extractives contribute to liquid and gas yields and mineral content is entrained in char. The general distribution of fast pyrolysis products from certain biomass components are shown in Figure 2.

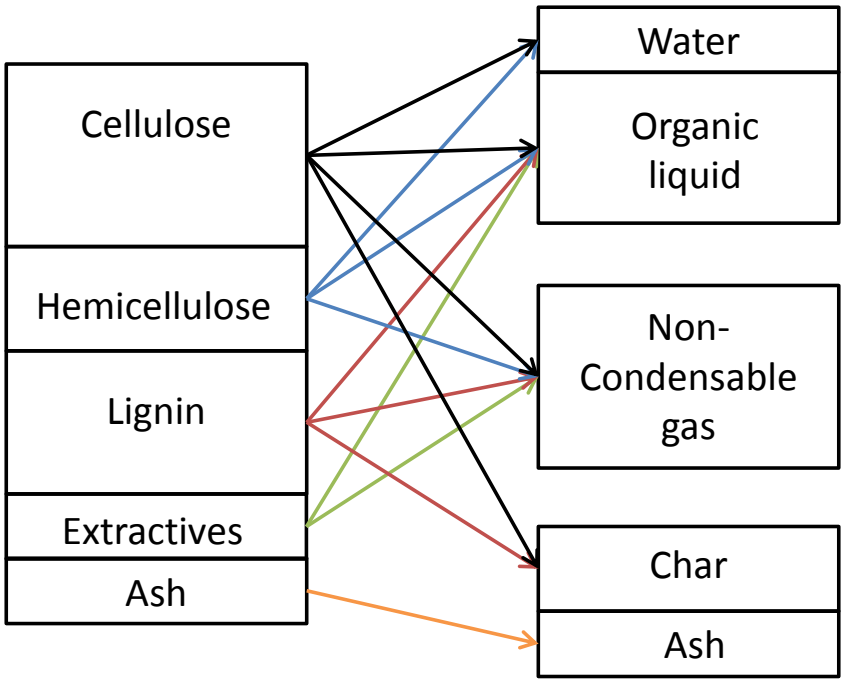


Figure 2 Distribution of fast pyrolysis products from certain biomass components

2.5.3 Fast pyrolysis of cellulose

Fast pyrolysis of cellulose starts at temperatures as low as 150 ^{o}C. Work by Evans et al. [72] showed that pyrolysis of cellulose at temperatures below 300 ^{o}C resulted in the formation of carbonyl, carboxyl and hydroperoxide groups, elimination of water, production of carbon monoxide and carbon dioxide with a char residue left over. Low temperatures will produce low yields of fast pyrolysis organic liquid products.

Pyrolysis of cellulose at temperatures above 300 ^{o}C results in yields of liquid products above 80 wt. %. Cellulose decomposes initially to form activated cellulose [122]. From the formation of activated cellulose two parallel reaction pathways occur, depolymerisation and fragmentation (ring scission), as shown in Figure 3. The main products of each parallel pyrolytic pathway are quite different as depolymerisation produces monomeric anhydrosugars, furans, cyclopentanones and pyrans and other related products [122-124]. As ring scission produces hydroxyacetaldehyde, linear carbonyls, linear alcohols, esters, and other related products [122-124].

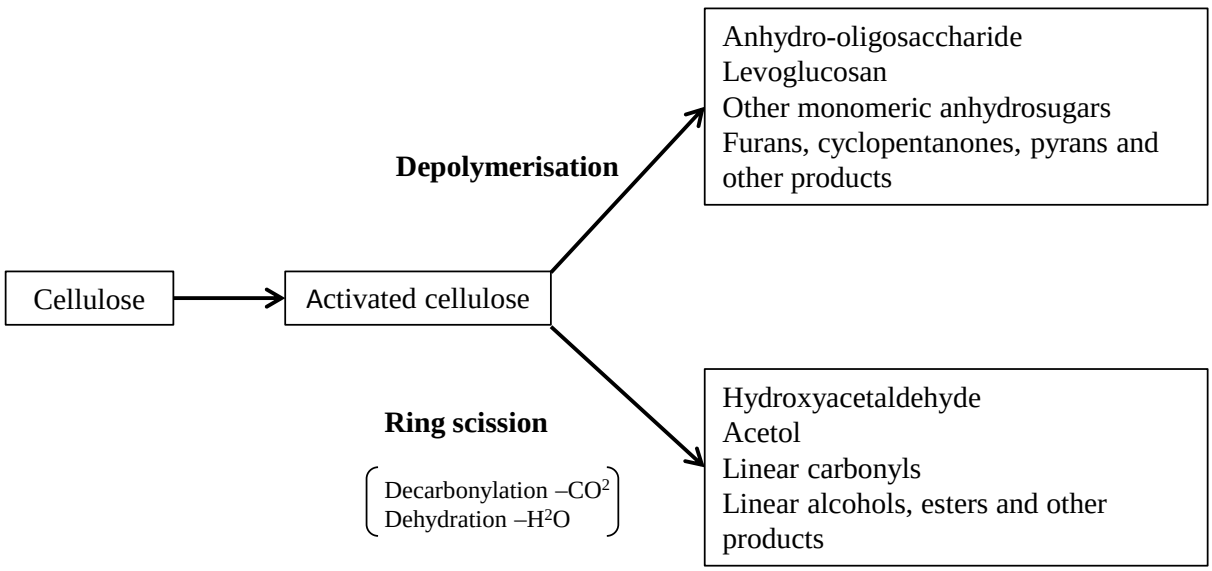


Figure 3 Cellulose fast pyrolysis parallel pyrolytic pathways

2.5.4 Fast pyrolysis of hemicellulose

The primary hemicellulose components are glucomannans and xylan which when pyrolysed form varying yields of char and depolymerisation products [123]. Glucomannans produce similar pyrolytic products to cellulose, as xylan produces higher char yields and not typical depolymerisation products such levoglucosan [123]. Pyrolysis of glucomannans is similar to cellulose as the glycosidic bonds are cleaved and able to form a stable monomeric anhydrosugars [125]. Xylan follows an alternative pyrolytic dehydration pathway which results in an increased char formation. Shen et al. [126] proposed possible pyrolytic pathways for xylan as shown in Figure 4.

Figure 4 Xylan fast pyrolysis major pyrolytic pathway [126]

2.5.5 Fast pyrolysis of lignin

Lignin is the most thermally stable component of biomass. Fast pyrolysis of lignin produces high char yields and low liquid yields compared to both cellulose and hemicellulose. The liquid product has three specific groups, large molecular oligomers which account for the majority of the liquid product [127]. The other two groups are monomeric phenolic compounds and light compounds such as acetic acid [127, 128].

2.5.6 Effect of biomass moisture content

The reason for considering biomass moisture content is due to the affect it can have on the final total water content of bio-oil. With increased water content the bio-oil is prone to phase separate which is undesirable.

Westerhof et al. [129] reported that the char and gas yield from pyrolysed biomass increased with increasing moisture content of feedstock. When biomass moisture contents were close to 20 wt. % (wet basis) organic vapours were lost when condensed as the proportion of fast pyrolysis product gas in the gas stream is reduced due to increased water vapour, but this is not a problem in feedstock that had moisture content below 10 wt. %. When the feedstock moisture content is reduced the proportion of organic vapours increases, but drying a high moisture content feedstock to this extent increases the overall energy requirement. Gray et al. [130] also observed that with increasing feedstock moisture content led to increased char yields. A feedstock of 16% moisture content resulted in a 5% char yield increase when compared to a dry feedstock, independent of ash content. This identifies that increased moisture content resulted in lower volatile yields and higher char yields, indicating that there must be some chemical interaction with water occurring in the fast pyrolysis reactions.

He et al. [131] studied the affect pyrolysis parameters have on the final products by varying the moisture content (5 - 15%) and the pyrolysis temperature (450 - 550 ^{o}C). It was found that bio-oil yields declined when pyrolysis temperature increased and moisture contents were held constant. The highest bio-oil yield was found at a pyrolysis temperature of 450 ^{o}C and a moisture content of 10%, and the lowest bio-oil yield was found at a pyrolysis temperature of 550 ^{o}C and a moisture content of 5%. As with other studies it was shown that as the moisture content increased so did the char yield. This work shows that to achieve the highest yield of bio-oil moderate moisture contents and lower pyrolysis temperatures are preferred. The work by He et al. [131] also showed that there were major differences in water content from 20 to 30% at different pyrolysis conditions. Generally higher moisture content feedstocks resulted in higher water content bio-oil which was expected.

Variation in senescence (refer to Section 2.4.2) is correlated with variation in moisture content in miscanthus [79] and consequently optimising moisture content through harvest time and senescence is one low energy route to controlling the water content in the feedstock.

2.6 Fast pyrolysis system

There are several parts to a complete fast pyrolysis system, starting with receiving and storage of feedstock biomass. Next is feedstock preparation for fast pyrolysis processing. Fast pyrolysis processing includes reactor configuration, char separation and liquid collection. Fast pyrolysis products can then be upgraded or a secondary reactor can be included to upgrade the pyrolysis vapours directly. This section describes briefly each stage of a fast pyrolysis system.

2.6.1 Reception and storage

Low capacity systems (3 t $h.^{-1}$) require a reception and storage area for biomass feedstock. This can consist of simply a concrete slab that is covered; the area needs to be covered to ensure that the feedstock does not become wetter due to rain therefore increasing drying requirements. Higher capacity systems will use a number of systems for reception and storage such as weighbridge, tipping units, conveyors, bunker storage and reclamation [119].

2.6.2 Feed drying

Drying is usually essential as all feed water ends up in the liquid products (refer to Section 2.5.6). The use of low grade process heat can be used to dry feed biomass, such as char combustion or flue gases from by product gas.

2.6.3 Grinding

The feedstock particle size has to be small enough so that rapid heating and heat transfer can occur to achieve optimal liquid yields (refer to Section 3.2 and 7.1). Different feed particle sizes can be used depending on the pyrolysis reactor type (refer to Section 2.5.1):

- less than 200 mm for a ablative reactor with rotating cone
- less than 6 mm for circulating fluidised bed reactor
- less than 2 mm for a fluidised bed reactor
- ablative reactors can use whole tree chips due to the difference in heat transfer

Grinding biomass to a suitable size fraction for fast pyrolysis results in reduced ash content for most crops (refer to Section 2.4.4 and Appendix 1).

2.6.4 Reactor configuration

There are a number of fast pyrolysis reactors that can be used depending on parameters and certain specifications. An overview of different fast pyrolysis reactors can be found in Section 2.5.1.

2.6.5 Char and ash separation

Almost all of the ash in biomass is retained in char, therefore efficient char removal results in successful ash removal. Char contributes to secondary cracking of fast pyrolysis vapours [19, 65-76], which results in increased reaction water yields and decreased organic yields in bio-oil. Due to these secondary cracking reactions rapid and complete char separation is desired and can be achieved by using a single cyclone unit or a number of cyclones in series.

2.6.6 Liquid collection

The collection of liquids from a fast pyrolysis unit typically uses two pieces of equipment, a quench column and an electrostatic precipitator (ESP). The quench column uses a quench media such as Isopar to contact hot fast pyrolysis vapours to rapidly cool them. Specific temperature control has to be monitored to ensure that blockages are avoided from condensation of heavy ends forming on plates within the quench column. An electrostatic precipitator is very effective in recovering the aerosols from the gaseous stream.

2.6.7 Improving pyrolysis technology

As pyrolysis technologies improve and the quest for suitable alternative and renewable energy sources continues fast pyrolysis will play a bigger role in reducing the reliance on fossil fuels. Generally there are two methods that can be used to improve the final quality of the bio-oil produced from fast pyrolysis. The first is to improve the quality of the source prior to the full scale production; in this case the biomass would need to be improved. This can be achieved by using certain ideal biomass that have the required composition, this ideal composition could also be achieved by using genetically modified sources of biomass [132], but this approach is very much debated. Or it can be achieved by pre-treatment of the biomass prior to pyrolysis (refer to Chapter 5 and 9). The second option is to upgrade the final product [133]; this can be achieved by introducing a catalyst to the pyrolysis reaction which in turn improves the quality of the bio-oil [134]. Upgrading bio-oil to a conventional transport fuel requires full deoxygenation, which can be accomplished by two main routes: catalytic vapour cracking and hydrotreating.

A second reactor can be coupled to a fast pyrolysis reactor so that the fast pyrolysis vapours are cracked before they are condensed (reactor temperature 350-600 ^{o}C, atmospheric pressure) [135]. In the presence of an acidic zeolite catalyst the volatiles produced from fast pyrolysis are cracked through a number of reactions such as deoxygenation (dehydration, decarboxylation, decarbonylation) which result in hydrocarbons being formed as well as carbon solids (coke) [135]. The main reason for cracking the vapours is to remove oxygen from the overall fast pyrolysis liquid content in the form of

water, carbon dioxide and carbon monoxide. Bio-oil has a low H/C ratio which is a limiting factor on hydrocarbon yield; methanol can be added to the process as a hydrogen donor [136]. The characteristics of the catalyst used can have a major effect on the products produced. Strong acid-shape HZSM-5 zeolites produce mostly aromatic hydrocarbons, as HY zeolites and silica-alumina produce mostly aliphatic hydrocarbons [137]. The majority of fast pyrolysis products (excluding water and carbon dioxide) are converted to hydrocarbons:

- alkenes
- single-ring aromatics
- naphthalenes
- methyl anthracene

Hydrotreating of bio-oil in general is the elimination of oxygen in the form of water by hydrogenation and hydrocracking of large molecules. It is carried out at high temperatures, high hydrogen pressure and in the presence of a catalyst (reactor temperature 250-400 ^{o}C, pressure 70-200 bar) [138]. The catalysts used are typically sulphided CoMo or NiMo [138].

Catalytic cracking has a few advantages over hydro treating:

- no or low need for hydrogen
- atmospheric pressure processing
- possibility of close coupling with pyrolysis

2.7 Fast pyrolysis products of biomass

This research project uses fast pyrolysis to convert biomass into fast pyrolysis liquid, fast pyrolysis char and fast pyrolysis gas. This section reviews fast pyrolysis products in terms of characteristics and properties.

2.7.1 Fast pyrolysis liquids

The main fast pyrolysis liquid product is known as bio-oil. Bio-oil has a low viscosity, dark brown colour and a smoky smell [139]. Fast pyrolysis liquids are non-miscible with hydrocarbons. Feedstock moisture content and water produced during fast pyrolysis can result in bio-oil having high water content, which can result in phase separation. Table 6 shows the typical properties of wood pyrolysis bio-oil.

Table 6 Typical properties of wood pyrolysis bio-oil [139]

Water content in bio-oil can be as high as 15-30 wt. % [139], derived from feedstock moisture content and reaction water produced during fast pyrolysis and storage. The presence of water has positive and negative effects on bio-oil characteristics; water lowers the heating value but reduces the viscosity. Bio-oil can separate into two phases due to increasing water contents [140]. A tar-like product with a high viscosity forms a bottom layer, with a low viscosity aqueous phase forming on top. The top layer comprises mainly of products from the decomposition of cellulose and hemicellulose [140]. The bottom layer comprises of high molecular lignin products [140]. Oxygen content of bio-oil is usually

35-40% [139], and is contained in over 300 compounds making up bio-oil. The high oxygen content results in a lower energy density when compared to conventional fuel by up to 50% [141]. Bio-oil contains large amounts of organic acids, such as acetic and formic acids, which leads to an acidic liquid with a low pH (pH value of 2-3) [141]. Due to the acidity of bio-oil it is very corrosive which requires specific construction materials being used for storage vessels or subsequent upgrading processes. Bio-oil has about half the energy density of fossil oil [142] due to higher water and oxygen content. Bio-oil viscosity can vary greatly depending on biomass, fast pyrolysis parameters, content of light compounds and storage time. Sipila et al. [143] found that viscosity was reduced in bio-oil with higher water contents and less water insoluble components. When bio-oil is stored it goes through an aging process which leads to an increase in viscosity [140] (refer to Section 2.8.2). There is an increase in viscosity due to condensation reactions taking place within the bio-oil. The majority of ash contained in biomass is concentrated in char, but small amounts can be entrained in bio-oil. Alkali metals within the ash are problematic, which can lead to cracking reactions within the bio-oil (refer to Section 2.8.2).

The composition of bio-oil is dependent on biomass composition and origin, pyrolysis temperature, residence time, heating rates, collection system and storage conditions [144]. The chemical composition of bio-oil is very complex, and in general is composed of water, organics, and a small amount of ash. The organic components consist mainly of alcohols, furans, phenols, aldehydes and organic acids [145]. Due to the number of compounds and complexity of fast pyrolysis bio-oil it has been difficult to characterise. GC analysis has been used to identify compounds within bio-oil but is limited due to a large fraction of the oil comprising of lignin and carbohydrate oligomers, which are not volatile enough to be detected by the GC analysis [19].

2.7.2 Fast pyrolysis char

Fast pyrolysis char is a by-product of fast pyrolysis which contains almost all of the ash contained in the feedstock biomass. The fast pyrolysis char can be either separated from the other products, as with in this research (refer to Section 7.1), where it can be used for other applications or it can be burned to provide process heat (circulating fluidised bed reactor) (refer to Section 2.5.1). It can be added to soil to improve upon its characteristics as a soil amendment (BIOCHAR) [146]. This is an interesting application due to the carbon sequestration benefit that BIOCHAR can have [147]. Fast pyrolysis char within this research was only collected for mass balance purposes.

2.7.3 Fast pyrolysis gas

Fast pyrolysis gas mostly consists of carbon dioxide, carbon monoxide and methane. Research by Yanik et al. [148] pyrolysed three agricultural wastes and found that carbon oxides made up

84-90 v v%.$^{-1}$ of the fast pyrolysis product gas, with methane accounting for 6-8 v v%.$^{-1}$ and C_2-C_4 minor amounts. The composition varied very little between all three agricultural waste product gases.

In some fast pyrolysis systems flue-gas or an inert gas can be used for fluidisation [149], this results in the fast pyrolysis product gas becoming diluted with the fluidising gas. The pyrolysis system that is used in this research uses nitrogen to fluidise the reactor bed material (refer to Section 7.1), resulting in the fast pyrolysis product gas being heavily diluted. The fast pyrolysis product gas was only used for analysis of gas composition and mass balance purposes (refer to Section 7.2.4).

2.8 Effect of inorganics on fast pyrolysis

Ash contains alkali metals which are known to catalyse cracking reactions of fast pyrolysis vapours and have a significant effect on fast pyrolysis product distribution including chemical composition of bio-oil [19, 65-76]. The sections below describe the effect biomass inorganic content can have on fast pyrolysis product distribution and bio-oil stability.

2.8.1 Effect of inorganics on fast pyrolysis products

Research by Sekiguchi and Shafizadeh [67] showed that inorganic compounds found naturally within biomass promote the formation of char and gas at the expense of pyrolysis liquid yield. An increase in char and gas yield at the expense of bio-oil due to the presence of ash during pyrolysis was observed in a number of studies for rice hull [68], sunflower stem [69] and miscanthus [70].

Thermogravimetric analysis (TGA) has been used extensively to study the effect of inorganic material on biomass pyrolysis. Studies by Nowakowski et al. [22, 71] found that pyrolysis product yields were influenced by the presence of potassium. Potassium catalysed the pyrolysis products increasing the char yield from 6.7 wt. % for HCl treated willow to 19.8 wt. % for K-impregnated willow samples. Also the potassium lowered the average first order activation energy for pyrolysis by up to 50 kJ Mol.$^{-1}$.

Ebringerova et al. [150] showed that the first step in the formation of volatile compounds during pyrolysis of cellulose was through the compound levoglucosan. It was shown that high concentrations of levoglucosan were found in all high standard bio-oils. By looking for the presence of this compound can help to identify the quality of bio-oil and if any unwanted side reactions have occurred. Evans et al. [72] showed that the presence of potassium in the feedstock promotes the decomposition of levoglucosan, as well as other anhydrosugars, and also leads to the decomposition of cellulose to

other unwanted products such as acetic acid and propanoic acid. This identifies that higher concentrations of potassium in feedstock lead to lower quality bio-oil as the content of levoglucosan has been reduced and increased acidic products are formed.

Sodium, potassium, magnesium and calcium are specific metal ions that are major inorganics within biomass (refer to Section 2.3). The effect of these metals on beech wood pyrolysis was studied by Niz-Azar et al. [73] and it was found that calcium was a weaker cracking catalyst than potassium and sodium. These findings were previously shown by Muller-Hagedorn et al. [74] who showed that these metal ions have an influence on fast pyrolysis product distribution (reduced liquid yield with an increased char and gas yield).

He et al. [131] found that solid content in bio-oil includes small char particles entrained with vapours into liquid products in the condensing process. Bio-oil is preferred with as low as possible solid content. The study varied pyrolysis temperatures and feedstock moisture contents, and found the solid content of bio-oil to range between 1.23% and 2.86%. From the results it was clear that the lower moisture content of the feedstock gave the lowest percentage of solid content in bio-oil, but there was no trend with the pyrolysis temperatures effect on solid content. A low bio-oil solid content is desired as it has a direct effect on bio-oil stability, as it catalyses reactions which take place within the bio-oil whilst in storage (refer to Section 2.8.2).

2.8.2 Bio-oil stability

Bio-oil is chemically and thermally instable due to its high content of reactive oxygen containing compounds. The instability of bio-oil can be observed by an increase in viscosity and water content over time, this is known as aging. Aging can be catalysed by bio-oil inorganic content [75, 76, 140, 151]. The change in viscosity is greater than in water content.

During bio-oil storage the chemical composition changes towards thermodynamic equilibrium this result in changes to the viscosity, molecular weight and co-solubility [75, 76]. Ideally a bio-oil should be single phase, but during storage the bio-oil can separate into two phases (refer to Section 2.7.1). Chemical reactions taking place during bio-oil aging change the polarity of the bio-oil components [151]. Certain reactions taking place produce water and compounds which are relatively nonpolar, therefore the overall water content is increased and the overall polarity of the organic content is decreased, this leads to an increased potential of phase separation occurring with the aged bio-oil. Aging of bio-oil leads to formation of larger molecules (increase in molecular weight) [152], this also increases the potential of phase separation as the compounds decrease in solubility. The bio-oil can

phase separate into a low viscosity aqueous phase and a high viscosity organic phase [140, 151, 153] (refer to Section 2.7.1).

Many reactions are possible to occur in a mixture of over 400 organic compounds. Diebold [151] reviewed several general chemical reactions which are thought to take place during bio-oil aging. Some of these reactions require a catalyst to take place, so depending on the amount of char (in particular the inorganic content) found within the bio-oil can have a direct effect on the aging progress of bio-oil. Below is a list of the general chemical reactions thought to take place during bio-oil ageing [151]:

- organic acids react with alcohols to form esters and water
- organic acids react with olefins to form esters
- aldehydes react with water to form hydrates
- aldehydes reacts with alcohols to form acetals and water
- aldehydes react with phenolics to form resins and water
- aldehydes react with proteins to form oligomers
- unsaturated compounds to form polyolefins
- air oxidation to form acids

Special care has to be taken in handling, transportation, storage and bio-oil use due to its instability. There is no standard method for measuring stability of bio-oils but a simple test can be used to compare bio-oil sample stability. To compare the stability of different fast pyrolysis bio-oils a simple test has been developed [75, 143, 154]. In the test, 45 ml of bio-oil in a 50 ml bottle is kept at 80 ^{o}C for 24 hours as this is claimed to simulate one year storage at ambient temperature. The increase in viscosity (measurement temperature at 40 ^{o}C) and water content is measured so that the stability of bio-oil can be determined. A slightly adapted version of this test was used in the research reported in this thesis to evaluate the stability of bio-oil produced (refer to Section 7.4.5).

3 Feedstock types and characterisation methods

This chapter gives an overview of each feedstock used regarding location of crop, specific growing conditions and harvesting times. Also specific feedstock preparation procedures are explained. Different sample particle sizes had to be prepared for feedstock preparation, analytical experiments and fast pyrolysis. Each feedstock was characterised by analytical techniques which are fully described.

3.1 Feedstocks

Miscanthus (*miscanthus x giganteus*) was used for the majority of the research due to a number of characteristics that make it an ideal biomass crop. Miscanthus is a C_4 perennial grass; gives consistently high yields; has low requirements for management and inputs, such as nitrogen fertiliser; and therefore has a relatively low energy requirement after crop establishment [155]. Miscanthus biomass has a high lignin content (~17% of cell wall composition) when compared to woody biomass or other agricultural residues [156-158]; a high C:N ratio (average of 142.6) throughout the growth season [7] and is capable of significant energy production per hectare [80] . Yield and crop quality in miscanthus are determined by the relative progression of senescence relative to harvest time [80].

Beech wood (*fagus sylvatica*) was used for impregnation studies within this research due to its low ash content (0.63 dry wt. %, refer to Section 6.1 Table 17). A low ash content biomass was desired because any changes in mass balance yields or bio-oil characteristics/stability can be assumed to be due to the chemicals that have been impregnated into the sample. If a high ash content biomass was used for impregnation it would be difficult to distinguish if any changes were due to the high ash content or the impregnated chemicals. Having a biomass with low ash content helps to avoid any 'parallel' catalytic cracking reactions, those taking place when alkali metals are present in the inorganic matter of biomass.

3.1.1 Senesced miscanthus at three harvest points and a commercial pellet

The biomass sample of miscanthus was grown on an experimental field at the Institute of Biological, Environmental and Rural Sciences (IBERS) in Aberystwyth University. The crop was established in April 2005 and did not receive any fertilisers or pesticides. The crop used for this study was harvested on 1st June 2009 (early summer harvest), 1st September 2009 (late summer harvest) and 1st February 2010 (conventional or winter harvest). For comparison, commercially available miscanthus pellets (0.5 cm diameter x 1-1.5 cm) were used. The pellets were made from miscanthus harvested and baled on 1st February 2010 (conventional or winter harvest); no other biomass or binders were used during pellet manufacture.

To generate sufficient biomass for fast pyrolysis a total of 30 stems were harvested from each of 4 replicate plots at each harvest time 5 cm ± 0.5 cm from soil level (to reduce soil contamination). From these 120 stems at each harvest time, ten stems were chosen at random so that a state of senescence could be determined. Senescence was assessed by determining the relative chlorophyll content of leaves by using a SPAD-502 meter (SPAD - Single Photon Avalanche Diode: Konica Minolta Sensing, Inc.). Measurements were taken on all fully expanded leaves (maximum leaf surface area) and a single average result recorded from five measurements taken along the length of the leaf. For senesced (brown) leaves the SPAD-502 meter did not produce a value due to the absence of chlorophyll; therefore were assigned a relative chlorophyll content of N/D (not detected).

3.1.2 Fresh miscanthus used for small scale demineralisation

The biomass sample of miscanthus was obtained from Rothamsted Research (Harpenden, Hertfordshire, UK). The crop was an early year cut, harvested in February - March 2008, when maximum senescence had occurred. No extra nitrogen was added to the plots during crop growth.

Three pre-treatment methods were used: a deionised water wash, 1.00% hydrochloric acid (HCl) wash and 0.10% Triton X-100 wash. Two different temperatures were used for each pre-treatment: 20 ^{o}C and 60 ^{o}C, with all washes duplicated. A carefully weighed sample of approximately 1 g was washed in a 100 ml three neck flask. One neck was used for a thermocouple so that the solution temperature could be monitored. The central neck was used for a water cooled condenser at 10-15 °C to make sure all vapours were collected due to elevated temperatures. The final neck was blocked. 1 g sample was washed with a 50 ml solution whilst being magnetically agitated for either 1, 2, or 4 hours. The solutions were made up on a weight percentage basis.

After the sample had been washed it was filtered and the flask was rinsed with 100 ml of deionised water to ensure the entire sample was removed. The HCl washed sample was then further washed with deionised water until the filtrate was Cl^- free. Sliver nitrate was used to ensure that the filtrate was Cl free. Samples were then dried in a vacuum oven at 60 ^{o}C ± 2 ^{o}C with a vacuum of -900 millbar for 24 hours. Thermogravimetric analyses were performed on biomass samples at 105 ^{o}C identifying that small quantities of light volatiles were released whilst drying. Therefore 60 ^{o}C was used as the drying temperature as it is high enough to dry samples swiftly but not so far that light volatiles were lost.

3.1.3 Fresh miscanthus used for large scale demineralisation

The biomass sample of miscanthus was grown at Woburn Experimental Farm (Bedfordshire, UK) on sandy soil. The crop was established in 2003; from 2005 until 2007 the crop was part of a large agronomic experiment. The whole experimental site received 50 kg K $ha.^{-1}$ (soluble potassium in an inorganic form) and 100 kg N $ha.^{-1}$ fertiliser, *Nitram* (ammonium nitrate), in 2008 to unify the yield across the field. The miscanthus for this work was harvested in February-March 2009 at this site.

The same three pre-treatment methods were used as the small scale demineralisation (refer to Section 3.1.2). Biomass samples were pre-treated at room temperature for a period of 4 hours (refer to Section 5.1). Miscanthus batches of 500 g (wet basis) were washed with a 10 litre solution whilst being agitated (300 rpm). The solutions were made up on a weight percentage basis. After the batch had been washed it was filtered and then the HCl washed sample was washed with deionised water until the filtrate was Cl^- free. Sliver nitrate was used to ensure that the filtrate was Cl free. The samples were left to stand for 24 hours. Batches were dried in a Swallow oven at 60 $^oC \pm 1$ ^oC for 48 hours. This type of oven was used as it can dry large quantities of biomass at one time. In order to accumulate sufficient untreated material for a fast pyrolysis experiment, successive washings were carried out until approximately 1.5 kg of pre-treated miscanthus was collected for each pre-treatment method.

3.1.4 Fresh miscanthus used for surfactant demineralisation

For information on the miscanthus sample used for surfactant demineralisation refer to Section 3.1.3. Miscanthus batches of 500 g (wet basis) were washed with a 10 litre Triton X-100 solution at different concentrations whilst being agitated (300 rpm) for 4 hours at room temperature. Four different concentrations were used 0.10, 0.25, 0.50 and 1.00 wt. % of Triton X-100. The batch was then filtered and left to stand for 24 hours. After the 24 hours the batch was dried in a Swallow oven at 60 $^oC \pm 1$ ^oC for 48 hours. In order to accumulate sufficient untreated material for a fast pyrolysis experiment, successive washings were carried out until approximately 1.5 kg of pre-treated miscanthus was collected for each Triton X-100 concentration.

A code was used to identify each different pre-treatment method:

MS – Untreated miscanthus sample
0.10 T - 0.10% Triton X-100 water wash at 20 ^oC (4 hours)
0.25 T - 0.25% Triton X-100 water wash at 20 ^oC (4 hours)
0.50 T - 0.50% Triton X-100 water wash at 20 ^oC (4 hours)
1.00 T - 1.00% Triton X-100 water wash at 20 ^oC (4 hours)

3.1.5 Beech wood used for impregnation

The biomass sample of beech wood (Fagus sylvatica) was purchased from J. Rettenmaier & Söhne GmbH + Co. KG D-73494 Rosenberg (Germany). Beech wood batches of 1 kg were impregnated with potassium in the form of potassium acetate (Sigma-Aldrich, ACS reagent, ≥ 99.0%) or phosphorus in the form of phosphoric acid (Sigma-Aldrich (FLUKA), 49-51%) to achieve concentrations of 0.10, 0.50, 1.00 and 2.00 wt. % of elemental potassium and phosphorus. The required amount of either potassium acetate or phosphoric acid was diluted in 5 litres of deionised water. The solution was then hand mixed (appropriate PPE was worn) with 1 kg of beech wood for 30 minutes. Each batch was left for 72 hours to ensure that the entire solution was absorbed. After 24 and 48 hours the beech wood was hand mixed for a further 30 minutes. After the 72 hours the batch was dried at 60 ^{o}C ± 2 ^{o}C for 48 hours.

3.2 Sample preparation

Biomass needs to be ground for fast pyrolysis to ensure high heat transfer rates and minimise vapour diffusion through the catalytically active external char layer. Biomass samples were ground (Retsch Ltd., Germany, Heavy-Duty Cutting Mill, Knife Mill Type SM2000) initially using a 10 mm screen followed by a second grinding using a 2 mm screen. The majority (95%) of ground biomass ended in the fraction size of 0.25-2.00 mm when sieved. Biomass samples are also ground so that the specific surface area of the untreated material increases and the biomass has an increased bulk density [159] (reduced volume). Reduced volume makes it more convenient for handling, transport and storage. Biomass processing by grinding also decreases the cellulose crystallinity, improving pre-treatments (washing) and thermal processing. There are a number of grinding devices that perform size reduction; a cutting mill has been used due to the majority of research being based on miscanthus. Research by Miao [159] found that particle size distributions (% w w.$^{-1}$), for miscanthus particles, had a higher percentage of fine particles per unit of biomass when processed with a knife mill compared to a hammer mill. This was ideal as small particle fraction sizes are required for certain studies (Table 7). Bulk densities for miscanthus processed by a knife mill were much higher when compared to a hammer mill [159], this is a positive as it improves handling, transport and storage on a laboratory scale. Also size reduction using shear failure instead of tensile failure is more energy efficient [160].

Varying fraction sizes were used for different experiments and feedstocks; refer to Table 7 for reasons why different fractions were used. The fraction of 0.15-0.25 mm was used for small scale demineralisation, 0.25-2.00 mm for large scale/surfactant demineralisation and 0.25-1.00 mm for impregnation studies. For fast pyrolysis processing the fraction size of 0.25-2.00 mm was used for senescence and large scale/surfactant demineralisation samples, 0.25-1.00 mm for impregnation samples. For thermogravimetric analysis (TGA) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) analysis biomass samples were ground and sieved to a fraction size of 0.15-0.25 mm. For

TGA and Py-GC-MS analyses a biomass splitter (Sepor Ltd., Sepor micro riffle splitter, Jones type, Model: 040G-000) was used to obtain a representative sample. Analytical sample size (0.15-0.25 mm) gives a homogenous sample this fraction size avoids mass transfer errors when heating big (2.00 mm) or small (0.05 mm) particles at the same time.

Table 7 Varying fraction sizes for different experiments

Objective	Fraction size	Why
Small scale demineralisation	0.15-0.25 mm	Analytical fraction size.
Large scale / surfactant demineralisation	0.25-2.00 mm	This fraction size is the minimum and maximum particle size that can be processed for the fast pyrolysis experiments (Section 7.1).
Impregnation studies	0.25-1.00 mm	A reduced fraction size was used so that a homogenous impregnated sample could be prepared, as the impregnation was achieved by soaking the biomass sample in a solution of water and potassium acetate or phosphoric acid.
TGA and Py-GC-MS	0.15-0.25 mm	Analytical fraction size.

3.3 Feedstock characterisation methods

This section explains feedstock characterisation techniques including elemental analysis, thermogravimetric analysis and analytical pyrolysis. The procedures for each technique are explained in detail.

3.3.1 Elemental analysis

The elemental analysis gives the composition of feedstock in wt. % of carbon, hydrogen, nitrogen. In order to give a good representation of the feedstock itself, ultimate analyses are performed on a dry basis; otherwise moisture is reported as additional hydrogen and oxygen. The elemental analyses are reported on a dry ash free basis; oxygen is calculated by difference.

For the elemental analysis for carbon, hydrogen and nitrogen a Carlo-Erba 1108 elemental analyser EA1108 was used. Carbon, hydrogen and nitrogen content (wt. % on dry basis) were analysed in

duplicate and average values were taken. Using Equation 1 [161] the higher heating value (HHV) was calculated. The lower heating value (LHV) was obtained using Equation 2 [162]:

Equation 1 Higher heating value

$$HHV_{Dry} = 3.55C^2 - 232C - 2230H + 51.2CH + 131N + 20600$$

Equation 2 Lower heating value

$$LHV_{Dry} = HHV_{Dry} - 2.442 * (8.936\ H/100)$$

Where:
C = Carbon, H = Hydrogen and N = Nitrogen

Metal and other inorganic components were analysed using a PerkinElmer Optima 7300 DV Induced Coupled Plasma (ICP) emission spectrometer. Prior to analysis the biomass was dried at 80 ^{o}C for 4 hours, 0.25 g was then digested in 5 cm^3 30% nitric acid and mixed for 2 hours at ambient temperature, then heated for 12 hours at 80 ^{o}C ± 2 ^{o}C. After the 12 hours 5 cm^3 of 25% hydrochloric acid was added and then heated for a further 4 hours at 80 ^{o}C ± 2 ^{o}C. The sample was then cooled and analysed by ICP emission spectrometer.

Feedstock ash content was calculated on a moisture free basis. Prior to analysis the feedstock was dried at 60 ^{o}C ± 2 ^{o}C for 24 hours. Ash content was calculated using E 1755 ASTM method [163]**.** Crucibles and lids (8-10) were put in a Carbolite AAF1100 furnace and heated to 575 ^{o}C for 3 hours; crucibles were then removed from the furnace and cooled in a desiccator. A desiccator was used to ensure the samples remained dry. The crucibles weight was recorded and then replaced in the furnace at 575 ^{o}C for a further hour, cooled and re weighed until the weights were within 0.1 mg. Approximately 0.5 to 1.0 g of dried feedstock was weighed into each crucible. Crucible, lid and sample were placed in furnace and heated to 250 ^{o}C at 10 ^{o}C min.$^{-1}$ and held for 30 minutes, then increased to 575 ^{o}C for 3 hours (crucible lids placed slightly off so not fully sealed). After 3 hours crucibles were removed and cooled in a desiccator. Each crucible was weighed to the nearest 0.1 mg. Crucibles were replaced in furnace and heated at 575 ^{o}C for 1 hour periods until crucible weight were constant to within 0.3 mg.

3.3.2 Thermogravimetric analysis (TGA)

Proximate analysis classifies the feedstock in terms of moisture, volatile matter, fixed carbon and ash. The volatile content consists of gases and vapours released during pyrolysis. Ash is the inorganic residue remaining after combustion of the feedstock. TGA data is equivalent to a standardised

proximate analysis. Two TGA tests are required for a complete proximate analysis, one performed in a nitrogen atmosphere the second in an air atmosphere. The first test in a nitrogen atmosphere shows the loss of moisture and volatiles. The moisture determined only includes water bound physically; water released by chemical reactions is part of the volatile matter. What remains after the pyrolysis is char consisting of fixed carbon and ash. The second test in an air atmosphere determines the ash content by combusting the fixed carbon contained in the char.

To study pyrolysis under dynamic heating for both treated and untreated feedstock samples (5 ± 0.1 mg), a PerkinElmer Pyris 1 thermogravimetric analyser was used. A pyrolysis heating rate of 20 ^{o}C min.$^{-1}$ was used, heating from ambient temperature to 550 ^{o}C in a nitrogen flow of 30 ml min.$^{-1}$ [164]**.** The ash content in biomass and fast pyrolysis char samples was determined using a heating rate of 2.5 ^{o}C min.$^{-1}$, heating from ambient temperature to 575 ^{o}C with a hold time of 15 minutes in an air purge rate of 30 ml min.$^{-1}$. Triplicate analysis (for TGA pyrolysis and ash content analysis) was undertaken for each sample.

3.3.3 Analytical pyrolysis by Py-GC-MS

Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) tests for both treated and untreated biomass samples were performed using a CDS 5200 pyrolyser closed coupled to a PerkinElmer Clarus 680 GC-MS. Approximately 1.5 mg of dried sample was placed in a 20 mm quartz tube between two quartz wool plugs. Pyrolysis experiments were carried out at 550 ^{o}C, at a heating rate of 500 ^{o}C s.$^{-1}$ and a pyrolysis time of 30 seconds. Pyrolysis vapours were trapped using a Tenax®-2 trap maintained at 45 ^{o}C, then desorbed at 280 ^{o}C (1 minute) and then transferred via a heated transfer line (310 ^{o}C) onto the GC column via an injection port kept at 300 ^{o}C. Separation was carried out on a PerkinElmer Elite-1701 column (crossbond: 14% cyanopropylphenyl and 86% dimethyl polysiloxane; 30 m, 0.25 mm i.d., 0.25 μm df), using a split ratio of 1:50. GC oven programme was as follows: held constant at 50 ^{o}C for 2 minutes, then ramped at 5 ^{o}C min.$^{-1}$ to 275 ^{o}C and held at 275 ^{o}C for 3 minutes. The programme lasts 50 minutes. Helium was used as the carrier gas with a constant flow of 15 ml min.$^{-1}$. Mass spectra were obtained for the molecular mass range m/z = 35–300, with a scan time of 0.35 seconds. Assignments of the main peaks were made from mass spectral detection (NIST05 MS library) and from literature [165, 166].

4 Feedstock senescence

This chapter covers the characterisation of three miscanthus samples harvested at different time points and a miscanthus commercial pellet, including results and discussion.

4.1 Senesced miscanthus characterisation

The C, H and N analysis for the four senescence feedstocks can be found in Table 8. The C, H and N analyses were all similar with a range of: 44.70-48.22% C; 5.98-6.02% H; 0.29-2.14% N. Accuracy is ± 0.30% absolute. C, H and N content was measured by elemental analysis technique and carried out by MEDAC Ltd. In general both low and high heating values were found to increase with senescence. Nitrogen content decreased from 2.14 % (early summer harvest) to 0.29% (conventional harvest) this showed that nitrogen was remobilised through senescence from aerial biomass to the rhizomes (below ground). A similar pattern of nutrient allocation was shown by other researchers [167], confirming the proposed translocation through senescence from leaves and stem to rhizomes. Nitrogen accumulation in above ground crop was measured using Near Infrared (NIR) spectroscopy using an Equinox 55 FTIR spectrometer.

Table 8 Senescence miscanthus feedstock characteristics

Measurement	1st June 2009	1st September 2009	1st February 2010	Commercial pellet
Biomass yield (as received, t ha.$^{-1}$)	6.96	21.28	14.96	-
Mean moisture content (wt. %)	78.6	66.7	46.1	-
Mean dried plant material yield (g kg.$^{-1}$)	214	333	539	-
Mean SPAD	42.8	26.3	N/D	-
Nitrogen accumulation in above ground crop (kg ha.$^{-1}$)	160	208	45	-
C (wt. % $^{d.b.}$)	44.70	45.65	47.40	48.22
H	6.02	5.98	5.93	6.01
N	2.14	0.92	0.29	0.97
O*	39.79	41.71	43.58	42.68
HHV (MJ kg.$^{-1}$)	18.0	18.2	18.8	19.2
LHV	16.6	16.0	17.5	17.9

Triplicate analyse were preformed
d.b. - dry basis
* - calculated by difference
N/D - not detected

Across the harvest period the relative chlorophyll content declined from 42.8 (early summer harvest), through an average of 26.3 (late summer harvest) to N/D (conventional harvest). Over this harvest period senescence is in progress and concentrations of photosynthetic protein and microelements are decreasing. This is shown in Figure 5 with leaf colour turning from green (early summer harvest) to a yellowy brown (late summer harvest) and finally brown (conventional harvest). Approximately 50% of leaf proteins are involved in photosynthesis and therefore a high correlation between nitrogen and chlorophyll content can be expected [168, 169]. The higher nitrogen content in commercial miscanthus pellet may have resulted from a high leaf content in the pelletised biomass which is caused by the bailing system which not only harvests stems, but also a significant amount of leaf material.

Figure 5 Typical miscanthus leaves contributing to the crop canopy at different senescence stages [170]

The biomass yields (as received, t ha.$^{-1}$) and total nitrogen concentration in above ground biomass (kg ha.$^{-1}$) were calculated based on two plants per m^2 and stem number per plant (data not shown) at each harvest time. Table 8 show that biomass yield was higher in September than at the conventional harvest time in February, but the quality of the harvested crop was better at the later harvest due to lower moisture and lower ash content.

The inorganic elemental analyses of the four senescence feedstocks are shown in Table 9. The majority of the metals decreased from the early summer harvest through to the winter harvest. High amounts of potassium, chlorine and phosphorous are seen in the early summer harvested biomass (0.800, 1.130 and 0.270 wt. %, respectively). The decrease in potassium, chlorine and phosphorus over

the winter prior to harvesting (0.270, 0.170 and 0.060 wt. %, respectively) may be due to a combination of senescence and natural leaching from rain over the winter period. Leaf fall over the winter period can also account for the reduction in elemental content of the feedstock as there is a higher percentage of inorganics found in the leaves compared to the stems [171].

Table 9 Elemental analysis of senescence's feedstock - inorganic matter content (single analysis)

Harvest	Na	K	Ca	Mg	Al	Cl	Si	P	Fe	Ti
	wt. % d.b.									
1st June 2009	0.016	0.800	0.610	0.270	0.004	1.130	0.620	0.270	0.009	0.0001
1st September 2009	0.007	0.560	0.600	0.170	0.012	0.520	0.420	0.180	0.011	0.0005
1st February 2010	b.d.l	0.270	0.140	0.036	0.010	0.170	0.550	0.060	0.009	0.0001
Commercial pellet	b.d.l	0.041	0.380	0.065	0.014	0.100	0.420	0.078	0.023	0.0011

d.b. - dry basis

b.d.l - below detection limit (1 ppm)

Pyrolysis differential thermogravimetric (DTG) results of all miscanthus samples harvested at different time points are shown in Figure 6 and Table 10. The main temperature peaks for 1st June 2009, 1st September 2009, 1st February 2010 and commercial pellet are: 352 °C, 375 °C, 362 °C and 379 °C respectively. Higher amounts of volatiles were observed for miscanthus harvested in February (82.8%). There are no major differences in volatile yields for all harvest points with the largest difference being 6.21%. A decrease of inorganics (particularly potassium) from the June harvest through to the conventional February harvest had a large impact on char formation; char yields decreased from 29.0% (June) to 19.5% (February). Char and volatile yields differ between the conventional February harvest and the commercial pellets may be due to the pelletisation process. Wet miscanthus (moisture - 15-20 wt. %) is pelletised by subjecting the biomass to pressure which heats the biomass up to 250 °C causing pre-pyrolysis with the partial removal of light volatiles.

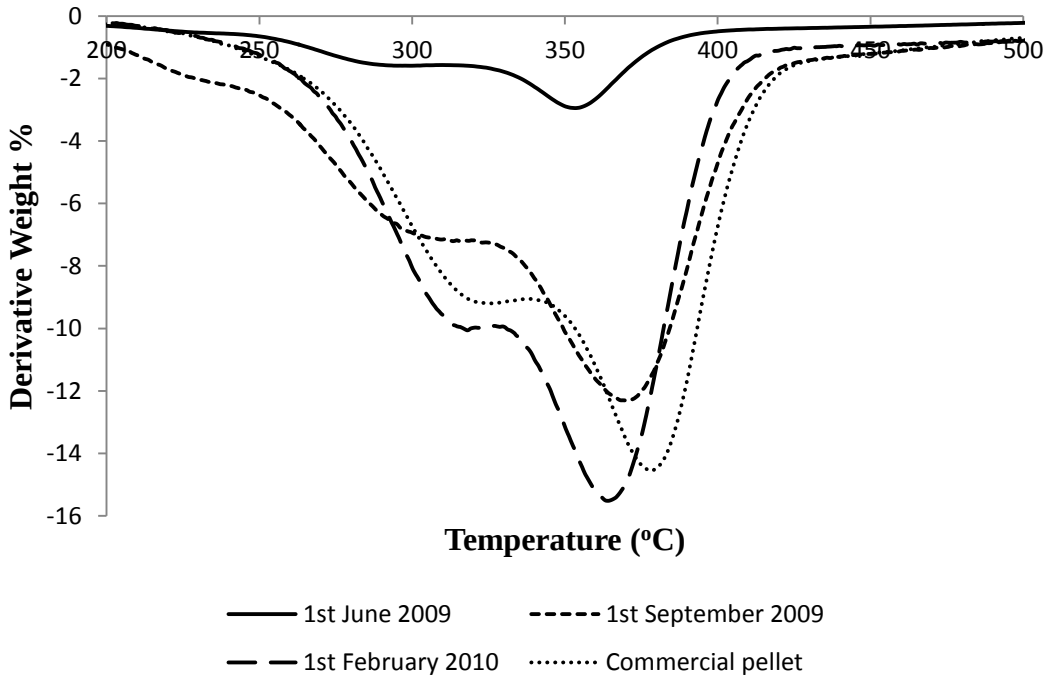


Figure 6 Pyrolysis DTG profiles of miscanthus samples harvested at different time points

Table 10 Thermogravimetric analysis data of senescence feedstock

Harvest	Volatile matter	Char	Fixed carbon	Ash	Volatile matter	T_0	T_s	Tp	T_f
	wt. % d.b.		wt. % d.b.	wt. % d.b.	wt. % d.a.f.	°C			
1st June 2009	70.98	29.02	21.66	7.36	76.62	172	230 and 297	352	444
1st September 2009	75.69	24.31	18.56	5.75	80.31	189	225 and 313	375	431
1st February 2010	80.51	19.49	16.69	2.80	82.83	232	322	362	447
Commercial pellet	77.59	22.41	19.86	2.55	79.62	229	334	379	438

T_0 - temperature corresponding to 1% mass loss on a dry basis

T_s - temperature of shoulder-like feature

T_p - pyrolysis peak temperature

T_f - temperature corresponding to 90% of mass loss on a dry basis

d.b. - dry basis

d.a.f. - dry ash free

4.2 Senesced miscanthus conclusion

There was a reduction of inorganic content from the early summer harvest and the conventional harvest; this may be due to a combination of senescence and natural leaching from rain water over the winter period. Leaf fall can account for a further reduction of inorganic content. Reduced inorganic content resulted in higher amounts of volatiles for the conventional harvest (82.8%), also char yields decreased from 29.0% (early summer harvest) to 19.5% (conventional harvest).

The main impact of early harvests on sustainable production of biomass from miscanthus is high nitrogen content. Nitrogen accumulation in above ground crop was at increased concentrations for early and late summer harvests (160 and 208 kg $ha.^{-1}$ respectively); lower levels are seen for conventional harvest (45 kg $ha.^{-1}$) due to significant remobilisation of nutrients through senescence. If the late summer harvest was used to generate bio-oil there could be a reduction in crop sustainability due to the lack of nutrient remobilisation resulting in a potential negative impact on crop yields for following growth years.

5 Feedstock demineralisation

This chapter covers the characterisation of all demineralised feedstocks, starting with small scale samples followed by large scale samples and surfactant demineralised samples, including results and discussion.

5.1 Small scale demineralised miscanthus characterisation

The C, H and N analysis for untreated miscanthus was as follows: 46.32% C; 5.81% H; 0.85% N. The C, H and N analyses for pre-treated miscanthus were all similar with a range of: 48.10-48.78% C; 5.68-6.27% H; 0.64-0.81% N. This shows around about a 2% increase in carbon, approximately the same hydrogen and a slight increase in nitrogen. Accuracy is ± 0.30% absolute.

DTG results comparing the influence of each pre-treatment method on miscanthus are shown in Figure 7 for deionised water, 1.00% HCl and 0.10% Triton X-100 washes. The pre-treatments have caused the main peak to shift slightly to a higher temperature; this shows that some catalytic species have been removed in this case alkali metals. The temperature peaks for untreated miscanthus, deionised water washed, 1.00% HCl washed and 0.10% Triton X-100 washed (at 20 ^{o}C for 2 hours) are: 355 ^{o}C, 392 ^{o}C, 380 ^{o}C and 397 ^{o}C respectively. There was a shoulder-like feature between the temperatures of 275 ^{o}C and 350 ^{o}C for the pre-treated miscanthus. This shoulder is attributed to the decomposition of hemicellulose and the initial degradation of cellulose; whilst the main peak is due to the final degradation of cellulose and the degradation of lignin [71]. The 1.00% HCl wash may have a lower temperature peak due to partial hydrolysis of hemicellulose.

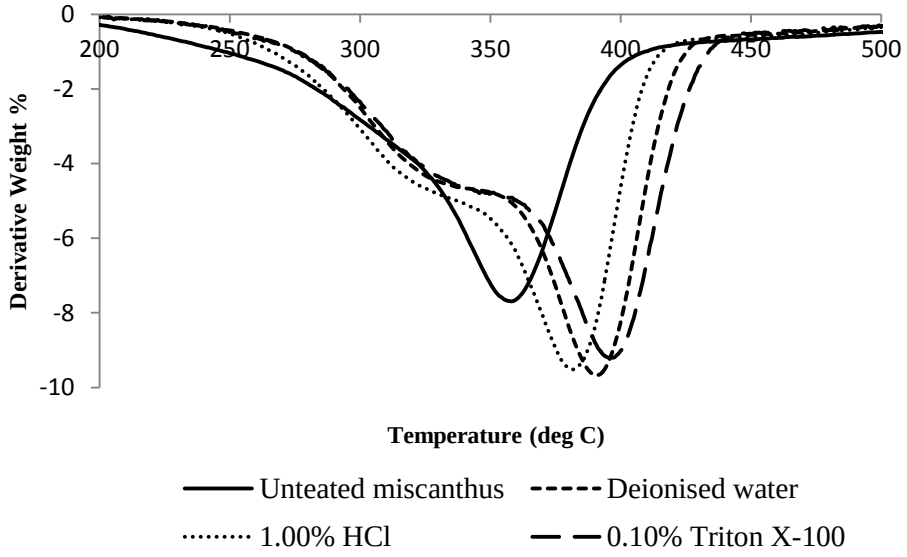


Figure 7 Pyrolysis DTG profiles for small scale demineralised miscanthus samples for deionised water, 1.00% HCl and 0.10% Triton X-100 washes

Each pre-treatment was run at two different temperatures; 20 ^{o}C and 60 ^{o}C. It was found that the temperature had no major effect on the pyrolysis profiles for all pre-treatments; this is shown by Figure 8. The main peak temperatures for 20 ^{o}C and 60 ^{o}C treatments are: 392 ^{o}C and 396 ^{o}C respectively. As there is no benefit by increasing the temperature of the washing solution means that no external energy source is required.

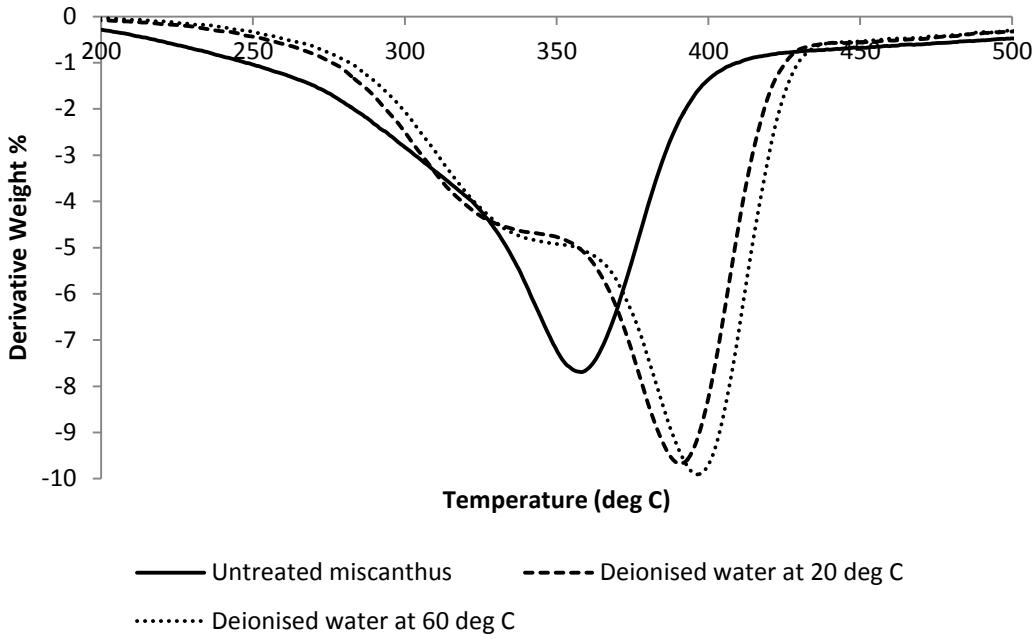


Figure 8 Pyrolysis DTG profiles for miscanthus washed with deionised water at 20 ^{o}C and 60 ^{o}C

Each pre-treatment was run for varying lengths of time; 1, 2 and 4 hours. It was found that the varying length of washing time had little effect on the pyrolysis profiles for all pre-treatments; this is shown by Figure 9. The main peak temperatures for 1, 2 and 4 hours 1.00% HCl treatments were: 390 ^{o}C, 380 ^{o}C and 390 ^{o}C respectively. There was a difference in peak temperatures for the 2 hour wash compared to that of the 1 and 4 hour washes; this could identify that alkali metals are removed from the miscanthus for up to an hour wash but then some alkali metals are reabsorbed for the 2 hour wash, then removed for anything longer than 2 hours. Further research on longer washing times could identify a trend of removal then absorption.

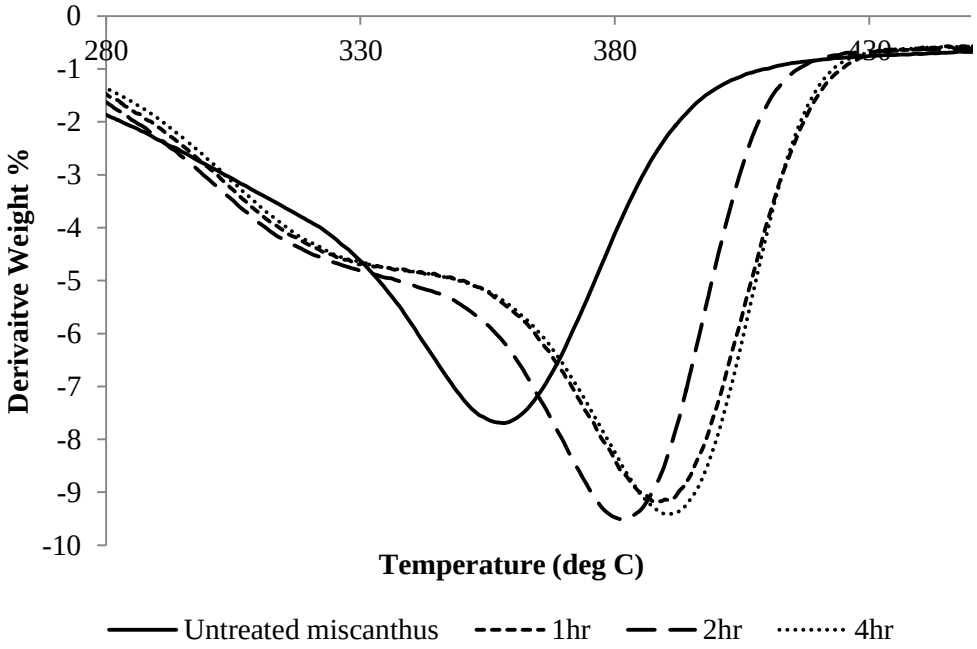


Figure 9 Pyrolysis DTG profiles for miscanthus washed with 1.00% HCl for 1, 2 and 4 hours

TGA Combustion of each pre-treated sample was studied as the combustion profiles easily identify if any catalytic species have been removed from the miscanthus. Combustion DTG results comparing the influence of each pre-treatment method on miscanthus are shown in Figure 10 for deionised water, 1.00% HCl and 0.10% Triton X-100 washes. The first main peak represents volatile release, ignition and combustion, while the second broader peak (ignoring the untreated miscanthus) was a result of slower char combustion. The first main peak has moved to slightly higher temperatures (335-343 ^{o}C) due to the removal of alkali metals which strongly catalyse the volatile release resulting in a shift to lower temperatures shown by the untreated miscanthus first peak (307 ^{o}C). For the pre-treated miscanthus the second broader peak (410-580 ^{o}C) was due to the demineralisation resulting in a very slow char combustion stage. In the case of the untreated miscanthus a sharp char combustion peak is present (445 ^{o}C) showing a fast, exothermic catalysed char combustion stage.

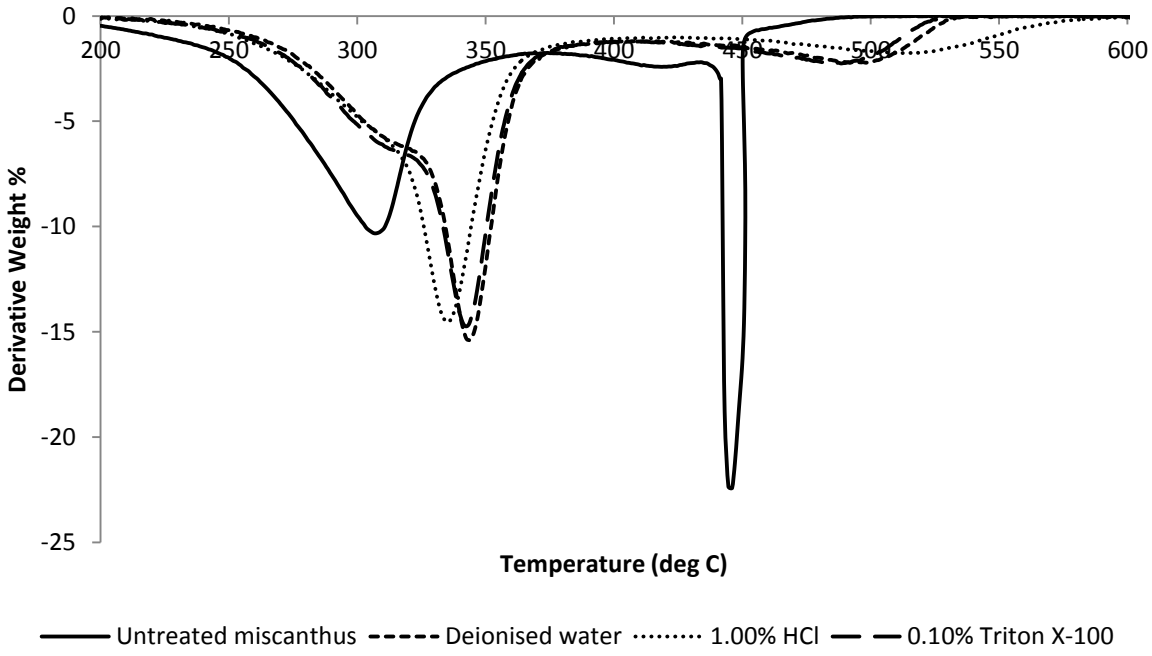


Figure 10 Combustion DTG profiles of small scale demineralised miscanthus samples for deionised water, 1.00% HCl and 0.10% Triton X-100 washed miscanthus samples

5.1.1 Small scale demineralisation conclusion

Miscanthus has been investigated on the influence pre-treatments have on pyrolysis and combustion behaviours on a small scale. Deionised water, 1.00% HCl and 0.10% Triton X-100 washes were used to remove alkali metals from the untreated miscanthus as they catalytically crack the volatile components in pyrolysis. The deionised water wash and 0.10% Triton X-100 wash moved the pyrolysis profile to a higher temperature identifying that they had a greater effect on removal of alkali metals than dilute acid wash. This was further identified with the combustion profiles which show that large amounts of alkali metals are removed due to the char burnout phase being much broader and slower, when compared to a sharp fast char burnout for high alkali metal contents in untreated miscanthus.

When different temperatures and varying times of washing were used the pyrolysis and combustion profiles were very similar. By varying the temperatures (20 ^{o}C and 60 ^{o}C) it identified that no external energy source is required for the pre-treatment stage as no major benefit was achieved that a room temperature pre-treatment cannot achieve. Varying the time of the washes showed that there could be a cycle of removal and then adsorption, with the 1 hour removing alkali metals then some being adsorbed for the 2 hour wash. This was shown by increased temperature peaks for the 1 hour and 4 hour washes, with a slight drop in peak temperature for the 2 hour wash. Further research is required for longer washing times to see if the trend continues or if the length of washing time has any beneficial value on the miscanthus. From these conclusions further demineralisation studies will be at room temperature for duration of 4 hours.

5.2 Large scale demineralised miscanthus characterisation

The C, H and N analysis for the untreated miscanthus was as follows: 49.06% C; 6.10% H; 1.07% N. The C, H and N analyses for the pre-treated miscanthus were all similar with a range of: 46.42-49.53% C; 5.73-6.01% H; 0.71-1.03% N. This shows approximately the same carbon and hydrogen, and a slight decrease in nitrogen compared to the untreated sample. Specific values can be found in Table 11. Accuracy is ± 0.30% absolute. The pre-treatment methods have similar HHV and LHV to untreated miscanthus.

Table 11 Elemental analysis of large scale miscanthus demineralisation

Measurement	Untreated miscanthus	Deionised water	1.00% HCl	0.10% Triton X-100
ASTM ash content (%)	3.68	1.92	3.52	1.53
C (wt. % $^{d.a.f}$)	49.06	46.42	49.53	48.71
H	6.10	5.73	6.01	5.99
N	1.07	1.03	0.81	0.71
O*	43.77	46.82	43.65	44.59
HHV (MJ kg.$^{-1}$)	19.62	18.46	19.76	19.40
LHV	18.29	17.21	18.45	18.09

d.a.f - dry ash free

* - calculated by difference

Results from the TGA analysis comparing the influence of each large scale pre-treatment method on miscanthus are shown in Figure 11 and Table 12. The main temperature peaks for untreated miscanthus, deionised water, 1.00% HCl and 0.10% Triton X-100 washes are: 341 ^{o}C, 366 ^{o}C, 361 ^{o}C and 383 ^{o}C respectively. The DTG profiles for large scale pre-treatment show that 0.10% Triton X-100 increases the main peak temperature the most (42 ^{o}C) compared to the deionised water wash and 1.00% HCl washes (25 and 20 ^{o}C respectively). As mentioned in Section 5.1, the main temperature peaks have shifted to higher temperatures shows that some catalytic species have been removed in this case alkali metals. The large scale 1.00% HCl wash shows the same trend as the small scale wash by having the lowest main peak temperature of the three pre-treatments, as mentioned in Section 5.1 this may be due to partial hydrolysis of hemicellulose. Higher amounts of volatiles were observed for deionised and Triton X-100 washes (99.58 and 94.79% respectively). There was a 1.73% decrease in volatile yield for the 1.00% HCl wash; this could be due to partial hydrolysis of hemicellulose. Char yields have been lowered for both deionised water and Triton X-100 washes (7.32 and 8.13% respectively) compared to untreated miscanthus (12.69%); this could be an indicator that inorganic

constituents (particularly potassium) that promote char formation have been removed from the miscanthus.

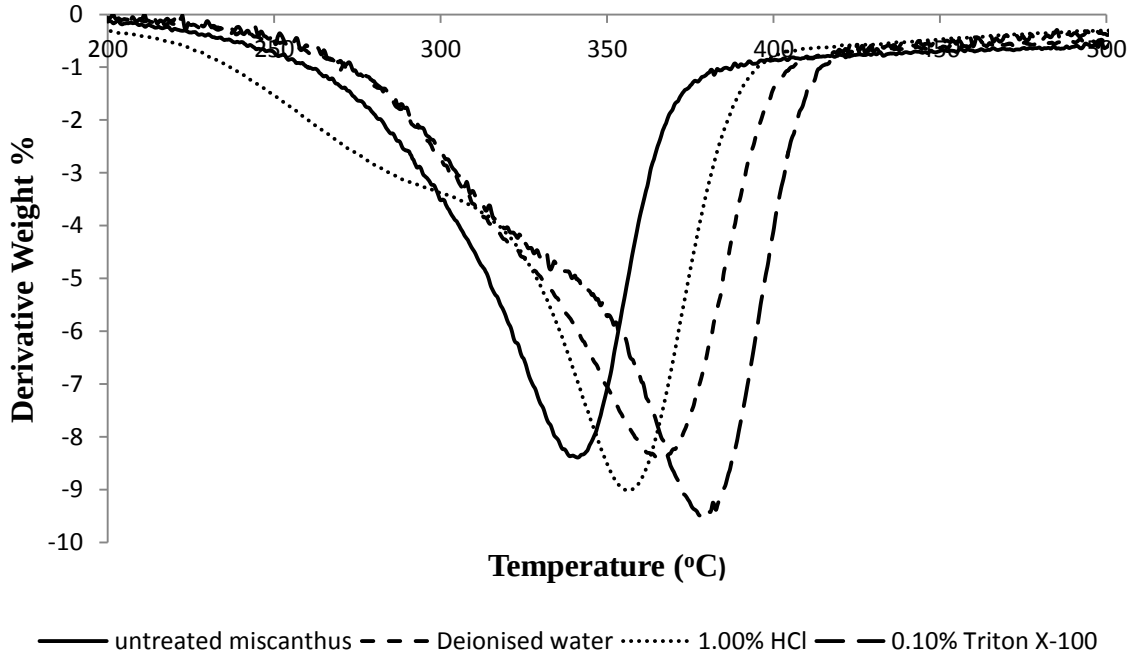


Figure 11 Pyrolysis DTG profiles of large scale demineralised miscanthus for deionised water, 1.00% HCl and 0.10% Triton X-100 washes

Table 12 Thermogravimetric analysis data of large scale demineralised miscanthus

Harvest	Volatile matter	Char	Fixed carbon	Ash	Volatile matter	Tp
	wt. % d.b.		wt. % d.b.	wt. % d.b.	wt. % d.a.f.	°C
Untreated miscanthus	87.31	12.69	8.26	4.43	91.36	341
Deionised water	92.68	7.32	3.40	3.92	99.58	366
1.00% HCl	87.65	12.35	10.14	2.21	89.63	361
0.10% Triton X-100	91.87	8.13	5.05	3.08	94.79	383

T_p - pyrolysis peak temperature

d.b. - dry basis

d.a.f. - dry ash free

5.2.1 Large scale demineralisation conclusion

All large scale pre-treatments had similar HHV and LHV, both being within 1.24 MJ $kg.^{-1}$. The Triton X-100 pre-treatment increased the main peak temperature of the pyrolysis profile the greatest (42 ^{o}C) when compared to untreated miscanthus. Deionised and HCl washes also increased the main peak temperature (25 and 20 ^{o}C respectively) showing that some catalytic species are removed from the miscanthus. Triton X-100 and deionised had the highest volatile content (94.79 and 99.58% respectively), but HCl washed miscanthus showed a reduction in volatile content compared to untreated miscanthus (1.73% reduction). This may be due to partial hydrolysis of hemicellulose. Char yields decreased for all large scale pre-treatments identifying that alkali metals have been removed from the untreated miscanthus.

5.3 Surfactant demineralised miscanthus characterisation

The C, H and N analysis for the untreated miscanthus was as follows: 48.63% C; 5.98% H; <0.10% N. The C, H and N analyses for the Triton X-100 treated miscanthus were all similar with a range of: 48.65-49.23% C; 5.89-6.18% H; <0.10% N. The surfactant washes had very little effect on CHN content of the miscanthus. Specific values can be found in Table 13. Accuracy is ± 0.30% absolute. The pre-treatment methods slightly increase both the HHV and LHV. Increasing concentrations of Triton X-100 resulted in reducing the ash content from 1.78% (miscanthus) to 0.68% (1.00% Triton X-100). Triton X-100 speeds up the wetting of the biomass permitting water to pass quicker through the biomass structure, also swelling the capillaries allowing water to wash the entirety of the biomass [110, 113]; therefore higher concentrations improve ash removal.

Table 13 Elemental analysis of surfactant demineralised miscanthus

Measurement	Untreated miscanthus	0.10 T	0.25 T	0.50 T	1.00 T
ASTM ash content (%)	1.78	1.11	0.95	0.85	0.68
C (wt. % $^{d.a.f}$)	48.63	48.65	48.65	48.92	49.23
H	5.98	5.89	6.01	6.10	6.18
N	<0.10	<0.10	<0.10	<0.10	<0.10
O*	45.29	45.36	45.24	44.88	44.49
HHV (MJ kg.$^{-1}$)	19.28	19.05	19.30	19.44	19.59
LHV	17.98	17.76	17.98	18.10	18.24

d.a.f - dry ash free

* - calculated by difference

Results from the TGA analysis comparing the influence of different Triton X-100 concentration pre-treatments on miscanthus are shown in Figure 12 and Table 14. The main temperature peaks for miscanthus (MS), 0.10 T, 0.25 T, 0.50 T and 1.00 T are: 367 ^{o}C, 389 ^{o}C, 389 ^{o}C, 388 ^{o}C and 392 ^{o}C respectively. The DTG profiles for the Triton X-100 pre-treatments are all similar with all main temperature peaks within 4 ^{o}C of each other. As mentioned in Section 5.1, the main temperature peaks have shifted to higher temperatures shows that some catalytic species have been removed. Volatile and char yields are similar for all Triton X-100 concentrations. The ash content decreases from 2.17% (miscanthus) to 1.40% (1.00% Triton X-100); this shows a trend of decreasing ash content with increased concentrations of Triton X-100.

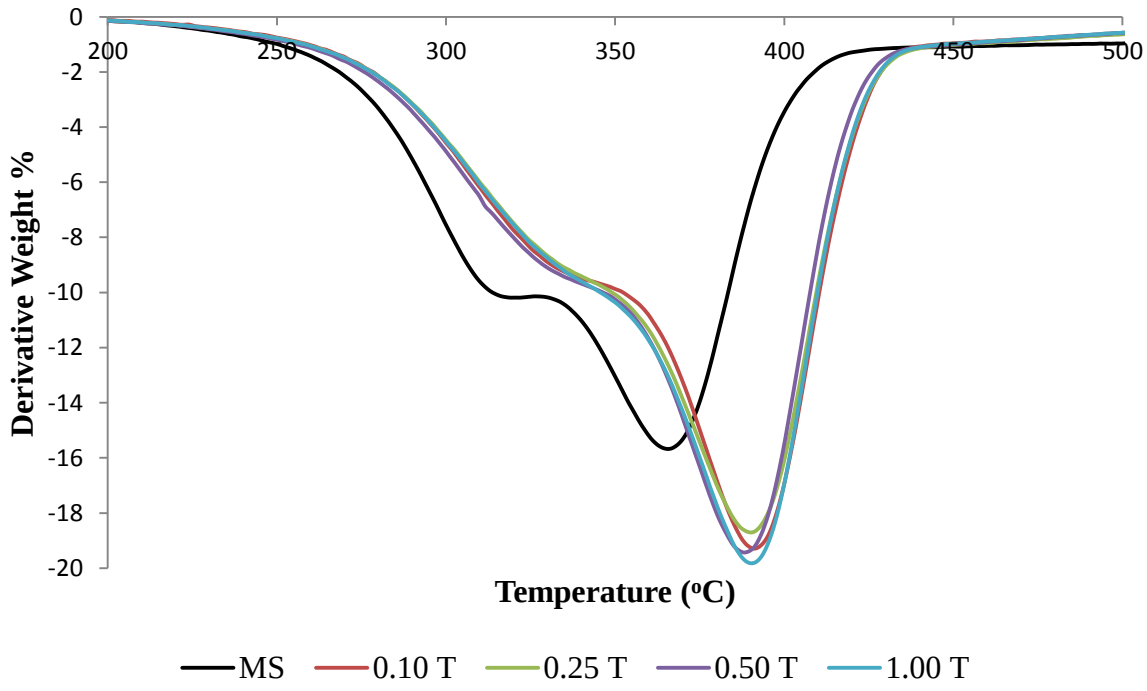


Figure 12 Pyrolysis DTG profiles for surfactant demineralised miscanthus

Table 14 Thermogravimetric analysis data of surfactant demineralised miscanthus

Harvest	Volatile matter	Char	Fixed carbon	Ash	Volatile matter	Tp
	wt. % d.b.		wt. % d.b.	wt. % d.b.	wt. % d.a.f.	°C
Untreated miscanthus	83.41	16.59	14.42	2.17	85.26	367
0.10% Triton X-100	83.50	16.50	14.78	1.72	84.96	389
0.25% Triton X-100	82.81	17.19	15.64	1.55	84.11	389
0.50% Triton X-100	83.67	16.33	14.80	1.53	84.97	388
1.00% Triton X-100	84.36	15.64	14.24	1.40	85.56	392

T_p - pyrolysis peak temperature

d.b. - dry basis

d.a.f. - dry ash free

Analytical pyrolysis chromatograms for untreated miscanthus, 0.10%, 0.25%, 0.50% and 1.00% Triton X-100 washed miscanthus are shown in Figure 13, also peak assignments for Py-GC-MS chromatograms are shown in Table 15 and Table 16. Untreated miscanthus, 0.10%, 0.25% and 0.50% Triton X-100 washed miscanthus have very similar Py-GC-MS chromatograms. The major volatile products are acetic acid (3.10 minutes), 3-Furaldehyde (7.08 minutes), 2-Hexene (11.87 minutes), pentanol (17.67 minutes), benzaldehyde 4-methyl (21.53 minutes), phenol 2 6-dimethyl (22.80 minutes) and Eugenol (24.77 minutes).

1.00% Triton X-100 has a significant effect on the decomposition profile of miscanthus. The major volatile products are acetic acid (3.53 minutes), oxirane 2-methyl-2-pentlyl (12.94 minutes), 2-cyclohexen-1-one 4 4 5-trimethyl (17.60 minutes), pentanol (18.13 minutes), benzaldehyde 4-methyl (21.59 minutes), benzaldehyde 3-methyl (21.69 minutes), phenol 2 6-dimethoxy (22.92 minutes), Eugenol (24.87 minutes) and vanillin (25.25 minutes). The abundance of acetic acid (3.53 minutes), pentanol (18.13 minutes) and benzaldehyde 4-methyl (21.59 minutes) all increased. Additional major volatile peaks of 2-cyclohexen-1-one 4 4 5-trimethyl (17.60 minutes) and benzaldehyde 3-methyl (21.69 minutes) occur due to increased Triton X-100 washing solution. It was observed that increased concentrations of Triton X-100 promote the removal and/or partial decomposition of hemicellulose. This would explain the decrease in yield of lighter volatile compounds.

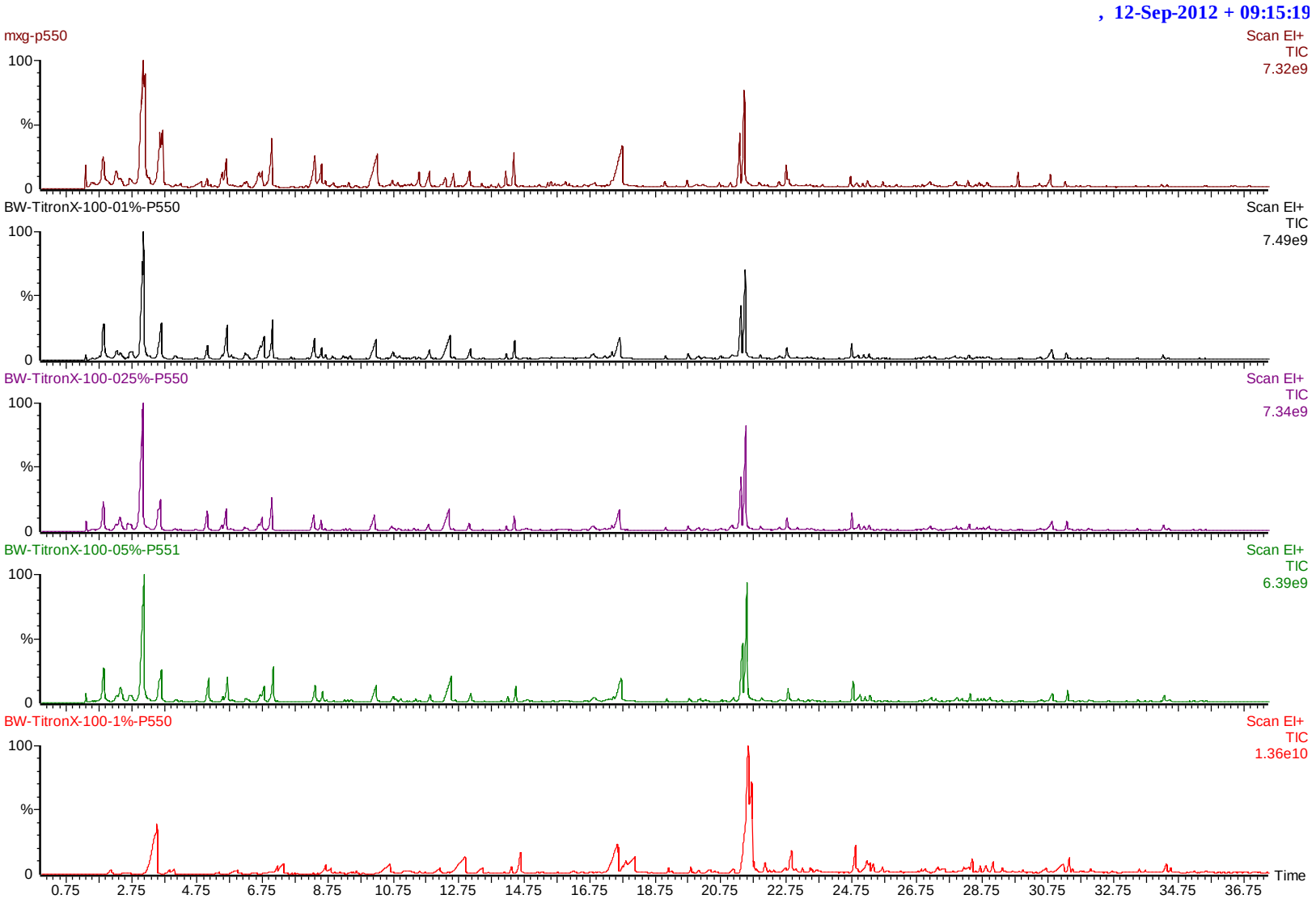


Figure 13 Py-GC-MS chromatogram for untreated miscanthus, 0.10%, 0.25%, 0.50% and 1.00% Triton X-100 washed miscanthus

Table 15 Untreated miscanthus, 0.10%, 0.25% and 0.50% Triton X-100 washed miscanthus peak assignments for Py-GC-MS chromatograms

RT (minutes)	Structure name	Formula	Molecular Weight
1.89	2, 4 (3H,-5H) -Furandione, 5, 5-dimethyl	C_6H_8O	128
2.41	2-Penten-1-ol	$C_5H_{10}O$	86
3.10	Acetic acid	$C_2H_4O_2$	60
3.66	Methyl ester	$C_3H_6O_2$	74
5.09	3-Buten-1-ol, 2-methyl	$C_5H_{10}O$	86
5.67	2-propanone, 1-(Acetyloxy)-	$C_5H_8O_3$	116
6.79	1, 2-propanediol, 2-Acetate	$C_5H_{10}O_3$	118
7.08	3-Furaldehyde	$C_5H_4O_2$	96
8.39	3-Furanmethanol	$C_5H_6O_2$	98
8.58	1,2-Ethanediol, diacetate	$C_6H_{10}O_4$	146
10.22	2, cyclopenten-1-one, 2-hydroxy	$C_6H_6O_2$	98
11.87	2-Hexene, (2)-	C_6H_{12}	84
12.45	Oxirane, 2-methyl-2-pentyl	$C_8H_{16}O$	128
13.12	2-cyclopenten-1-one, 2-hydroxy-3-methyl	$C_6H_8O_2$	112
14.48	Phenol, 2-methoxy	$C_7H_8O_2$	124
17.67	Pentanol	$C_5H_{10}O$	86
19.07	Phenol, 3-ethyl, Acetate	$C_{10}O_2$	164
19.79	Phenol, 4-ethyl, 2-methoxy	$C_9H_{12}O_2$	152
21.39	2-methoxy-4-vinylphenol	$C_9H_{10}O_2$	150
21.53	Benzaldehyde, 4-methyl	C_8H_8O	120

22.80	Phenol, 2, 6-dimethoxy	$C_8H_{10}O_3$	154
24.77	Eugenol	$C_{10}H_{12}O_2$	164
25.29	Vanillin	$C_8H_8O_3$	152
30.88	D-allose	$C_6H_{12}O_6$	180

Table 16 1.00% Triton X-100 washed miscanthus peak assignments for Py-GC-MS chromatogram

RT (minutes)	Structure name	Formula	Molecular Weight
2.11	Isobutyric acid	$C_7H_{12}O_2$	128
3.53	Acetic acid	$C_2H_4O_2$	60
4.05	Methyl ester	$C_3H_6O_2$	74
7.21	Propanoic acid	$C_4H_6O_3$	102
7.40	Furan, 2, 5-dimethyl	C_6H_8O	96
10.65	2-cyclopenten-1-one, 2-hydroxy	$C_5H_6O_2$	98
12.16	2-Hexene	C_6H_{12}	84
12.94	Oxirane, 2-methyl-2-pentlyl	$C_8H_{16}O$	128
13.48	2-cyclopenten-1-one, 2-hyroxy-3-methyl	$C_6H_8O_2$	112
14.64	Phenol, 2-methoxy	$C_7H_8O_2$	124
17.60	2-cyclohexen-1-one, 4, 4, 5-trimethyl	$C_9H_{14}O$	138
18.13	Pentanol	$C_5H_{10}O$	86
21.59	Benzaldehyde, 4-methyl	C_8H_8O	120
21.69	Benzaldehyde, 3-methyl	C_8H_8O	120

22.92	Phenol, 2, 6-dimethoxy	$C_8H_{10}O_3$	154
24.87	Eugenol	$C_{10}H_{12}O_2$	164
25.25	Vanillin	$C_8H_8O_3$	152
25.71	Formic acid	$C_5H_{10}O_2$	102
31.23	D-allose	$C_6H_{12}O_6$	180
31.41	Phenol, 2, 6-dimethoxy-(2-propemyl)	$C_{11}H_{14}O_3$	194
32.06	Benzoic acid	$C_9H_{10}O_4$	182

5.3.1 Surfactant demineralisation conclusion

Both HHV and LHV increased with increased Triton X-100 washing solutions. Increased concentrations of Triton X-100 resulted in the ash content being reduced from 1.78% (miscanthus) to 0.68% (1.00% Triton X-100). Triton X-100 swells the capillaries of the biomass allowing the wash solution to access a larger proportion of the biomass. All Triton X-100 concentrations had similar DTG profiles with all main peak temperatures within 4 ^{o}C of each other. Volatile and char yields are similar for all concentrations (2 wt. % $^{d.b.}$ difference). Untreated miscanthus, 0.10%, 0.25% and 0.50% Triton X-100 washed miscanthus have very similar Py-GC-MS chromatograms. 1.00% Triton X-100 washed miscanthus has a decreased yield of lighter volatile components which could be due to the removal and/or partial decomposition of hemicellulose.

6 Feedstock impregnation

This chapter covers the characterisation of all impregnated beech wood samples, including results and discussion.

6.1 Beech wood and impregnated beech wood characterisation

The C, H and N analysis for beech wood was as follows: 49.66% C; 6.29% H; <0.10% N. Accuracy is ± 0.30% absolute. An elemental analysis was not performed for each impregnated beech wood sample as it was assumed that each sample would have the same elemental content as untreated beech wood. All samples of beech wood were from a single batch. Potassium and phosphorus content of untreated and impregnated beech wood samples are shown in Table 18.

Table 17 Elemental analysis of beech wood

Measurement	Beech wood
ASTM ash content (wt. % $^{d.b.}$)	0.63
C (wt. % $^{d.a.f}$)	49.66
H	6.29
N	<0.10
O*	43.95
HHV (MJ kg.$^{-1}$)	19.81
LHV	18.44

d.b. – dry basis

d.a.f – dry ash free

* – Calculated by difference

Table 18 Elemental analysis of impregnated beech wood– potassium and phosphorus content

	Beech wood	0.10 K	0.50 K	1.00 K	2.00 K
K (wt. % $^{d.b.}$)	0.05	0.16	0.74	0.94	1.13
	Beech wood	0.10 P	0.50 P	1.00 P	2.00 P
P (wt. % $^{d.b.}$)	0.01	0.11	0.96	0.94	0.89

d.b. – dry basis

DTG profiles for each K and P-impregnated beech wood sample are shown in Figure 14 and Figure 15. Pyrolysis decomposition of all impregnated samples began around 200 ^{o}C, major mass loss occurs at the temperature range between 250 and 450 ^{o}C during which volatile matter is released, with the formation of char and evolution of secondary gases.

The main temperature peaks for untreated beech wood, 0.10% K, 0.50% K, 1.00% K and 2.00% K are: 378 ^{o}C, 375 ^{o}C, 358 ^{o}C, 330 ^{o}C and 343 ^{o}C respectively. The DTG profiles for K-impregnated beech wood show that as the concentration of elemental potassium increases the main peak temperature decreases gradually. The 0.10% potassium had little effect on the main peak temperature compared to the untreated beech wood (3 ^{o}C difference); 0.50% K, 1.00% K and 2.00% K lower the temperature of the main peak even further (20 ^{o}C, 48 ^{o}C and 35 ^{o}C difference respectively). The 2.00% K impregnation was expected to have the lowest main peak temperature as it had the highest potassium content (1.13 wt. %$^{d.b.}$). There is a reduction in main peak temperature because as the amount of potassium present in biomass increases it becomes more effective in catalysing pyrolysis [71]. Lower amounts of volatiles were observed for higher concentrations of potassium (71.25% for 1.00 K) compared to beech wood (77.81%) identifying increased catalytic cracking. Increased potassium content had a large impact on char formation; char yields increased from 22.19% (beech wood) to 28.75% (1.00 K). Char yields increased due to alkali metal content (in particular potassium) which acts as a catalyst for promoting char formation [130, 172]. Ash content increases with increased concentrations of potassium, this was expected.

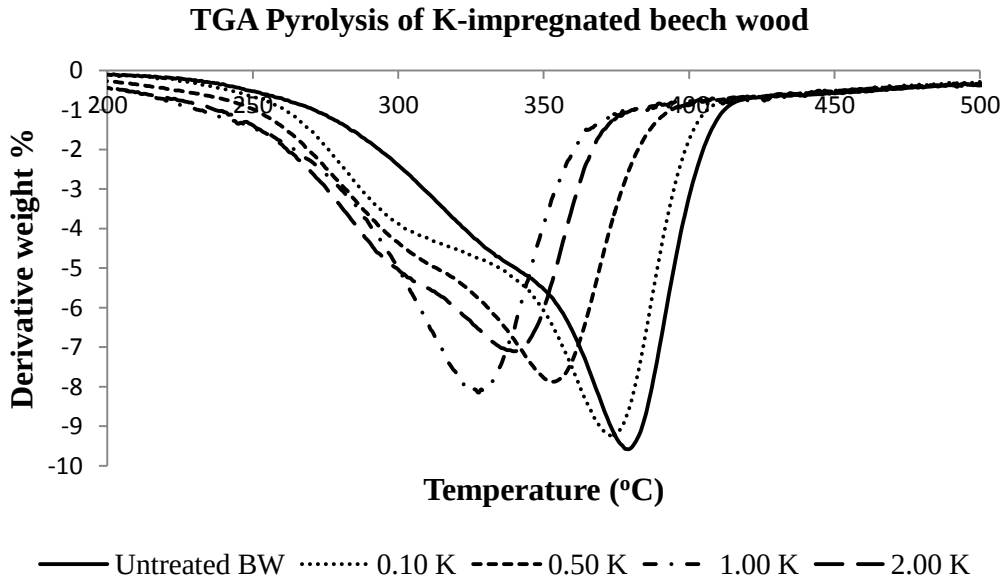


Figure 14 Pyrolysis DTG profile for K-impregnated beech wood

Table 19 Thermogravimetric analysis data of K-impregnated beech wood

Harvest	Volatile matter	Char	Fixed carbon	Ash	Volatile matter	Tp
	wt. % d.b.		wt. % d.b.	wt. % d.b.	wt. % d.a.f.	°C
Beech wood	77.81	22.19	21.24	0.95	78.56	378
0.10% K	80.46	19.54	18.33	1.21	81.45	375
0.50% K	75.58	24.42	22.07	2.35	77.40	358
1.00% K	71.25	28.75	26.13	2.62	73.17	330
2.00% K	73.69	26.31	23.22	3.09	76.04	343

T_p - pyrolysis peak temperature

d.b. - dry basis

d.a.f. - dry ash free

The main temperature peaks for untreated beech wood, 0.10% P, 0.50% P, 1.00% P and 2.00% P are: 378 ^{o}C, 377 ^{o}C, 310 ^{o}C, 291 ^{o}C and 301 ^{o}C respectively. The DTG profiles for P-impregnated beech wood show that as the concentration of elemental phosphorus increases the main peak temperature decreases dramatically. The 0.10% phosphorus had little effect on the main peak temperature compared to the untreated beech wood (10 ^{o}C difference); 0.50% P, 1.00% P and 2.00% P lower the temperature of the main peak even further (68 ^{o}C, 87 ^{o}C and 77 ^{o}C difference respectively). It seems that phosphorus is more effective at catalysing pyrolysis as shown by lowering main peak temperatures and increasing char yields. Lower amounts of volatiles were observed for higher concentrations of phosphorus (58.70% for 2.00 P) compared to beech wood (77.81%). Increased phosphorus content had a large impact on char formation; char yields increased from 22.19% (beech wood) to 41.30% (2.00 P). Phosphorus compounds are well known flame-retardants [104, 105], resulting in increased char yields. Ash content increases with increased concentrations of phosphorus.

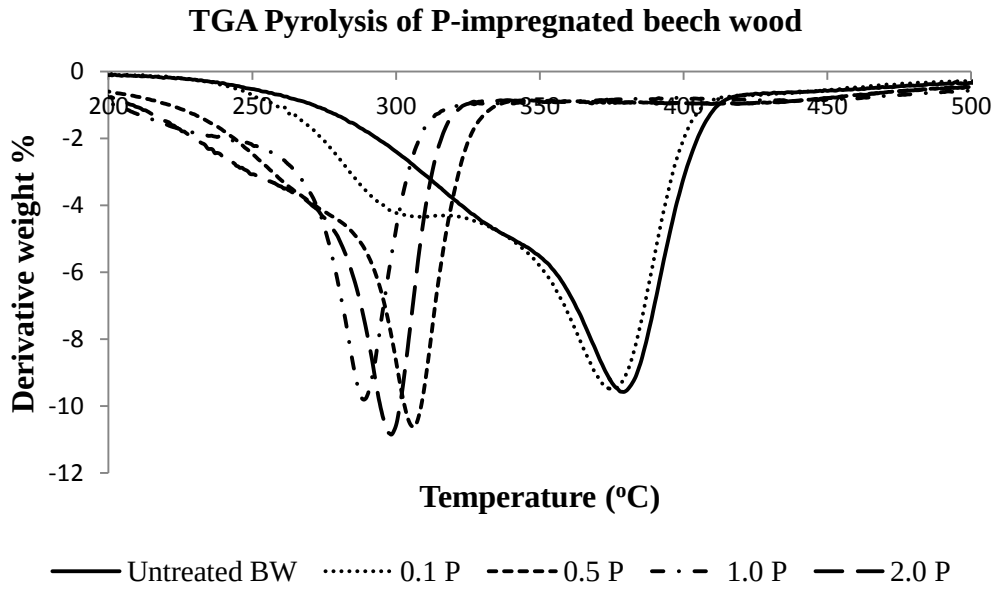


Figure 15 Pyrolysis DTG profile for P-impregnated beech wood

Table 20 Thermogravimetric analysis data of P-impregnated beech wood

Harvest	Volatile matter	Char	Fixed carbon	Ash	Volatile matter	Tp
	wt. % d.b.		wt. % d.b.	wt. % d.b.	wt. % d.a.f.	°C
Beech wood	77.81	22.19	21.24	0.95	78.56	378
0.10% P	81.95	18.05	16.82	1.23	82.17	377
0.50% P	69.48	30.52	23.09	7.43	75.06	310
1.00% P	62.18	37.82	28.79	9.03	68.35	291
2.00% P	58.70	41.30	32.50	8.80	64.36	301

T_p - pyrolysis peak temperature

d.b. - dry basis

d.a.f. - dry ash free

Analytical pyrolysis chromatograms for untreated beech wood, 1.00% potassium and 1.00% phosphorus impregnated beech wood are shown in Figure 16, Figure 17 and Figure 18 respectively; also peak assignments for Py-GC-MS chromatograms are shown in Table 21. The major volatile products of untreated beech wood are acetic acid (2.60 minutes), methyl ester (3.15 minutes), phenol (13.35 minutes), 2–methoxy–phenol (Guaiacol) (13.52 minutes), 2-methyoxy-4(1-prophenyl)-phenol (16.56 minutes), D-allose (28.55 minutes) and 1, 6 anhydro-β-D-glucopyranose (levoglucosan) (30.70 minutes).

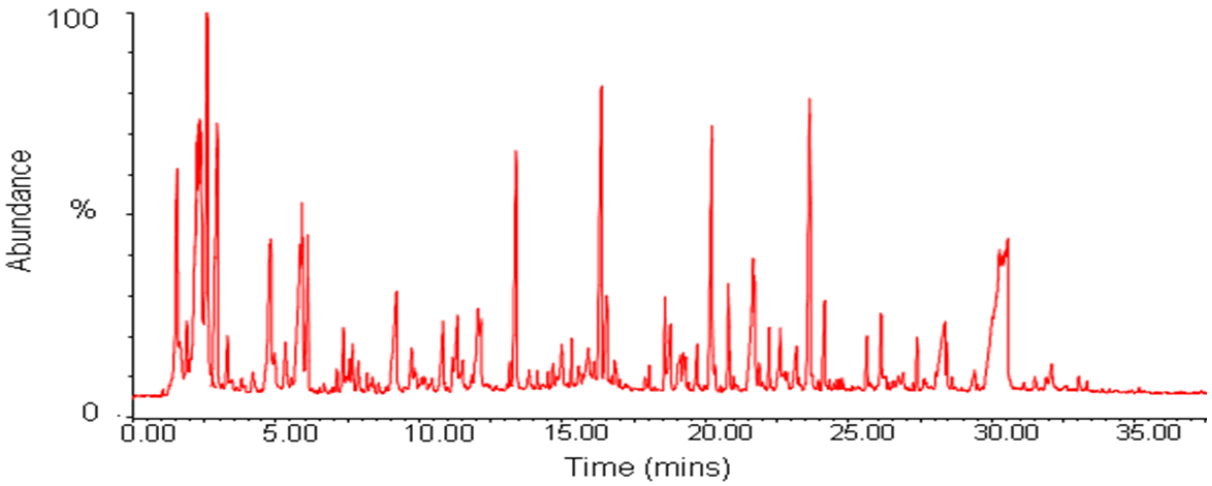


Figure 16 Py-GC-MS chromatogram for untreated beech wood

Potassium impregnated beech wood shows some similarity to the untreated beech wood chromatogram, with the major volatile organic products being acetic acid (2.60 minutes), methyl ester (3.15 minutes), 2 – Methoxy– phenol (Guaiacol) (13.52 minutes) and 2-Methoxy-4 (2-Prophenyl)-phenol (Eugenol) (20.99 minutes). Potassium has a significant influence on biomass decomposition markers (products). The formation of levoglucosan (30.70 minutes) decreases considerably compared to that of untreated beech wood, this is due to the catalytic effect of potassium. The presence of potassium leads to the formation of lower molecular weight compounds at the expense of levoglucosan and anhydrosugars. These results are supported by previous studies that have been carried out in this area [22].

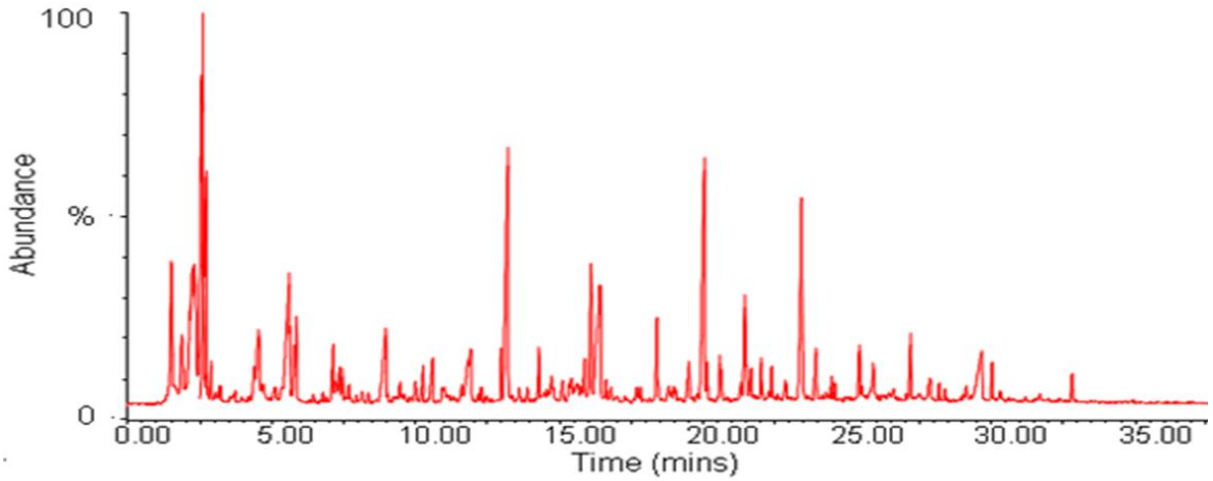


Figure 17 Py-GC-MS chromatogram for 1.00% K-impregnated beech wood sample

Phosphorous has a significant effect on the decomposition profile of beech wood. The major volatile products are 3-furaldehyde (6.38 minutes), 5-methyl-2-furancarboxaldehyde (10.03 minutes), 2-methoxy-4-methyl-phenol (16.56 minutes), levoglucosenone (17.04 minutes), 1, 4:3, 6-Dianhydro-α-D-glucopyranose (20.01 minutes) and levoglucosan (30.70 minutes). The abundance of acetic acid (2.60 minutes) is dramatically reduced and methyl ester (3.15 minutes) is not present. Additional peaks of 3-furaldehye (6.38 minutes) and 5-methyl-2-furancarboxaldehyde (10.03 minutes) occur due to phosphorus which is not present on the untreated beech wood chromatogram. The levoglucosenone peak is more prominent and the levoglucosan peak hardly noticeable. This identifies that phosphorous promotes the cracking of levoglucosan.

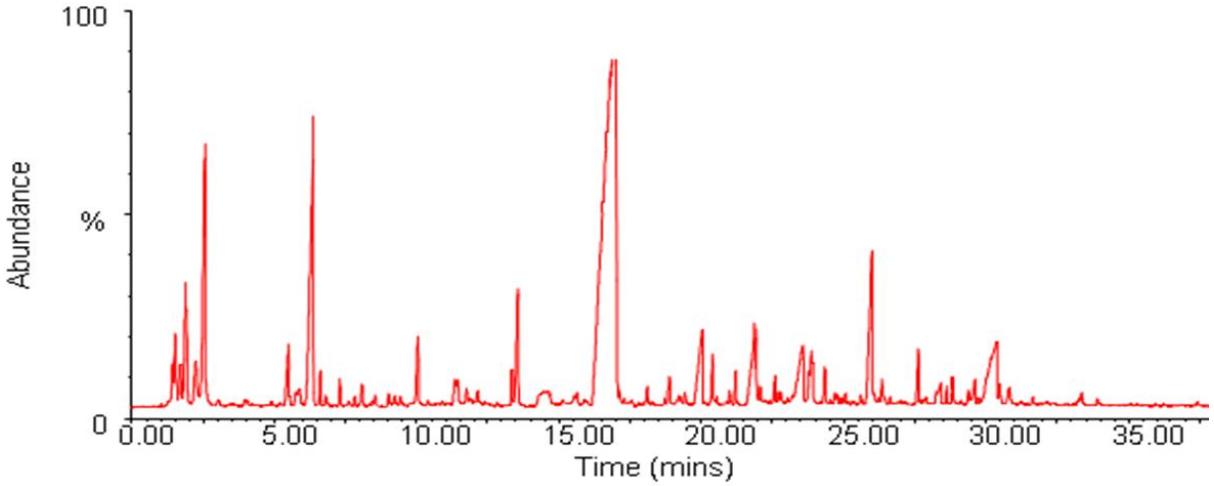


Figure 18 Py-GC-MS chromatogram for 1.00% P-impregnated beech wood sample

Table 21 Untreated beech wood, 1.00% K-impregnated beech wood and 1.00% P-impregnated beech wood peak assignments for Py-GC-MS chromatograms

RT (minutes)	Structure name	Formula	Molecular Weight
2.60	Acetic acid	$C_2H_4O_2$	60
3.15	Methyl ester	$C_3H_6O_2$	74
4.96	1,2-Ethanediol, monoacetate	$C_4H_8O_3$	104
6.01	1-Butoxy-2-propanol acetate	$C_9H_{18}O_3$	174
6.38	3-Furaldehyde	$C_5H_4O_2$	96
7.54	2-Furanmethanol	$C_5H_6O_2$	98
7.87	2-Butanone	C_4H_8O	72
9.40	2- hydroxyl-2-cyclopentane-1-one	$C_5H_6O_2$	98
10.03	5-methyl-2-furancarboxaldehyde	$C_6H_6O_2$	110
13.35	Phenol	C_6H_6O	94
13.52	Guaiacol	$C_7H_8O_2$	124
16.56	2-methoxy-4-methyl-phenol	$C_8H_{10}O_2$	138
16.81	Pentanal	$C_5H_{10}O$	86
17.04	Levoglucosaenone	$C_6H_6O_3$	126
18.78	4-Ethyl-2-methoxy-phenol	$C_9H_{12}O_2$	152
20.01	1,4:3,6-Dianhydro-.α.-d-glucopyranose	$C_6H_8O_4$	144
20.41	2-Methoxy-4-vinyl-phenol	$C_9H_{10}O_2$	150
20.99	Eugenol	$C_{10}H_{12}O_2$	164
21.89	Catechol	$C_6H_6O_2$	110
22.41	2-Methoxy-6 (2-Prophenyl)-phenol	$C_{10}H_{12}O_2$	164
22.80	3-Methyl-1,2 Benzenediol	$C_7H_8O_2$	124

23.83	2-Methoxy-4 (1-Prophenyl)-phenol	$C_{10}H_{12}O_2$	164
24.36	Vanillin	$C_{10}H_{12}O_2$	152
25.83	2-Methoxy-4-propyl-phenol	$C_{10}H_{14}O_2$	166
26.32	1-(4-Hydroxy-3-Methoxy phenyl) Ethanone	$C_9H_{10}O_3$	166
27.59	1-(4-Hydroxy-3-Methoxy phenyl)-2-Propanone	$C_{10}H_{12}O_3$	180
28.55	D -Allose	$C_6H_{12}O_6$	180
28.63	4-Ethyl-2-Methoxy – Phenol	$C_9H_{12}O_2$	152
30.70	Levoglucosan	$C_6H_{10}O_5$	162

6.1.1 Beech wood impregnation conclusion

Both potassium and phosphorus impregnated beech wood lowered the main peak temperature of the pyrolysis profiles. Phosphorus impregnated beech wood lowered the temperature the greatest (beech wood - 378 ^{o}C, K - 330 ^{o}C and P - 291 ^{o}C). Lower amounts of volatiles were observed for higher concentrations of potassium and phosphorus (71.25% for 1.00% K and 58.70% for 2.00% P) compared to beech wood (77.81%). Increased potassium content increased char yields as it acts as a catalyst for promoting char formation. Phosphorus compounds are well known flame-retardants resulting in increased char yields. Ash content increased with increased impregnation concentrations, which was to be expected.

Potassium has a significant influence on biomass decomposition markers (products). The formation of levoglucosan is dramatically decreased this is due to the catalytic effect of potassium. The presence of potassium leads to the formation of lower molecular weight compounds at the expense of levoglucosan and anhydrosugars. The tar compounds produced from phosphorus-impregnated beech wood were very different from untreated beech wood. Furfural and levoglucosenone become more dominant products upon P-impregnation pointing to new rearrangement and dehydration routes of cell wall components of biomass.

7 Thermal processing and product analysis

This chapter describes the methods used to fast pyrolyse biomass and characterise the products. Results are presented in subsequent chapters. Reproducibility of the fast pyrolysis results is discussed in this chapter to establish if thermal processing repeats are required for each feedstock.

7.1 Fast pyrolysis rig

The fast pyrolysis experiments were carried out in a 1 kg $h.^{-1}$ continuous bubbling fluidised bed reactor (#4). A flow sheet of the 1 kg $h.^{-1}$ fast pyrolysis rig set-up is shown in Figure 19. The rig is composed of three sections: the feeding system, the fast pyrolysis reactor and product collection. The feeding system consists of an air-tight hopper (#1) with a nitrogen purge with speed regulated twin metering screws to supply up to 1 kg $h.^{-1}$ of feedstock to the high speed feed screw (#2) which is water cooled at the feed point to minimise pre-pyrolysis. Low biomass moisture content is desirable (refer to Section 2.5.6) as it helps to reduce the risk of pre-pyrolysis with in the feed screw as the heat is used to evaporate the water therefore reducing the possibility of pyrolysis taking place. The biomass fraction size has to be between 0.25-2.00 mm (refer to Section 3.2), as blockages in the hopper or feed screw can occur with smaller or larger particle sizes. The main aim is to bring the biomass particles to the optimum pyrolysis temperature and minimize exposure to lower temperatures which favour the formation of char [117]; this can be achieved by using smaller particle sizes ideally below 2.00 mm.

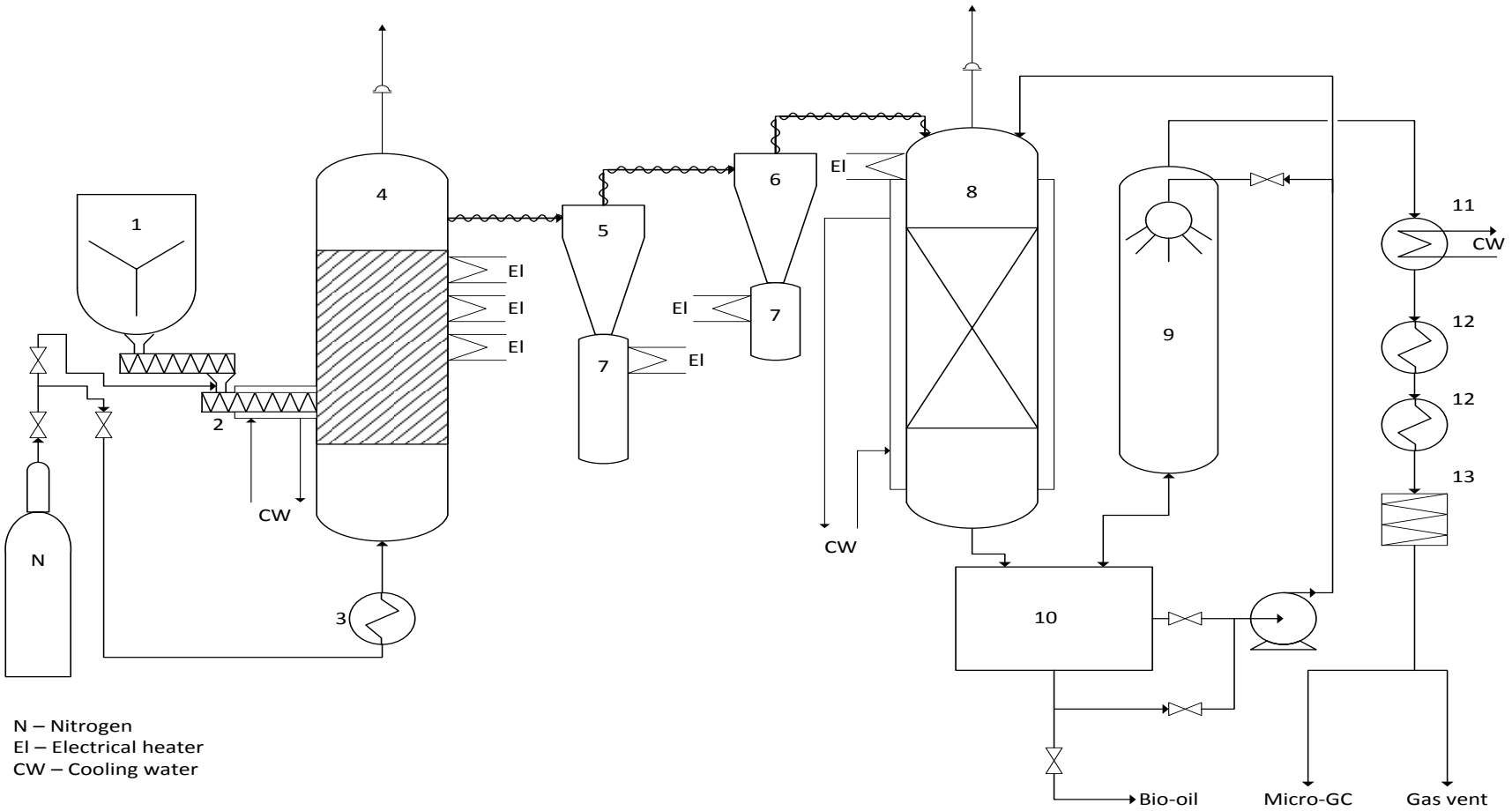


Figure 19 1 kg h.$^{-1}$ fast pyrolysis rig set-up

1 - feed hopper, 2 - fast screw, 3 - nitrogen preheater, 4 - bubbling fluidised bed reactor, 5 - cyclone one, 6 - cyclone two, 7 - char pot, 8 - quench column, 9 - electrostatic precipitator, 10 - collection tank, 11 - water cooled condenser, 12 - dry ice / acetone condenser, 13 - cotton wool filter

The biomass was fed into the lower part of the fluid bed reactor, 10.16 cm above the distributor plate. The distributor plate is a porous plate at the bottom of the reactor that disperses the fluidising gas and supports the reactor fluid bed material. The reactor bed material is 1 kg of sieved quartz sand with a particle size between 600 and 710 µm. The minimum particle size that could be used was determined by the diameter of the holes in the distributor plate of 500 µm. Silica sand was chosen as it is a very efficient heat transfer material due to its high solid density, it is also robust, thermally stable and cheap. Being thermally stable is important as the silica sand is burnt off after each experiment to remove char (refer to Section 7.2.3). Based on previous research at Aston University Bioenergy Research Group (BERG) [173] it was known that the particle size fraction, 600-710 µm, was suitable for both beech wood and miscanthus processing at a moderate nitrogen flow 51 l $min.^{-1}$ (atmospheric test pressure - ATP). 51 l $min.^{-1}$ of nitrogen resulted in fluidisation of the bed material and good char particle entrainment (no bed material is entrained).

The reactor was fluidised with three times the minimum fluidising velocity (17 dm^3 $min.^{-1}$) [174] of preheated nitrogen used on a single pass basis. A single pass basis was used so that the gas stream (nitrogen and product gas) can be analysed every 150 seconds, therefore the product gas composition can be studied at any point during a fast pyrolysis experiment. The nitrogen was preheated (#3) electrically in a chamber below the fluid bed reactor. All experiments were carried out with the aim of achieving an average pyrolysis temperature of 535 ± 5 ^oC (to reduce number of process parameters that have an impact on product yields and improve comparability of experiments); this is an average temperature between the middle (T1) and bottom (T2) of the reactor zone. Figure 20 shows the positioning of middle (T1) and bottom (T2) thermocouples within the reactor (all measurements are in centimetres). The residence time of the vapours in the reactor and associated hot pipework and cyclones was calculated to be below 1.1 seconds [174]. The hot vapour residence time in the reactor and associated hot pipework and cyclones is directly dependent on the fluidisation gas flow rate.

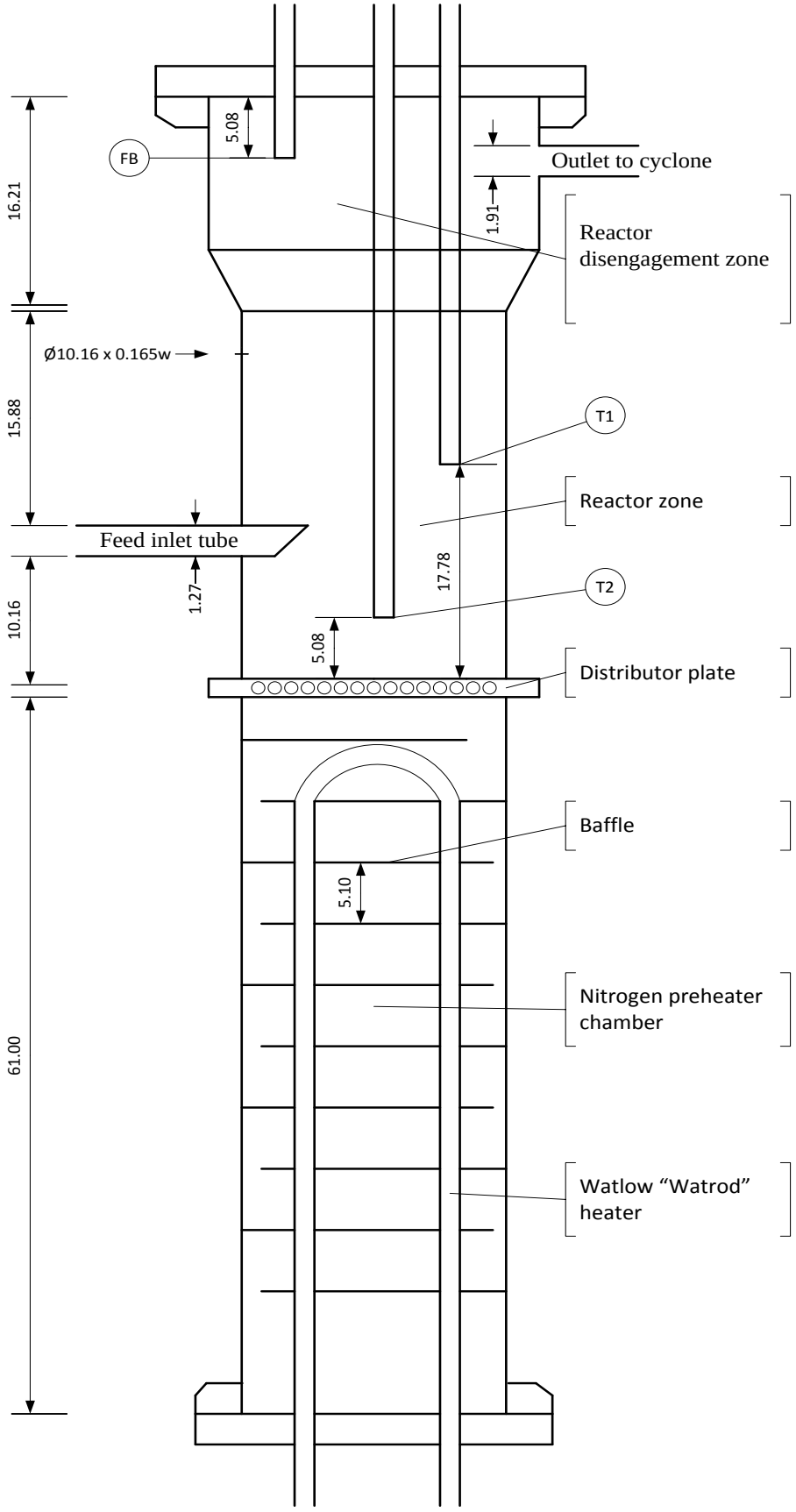


Figure 20 Reactor dimensions

As the vapour and gas stream leaves the reactor it passes through two heated cyclones in series (#5 and 6) where the char is separated. The first cyclone collects the coarse char (above 10 μm particle diameter) and the second collects the fine char (5-10 μm particle diameter). The cyclones and pipework are all trace heated to at least 425 ^{o}C to minimise tar condensation leading to blockages and not above 460 ^{o}C to minimise thermal cracking. Following the cyclones the vapours are condensed in a cooled quench column (#8) directly contacted with ISOPAR™ (Isopar V. CAS number: 64742-46-7. Supplier: Multisol Limited) as the quenching media controlled to between 20 and 25 °C, by a water jacket surrounding the quench column. Isopar is an iso-paraffinic hydrocarbon which is not miscible with fast pyrolysis liquid [116]. 12 litres of Isopar was circulated in the system at a flow of approximately 9 l min.$^{-1}$. The aerosols are coalesced in a wet walled electrostatic precipitator (#9), working at 20 kV and 0.2 mA, flushed with Isopar. The electrostatic precipitator consists of two electrodes, a central wire cathode and an outer cylindrical anode. The central cathode charges the aerosols so that they migrate to the outer cylindrical anode. As the electrostatic precipitator is wet walled the Isopar removes the coalesced aerosols and returns them to the condensed fast pyrolysis oil in the collection tank. Isopar is pumped from the middle of the collection tank (#10) back to the top of the quench column and the top of the electrostatic precipitator. There is no specific ratio of Isopar to the quench column and electrostatic precipitator as the flow of Isopar can be varied to the quench column to maintain Isopar temperature between 20 and 25 °C. The bio-oil is periodically run-off from the collection tank and collected in the bottom of the tank.

Following the electrostatic precipitator the gas passes through a water cooled condenser (#11) at 10-15 °C, two dry ice / acetone condensers (#12) in series at -70 °C and finally a cotton wool filter (#13), followed by 250 g of silica gel (silica gel orange, Sigma Aldrich, reference: 13767, CAS number: 112926-00-8, particle size 2-5 mm), to collect as much water vapour still in the gas stream as possible. A detailed mass balance (refer to Section 7.2) was performed for each experimental run and enabled a final mass balance closure of usually better than 90%. For details on mass balance losses/errors refer to Section 7.2.5. With the addition of silica gel to the cotton wool filter mass balance closures were increased by 2-3% as collection of moisture was improved.

An on-line Varian CP 4900 Micro-GC microgas chromatograph with a thermal conductivity detector (TCD) and two columns (Varian CP-5A molsieve and CP-PortaPLOT) was used for interval analysis (every 150 seconds) of the non-condensable gases for each fast pyrolysis run. Any excess gas was vented to the fume hoods.

Temperatures were measured and recorded using K-type thermocouples joined to a Microlink 751 ADC unit using Windmill data logging software. As the pyrolysis temperature needs to be regulated and controlled to a specific temperature range a number of temperatures are monitored:

- Nitrogen pre-heater
- Fluidising gas before distributor plate
- Electric knuckle heaters (around the outside of reactor)
- Bottom of reaction zone (T2)
- Middle of reaction zone (T1)
- Freeboard in the reactor disengagement zone (FB)

System pressures are measured by analogue instrumentation at varying points, so that any blockages or leaks can be identified. The fluidised bed is also monitored to ensure it is operating suitably. The list below identifies where the pressure differences were measured:

- Distributor plate - top of reactor
- Reactor outlet - quench column inlet
- Quench column inlet – Electrostatic precipitator outlet
- Electrostatic precipitator outlet - gas meter outlet

7.2 Mass Balance

Mass balances (wt. % on dry feed basis) were calculated based on mass of dry biomass processed and final fast pyrolysis products of bio-oil, char and non-condensable gases. An extensive mass balance is performed so that good overall closures are achieved which allows for comprehensive conclusions to be made on product yields. Once a fast pyrolysis experiment was completed the rig was left to stand until reaching room temperature, at which point it was partially dismantled. Dismantling includes all metal pipework between reactor output and quench input, including both cyclones and char pots. The rest of the fast pyrolysis rig cannot be measured directly as dismantling is time consuming and certain parts are too heavy to achieve an accurate weight measurement. Table 22 shows how each aspect of the mass balance was achieved for input material, fast pyrolysis liquid products, fast pyrolysis char products and fast pyrolysis gas products which are then described in more detail in the following sections.

Table 22 Mass balance for 1 kg h.$^{-1}$ fast pyrolysis rig

Material	Equipment	Method
Input material:		
Biomass	Feed hopper	Difference in weight of biomass added to hopper and biomass left in hopper after run
Sand	Reactor	Difference in weight before run and bed material after being burnt off
FP liquid products:		
Fast pyrolysis liquid	Collection tank	Directly weighed after separation from Isopar
Fast pyrolysis liquid hold up	Quench column	Difference in weight before and after run
Secondary condensate	Water cooled condenser	Difference in weight before and after run
Secondary condensate	Dry ice / acetone condenser 1 plus collection flask	Difference in weight before and after run
Secondary condensate	Dry ice / acetone condenser 2 plus collection flask	Difference in weight before and after run
Secondary condensate	Glass pipework	Difference in weight before and after run
Secondary condensate	Cotton wool filter plus 150 g of silica gel	Difference in weight before and after run
FP char products:		
Char and char coating sand	Reactor	Difference in bed material after run and when bed material has been burned off
Char	Cyclone 1 and 2 including both char pots	Directly removed and weighed
Char	Metal pipework	Directly removed and weighed
FP gas products:		
Pyrolysis gas	Varian micro GC and diaphragm gas meter	Pyrolysis gas mass measured by average gas composition and total gas volume

7.2.1 Input material

The biomass was weighed before being poured into the feed hopper and then re-weighed after the fast pyrolysis experiment; the difference between them was the amount of biomass processed. The bed material (silica sand) in the reactor was weighed before and after each run. The bed material after the run includes course char particles and char coating the sand particles (refer to Section 7.2.3) which has to be deducted from the input mass balances.

7.2.2 Fast pyrolysis liquid products

Liquid products were collected from the collection tank via a tap using a separation funnel. The liquid was allowed to flow into the separation funnel till visibly no more bio-oil could be extracted from the collection tank. These liquid products were left 24 hours to separate from Isopar, that can also be removed from the collection tank and should not be included in the mass balance. The quench column and ESP were then drained of any remaining Isopar and washed with ethanol to remove bio-oil hold-up (average bio-oil hold-up in the quench column was around 10 g which was comparable to previous operators of the 1 kg $h.^{-1}$ fast pyrolysis rig using similar feedstocks). The hold-up was directly measured by removing the plates within the quench column before and after a fast pyrolysis run and measuring the difference in weight. This value was used then in every mass balance as a fixed value as dismantling the quench column is very time consuming.

The water cooled condenser, two dry ice/acetone condensers and accompanying glassware were weighed before and after a run so that the difference could be calculated. Reaction water was measured by determining the feedstock moisture content and the fast pyrolysis liquid product moisture content (refer to Section 7.4.3). The reaction water can be regarded as the difference between the sum of moisture in the fast pyrolysis liquids and the moisture in the processed feedstock.

7.2.3 Fast pyrolysis char products

Char was directly collected and weighed from both cyclones accompanying char pots and metal pipework. Coarse char and char coating the sand within the reactor has to be included in the char products. This was calculated by weighing the overall bed material after a fast pyrolysis run, the bed material was then placed in an oven and heated to 600 ^{o}C for 2 hours which burns off the char. The bed material was left to cool to room temperature and reweighed; the difference was concluded to be char product. For the purpose of the mass balance it was assumed that no char was entrained into the bio-oil.

7.2.4 Fast pyrolysis gas products

A Varian Star Chromatography Workstation 6.0 was used for quantification of non-condensable gases produced during the fast pyrolysis run. The pyrolysis gas products were sampled every 150 seconds exactly. The CP-PortaPLOT column was used for separation of carbon dioxide, ethane, ethene,

propane, propene and n-butane. The molecular sieve CP-5A column was used for separation of carbon monoxide, hydrogen, oxygen, nitrogen and methane. A range of BOC gas mixtures of known compositions of non-condensable gases were used to calibrate the columns prior to all pyrolysis runs. A diaphragm gas meter was used to measure the total gas output. By using the total gas output and the Varian Star Chromatography Workstation 6.0 the mass of the gas can be calculated.

7.2.5 Errors/Losses

Losses in the mass balance are down to undetected and unidentified permanent gases, bio-oil holdup in the quench column, partial dissolution of some pyrolysis products in the Isopar and non-condensed water vapour.

Gas detection was limited to the calibrated gases; also the pyrolysis product gas is diluted in fluidising nitrogen. Pyrolysis product gas can account for as little as 5% of the overall analysed gas stream. Therefore small errors in analysis of the fast pyrolysis gas products have a large knock on effect on the overall mass balance.

Isopar was found not to be fully separated from bio-oil after leaving in a separation funnel for 24 hours. Therefore prior to any analysis all bio-oil samples were centrifuged using an Eppendorf 5702 centrifuge at 2500 rpm for 5 minutes. This resulted in the less dense Isopar forming a layer above the bio-oil sample as seen in Figure 21. The purpose of removing the Isopar was because it would affect the actual moisture content of the bio-oil sample therefore changing the mass balance (reaction water yield). Also when samples were measured for viscosity major fluctuations occurred. This is because Isopar and bio-oil have different viscosities which meant that the Brookfield Viscometer model DV-II+pro rotational viscometer (refer to Section 7.4.2) could not distinguish between the two liquids. Fresh Isopar is a clear liquid but after a pyrolysis run it becomes a light brown colour as seen in Figure 21. This identifies partial dissolution of some pyrolysis products into the Isopar, resulting in a loss in fast pyrolysis liquid.

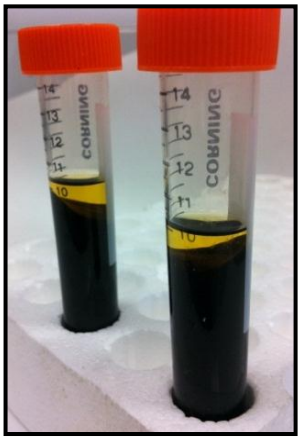


Figure 21 Bio-oil samples with a top layer of Isopar after centrifuging

7.3 Reproducibility

To discover if the results from the 1 kg $h.^{-1}$ fast pyrolysis rig were reproducible two fast pyrolysis experiments were performed using beech wood as a feedstock (refer to Section 3.1.5). The same fast pyrolysis temperature, biomass feed rate and length of run were used for both experiments to ensure results could be compared accurately. The resulting mass balances were compared to see how similar the results were to each other. This would allow for further fast pyrolysis experiments only requiring one run if reproducible results were obtained or in duplicate/triplicate if results are not reproducible. Reproducible results are defined as yields of bio-oil, char and gas being within a 5% range. If yields were outside this range it would show that processing the same feedstock would produce different results and therefore an average of yields would have to be taken from multiple runs. Also the bio-oil has to be single phase. Mass balance closures are acceptable above 90%.

The resulting mass balances are shown in Table 23. Both of the mass balance closures are above 90% and within 2.50% of each other. Yields of char, bio-oil and gas were very similar with wt. % of 13.18-14.35, 67.99-70.68 and 10.53-11.26 respectively. Bio-oils were single phase (refer to Section 7.4.3) and have similar organic and reaction water contents (58.90-63.41 and 7.27-9.09 wt. % respectively). As both fast pyrolysis mass balances and individual yields are within the 5% range it can be expected that further fast pyrolysis experiments would produce reproducible results, therefore only one experiment was performed for each feedstock.

Viscosity or pH cannot be used as criteria for reproducibility as they can be greatly affected by feedstock water content. Even a difference as little as 0.50% in feedstock water content can result in dramatic variation in viscosity or pH, mainly viscosity. Yield of reaction water is a more accurate way to distinguish reproducible results.

Table 23 Fast pyrolysis mass balances for beech wood

Reproducibility		
	Beech wood 1	Beech wood 2
Yield, (wt. % on dry feed basis)		
Char	**13.18**	**14.35**
Bio-oil (organics and reaction water)	**70.68**	**67.99**
Phase	Single	Single
Organics	63.41	58.90
Reaction water	7.27	9.09
Gas	**11.37**	**10.53**
Mass balance closure	**95.23**	**92.88**

7.4 Fast pyrolysis product analysis

This section describes different fast pyrolysis product analysis techniques including GC-MS/FID, dynamic viscosity, water content, pH and an accelerated storage experiment. The procedure for each technique is explained in detail. Results for each analysis technique can be found in Chapters 8, 9 and 10.

7.4.1 GC-MS/FID analysis of fast pyrolysis bio-oils

Analysis of bio-oil samples were performed using a PerkinElmer Clarus 680 GC-MS system. GC samples were prepared by mixing bio-oil with GC grade acetone (1:5 v $v.^{-1}$). 1 µl of the GC sample was filtered using a 0.2 µm pore size Sartorius filter, and was injected into the GC column via an injection port maintained at 300^{o}C, with 1:50 split ratio. Separation was carried out on a Perkin Elmer Elite-1701 column (crossbond: 14% cyanopropylphenyl and 85% dimethyl polysiloxane; 30 m, 0.25 mm i.d., 0.25 µm df). The GC oven programme was as follows: held constant at 50 ^{o}C for 2 minutes, then ramped at 5 ^{o}C $min.^{-1}$ to 275 ^{o}C and held at 275 ^{o}C for 3 minutes. The programme lasts 50 minutes. Helium was used as the carrier gas with a constant flow of 15 ml $min.^{-1}$. A column splitter was used to enable simultaneous detection of compounds separated on the columns by MS and FID detectors. Mass spectra were obtained using 70 eV ionisation energy in the molecular mass range of m/z = 35–300, with a scan time of 0.35 seconds. Assignments of the main peaks were made from mass spectral detection (NIST05 MS library) and from the literature [165, 166]. The FID make-up gas was a mixture of hydrogen (45 ml $min.^{-1}$) and air (450 ml $min.^{-1}$). The detector temperature was 250 ^{o}C.

7.4.2 Dynamic viscosity of bio-oil

A Brookfield Viscometer model DV-II + pro rotational viscometer was used to measure the dynamic viscosity of bio-oil samples. Prior to use, the viscometer (accuracy, ± 1% full-scale range; repeatability, 0.2% full-scale range) was calibrated with 4.7 cP Brookfield silicone viscosity calibration standard. Different spindles (CS4-18 and CS4-34) were used depending on how viscous the sample appeared. A computer programme was used to set an initial speed resulting in a 10% torque reading, then after every minute the speed was increased by 0.5 rpm for 120 minutes. A temperature controlled water bath (temperature 40 ± 0.1 ^{o}C) was used.

7.4.3 Water content

Volumetric Karl-Fischer (KF) titration was used to determine the water content of all the fast pyrolysis liquid products. A Mettler Toledo V20 KF titrator with Hydranal (R) K as a working medium and Hydranal (R) Composite 5K as a titrant. Prior to analysis the KF instrument was calibrated with HPLC-grade water and the system was flushed with working medium between different samples. All analyses were performed in triplicate with the water content reported visually after being calculated automatically by the KF, based on the weight of bio-oil sample used.

To find out if a bio-oil sample was single phase the water content has to be measured at three separate points (33, 50 and 66% from the top of sample). The bio-oil can be classed as single phase if the difference between two consecutive points was lower than 4 wt. %. If any one of the three readings falls outside of the 4 wt. % range then the bio-oil sample was classed as separated.

7.4.4 pH analysis

A Sartorius PB-11 pH meter was used to measure the acidity of the bio-oils. Prior to each measurement the pH meter was calibrated with pH buffers (pH = 2, 4, 7 and 10) which were provided by Sartorius. Calibrations were repeated for each sample to ensure that exact readings were recorded and the probe was cleaned between sample analyses to ensure no cross contamination occurred.

7.4.5 Bio-oil accelerated storage experiment

Each main bio-oil sample was centrifuged to remove all the Isopar. A maximum of 96 ml (8 x 12 ml samples) of bio-oil could be centrifuged at a single time; therefore after the Isopar was removed each sample was poured into a single glass vial and left to stand until air bubbles dissipated. 75 ml of each bio-oil were placed in 100 ml glass bottle which had been dried at 105 ^{o}C for 4 hours to remove all moisture. The lids were replaced on the bottles and then placed in an oven at 80 ^{o}C for 24 hours, as this has been shown to simulate one year degradation at ambient temperature [143]. After the first 10 minutes the bottle lids were re-tightened. After 24 hours the bio-oil was removed from the oven and left to cool to ambient temperature. The viscosity and water content were re-measured so a viscosity and water content index could be calculated (Equation 3 and Equation 4). An index of 1.00 indicates a perfectly stable liquid in which the viscosity or water content does not change with heating or time. Most applications for bio-oil require the bio-oil to retain its initial physical properties during storage, transport and use. Stability of bio-oil is discussed in Section 2.8.

Equation 3 Viscosity index (v_I)

$$v_I = 1 + \frac{v_1 - v_0}{v_0}$$

v_0 - viscosity before the accelerated storage experiment (0 h)

v_1 - viscosity after the accelerated storage experiment (24 h)

Equation 4 Water content index (w_I)

$$w_I = 1 + \frac{w_1 - w_0}{w_0}$$

w_0 - water content before the accelerated storage experiment (0 h)

w_1 - water content after the accelerated storage experiment (24 h)

8 Impact of senescence times on fast pyrolysis bio-oils – results and discussion

This chapter shows results from fast pyrolysis and bio-oil storage experiments for miscanthus harvested at three different time points and commercial pellets. The chapter covers the potential of harvesting miscanthus earlier than conventional harvest (February-March), allowing the harvest window to be extended whilst maintaining bio-oil quality (low viscosity and water content indexes plus single phase).

8.1 Fast pyrolysis and bio-oil storage experiments

The fast pyrolysis mass balance for the three senescence stages of miscanthus and the commercial pellets are summarised in Table 24. Acceptable mass balance closures were achieved for all four feedstock's (>90%).

The total bio-oil yields obtained with all miscanthus samples ranged from 50.9 wt. % (for early harvest-June) and 63.3 wt. % (for conventional harvest-February). For commercial miscanthus pellets the total bio-oil yield was obtained at a level of 62.1 wt. % which was close to the obtained yield from conventional harvest. The highest organic content in bio-oil was observed for commercial pellets and the conventional harvest at 52.9 wt. % and 52.5 wt. % respectively. The reaction water was found to be lowest in bio-oil derived from commercial pellets (9.2 wt. %), and was similar to bio-oil derived from the late summer harvest (9.5 wt. %). Bio-oil obtained from the early harvested crop had the highest reaction water yield (14.0 wt. %) due to the cracking of organics to water and carbon dioxide by higher concentrations of alkali metals (refer to Section 4.1 Table 9).

Elemental analysis of fast pyrolysis char and bio-oil samples are given in Table 24. The HHV of char increased with plant development, early summer harvest having a HHV of 21.4 MJ $kg.^{-1}$ and peaking with conventional harvest (February) at 25.2 MJ $kg.^{-1}$. The HHV for the bio-oil showed no specific trend with it fluctuating, peaking with late summer harvest at 20.0 MJ $kg.^{-1}$ and troughing with conventional harvest at 18.0 MJ $kg.^{-1}$.

Table 24 Senesced miscanthus fast pyrolysis mass balances and product properties

	Harvest time/senescence stage			
	1st June 2009	1st September 2009	1st February 2010	Commercial pellet
Yield, (wt. % on dry feed basis)				
Char	**26.1**	**16.3**	**14.5**	**13.7**
Bio-oil	**50.9**	**59.1**	**63.3**	**62.1**
Phase	Single	Single	Single	Single
Organics	36.9	49.6	52.5	52.9
Reaction water	14.0	9.5	10.8	9.2
Gas	**15.3**	**15.1**	**12.8**	**15.0**
Mass balance closure	**92.3**	**90.5**	**90.6**	**90.8**
Char properties				
Ash (wt. % d.b.)	29.50	23.41	13.49	10.52
C (wt. % d.a.f.)	57.64	60.20	68.05	67.79
H	2.92	3.06	3.12	3.09
N	1.93	1.26	0.45	0.97
O*	37.51	35.48	28.38	28.15
HHV (MJ kg.-1)	21.4	22.3	25.2	25.2
LHV	20.8	21.6	24.6	24.5
Bio-oil properties				
Ash (wt. % d.b.)	-	-	-	-
C (wt. % d.a.f.)	42.62	48.81	45.00	49.52
H	8.08	7.86	7.66	8.76
N	2.17	0.79	0.39	0.28
O*	47.13	42.54	46.95	41.44
HHV (MJ kg.-1)	17.1	20.0	18.0	20.6
LHV	15.3	18.3	16.3	18.7

d.b. - dry basis

d.a.f. - dry ash free

* - by difference

- - not analysed

The char yield from miscanthus samples decreased from 26.1 wt. % (the highest value, for early summer harvest) to 14.5 wt. % (for conventional harvest). Results from ash content analysis of fast pyrolysis chars show that as plant development progressed the ash content decreased. This was also correlated to the ash content of the feedstock (refer to Section 4.1 Table 8). It is known that during the fast pyrolysis process the inorganic compounds in the form of ash catalyse biomass decomposition and char-forming reactions. High ash content leads to reductions in liquid yield, and increased yield of char and non–condensable gases.

Results for the bio-oil accelerated storage experiments are shown in Table 25. Bio-oil contains a large number of oxygenated organic compounds with a wide range of molecular weights. The chemical composition of the bio-oil during storage changes towards the thermodynamic equilibrium, which results in changes in the viscosity, molecular weight, and co-solubility of its many compounds [151]. When the bio-oil samples were placed in the accelerated storage experiment, an increase in viscosity for all of the samples was observed. The viscosity index shows that the early summer harvest produces the most unstable bio-oil (1.77), compared to the other three harvests which produce similar stability bio-oils (1.27-1.34). The water index shows a similar trend except that the late harvested material suggests a perfectly stable liquid, although this is not entirely in line with the viscosity index. The majority of inorganics are concentrated in the char, but small amounts of char can be entrained in the pyrolysis vapours and therefore small amounts of ash may end up in the bio-oil.

The reduction in pH of the bio-oil samples (Table 25) could be an indication of the decomposition of levoglucosan and other anhydrous sugars due to the presence of alkali metals. This decomposition leads to formation of low molecular weight products such as formic acid, acetic acid and propanoic acid, which increase the acidity of the bio-oil. After the accelerated storage experiment, some phase separation was observed in early summer harvest bio-oil as a noticeable thin bottom layer of polymerised material. Bio-oil phase separation results from polymerisation reactions, where larger molecules are formed. Etherification and esterification reactions, in which water is a by-product, can also lead to phase separation. Larger molecules create a ‘tar like’ bottom layer and the top layer has higher water content and is more acidic [175].

Table 25 Results for the stability of bio-oils derived from miscanthus biomass harvested at three time points and from commercial pellets

Analysis	Harvest time/senescence stage							
	1st June 2009		1st September 2009		1st February 2010		Commercial pellet	
	0h	**24h**	**0h**	**24h**	**0h**	**24h**	**0h**	**24h**
Viscosity (cP)	93	165	187	245	70	89	83	111
Stability index based on viscosity	1.77		1.31		1.27		1.34	
Water content increase (%)	24.94	33.85	13.12	14.64	19.42	19.43	17.65	17.66
Stability index based on water content	1.36		1.12		1.00		1.00	
pH	3.92	3.62	3.42	3.05	3.05	2.95	3.00	2.74

Viscosity, water content and pH measured after aging of bio-oil by heating at 80 ^{o}C for 24 hours

During the accelerated storage experiment the water content of the bio-oil samples derived from the conventionally harvested and commercial pellets was stable with a water content index of 1.00 (Table 25). The late summer harvest bio-oil sample had a slightly less stable water content index of 1.12, but the early summer harvest bio-oil had the least stable water content index of 1.36. The accelerated storage experiment revealed that the most stable bio-oil was achieved using miscanthus harvested in February (viscosity index 1.27, water content index 1.00). The late summer harvest bio-oil had a similar viscosity index as conventionally harvested material (winter) but a slightly higher water content index (viscosity index 1.31, water content index 1.12) compared to the conventional harvest, but can still be classed as a good quality bio-oil as no phase separation was apparent [176].

The main bio-oils generated during the fast pyrolysis experiment before and after storage were compared using the GC-MS analysis and the results can be found in the Figure 22 a-d (June and commercial pellet not shown). No major differences were observed in the chemical composition of bio-oils obtained from miscanthus harvested in September and February. After storage at the elevated temperature of 80 ^{o}C additional low molecular weight components such as methanol, 1-hydroxy-2-propanone and 2-hydroxy-butanone were observed in both bio-oils. It was postulated by Ortega et al. [175] that organic constituents of bio-oil undergo oxidation reactions, this results in alcohols being formed, followed by ketones or aldehydes and then carboxylic acids. The carboxylic acid molecules dissociate in the aqueous element of the liquid which increases the acidity of the bio-oil. Esterification can also take place between organic acids and alcohol, where water is produced as a by-product [66]. Changes in the water content in the fast pyrolysis bio-oils can be also related to possible cracking reactions during the accelerated storage at 80 ^{o}C promoted by alkali metals (such as potassium) present in the bio liquid.

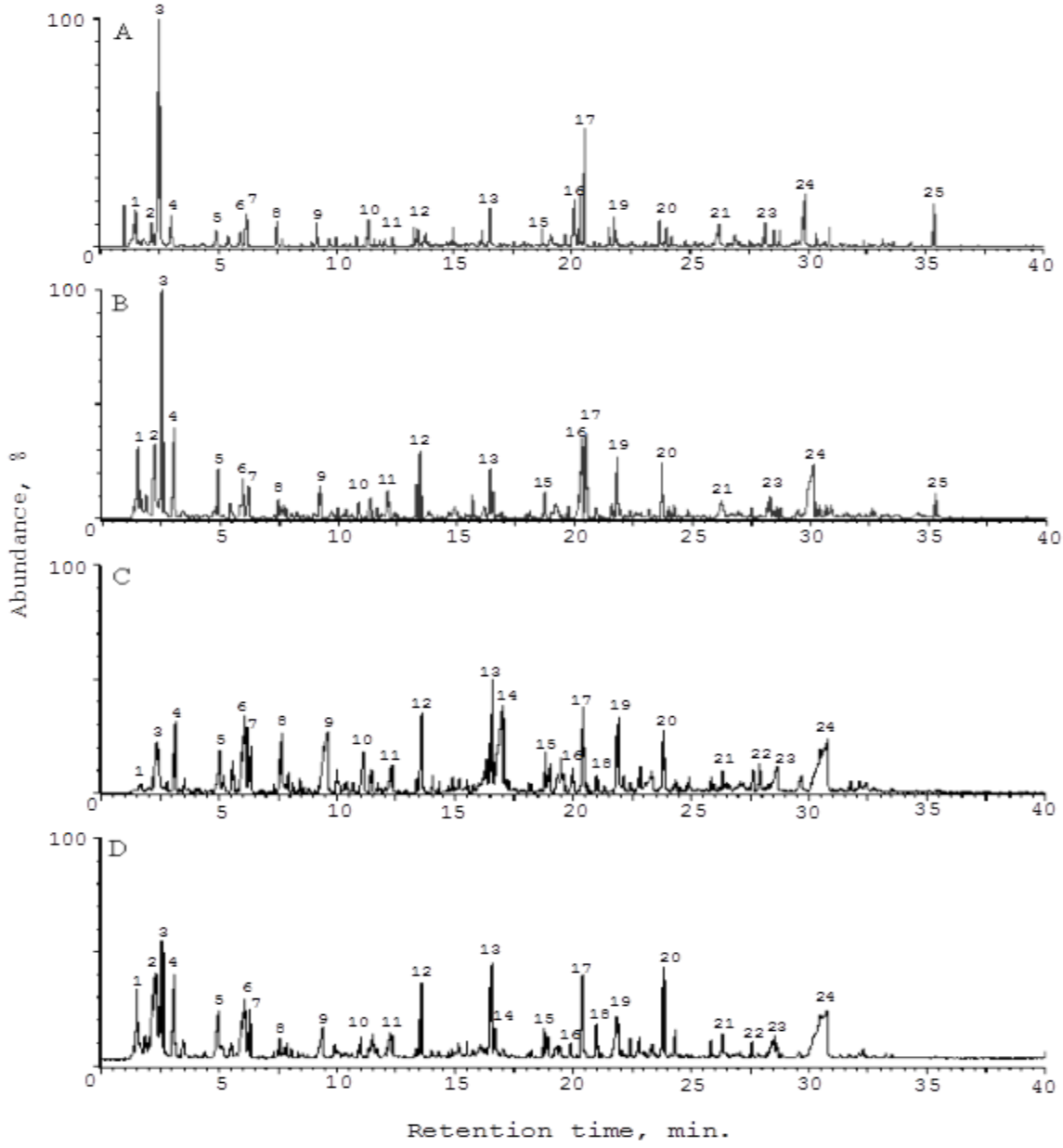


Figure 22 Senesced miscanthus bio-oil GC-MS chromatograms

A - September harvest before accelerated storage experiment; B - September harvest after accelerated storage experiment; C - February harvest before accelerated storage experiment; D - February harvest after accelerated storage experiment

Peak assignments: 1) pyrovaldehyde; 2) methanol; 3) acetic acid; 4) 1-hyrdoxy-2-propanone; 5) 1-hydroxy-2-butanone; 6) 3-furalaldehyde; 7) 2-methyl-2-cyclopentene-1-one; 8)1,3-cyclopentanedione; 9) 2-methoxyphenol; 10) 2-methylphenol; 11) 4-ethylphenol; 12) 1,2-benzenediol; 13) 2-methoxy-4-vinylphenol; 14) 4-ethyl-2-methoxyphenol; 15) 2,6-dimethoxyphenol; 16) 2-methoxy-4-methylphenol; 17) Vanillin; 18) 1,2,4-trimethoxybenzene; 19) 2-methoxy-4-(1-propenyl)-phenol; 20) 1-(4-hydroxy)-3-methylphenyl)-ethanone; 21) 1,2-dimethoxy-4-(2-methoxyethyl)-benzene; 22) 1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone; 23) 2,6-dimethoxy-4-(2-propenyl)-phenol; 24) levoglucosan

8.1.1 Sustainable production of fast pyrolysis bio-oil from miscanthus

A summary of the results considering the impact of the miscanthus harvest times on bio-oil storage, heating values and nitrogen accumulation in the crop is given in Figure 23. The sustainable production of bio-oil from miscanthus biomass should be optimised so that minimal energy input is required for biomass growth, for example from fertiliser requirements while achieving optimal bio-oil quantity and quality in terms of stability. It has been shown that the harvest window for miscanthus can be extended while maintaining similar bio-oil qualities to that produced from the conventional timed harvest (harvested on 1st February 2010). To maintain sustainable crop production nutrient remobilisation has to be taken into account if the harvest window can be extended. Nitrogen fixation from bacteria could replenish some soil nitrogen [177], but nitrogen concentrations in the harvested crop should be kept to a minimum to reduce the potential need for fertiliser application. Nitrogen concentrations in the above ground biomass for September were considered too high (208 kg ha.$^{-1}$) to maintain a crop sustainably when compared to a more sustainable level of nitrogen off take for the 1st of February harvest (45 kg ha.$^{-1}$). Further research could be conducted to identify more accurately the time (exact week) of harvest, between 1st September and 1st February (highlighted in grey in Figure 23) and the precise relationship with developmental senescence, when the level of nutrients in the above ground biomass reaches a level that does not compromise the sustainability of miscanthus production.

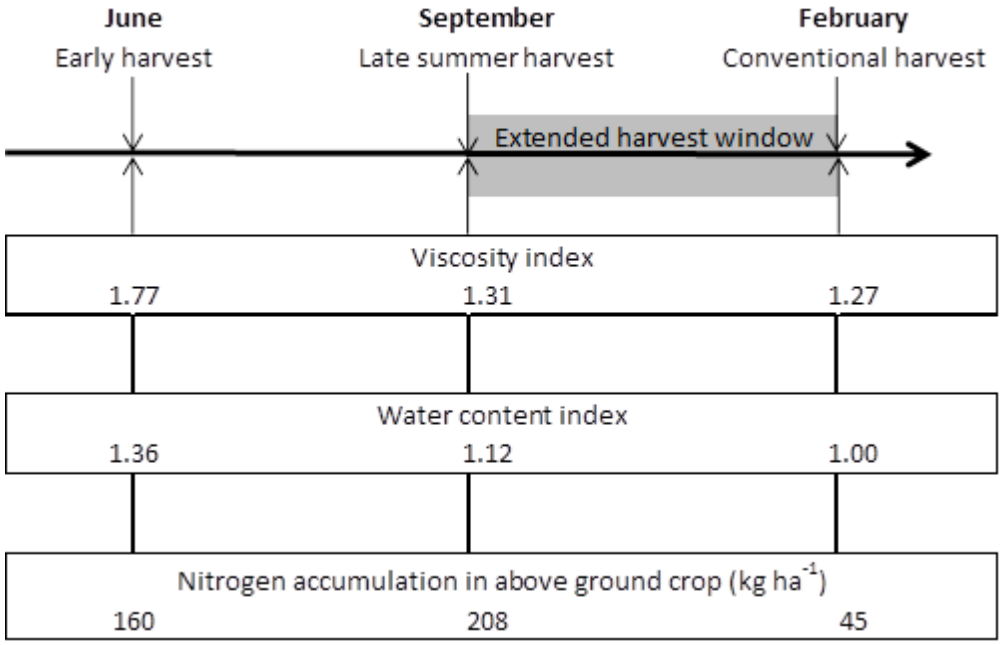


Figure 23 Impact of harvest time on bio-oil characteristics

8.1.2 Conclusion

Miscanthus has been investigated for the influence of senescence and harvest time on the quality of bio-oils produced from fast pyrolysis, as defined by a single phase bio-oil, viscosity index and water content index. From the elemental analysis of each feedstock it was seen that alkali metals (such as potassium) are reduced during senescence which leads to less cracking of the pyrolysis vapours; therefore, increasing the organic liquids and reducing char and reaction water. From the mass balances performed for the fast pyrolysis runs for each feedstock, the June harvest gave the lowest total liquid yield (50.9 wt. %) and the highest char and reaction water yields (26.0 and 14.0 wt. % respectively). The other three feedstocks produced similar liquid (59.1-63.3 wt. %), char (13.7-16.3 wt. %) and reaction water yields (9.2-10.8 wt. %). These similar yields suggest that the miscanthus could be harvested earlier than the conventional harvest date of spring the following year, extending the harvest window by two months. Concentrations of inorganics (nutrients) present in biomass should be taken into consideration to obtain a fast pyrolysis bio-oil which is single phase, and has a low viscosity index and low water content index.

The viscosity index showed that the early summer harvest bio-oil was the least stable (viscosity index 1.77), the other two harvests were of comparable stability. The conventional harvest and commercial pellets had a stable water content index of 1.00 (perfectly stable). No major differences were observed in the chemical composition of bio-oils obtained from miscanthus harvested in September and February analysed by GC-MS, except a small number of low molecular weight components generated during the accelerated storage at 80 ^{o}C. All four bio-oil viscosities increased over the storage experiment which was to be expected due to polymerisation resulting in increasing the average molecular weight. Viscosity index seems to be a more reliable predictor of bio-oil stability.

Sustainable production of bio-oil from miscanthus biomass should be optimised for minimal external energy input for biomass growth, for example from fertiliser requirements and for bio-oil quantity and quality in terms of stability. It has been shown that the harvest window for miscanthus plantation can be extended allowing for a similar bio-oil to be produced to that of the conventional harvest (harvested on 1st February 2010). To maintain a sustainable crop production the harvest window can be extended but the nutrient remobilisation has to be taken into account. Nitrogen fixation from bacteria will replenish some soil nitrogen content, but nitrogen content in harvested crop should be kept at a minimum to reduce the potential need for nitrogen fertiliser application. Nitrogen content in above ground biomass for September were too high (208 kg ha.$^{-1}$) for harvest while maintaining a sustainable crop when compared to a more sustainable content of nitrogen removal for the 1st of February harvest (45 kg ha.$^{-1}$). It is proposed that the harvest time of miscanthus can be extended to cover a wider harvest window whilst still maintaining bio-oil quality.

9 Demineralisation - results and discussion

This chapter shows results from fast pyrolysis and bio-oil storage experiments for large scale and surfactant demineralised miscanthus. The first part of the chapter covers three different large scale demineralised miscanthus samples comparing fast pyrolysis mass balances and stability indexes of bio-oil after accelerated storage. The second part of the chapter covers the potential different concentrations of surfactant (Triton X-100) have on bio-oil production and the effect they have on the stability of bio-oil after accelerated storage experiments.

9.1 Fast pyrolysis and bio-oil storage experiments for demineralised miscanthus

The fast pyrolysis mass balance for large scale demineralised miscanthus are summarised in Table 26. Acceptable mass balance closures were achieved for all four feedstock's (>88%). The total bio-oil yield obtained from large scale demineralised miscanthus stayed stable for demineralised water and HCl washes (62.44 and 64.13 wt. % respectively) when compared to untreated miscanthus (64.05 wt. %) which suggests that these washes have no benefit in terms of bio-oil yield . Triton X-100 washed miscanthus increased the bio-oil yield to 76.21 wt. % due to reduced cracking of organics to water and carbon dioxide as a result of a lowered ash content (refer to Section 5.2 Table 11). Untreated and demineralised water washed miscanthus also had similar organic (53.32 and 55.94 wt. % respectively) and reaction water yields (10.53 and 8.19 wt. % respectively). HCl washed miscanthus had decreased yields of organics (49.21 wt. %) and increased yields of reaction water (13.23 wt. %). This could be due to increased cracking of organics to water and carbon dioxide [172] as the second deionised water wash may not have removed all of the chlorine (as a result of HCl wash). Triton X-100 washed miscanthus had higher yields of organics (68.93 wt. %) compared to untreated and other washed miscanthus samples, also reaction water yields were the lowest (7.29 wt. %). Triton X-100 can increase cell permeability [110] allowing for the washing solution to wash the entire biomass sample removing increased quantities of inorganics therefore reducing organic cracking.

Table 26 Large scale demineralisation fast pyrolysis mass balances and product properties

	Large scale washing experiments			
	Untreated miscanthus	Deionised water	1.00% HCl	0.10% Triton X-100
Yield, (wt. % on dry feed basis)				
Char	**13.70**	**12.97**	**10.69**	**9.77**
Bio-oil	**64.05**	**64.13**	**62.44**	**76.21**
Phase	Single	Single	Single	Single
Organics	53.52	55.94	49.21	68.93
Reaction water	10.53	8.19	13.23	7.29
Gas	**12.33**	**11.01**	**15.16**	**8.25**
Mass balance closure	**90.08**	**88.11**	**88.29**	**94.24**
Char properties				
Ash (wt. % $^{d.b.}$)	13.77	14.86	15.82	17.65
C (wt. % $^{d.a.f.}$)	82.88	75.76	79.79	84.99
H	3.47	3.72	3.22	4.00
N	0.12	1.37	2.38	0.12
O*	13.53	19.15	14.61	10.89
HHV (MJ kg.$^{-1}$)	40.32	37.82	37.99	43.74
LHV	39.56	37.01	37.29	42.87
Bio-oil properties				
Ash (wt. % $^{d.b.}$)	-	-	-	-
C (wt. % $^{d.a.f.}$)	55.70	52.02	50.58	54.95
H	11.18	8.54	7.50	8.79
N	0.15	0.81	0.63	0.56
O*	28.97	38.63	41.29	35.70
HHV (MJ kg.$^{-1}$)	25.66	21.95	20.73	23.77
LHV	23.22	20.08	19.09	21.85

d.b. - dry basis

d.a.f. - dry ash free

* - by difference

- - not analysed

Char yields decrease for all large scale demineralised miscanthus samples, with Triton X-100 having the lowest char yield (9.77 wt. %) when compared to untreated miscanthus (13.70 wt. %). As Triton X-100 is able to lower the inorganic content of miscanthus the most (assumed from miscanthus ash content, refer to Section 5.2 Table 13) it results in lower char yields due to reduced catalysis of char forming reactions. Gas yields decrease for deionised and Triton X-100 washed miscanthus (11.01 and 8.25 wt. %) when compared to untreated miscanthus (12.33 wt. %), but HCl washed miscanthus results in higher gas yields (15.16 wt. %). As mentioned previously increased reaction water and gas yields can be due to cracking of organics to water and carbon dioxide. All bio-oil produced was single phase.

Char higher heating values decreased for deionised and HCl washed miscanthus (37.82 and 37.99 MJ $kg.^{-1}$ respectively) but increased for Triton X-100 washed miscanthus (43.74 MJ $kg.^{-1}$) when compared to untreated miscanthus (40.32 MJ $kg.^{-1}$). Bio-oil higher heating values decreased for deionised, HCl and Triton X-100 washed miscanthus (21.95, 20.73 and 23.77 MJ $kg.^{-1}$ respectively) when compared to untreated miscanthus (25.66 MJ $kg.^{-1}$).

The bio-oil stability experiments for untreated miscanthus and large scale demineralised miscanthus are summarised in Table 27. As expected viscosity of all bio-oil samples placed in accelerated storage increased. The viscosity index shows that each different washing solution had a positive effect by reducing the index (towards one) compared to untreated miscanthus. As the demineralisation washes have reduced the ash content of the feedstock results in a lower inorganic content of the char, which as mentioned (refer to Section 8.1) small amounts of char can be entrained in the fast pyrolysis vapours and therefore ash may end up in the bio-oil. Reduced inorganic content in the bio-oil reduces aging reactions, therefore the viscosity and water content indexes are closer to one (entirely stable). HCl and Triton X-100 washed miscanthus have the lowest viscosity index (1.40 and 1.44 respectively) with deionised water washed miscanthus having a slightly higher index (1.63). The water content index shows that Triton X-100 washed miscanthus produces the most stable bio-oil (1.06), compared to deionised and HCl washed miscanthus (1.18 and 1.21 respectively). Overall Triton X-100 washed miscanthus bio-oil samples are more stable in both viscosity and water content indexes compared to the other large scale washings. This could be because the char that is entrained in the bio-oil contains less inorganics (such as potassium and phosphorous) therefore reducing any further catalytic cracking or aging reactions.

Table 27 Results for the stability of bio-oils derived from large scale washing experiments

Analysis	Large scale washing experiments							
	Untreated miscanthus		Deionised water		1.00% HCl		0.10% Triton X-100	
	0h	**24h**	**0h**	**24h**	**0h**	**24h**	**0h**	**24h**
Viscosity (cP)	12.10	38.15	339.55	555.03	125.06	175.67	65.65	94.21
Stability index based on viscosity	3.15		1.63		1.40		1.44	
Water content increase (%)	24.35	32.70	17.67	20.80	15.16	18.27	29.02	30.63
Stability index based on water content	1.34		1.18		1.21		1.06	
pH	2.43	2.31	3.11	3.01	3.35	3.13	2.96	2.85

Viscosity, water content and pH measured after aging of bio-oil by heating at 80 ^{o}C for 24 hours

9.1.1 Conclusion

Miscanthus has been investigated for the influence three different washing solutions have on the quality of bio-oil produced from fast pyrolysis, as defined by a single phase bio-oil, viscosity index and water content index. From the mass balances performed for the pyrolysis runs for each demineralised feedstock, the 0.10% Triton X-100 washed miscanthus gave the highest total liquid yield (76.21 wt. %) and the lowest char and reaction water yields (9.77 and 8.25 wt. % respectively). The other two washed miscanthus feedstocks produced similar liquid (62.44-64.13 wt. %), char (10.69-12.97 wt. %) and reaction water yields (8.19-13.23 wt. %) when compared to untreated miscanthus. These similar yields suggest that there is no advantage to washing miscanthus with either deionised water or 1.00% HCl. Bio-oil quality should be taken into consideration as the viscosity index and water content could be improved by each different solution wash, even if there was no major difference in yields.

The viscosity index showed that all washing solutions improved the stability with 1.00% HCl and Triton X-100 being the most stable (1.40 and 1.44 respectively). All washing solutions also improved the water content index with Triton X-100 being the most stable (1.06). Of the three washing solutions Triton X-100 produced the most stable bio-oil with a low viscosity index and the lowest water content index.

As 0.10% Triton X-100 washed miscanthus had the highest total liquid yield (plus lowest char and reaction water yields) as well as the most stable bio-oil further research was performed focusing on different washing solution concentrations. Refer to Section 9.2 for fast pyrolysis and bio-oil storage experiments for surfactant demineralised miscanthus.

9.2 Fast pyrolysis and bio-oil storage experiments for surfactant demineralised miscanthus

The fast pyrolysis mass balance for the surfactant demineralised miscanthus are summarised in Table 28. Acceptable mass balance closures were achieved for all feedstock's (>84%). The total bio-oil yield obtained from Triton X-100 washed miscanthus stayed stable for low concentrations of Triton X-100 from 56.34 to 57.43 wt. % (0.25% and 0.10% Triton X-100 respectively) compared to a untreated miscanthus yield of 56.86 wt. %. As the concentrations of Triton X-100 increased so did the bio-oil yields to 63.59 and 64.54 wt. % (0.50% and 1.00% Triton X-1000 respectively) suggesting that increased concentrations of Triton X-100 result in more effective removal of inorganic matter due to reduced catalytic cracking of fast pyrolysis vapours. As expected the organic content in bio-oil was increased from 43.03 wt. % (untreated miscanthus) to 55.28 wt. % (1.00% Triton X-100). Triton X-100 decreases char and water produced whilst increasing liquid phase organics. Reaction water yields decrease from 13.83 wt. % (untreated miscanthus) down to 9.26 wt. % (1.00% Triton X-100), due to the decreased amount of cracking of organics to water and carbon dioxide.

Char yields decrease with increased concentrations of Triton X-100 from 14.56 wt. % (untreated miscanthus) to 10.43 wt. % (1.00% Triton X-100). The char yields seem to become stable as the concentration of Triton X-100 goes above 0.50% suggesting that further concentration increases would result in no improved reductions on char yields. Gas yields decrease with increased Triton X-100 concentrations from 17.58 wt. % (0.10% Triton X-100) to 12.73 wt. % (1.00% Triton X-100), but when the concentrations of Triton X-100 reached 0.50 % the gas yield stabilised at 12.82 – 12.73 wt. % (0.50% and 1.00% Triton X-100 respectively). All bio-oil produced was single phase.

Char higher heating values increased as Triton X-100 concentration increased from 40.93 to 47.28 MJ $kg.^{-1}$ (0.10 and 0.50% Triton X-100 respectively), apart from 1.00% Triton X-100. The expected heating value was to be above 47.28 MJ $kg.^{-1}$ but dropped to 43.09 MJ $kg.^{-1}$, this could be due to removal and/or partial decomposition of hemicellulose at higher concentrations of Triton X-100 (refer to Section 5.3). Bio-oil higher heating values were similar for untreated miscanthus, 0.10%, 0.50% and 1.00% Triton X-100 (21.66, 21.04, 21.73 and 20.58 MJ $kg.^{-1}$ respectively), but when the concentration of Triton X-100 was at 0.25% the heating value increased to 24.17 MJ $kg.^{-1}$.

Table 28 Surfactant fast pyrolysis mass balances and product properties

	Triton X-100 washes				
	Untreated miscanthus	0.10 T	0.25 T	0.50 T	1.00 T
Yield, (wt. % on dry feed basis)					
Char	**14.56**	**10.78**	**12.74**	**10.87**	**10.43**
Bio-oil	**56.86**	**57.34**	**56.34**	**63.59**	**64.54**
Phase	Single	Single	Single	Single	Single
Organics	43.03	41.00	46.31	52.56	55.28
Reaction water	13.83	11.33	10.03	11.03	9.26
Gas	**18.75**	**17.58**	**15.68**	**12.82**	**12.73**
Mass balance closure	**90.17**	**85.70**	**84.76**	**87.28**	**87.87**
Char Properties					
Ash (wt. % $^{d.b.}$)	13.51	13.81	22.99	20.57	14.34
C (wt. % $^{d.a.f.}$)	82.89	81.74	90.95	89.41	84.38
H	3.60	3.76	4.13	4.20	3.93
N	0.12	0.20	0.35	0.28	0.12
O*	13.39	14.30	4.57	6.11	11.57
HHV (MJ kg.$^{-1}$)	40.87	40.93	47.93	47.28	43.09
LHV	40.08	40.10	47.03	46.37	42.24
Bio-oil properties					
Ash (wt. % $^{d.b.}$)	-	-	-	-	-
C (wt. % $^{d.a.f.}$)	52.56	52.03	56.57	52.96	50.76
H	7.42	6.65	7.98	7.16	7.04
N	0.19	0.10	0.10	0.10	0.10
O*	39.83	41.22	35.35	39.78	42.10
HHV (MJ kg.$^{-1}$)	21.66	21.04	24.17	21.73	20.58
LHV	20.04	19.59	22.43	20.17	19.04

d.b. - dry basis

d.a.f. - dry ash free

* - by difference

- - not analysed

The bio-oil stability experiments for untreated miscanthus and Triton X-100 treated miscanthus are summarised in Table 29. As expected viscosity of all bio-oil samples placed in accelerated storage increased. The viscosity index shows that 1.00% Triton X-100 produces the most stable bio-oil (2.43), compared to untreated miscanthus bio-oil (2.69). The viscosity index decreases as the concentration of Triton X-100 increases. Higher concentration washes have to be studied to find out if at a certain point the stability of bio-oil becomes consistent. The water content index shows that 1.00% Triton X-100 produces the most stable bio-oil (1.01), compared to untreated miscanthus bio-oil (1.34). The water content index shows a similar trend to the viscosity index as the concentration of Triton X-100 increases the water content index decrease, showing that the bio-oil becomes more stable. As the water content index for 1.00% Triton X-100 is close to 1 (indicating a perfectly stable bio-oil), it can be concluded that concentrations above 1.00% would produce a perfectly stable bio-oil when considering water content. An increased concentration of Triton X-100 was expected to improve the stability of bio-oil in both viscosity and water content due to more effective removal of inorganic content of biomass prior to fast pyrolysis processing (refer to Section 5.3 Table 13), therefore reducing any further catalytic cracking or aging reactions (refer to Section 2.8.2). Overall 1.00% Triton X-100 miscanthus bio-oil samples are more stable in both viscosity and water content indexes compared to lower concentrations, which was to be expected.

Table 29 Results for the stability of bio-oils derived from miscanthus washed with varying concentrations of Triton X-100

Analysis	Triton X-100 washes									
	Untreated miscanthus		0.10 T		0.25 T		0.50 T		1.00 T	
	0h	**24h**	**0h**	**24h**	**0h**	**24h**	**0h**	**24h**	**0h**	**24h**
Viscosity (cP)	110.75	298.46	684.51	1758.55	311.50	785.29	165.50	420.50	154.09	375.00
Stability index based on viscosity	2.69		2.57		2.52		2.54		2.43	
Water content increase (%)	16.22	21.67	5.17	5.55	7.35	7.75	8.73	9.26	8.21	8.32
Stability index based on water content	1.34		1.07		1.05		1.06		1.01	
pH	2.87	2.65	2.95	2.81	2.76	2.64	3.09	2.89	2.46	2.32

Viscosity, water content and pH measured after aging of bio-oil by heating at 80 ^{o}C for 24 hours

9.2.1 Conclusion

Miscanthus has been investigated for the influence of different concentrations of Triton X-100 wash solutions on the quality of bio-oil produced from fast pyrolysis, as defined by a single phase bio-oil, viscosity index and water content index. From the mass balances performed for the pyrolysis runs for each surfactant demineralised feedstock, the 1.00% Triton X-100 gave the highest total liquid yield (64.54 wt. %) and the lowest char and reaction water yields (10.43 and 12.73 wt. % respectively). The lower concentrations increased the total bio-oil yield and lowered the char and reaction water yields but not to the extent of the higher concentration of Triton X-100. As the concentration of Triton X-100 reached 0.50% and above the increase in total liquid yield and decrease in char and reaction water yields began to become stable, indicating that concentrations above 1.00% would have no more effect on mass balances yields.

The viscosity index showed that concentrations of Triton X-100 between 0.10% and 0.50% had similar stability (viscosity index range of 2.52-2.57), 1.00% Triton X-100 was the most stable (2.43) when compared to untreated miscanthus (2.69). A similar result occurred with the water content index. Concentrations of Triton X-100 between 0.10% and 0.50% has similar stability (water content index range 1.05-1.07), 1.00% Triton X-100 was the almost completely stable (1.01). As there was no major changes in both the viscosity index and water content index is another indicator that concentrations above 1.00% would have no more effect on mass balance yields or bio-oil stability.

It is proposed that a batch of miscanthus to be washed with 2.00% Triton X-100 to confirm that concentrations over 1.00% have little or no effect on mass balance yields or bio-oil stability.

10 Impregnation studies - results and discussion

This chapter shows results from fast pyrolysis and bio-oil storage experiments for beech wood impregnated with potassium or phosphorus. By studying bio-oil produced from impregnated biomass highlights the affect these elements have on bio-oil production and bio-oil storage capabilities.

10.1 Fast pyrolysis and bio-oil storage experiments

The fast pyrolysis mass balances for untreated beech wood and K-impregnated beech wood are summarised in Table 30. Acceptable mass balance closures were achieved for all feedstock's (>87%). The char and bio-oil elemental analysis are displayed on a dry basis; this is because with beech wood being impregnated with other compounds it can lead to an overall CHN analysis above 100% if completed on a dry ash free basis.

The total bio-oil yields obtained for K-impregnated beech wood decrease as the weight per cent of potassium impregnated increases from 58.09 wt. % (0.10% potassium) to 34.36 wt. % (2.00% potassium). As expected the organic content in bio-oil was reduced dramatically from 63.41 wt. % (untreated beech wood) to 21.23 wt. % (2.00% potassium). Potassium increased char and water produced at the expense of the liquid phase organic products [178]. Increased potassium content resulted in the reaction water yield to increase from 7.27 wt. % (untreated beech wood) up to 15.2 wt. % (1.00% potassium), due to the increased amount of cracking of organics to water and carbon dioxide.

Char yields increase with increased potassium concentrations from 14.8 wt. % (0.10% potassium) to 28.94 wt. % (2.00% potassium); this would suggest that char yields would continue to rise until levelling at a certain concentration of K-impregnation. The changes in liquid and char yields can be attributed to the increased potassium content which acts as a catalyst for promoting char formation [172]. Gas yields increase also with increased potassium concentration from 14.71 wt. % (0.10% potassium) to 24.26 wt. % (2.00% potassium), but when the concentration of potassium reached 1.00% the gas yield levelled out at 24.26 - 24.29 wt. % (2.00% potassium and 1.00% potassium respectively).

A main factor in bio-oil quality is whether the bio-oil is single phased; some point between 0.50% and 1.00% K-impregnation the bio-oil produced becomes separated (due to increased yields of reaction water). As the water content increases the bio-oil is expected to phase separate; an upper phase which is a water-rich phase and a lower phase which is viscose with high tar content [179]. This identifies that potassium concentrations have to be kept below a certain concentration so that the quality of bio-oil can be maintained. Potassium has a chemical effect on the primary decomposition paths of cellulose, hemicellulose and lignin and increases the activity of secondary reactions. The addition of

potassium, even in low amounts, causes major changes on the yields of char, water and gas formation all at the expense of organic yields. Alkali metals favour dehydration, demethoxylation, decarboxylation, demethylation and char formation [180, 181] in the primary decomposition of lignin. While processing K-impregnated beech wood no processing problems occurred.

Char higher heating values were similar for untreated beech wood, 0.10 and 0.50% K (30.69, 31.37 and 33.89 MJ $kg.^{-1}$ respectively), but when the concentration of potassium was increased to 1.00 and 2.00% the heating value increased to 40.00 and 38.40 MJ $kg.^{-1}$ respectively. Heating values for bio-oil produced from K-impregnated beech wood showed no specific trend, with 1.00% K having the highest value (26.46 MJ $kg.^{-1}$) and 0.50% K having the lowest value (18.49 MJ $kg.^{-1}$).

Table 30 K-impregnation fast pyrolysis mass balances and product properties

	K-impregnation				
	Beech wood	0.10 K	0.50 K	1.00 K	2.00 K
Yield, (wt. % on dry feed basis)					
Char	**13.18**	**14.80**	**18.02**	**24.62**	**28.94**
Bio-oil	**70.69**	**58.09**	**52.12**	**40.42**	**34.84**
Phase	Single	Single	Single	Separated	Separated
Organics	63.41	46.70	35.42	25.23	21.23
Reaction water	7.27	11.40	16.70	15.20	13.61
Gas	**11.37**	**14.71**	**17.68**	**24.29**	**24.26**
Mass balance closure	**95.23**	**87.60**	**87.83**	**89.33**	**88.04**
Char Properties					
Ash (wt. % $^{d.b.}$)	3.58	5.79	10.53	19.54	27.91
C (wt. % $^{d.a.f.}$)	75.70	80.85	84.59	94.47	92.65
H	3.51	3.28	3.57	3.67	3.48
N	0.37	0.47	0.11	0.51	0.55
O*	20.42	15.40	11.73	1.35	3.32
HHV (MJ kg.$^{-1}$)	30.69	31.37	33.89	40.00	38.40
LHV	29.93	30.66	33.11	39.20	37.64
Bio-oil properties					
Ash (wt. % $^{d.b.}$)	-	-	-	-	-
C (wt. % $^{d.a.f.}$)	46.19	51.40	46.09	59.36	56.56
H	7.91	8.26	7.91	8.79	7.39
N	0.22	0.10	0.10	0.10	0.10
O*	45.68	40.24	45.90	31.75	35.95
HHV (MJ kg.$^{-1}$)	18.55	21.39	18.49	26.46	23.77
LHV	16.83	19.58	16.76	24.55	22.16

d.b. - dry basis

d.a.f. - dry ash free

* - by difference

\- - not analysed

The fast pyrolysis mass balances for untreated beech wood and P-impregnated beech wood are summarised in Table 31. Acceptable mass balance closures were achieved for all feedstock's (>88%). The total bio-oil yields obtained for the P-impregnated beech wood decrease as the weight per cent of phosphorus impregnated increases from 66.62 wt. % (0.10% phosphorus) to 52.38 wt. % (2.00% phosphorus). The organic content in bio-oil was reduced from 63.41 wt. % (untreated beech wood) to between 30.74 and 36.09 wt. % (0.50% phosphorus and 2.00% phosphorus respectively). Reaction water yields increased from 7.27 wt. % (untreated beech wood) up to 19.47 wt. % (0.50% phosphorus) indicating more dehydration reactions taking place during fast pyrolysis. The primary breakdown of the cellulose structure due to pyrolysis at low temperatures results in the main products being carbon dioxide, carbon monoxide, water and char (this dehydration of cellulose favours low temperatures) (refer to Section 2.5.3) [182], phosphorus reduces the temperature of fast pyrolysis (refer to Section 6.1, Table 20) therefore favouring the dehydration pathway (increasing reaction water yields).

Char yields increased with increased phosphorus concentrations from 9.41 wt. % (0.10% phosphorus) to between 25.49 and 30.21 wt. % (0.50% phosphorus and 1.00% phosphorus respectively). The increase in char yields is due to acid catalysed condensation reactions [183]; higher phosphorous content increases the char formation due to increased catalysis of condensation reactions. It is also well known that phosphorus compounds are flame-retardants [104, 105], resulting in increased char yields. Increased amounts of phosphorus above 0.50% do not seem to greatly affect char yield. All P-impregnated beech wood bio-oil samples were single phase.

Char higher heating values cannot be compared as the ash content of char samples for concentrations above 0.50% could not be determined. This was because the phosphorus formed a flame retardant layer which meant that the carbon beneath this layer was not combusted therefore the actual char ash content could not be calculated. Therefore the CHN results are on a dry basis for 1.00 and 2.00% phosphorus and on a dry ash free basis for 0.10 and 0.50% phosphorus. Char higher heating values decreased as the concentration of phosphorus increased from 30.69 to 26.09 MJ $kg.^{-1}$ (untreated beech wood and 0.50% P respectively). Heating values for bio-oil produced from P-impregnated beech wood showed no specific trend, with 1.00% P having the highest value (22.39 MJ $kg.^{-1}$) and 0.50% P having the lowest value (18.77 MJ $kg.^{-1}$).

While processing P-impregnated beech wood it was noticed that with increased phosphorus concentrations the processing became more problematic. This was due to bed temperatures dropping resulting in a large temperature difference between the middle (T1) and bottom (T2) of the reactor (refer to Section 7.1 Figure 20). When the bed material (1 kg sieved silica sand) was removed from the reactor it was found to have agglomerated into large clumps due to char formation within the reactor (Figure 24), therefore affecting the fluidisation and heat transfer. By regularly increasing the flow rate of preheated fluidising nitrogen, from 45 dm^3 $min.^{-1}$ to 60 dm^3 $min.^{-1}$, reduced the bed temperature

difference by breaking up the agglomerated char and sand. Figure 24 shows the agglomerated char and sand from the reactor due to increased concentrations of phosphorus.

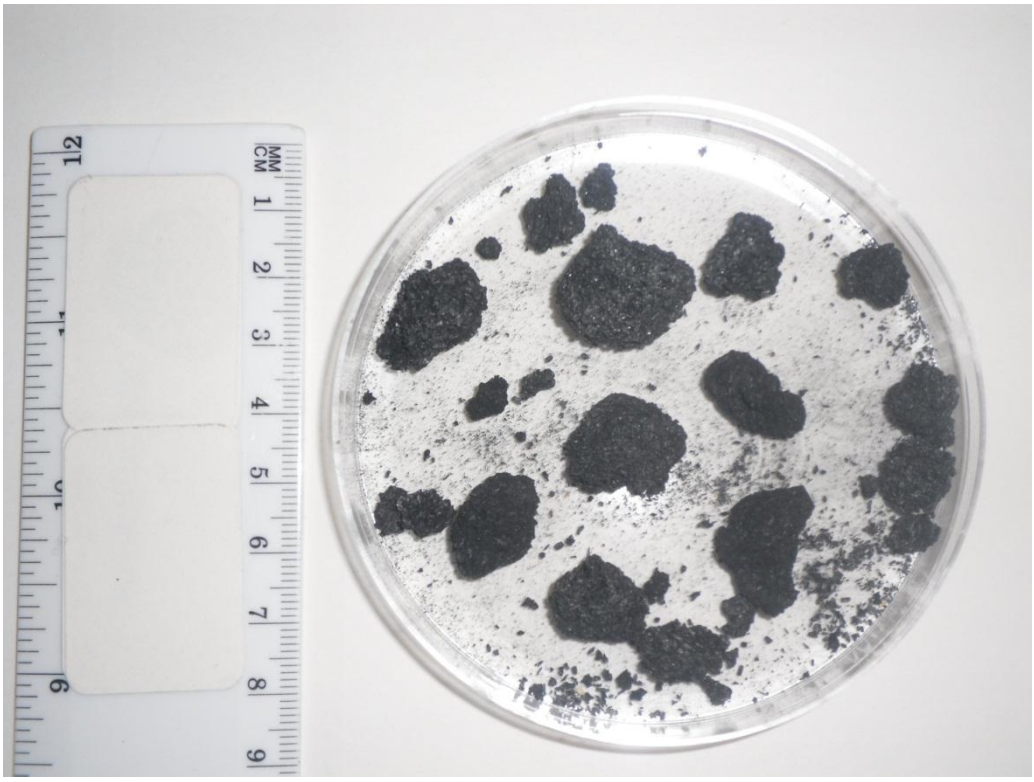


Figure 24 Agglomerated char and sand from reactor

When concentrations of phosphorus are at 0.50% or above the yields of bio-oil, char and gases stay within a similar range (5 wt. %) suggesting that increased concentration of phosphorus (above 0.50%) have little or no effect on the mass balance. But on the processing side, concentrations of phosphorus at 0.50% and above lead to problems due to an increased rate of sand/char agglomeration within the reactor.

Table 31 P-impregnation fast pyrolysis mass balances and product properties

	P-impregnation				
	Beech wood	0.10 P	0.50 P	1.00 P	2.00 P
Yield, (wt. % on dry feed basis)					
Char	**13.18**	**9.41**	**25.49**	**30.21**	**26.00**
Bio-oil	**70.69**	**66.62**	**50.21**	**52.84**	**52.38**
Phase	Single	Single	Single	Single	Single
Organics	63.41	55.77	30.74	34.69	36.09
Reaction water	7.27	10.85	19.47	18.15	16.29
Gas	**11.37**	**15.79**	**13.26**	**15.59**	**11.25**
Mass balance closure	**95.23**	**91.82**	**88.96**	**98.65**	**89.64**
Char Properties					
Ash (wt. % $^{d.b.}$)	3.58	8.05	18.72	n/d	n/d
C (wt. % $^{d.a.f.}$)	75.70	82.37	88.28	76.15$^{\#}$	78.72$^{\#}$
H	3.51	3.40	3.25	3.12$^{\#}$	3.00$^{\#}$
N	0.37	0.54	0.43	0.41$^{\#}$	0.45$^{\#}$
O*	20.42	13.69	8.04	20.32$^{\#}$	17.83$^{\#}$
HHV (MJ kg.$^{-1}$)	30.69	28.60	26.09	28.78	29.80
LHV	29.93	27.92	25.51	28.10	29.14
Bio-oil properties					
Ash (wt. % $^{d.b.}$)	-	-	-	-	-
C (wt. % $^{d.a.f.}$)	46.19	50.82	47.04	52.26	47.35
H	7.91	7.22	6.80	9.39	7.62
N	0.22	0.36	0.10	0.24	0.10
O*	45.68	41.60	46.06	38.25	44.93
HHV (MJ kg.$^{-1}$)	18.55	20.71	18.77	22.39	19.07
LHV	16.83	19.14	17.28	20.34	17.40

d.b. - dry basis

d.a.f. - dry ash free

* - by difference

\- - not analysed

n/d - not determined

\# - CHN results on a dry basis

Untreated beech wood bio-oil was single phase which is identified by the limited amount of lighter coloured small spots (water emulsion); also the bio-oil has a low viscosity (58.00 cP, Table 32) this is shown by the bio-oil flowing over a large proportion of the petri dish (Figure 25 A). Bio-oil obtained from 1.00% potassium impregnated beech wood was phase separated; the water emulsion is clearly shown by the increased amount of lighter coloured spots and streaking of the bio-oil (Figure 25 B). Bio-oil obtained from 1.00% phosphorus impregnated beech wood was single phase and had a high viscosity (145.00 cP, Table 33) this is shown by the limited flow of bio-oil over the petri dish (Figure 25 C).

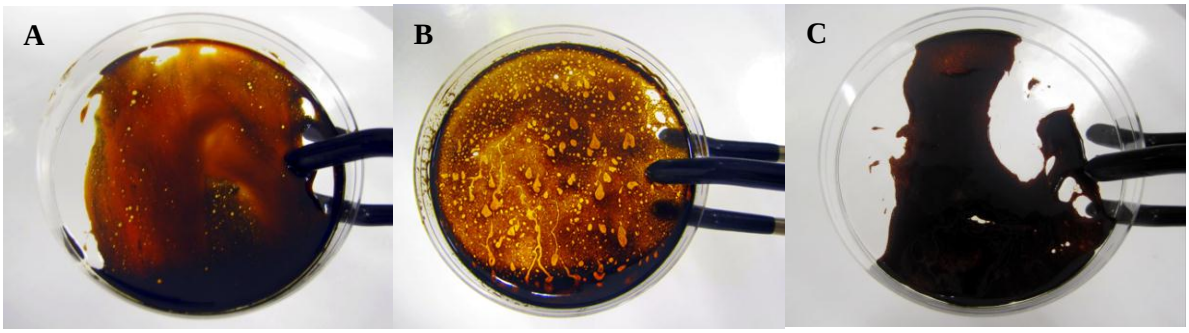


Figure 25 Bio-oils samples produced from beech wood, 1.00% K and 1.00% P impregnated beech wood

A - bio-oil obtained from untreated beech wood (single phase), B - bio-oil obtained from 1.00% K impregnated beech wood (phase separated), C - bio-oil obtained from 1.00% P impregnated beech wood (single phase but higher viscosity)

The bio-oil stability experiments for untreated beech wood, K-impregnated and P-impregnated beech wood are summarised in Table 32 and Table 33. When the bio-oil samples were placed in the accelerated storage experiment an increase in viscosity for all impregnated samples was observed. The viscosity index shows that K-impregnated beech wood samples produce the most unstable bio-oils (2.13 to 2.68), compared to the P-impregnated beech wood bio-oils (1.76-1.98). The increase in viscosity index for the potassium samples suggests that increased potassium concentrations would result in the index continuing to rise. If potassium concentrations increased this would result in higher concentrations being entrained in char therefore having a greater effect on bio-oil stability. Presence of char in bio-oil seems to catalyse reactions leading to viscosity of bio-oil increasing [184]. The viscosity index for the phosphorus samples begins to settle between 1.93 and 1.98, for 1.00% phosphorus and 2.00% phosphorus respectively.

The water content index shows a similar trend as the viscosity index for K-impregnated beech wood bio-oil samples as the index increases from 1.14 (0.10% K) to 1.22 (2.00% K). Etherification and

esterification occurring between hydroxyl, carbonyl and carboxyl group components results in water being a by-product [66], as seen by the increase in water content index. P-impregnated beech wood bio-oil samples have similar water content indexes (1.08-1.11), as these indexes are similar to the untreated beech wood water content index (1.06) it suggests that phosphorus has little or no effect on the water content of the bio-oil during storage. Water content indexes do not vary much as the water release during aging is small and is over compensated by the average molecular weight increase of the bio-oil [140]. Overall P-impregnated beech wood bio-oil samples are more stable in both viscosity and water content indexes compared to the K-impregnated beech wood bio-oil samples.

Table 32 Results for the stability of bio-oils derived from K-impregnated beech wood

Analysis	K-impregnation									
	Beech wood		0.10 K		0.50 K		1.00 K		2.00 K	
	0h	**24h**	**0h**	**24h**	**0h**	**24h**	**0h**	**24h**	**0h**	**24h**
Viscosity (cP)	58.00	75.06	38.50	82.00	14.80	29.76	45.00	101.00	47.50	127.25
Stability index based on viscosity	1.29		2.13		2.01		2.24		2.68	
Water content increase (%)	18.20	19.25	13.69	15.55	22.18	26.09	31.00	37.54	32.36	39.54
Stability index based on water content	1.06		1.14		1.18		1.21		1.22	
pH	2.43	2.31	3.02	2.71	3.15	3.07	3.35	3.13	3.35	3.13

Viscosity, water content and pH measured after aging of bio-oil by heating at 80 ^{o}C for 24 hours

Table 33 Results for the stability of bio-oils derived from P-impregnated beech wood

Analysis	P-impregnation									
	Beech wood		0.10 P		0.50 P		1.00 P		2.00 P	
	0h	**24h**	**0h**	**24h**	**0h**	**24h**	**0h**	**24h**	**0h**	**24h**
Viscosity (cP)	58.00	75.06	82.50	145.36	100.80	198.30	145.00	280.00	12.90	25.60
Stability index based on viscosity	1.29		1.76		1.97		1.93		1.98	
Water content increase (%)	18.20	19.25	9.23	10.11	14.95	16.62	17.16	19.02	16.31	17.67
Stability index based on water content	1.06		1.10		1.11		1.11		1.08	
pH	2.43	2.31	3.11	2.73	3.17	2.86	3.27	2.85	3.51	2.94

Viscosity, water content and pH measured after aging of bio-oil by heating at 80 ^{o}C for 24 hours

The chromatogram from GC-MS analysis for bio-oil from untreated beech wood is shown in Figure 26. Bio-oil produced from untreated beech wood compromised of 23 key components and this is only a fraction of the components that are contained in bio-oil. The main components are organic acids, furans, phenols and anhydrosugars. The major organic compounds along with their retention time, structure name, molecular formula and molecular weight are shown in Table 34.

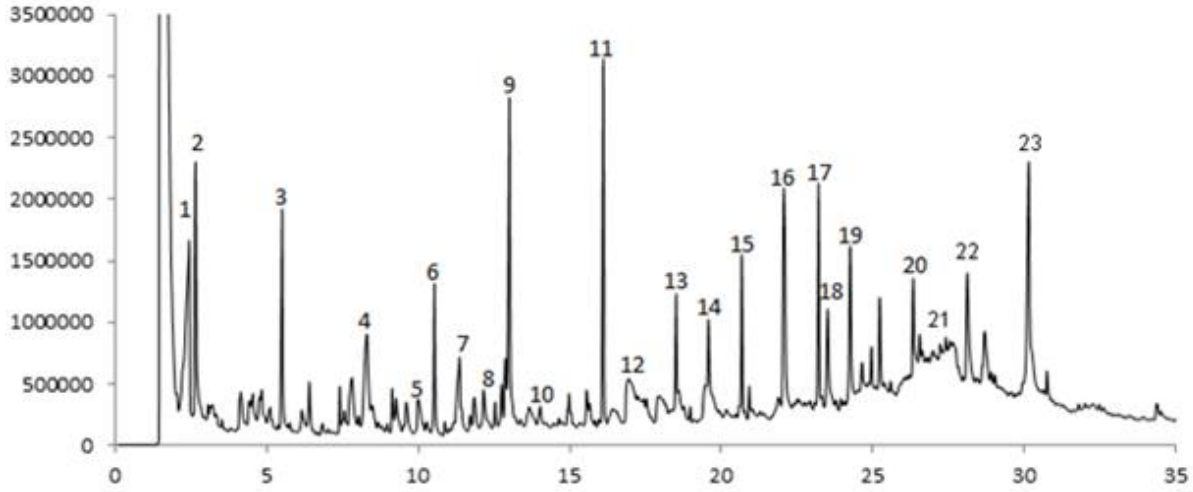


Figure 26 GC-MS chromatogram for bio-oil from untreated beech wood

The chromatogram from GC-MS analysis for bio-oil from 1.00% potassium impregnated beech wood is shown in Figure 27. The major difference observed between untreated beech wood bio-oil and potassium impregnated beech wood bio-oil was the yield of levoglucosan which dramatically reduces. As previously mentioned the presence of potassium and other alkali metals in the feedstock promotes the decomposition of levoglucosan [72] (refer to Section 2.8.1). Potassium impregnation also promotes the production of phenol and its derivatives such as 2-methoxy-4-vinyl-phenol, 2-Methoxy-4 (1-Prophenyl)-phenol. It was also observed that potassium impregnation suppresses the formation of acid compounds such as acetic acid and butanedioic acid compared to untreated beech wood. A decrease in bio-oil acidity with increasing concentration of potassium is shown in Table 32, which supports the fact that the formation of acid compounds was inhibited.

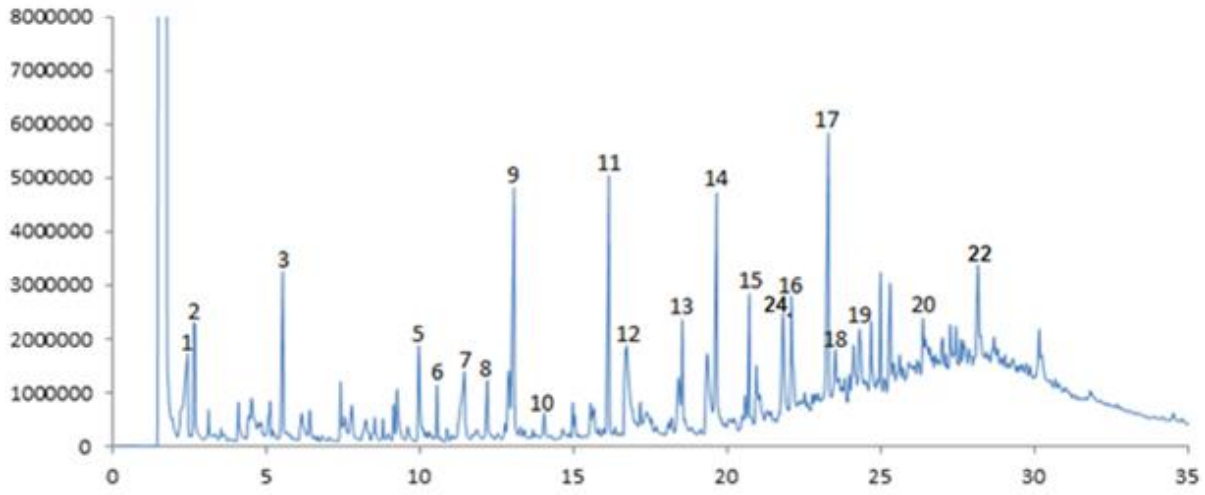


Figure 27 GC-MS chromatogram for bio-oil from 1.00% potassium impregnated beech wood

The chromatogram from GC-MS analysis for bio-oil produced from 1.00% phosphorus impregnated beech wood is shown in Figure 28. The highest yields observed for phosphorus impregnated beech wood bio-oil were for the following markers: Guaiacol, 2-methoxy-4-propyl-phenol, 3-furanmethanol, 3-furaldehyde and levoglucosenone. The presence of phosphorus promoted the formation of phenolic compounds whilst levoglucosan was not produced. Phosphorous promotes decomposition of anhydrosugars during fast pyrolysis to lighter volatile compounds. Levoglucosenone is an anhydrosugar formed from the pyrolytic cracking of levoglucosan. Similar results were observed for analytical pyrolysis experiments for the same set of samples (refer to Section 6.1).

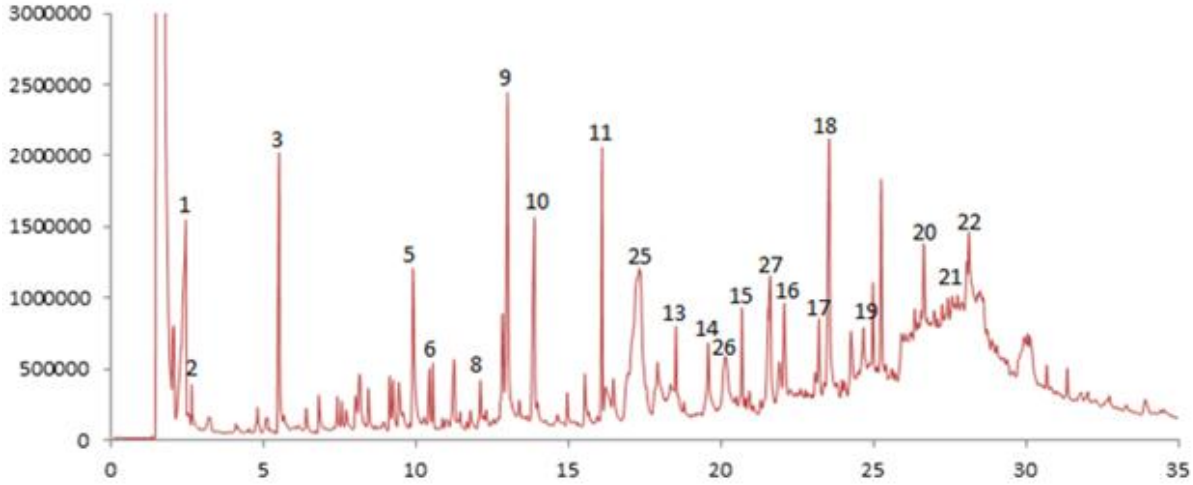


Figure 28 GC-MS chromatogram for bio-oil from 1.00% phosphorus impregnated beech wood

The bio-oil GC-MS results for 0.10, 0.50 and 2.00% potassium and phosphorus impregnated beech wood have been analysed but results are not shown. Chromatograms obtained from those samples were very similar to that of either untreated beech wood or 1.00% potassium/phosphorus impregnated beech wood.

Table 34 Peak assignments for GC-MS chromatograms of bio-oil from untreated beech wood and 1.00% potassium and phosphorus impregnated beech wood

Peak ID	RT (minutes)	Structure name	Formula	Molecular Weight
1	2.10	Acetic acid	$C_2H_4O_2$	60
2	2.65	Acetic acid, methyl ester	$C_3H_6O_2$	74
3	5.50	3-furaldehyde	$C_5H_4O_2$	96
4	8.42	5-methyl-2(3H)- furanone	$C_5H_6O_2$	98
5	10.06	Phenol	C_6H_6O	94
6	10.50	Butanedioic acid, dimethyl ester	$C_6H_{10}O_4$	146
7	11.40	2-hydroxy-3-methyl-2-cyclopenten-1-one	$C_6H_8O_2$	112
8	12.00	2-methyl-phenol	C_7H_8O	108
9	12.90	2 – Methoxy – phenol (Guaiacol)	$C_7H_8O_2$	124
10	13.85	3-Furanmethanol	$C_5H_6O_2$	98
11	16.09	2-methoxy-4-methyl-phenol	$C_8H_{10}O_2$	138
12	17.25	2-Methoxy-4 (2-Prophenyl)-phenol	$C_{10}H_{12}O_2$	164
13	18.51	4-ethyl-2-methoxy-phenol	$C_9H_{12}O_2$	152
14	19.58	2-methoxy-4-vinyl-phenol	$C_9H_{10}O_2$	150
15	20.65	Eugenol	$C_{10}H_{12}O_2$	164
16	22.06	Vanillin 4-Hydroxy-3-methoxy-benzaldehyde	$C_{10}H_{12}O_2$	152
17	23.2	2-Methoxy-4 (1-Prophenyl)-phenol	$C_{10}H_{12}O_2$	164
18	23.51	2-Methoxy-4-propyl-phenol	$C_{10}H_{14}O_2$	166
19	24.26	1-(4-hydroxy-3-methoxyphenyl)-ethanone	$C_9H_{10}O_3$	166
20	25.22	1-(4-hydroxy-3-methoxyphenyl)-2-propanone	$C_{10}H_{12}O_3$	180

21	27.49	Levoglucosan	$C_6H_{10}O_5$	162
24	21.74	4-Ethyl-1,3-benzenediol	$C_8H_{10}O_2$	138
25	17.31	Levoglucosenone	$C_6H_6O_3$	126
26	20.15	1,4:3,6-Dianhydro-.α.-D-glucopyranose	$C_6H_8O_4$	144
27	21.60	2,3-Anhydro-D-mannosan	$C_6H_8O_4$	144

10.1.1 Conclusion

Beech wood has been investigated for the influence of potassium and phosphorus on the quality of bio-oil produced from fast pyrolysis, as defined by a single phase bio-oil, viscosity index and water content index. From the mass balances for the potassium impregnated beech wood the total liquid yield decreases from 58.09 wt. % (0.10% potassium) to 34.84 wt. % (2.00% potassium). Potassium increased char and water produced at the expense of the liquid phase organic products. At some point between 0.50% and 1.00% K-impregnation the bio-oil produced became separated (due to increased yields of reaction water), therefore reducing the quality. From the mass balances for the phosphorus impregnated beech wood the total liquid yield decreases from 66.62 wt. % (0.10% phosphorus) to 52.38 wt. % (2.00% phosphorus). Char yields increased from 9.41 wt. % (0.10% phosphorus) to between 25.49 and 30.21 wt. % (0.50% phosphorus and 1.00% phosphorus respectively). The increase in char yields is due to acid catalysed condensation reactions; higher phosphorus content increases the char formation due to increased catalysis of condensation reactions. All P-impregnated beech wood bio-oil samples were single phase.

The viscosity index showed that K-impregnated beech wood samples produce the most unstable bio-oils (2.13 to 2.68) when compared to P-impregnated beech wood bio-oils (1.76-1.98). If concentrations of potassium were increased above 2.00% the results suggest that the bio-oil would continue to become less stable. A similar trend is seen for the water content index which rises as the concentration of potassium increases. The viscosity index for P-impregnated beech wood stabilises at concentrations at and above 0.50% suggesting that higher concentrations of phosphorus would have little or no effect on the bio-oil stability. This is further justified by the water content index which stays consistent for all concentrations of phosphorus when compared to untreated beech wood. Overall P-impregnated beech wood bio-oil samples are more stable in both viscosity and water content indexes compared to the K-impregnated beech wood bio-oil samples.

The major difference observed between untreated beech wood bio-oil and potassium impregnated beech wood bio-oil analysed by GC-MS was the yield of levoglucosan which dramatically reduced due to potassium promoting its decomposition. Also potassium impregnation suppresses the formation of acid compounds therefore decreasing bio-oil acidity. The major difference observed between untreated beech wood bio-oil and phosphorus impregnated beech wood bio-oil analysed by GC-MS was that the presence of phosphorus caused levoglucosan to be catalytically cracked to levoglucosenone. Therefore the bio-oil consisted of lighter volatile compounds.

11 Summary

This chapter summarises results from each of the three subtasks which have been investigated and presented in this thesis.

11.1 Subtask 1: Senescence

Impact of miscanthus senescence was studied for its effect on fast pyrolysis bio-oil quality and stability as well as the impact of utilising biomass of different harvest time on nitrogen remobilisation. Ash (inorganic content) in miscanthus was naturally reduced over the winter period from the early summer harvest (June) to the conventional harvest (February) due to a combination of senescence and natural leaching from rain water. TGA results showed that due to this reduction of inorganics higher amounts of volatiles were produced for the conventional harvest (82.8%), also char yields decreased from 29.0% (early summer harvest) to 19.5% (conventional harvest).

Inorganic content reduction during senescence is an advantage for fast pyrolysis processing as it leads to less cracking of pyrolysis vapours; therefore increasing yields of organic liquids and reducing char and reaction water yields. The early summer harvested miscanthus had the highest inorganic content and when thermally processed produced the lowest total liquid yield (50.9 wt. %) and the highest char and reaction water yields (26.0 wt. % and 14.0 wt. % respectively). The other three feedstocks produced similar liquid (59.1-63.3 wt. %), char (13.7-16.3 wt. %) and reaction water (9.2-10.8 wt. %) yields. These similar yields identify that the miscanthus harvest window could possibly be extended depending on bio-oil quality and stability.

The conventional and late summer harvest (September) had comparable stability with viscosity indexes between 1.27-1.31 and water content indexes between 1.00-1.12 (1.00 is perfectly stable). No major differences were observed in the chemical composition of bio-oils obtained from late summer and conventional harvest analysed by GC-MS. The late summer harvest bio-oil is similar to the conventional harvest in viscosity and water content indexes as well as chemical composition the miscanthus harvest window can be extended when considering bio-oil quality and stability.

Even though bio-oil quality and stability can be maintained whilst extending the miscanthus harvest window the sustainable production of bio-oil should be optimised for minimal fertiliser input for biomass growth. To maintain a sustainable crop production the harvest window can be extended but the nutrient remobilisation has to be taken into account. Nitrogen concentration in harvested crops should be kept at a minimum to reduce the need for fertiliser application. Nitrogen accumulation in above ground crop was at its highest level for late summer harvest (208 kg $ha.^{-1}$); lower levels are seen for conventional harvest (45 kg $ha.^{-1}$) due to significant remobilisation of nutrients through senescence.

If the late summer harvest was used to generate bio-oil there could be a reduction in crop sustainability due to the lack of nutrient remobilisation resulting in a potential negative impact on crop yields for following growth years. At a certain time point between the late summer and conventional harvest crop nitrogen content is at a certain level that allows for the harvest window to be extended whilst maintaining sustainable crop production.

11.2 Subtask 2: Demineralisation

Deionised water, 1.00% HCl and 0.10% Triton X-100 washes were used to reduce ash (inorganic content) of miscanthus as some components of ash catalytically crack the volatile components in fast pyrolysis. Deionised water and 0.10% Triton X-100 washes increased the peak pyrolysis temperature to a greater affect than 1.00% HCl wash identifying that they had an increased effect on removal of inorganic matter. Different temperatures (20 ^{o}C and 60 ^{o}C) and washing durations (1, 2 and 4 hours) were used to identify the ideal washing conditions. No major benefit was achieved by increasing the washing solution temperature; therefore room temperature washing solutions can be used. Varying the duration of washes showed that there could be a cycle of removal and then adsorption, with the 1 hour removing inorganic matter then some being adsorbed for the 2 hour wash. This was shown by increased temperature peaks for the 1 and 4 hour washes, with a slight drop in peak temperature for the 2 hour wash. From these results large scale demineralisation experiments were conducted at room temperature for duration of 4 hours.

Miscanthus washed on a large scale (0.50 kg batches) was processed by fast pyrolysis so that mass balance yields and products could be analysed and compared. Miscanthus washed with 0.10% Triton X-100 gave the highest total liquid yield (76.21 wt. %) and the lowest char and reaction water yields (9.77 wt. % and 8.25 wt. % respectively). Deionised water and 1.00% HCL washes gave similar liquid (62.44-64.13 wt. %), char (10.69-12.97 wt. %) and reaction water (8.19-13.23 wt. %) yields. In terms of bio-oil stability Triton X-100 produced the most stable bio-oil of the three washing solutions with a low viscosity index (1.44) and the lowest water content index (1.06). As 0.10% Triton X-100 washed miscanthus had the highest total liquid yield (plus lowest char and reaction water yields) as well as the most stable bio-oil further research was performed focusing on different Triton X-100 washing solution concentrations.

Increased concentrations of Triton X-100 resulted in ash content being reduced from 1.78 wt. % (untreated miscanthus) to 0.68 wt. % (1.00% Triton X-100). Untreated miscanthus, 0.10%, 0.25% and 0.50% Triton X-100 washed miscanthus have very similar Py-GC-MS chromatograms. 1.00% Triton X-100 washed miscanthus has a decreased yield of lighter volatile components which could be due to the removal and/or partial decomposition of hemicellulose.

Miscanthus washed with 1.00% Triton X-100 gave the highest total liquid yield (64.54 wt. %) and the lowest char and reaction water yields (10.43 wt. % and 12.73 wt. % respectively). All concentrations of Triton X-100 increased the total liquid yield and decreased char and reaction water yields compared to untreated miscanthus yields. As the concentration of Triton X-100 approached 1.00% the increase in liquid yield and decrease in char and reaction water yield began to stabilise indicating that concentrations above 1.00% would have no more effect on mass balance yields. In terms of bio-oil stability 1.00% Triton X-100 produced the most stable bio-oil with the lowest viscosity index (2.43) and the lowest water content index (1.01).

11.3 Subtask 3: Impregnation with potassium and phosphorus

Beech wood was impregnated with potassium and phosphorus so that their effect on fast pyrolysis processing, mass balance yields and bio-oil quality and stability could be studied. Both potassium and phosphorus impregnated beech wood lowered the main peak temperature of the pyrolysis profiles. Ash content increased with increased impregnation concentrations. Py-GC-MS analysis showed that potassium had a significant influence on biomass decomposition markers (products). The formation of levoglucosan was dramatically decreased due to the catalytic effect of potassium. The presence of potassium leads to the formation of lower molecular weight compounds at the expense of levoglucosan and anhydrosugars. Phosphorus also had significant influence on biomass decomposition markers (pyrolytic decomposition products). Furfural and levoglucosenone become more dominant products pointing to new rearrangement and dehydration routes of cell wall components of biomass.

Impregnated beech wood samples were processed by fast pyrolysis so that mass balance yields and products could be analysed and compared. An increasing concentration of potassium caused the total liquid yield to decrease from 58.09 wt. % (0.10% potassium) to 34.84 wt. % (2.00% potassium). Potassium catalytically cracks the pyrolysis liquids in the vapour phase resulting in increased char and water yields at the expense of liquid phase organic yields. A phase separated bio-oil (due to increased yields of reaction water) was produced for 1.00% K-impregnation therefore reducing quality. Increased concentrations of phosphorus also caused the total liquid yield to decrease from 66.62 wt. % (0.10% phosphorus) to 52.38 wt. % (2.00% phosphorus). Char yields increased from 9.41 wt. % (0.10% phosphorus) to between 25.49 and 30.21 wt. % (0.50% phosphorus and 1.00% phosphorus respectively). The increase in char yields is due to acid catalysed condensation reactions; higher phosphorus content increases the char formation due to increased catalysis of condensation reactions. All P-impregnated beech wood bio-oil samples were single phase.

No processing problems occurred for K-impregnated beech wood, but P-impregnated beech wood caused the reactor temperature to drop. When the bed material (1 kg sieved silica sand) was removed

from the reactor it was found to have agglomerated into large clumps due to char formation within the reactor, therefore affecting the fluidisation and heat transfer.

As the concentration of potassium increased the bio-oil became less stable which was shown by increased viscosity (2.13 for 0.10% K and 2.68 for 1.00% K) and water content (1.14 for 0.10% K and 1.22 for 1.00% K) indexes. Potassium from biomass is concentrated in fast pyrolysis char which can be entrained into bio-oil; char in bio-oil seems to catalyse reactions leading to viscosity of bio-oil increasing. The viscosity index for P-impregnated beech wood stabilises at concentrations at and above 0.50% P suggesting that higher concentrations of phosphorus would have little or no effect on the bio-oil stability. Phosphorus water content indices were stable for all concentrations of phosphorus.

Major differences were observed for bio-oil analysed by GC-MS between beech wood and potassium impregnated beech wood. Levoglucosan yields were dramatically reduced due to potassium promoting its decomposition, also the formation of acid compounds were suppressed therefore reducing bio-oil acidity. Differences were also observed for phosphorus impregnated beech wood which caused levoglucosan to be catalytically cracked to levoglucosenone; therefore the bio-oil consisted of lighter volatile compounds.

12 Conclusion

The main aims of this PhD research project were to investigate ash control methods to limit the inorganic content within biomass prior to fast pyrolysis and investigate the effect of specific ash components (particularly potassium and phosphorus) on fast pyrolysis processing, mass balance yields and bio-oil quality and stability. The main aim was divided into three subtasks which have been investigated and presented in this thesis. All measurable aims were achieved.

Two harvesting locations were used to obtain miscanthus, IBERS research fields in Aberystwyth and Woburn experimental farm in Woburn. The miscanthus obtained from Aberystwyth (refer to Section 3.1.1) was used to study the impact of senescence times on fast pyrolysis bio-oils and the miscanthus obtained from Woburn (refer to Section 3.1.3) was used for demineralisation experiments. Both miscanthus batches were harvested between February and March. Pre-treatment and thermal processing was completed within one month of harvesting to minimise natural decomposition. A comparison of mass balances for miscanthus harvested from the two locations is shown in Table 35. The mass balance yields for both miscanthus batches are very similar for all fast pyrolysis products. This shows that miscanthus harvested from different locations (within the same harvest period and processed within a month of harvesting) has little or no effect on mass balance yields. It was observed that the bio-oil organic and reaction water yields were within 1.02 wt. %, if there was any difference in miscanthus depending on location the biggest changes would occur in the bio-oil organic and reaction water yields. Conducted research showed that the growing location of miscanthus has little or no effect on fast pyrolysis mass balance yields when harvested within the same time period and processed within a month harvesting.

Table 35 Comparison of mass balances for miscanthus harvested in two different locations

	Aberystwyth	Woburn
	Untreated miscanthus	Untreated miscanthus
	Yield, (wt. % on dry feed basis)	
Char	**14.50**	**13.70**
Bio-oil	**63.30**	**64.05**
Phase	Single	Single
Organics	52.50	53.52
Reaction water	10.80	10.53
Gas	**12.80**	**12.23**
Mass balance closure	**90.60**	**90.08**

The investigated pre-treatment methods were applied to improve fast pyrolysis mass balance yields (increase bio-oil yield and decrease char and gas yields) and bio-oil stability in terms of viscosity and water content. When different sets of experiments were directly compared, a difference in both mass balance yields and bio-oil stability became apparent. A comparison of mass balance yields and bio-oil stability results for demineralised and surfactant demineralised miscanthus are summarised in Table 36 and Table 37. Each set of experiments used the same miscanthus batch and fast pyrolysis parameters the only difference was a nine month gap between each set of experiments being completed. The demineralised miscanthus set of experiments were performed prior to the surfactant demineralised miscanthus experiments. Over this nine month gap the miscanthus was stored in a dry environment but natural decomposition may have occurred which has changed the composition of the miscanthus (cellulose, hemicellulose and lignin content). Organic matter breakdown is a natural process that involves many physical, chemical and biological activities [185]. A negative exponential rate of breakdown occurs identifying that the organic matter loss rate declines over time [186], the initial loss is due to decomposition of sugar derived components leaving more resistant components (lignin). It was anticipated that some portions of hemicellulose and cellulose have decomposed over the nine month gap leaving the more resistant lignin component. This decrease in hemicellulose can account for the difference in mass balance yields between the two sets of experiments. By reducing the hemicellulose content of the miscanthus results in a reduced bio-oil organic yield (demineralised miscanthus - 53.52 wt. %, surfactant demineralised miscanthus - 43.03 wt. %), as the fast pyrolysis products from hemicellulose greatly contribute to the bio-oil organic fraction (refer to Section 2.5.4). Decreased hemicellulose content results in an increased lignin fraction therefore having a direct effect on char and gas yields (increased from 13.70 to 14.56 wt. % and 12.33 to 18.75 wt. % respectively) (refer to Section 2.5.5).

As the hemicellulose content has been decreased for the surfactant demineralised experiments the pre-treatments have a reduced effect on the mass balance yields when compared to untreated miscanthus. The factor of reduced hemicellulose and increased lignin content has a greater effect on fast pyrolysis product yields than feed stock alkali metal content, this is because there is a reduced yield of fast pyrolysis vapours in which alkali metals are able to catalytically crack.

Table 36 Comparison of demineralised miscanthus and surfactant demineralised mass balances

	Demineralised		Surfactant demineralised	
	Untreated miscanthus	0.10% Triton X-100	Untreated miscanthus	0.10% Triton X-100
Yield, (wt. % on dry feed basis)				
Char	**13.70**	**9.77**	**14.56**	**10.78**
Bio-oil	**64.05**	**76.21**	**56.86**	**57.34**
Phase	Single	Single	Single	Single
Organics	53.52	68.93	43.03	41.00
Reaction water	10.53	7.29	13.83	11.33
Gas	**12.33**	**8.25**	**18.75**	**17.58**
Mass balance closure	**90.08**	**94.24**	**90.17**	**85.70**

It was observed that natural decomposition of miscanthus may have little or no effect on the fast pyrolysis liquids stability index based on water content as shown in Table 37. The stability index based on viscosity should be used for comparisons of viscosity. Viscosity results cannot be directly compared as the results do not take into account the water content of the bio-oil, this is shown when comparing untreated miscanthus bio-oil viscosities for demineralised and surfactant demineralised experiments (12.10 cP - 24.35% water content and 110.75 cP - 18.22% water content respectively) identifying a large difference in viscosity with a small difference in water content. As the water content of a bio-oil increases the viscosity decreases.

The stability index based on viscosity for 0.10% Triton X-100 varies between the demineralised and surfactant demineralised miscanthus experiments. As mentioned the proportion of lignin may have been increased (due to hemicellulose decomposition) for the surfactant demineralised experiment resulting in an increased amount of large molecular oligomers [127], monomeric phenolic compounds and light compounds such as acetic acid [127, 128] being produced (refer to Section 2.5.5) which was measured by GC/MS of bio-oil samples. These compounds have a direct effect on bio-oil stability as discussed in Section 2.8.2. It also highlights that pre-treatment of naturally decomposing biomass has little or no effect on bio-oil stability based on viscosity index as shown by a small decrease, 2.69 (untreated miscanthus) to 2.57 (0.10% Triton X-100).

The age of feedstock (after harvest) has a direct link to whether pre-treatment is required or if the feedstock can be directly processed. Ideally the feedstock should be pre-treated and thermally processed as soon as possible after harvesting to minimise natural decomposition and achieve the highest yield and most stable bio-oil in terms of viscosity index.

Table 37 Comparison of demineralised miscanthus and surfactant demineralised bio-oil storage experiments

Analysis	Demineralised				Surfactant demineralised			
	Untreated miscanthus		0.10% Triton X-100		Untreated miscanthus		0.10% Triton X-100	
	0h	**24h**	**0h**	**24h**	**0h**	**24h**	**0h**	**24h**
Viscosity (cP)	12.10	38.15	65.65	94.21	110.75	298.46	684.51	1758.55
Stability index based on viscosity	3.15		1.44		2.69		2.57	
Water content increase (%)	24.35	32.70	29.02	30.63	16.22	21.67	5.17	5.55
Stability index based on water content	1.34		1.06		1.34		1.07	
pH	2.43	2.31	2.96	2.85	2.87	2.65	2.95	2.81

Viscosity, water content and pH measured after aging of bio-oil by heating at 80 ^{o}C for 24 hours

13 Recommendations

This chapter provides recommendations for further research on the topic of 'Ash control methods to limit biomass inorganic content and its effect on fast pyrolysis bio-oil stability'.

For further fast pyrolysis processing a more suitable quenching medium may be required due to partial dissolution of some pyrolysis products into the current quench medium (Isopar), resulting in a loss in fast pyrolysis liquid (see Section 7.2.5). Isopar was also found to not fully separate from bio-oil after being left in a separation funnel for 24 hours, therefore bio-oil samples had to be centrifuged prior to all analysis.

As it has been identified that the harvest window for miscanthus can be extended whilst maintaining bio-oil quality and yield (see Chapter 8), it should be studied if a sustainable crop can be produced using the extended harvest window over a number of harvests. This should be performed on a single field growing miscanthus over a number of years using the extended harvest window. Miscanthus samples can then be compared for each harvest to see if the crop has the same characteristics and yields for each year. This will identify if any fertilisers, in particular nitrogen fertiliser, are required to maintain a sustainable crop whilst using the extended harvest window.

This research project only looked at one type of surfactant (Triton X-100) for pre-treatment of miscanthus. Further research into other surfactants could identify a surfactant that could lower the inorganic content further or by the same extent using a lower concentration compared to Triton X-100. Other surfactants could increase the permeability of the biomass compared to Triton X-100 therefore improving the surfactant wash (lowering the inorganic content). Surfactants for future research should be evaluated on type (non-ionic, anionic or cationic), cost and disposal options. Ideally the surfactant should be bio-degradable.

As miscanthus was washed with Triton X-100 concentrations of 1.00% and below an increased concentration of 2.00% should be used to confirm that concentrations over 1.00% have little or no further effect on mass balance yields and bio-oil quality and stability.

GC-MS should be performed on all bio-oil samples produced from miscanthus washed with varying Triton X-100 concentrations so that results can be compared to Py-GC-MS results. This would identify if the composition of bio-oil changed with increased concentrations. It was highlighted by Py-GC-MS analysis that 1.00% Triton X-100 could possibly promote removal and/or partial

decomposition of hemicellulose which could be confirmed if the composition of 1.00% Triton X-100 washed miscanthus bio-oil contained lower yields of hemicellulose decomposition markers.

A techno-economic feasibility study should be performed based on the findings of this research project to establish the costs for miscanthus surfactant pre-treatment followed by fast pyrolysis processing. This would highlight if the increased operation cost due to surfactant pre-treatment is worthwhile to achieve increased yields and improved quality and stability of bio-oil.

Further impregnation work should be studied so that the effect of other elements, mainly sodium as it is an alkali metal, can be determined in terms of fast pyrolysis processing, mass balance yields and bio-oil quality and stability.

The outcome of this research project in combination with the above recommendations should provide enough information for a complete evaluation of specific ash control methods to limit the inorganic content within biomass prior to fast pyrolysis, as well as the effect of specific ash components on fast pyrolysis processing, mass balance yields and bio-oil quality and stability.

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Appendix 1: Influence of particle size on ash content

As varying particle size fractions were to be used for pre-treatments and analysis techniques (refer to Section 3.2) the influence of particle size on ash content was studied. By measuring ash content for different particle size ranges can help to identify an ideal particle size for pre-treatment and fast pyrolysis processing (limit ash content of feedstock).

Materials

Four different biomass samples were studied: Miscanthus, switch grass, rape straw and wheat straw. All samples were obtained from Rothamsted Research (Harpenden, Hertfordshire, UK). Miscanthus was an early year cut and taken before bailing, rape straw was harvested early 2008, wheat straw was harvested early 2008 then stored outside in a commercial stock and collected June 2009, and switch grass was harvested early 2008. Early harvest refers to between February and March. The samples were ground and sieved (refer to Section 3.2).

The ground biomass was sieved into four particle size ranges; < 0.075 mm, 0.15-0.25 mm, 0.50-1.00 mm, and 1.00-2.00 mm. The fractions water content or total solid content was then calculated using a modified E 1756 ASTM method for the determination of total solids in biomass. Biomass samples were dried at 60 ^{o}C instead of 105 ^{o}C to ensure that only water was removed from the biomass and no light volatiles. The ash content was calculated on a moisture free basis so after the total solid content was calculated samples were stored in sealed containers (pre-dried at 105 ^{o}C for 24 hours) to keep samples dry. Ash content was calculated using E 1755 ASTM method.

Results and discussion

The total solid and ash content for different particle fraction sizes for four biomass types is shown in Table 38. For all four biomass samples moisture content slightly increases as particle size decreases, this could be due to an increased surface area. Ash content increases as particle size decreases. A simple explanation for increased ash content can be due to dust particles. Dust particles are very fine, and when sieved with biomass will end up in smaller fraction sizes therefore increasing ash content. Dust is picked up by biomass when it is stored before transport or through soil contamination when harvested and baled (refer to Section 2.2). To improve this experiment the biomass could be dip washed before milling to try and remove any dust build up on the surface so when the ash content is calculated it only takes into account the ash within the biomass. A dip wash is a simple procedure that removes surface dust by submersing biomass in water for a few seconds.

Table 38 Total solid and ash content for different particle fraction sizes for miscanthus, switch grass, rape straw and wheat straw

Size fraction (mm)	Total solid content (% T_{60})	Ash content (% ash)
Miscanthus		
< 0.075	94.5	5.2
0.15-0.25	93.9	3.6
0.50-1.00	91.0	2.8
1.00-2.00	89.9	2.7
Switch grass		
< 0.075	94.2	17.6
0.15-0.25	92.3	13.7
0.50-1.00	90.8	6.9
1.00-2.00	90.4	4.2
Rape straw		
< 0.075	92.0	10.0
0.15-0.25	90.8	4.9
0.50-1.00	89.2	4.8
1.00-2.00	88.7	4.8
Wheat straw		
< 0.075	92.7	16.2
0.15-0.25	92.3	7.4
0.50-1.00	90.8	7.0
1.00-2.00	90.1	5.8