THE PRE-TREATMENT AND PYROLYSIS OF BIOMASS FOR THE PRODUCTION OF LIQUIDS FOR FUELS AND SPECIALITY CHEMICALS

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SUMMARY

Fast pyrolysis of biomass is a significant technology for producing pyrolysis liquids [also known as bio-oil], which contain a number of chemicals. The pyrolysis liquid can be used as a fuel, can be produced solely as a source of chemicals or can have some of the chemicals extracted and the residue used as a fuel. There were two primary objectives of this work. The first was to determine the fast pyrolysis conditions required to maximise the pyrolysis liquid yield from a number of biomass feedstocks. The second objective was to selectively increase the yield of certain chemicals in the pyrolysis liquid by pre-treatment of the feedstock prior to pyrolysis.

For a particular biomass feedstock the pyrolysis liquid yield is affected by the reactor process parameters. It has been found that, providing the other process parameters are restricted to the values shown below, reactor temperature is the controlling parameter. The maximum pyrolysis liquid yield and the temperature at which it occurs has been found by a series of pyrolysis experiments over the temperature range 400-600°C.

- high heating rates >1000°C/s,
- pyrolysis vapour residence times <2 seconds,
- pyrolysis vapour temperatures >400 but <500°C,
- rapid quenching of the product vapours.

Pre-treatment techniques have been devised to modify the chemical composition and/or structure of the biomass in such a way as to influence the chemical composition of the pyrolysis liquid product. The pre-treatments were divided into two groups, those that remove material from the biomass and those which add material to the biomass. Component removal techniques have selectively increased the yield of levoglucosan from 2.45 to 18.58 mf wt.% [dry feedstock basis]. Additive techniques have selectively increased the yield of hydroxyacetaldehyde from 7.26 to 11.63 mf wt.% [dry feedstock basis].

Techno-economic assessment has been carried out on an integrated levoglucosan production process [incorporating pre-treatment, pyrolysis and chemical extraction stages] to assess which method of chemical production is the more cost effective. It has been found that it is better to pre-treat the biomass in order to increase the yield of specific chemicals in the pyrolysis liquid and hence improve subsequent chemicals extraction.

Future development of this work would be to investigate the pyrolysis conditions, which produce the best quality liquid for use as a fuel. However, in order to do this a measure of the pyrolysis liquid quality must be established. The measure of quality may be a function of viscosity or liquid chemical composition.

ACKNOWLEDGEMENTS

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1. INTRODUCTION

Fast pyrolysis of biomass at moderate temperatures [400-600°C] produces three products; pyrolysis liquid [also known as bio-oil], char and gas. The pyrolysis liquid can be combusted as an alternative to fuel oil. However, the pyrolysis liquid also contains a number of potentially valuable chemicals. There may be markets for these chemicals if they can be extracted from the pyrolysis liquids economically.

This project has two objectives. Firstly, to determine the pyrolysis process conditions, which result in the maximum production of pyrolysis liquid from a number of biomass feedstocks. Secondly, to develop feedstock pre-treatment processes, which result in a selective increase in the yield of certain chemicals in the fast pyrolysis liquid.

1.1 BACKGROUND

The introduction of the Common Agricultural Policy [CAP], more efficient farming and policies such as "set-aside" have encouraged alternative use of land normally used for food production. Factors such as increased levies on landfill have also made it necessary for companies to find alternative uses for their waste products and residues.

Growth of biomass for fast pyrolysis offers an alternative use for land normally used for the production of food. Fast pyrolysis may also be capable of utilising some residues/waste normally assigned to landfill. Biomass can cover a wide range of substances. Examples of biomass types are woods, forestry residues, energy crops, agricultural crops, agricultural residues, food processing residues and wastes.

Fast pyrolysis is defined as the thermal degradation and chemical reactions that occur when biomass is heated in the absence of an oxidising atmosphere. Providing the feedstock is suitable, fast pyrolysis at moderate temperatures [400-600°C] gives three products. The major product is a liquid in yields of up to 80mf wt.% on a dry feedstock basis, with char and gas making up the remainder. Pyrolysis liquid can be used as a fuel and has been successfully combusted in a dual fuel engine to produce electricity (1).

As well as being used as a fuel, pyrolysis liquids can contain hundreds of potentially valuable chemicals. However, only approximately 20 of these are present in concentrations high enough to make them suitable for extraction [i.e. 1mf wt.% on a dry feedstock basis is estimated to be the cut-off point]. The speciality chemicals levoglucosan and hydroxyacetaldehyde are generally present in the highest yields [concentrations of 2-10 mf wt.%]. Levoglucosan is an anhydrosugar with potential uses as a biodegradable polymer or plastic, high value speciality chemicals precursor or low calorie food filler (2, 3, 4, 5, 6, 7, 8, 9). Hydroxyacetaldehyde can be used as a food flavouring and colouring agent (10, 11) and a tanning agent. It is currently marketed as aqueous smoke flavouring (12). Bio-oil also contains some commodity chemicals such as acetic acid, methanol and ethanol.

1.2 OBJECTIVE

There are two primary objectives to this project. The first objective concentrates on the use of fast pyrolysis to produce liquids for use as a fuel. For a particular feedstock the pyrolysis process parameters determine the yield of pyrolysis products. Thus, the pyrolysis process parameters have been investigated in order to determine what conditions are required to maximise the pyrolysis liquid yield. This study has determined the maximum pyrolysis liquid yield and the pyrolysis reactor temperature, at which this yield occurs, for a number of previously untested biomass feedstocks.

Production of the maximum amount of pyrolysis liquid does not necessarily mean that the best quality fuel is obtained. It may be better to produce smaller amounts of better quality fuel. However, the assessment of the maximum liquid yields and corresponding pyrolysis reactor temperatures does provide a starting point for the assessment of the liquid quality. The assessment of liquid quality is possibly a topic for a PhD in its own right and therefore is a recommendation for further work.

The second objective of this work is to develop feedstock pre-treatment techniques, which selectively enhance the yield of certain chemicals in the fast pyrolysis liquid. Pre-treatments can be used to either remove components from the biomass or add chemicals into the biomass.

Pre-treatment of biomass by chemical component removal can selectively increase the concentration of specific chemicals in the pyrolysis liquid. However, the removal of some of the biomass will result in an overall reduction in pyrolysis liquid yield [since less biomass is pyrolysed]. It may be better to extract small amounts of a particular chemical from a large volume of pyrolysis liquid and hence avoid the cost of pre-treatment. Alternatively it may be more cost effective to pre-treat the biomass and extract the chemical from a smaller amount of pyrolysis liquid containing a higher concentration of chemical. The processes involved in pre-treating biomass have been extensively reviewed and a number have been selected and tested. The findings of the literature review and the results of experiments are reported in the following chapters.

The addition of certain chemicals into the biomass is known to increase the yield of specific chemicals in the pyrolysis liquid. The chemicals which have been used to influence the fast pyrolysis reaction have been extensively reviewed and a number of promising chemicals have been selected and tested. The results are reported later in the thesis.

1.3 STRUCTURE OF THE THESIS

The thesis is arranged into the following chapters:

Chapter 2, Biomass Composition

This Chapter illustrates the two key areas which influence the pre-treatment and fast pyrolysis of biomass. The first area is the structural arrangement of the biomass. The second area is the chemical content of the components, which make up biomass.

The structure of biomass has a profound effect on how easy or hard it is to break apart, both chemically and physically. It is also important to know where the individual biomass components are held in the structure in order to determine the type of pre-treatment required to remove them.

For the production of chemicals from fast pyrolysis of biomass it is important to know the chemical composition of a particular biomass type. The chemical components contained in biomass are known to degrade to certain chemicals during fast pyrolysis. Thus if the chemical components are known, it may be possible to predict the yield of chemicals from fast pyrolysis of that biomass type.

Chapter 3, Fast Pyrolysis

Fast pyrolysis uses moderate temperatures [400-600°C] to break down biomass into liquid, char and gas. The yields of these products are controlled by process and feedstock parameters. This Chapter describes the fast pyrolysis process and investigates the parameters, which control it. The parameters which have the greatest influence are reviewed in more detail. This Chapter forms the basis for the experimental work described in Chapter 6, 7 and 8.

Chapter 4, Pre-treatment

This chapter reviews past and current work in the area of biomass pre-treatment. Pre-treatment is defined as a chemical process carried out prior to pyrolysis, which either modifies the biomass lignocellulose polymers or adds substances, for example catalysts, into the lignocellulose complex.

This chapter deals specifically with the removal of parts of components or complete biomass components from the feedstock material. The purpose of this is to modify the pyrolysis reaction and hence increase the yield of some specific chemicals.

Chapter 5, Additives

This chapter reviews the effect of biomass additives on pyrolysis products with particular reference to selectively increasing the yields of specific chemicals in the fast pyrolysis liquid.

Much of the literature involving the addition of substances to biomass investigates the effects by thermogravimetric [TGA] studies involving slow heating rates. Only a few of the literature sources investigate the effects of additives on the yields of chemicals in the pyrolysis liquid; hence these will be the primary focus.

Chapter 6, Experimental Programme

One of the objectives of the project was to evaluate and compare different feedstocks. The feedstocks, which have been tested are described and characterised in this Chapter. The received condition of the feedstock and any preparation methods used prior to pre-treatment or pyrolysis are also described.

The pyrolysis experiments used to evaluate the feedstocks were carried out in a 150g/h reactor system. The equipment is described and procedures for operating the pyrolysis system, analytical equipment and obtaining mass balances are described. A critical assessment of the mass balance and analytical procedures is included.

Chapter 7, Pyrolysis of Untreated Feedstocks

A number of previously untested feedstocks have been fast pyrolysed over a range of temperatures [450-600°C]. In all cases the maximum yield of organics has been determined along with the temperature at which this maximum occurs. The results are compared, where possible, to work by other institutes carried out on similar feedstocks at similar conditions. In all cases chemical analysis of one or more of the pyrolysis liquid samples from each feedstock has been carried out. The results are presented and critically compared.

Chapter 8, Pre-treatment Experiments

Pre-treatment methods were investigated in Chapters 4 and 5. From this the most promising areas of pre-treatment for the production of selected chemicals from fast pyrolysis have been selected.

This chapter describes the pre-treatment experiments which were used, along with experimental results, which attempt to assess how effective each pre-treatment was.

Chapter 9, Pyrolysis of Pre-treated Feedstocks

Fast pyrolysis of pre-treated feedstocks has been carried out at 500°C using a 150g/h reactor. This temperature was found [in Chapter 7] to give the highest yield of organics for most feedstock types. The yields of pyrolysis products and chemicals are reported along with critical assessment and comparison with the results of similar experiments from other institutes. The following sections present the results from the pyrolysis experiments and also results from HPLC analysis of the pyrolysis liquids.

Chapter 10, Techno-Economic Assessment

This Chapter investigates and compares the total plant and operating costs for a number of integrated levoglucosan production systems. It compares the costs of five possible scenarios utilising biomass: no chemical pre-treatment, water washing, water pre-wash followed by acid washing, acid hydrolysis and purchasing commercially available cellulose.

The results and procedures from the experimental work reported earlier have been used to provide process schemes and operating data for all but the commercial cellulose scheme. The most economic method for producing levoglucosan from fast pyrolysis of biomass is determined along with levoglucosan production costs and return on investment. Sensitivity studies have been carried out to find out which factors have the largest influence.

Chapter 11, Conclusions

This chapter draws conclusions from previous chapters.

Chapter 12, Recommendations

This chapter gives recommendations for the continuing development of pre-treatment and pyrolysis for the production of fuels and speciality chemicals.

2. BIOMASS

This Chapter illustrates the two key areas, which influence the pre-treatment and fast pyrolysis of biomass. The first area is the structural arrangement of the biomass. The second area is the chemical content of the components which make up biomass.

The structure of biomass has a profound effect on how easy or hard it is to break apart, both chemically and physically. It is also important to know where the individual biomass components are held in the structure in order to determine the type of pre-treatment required to remove them.

For the production of chemicals from fast pyrolysis of biomass it is important to know the chemical composition of a particular biomass type. The chemical components contained in biomass are known to degrade to certain chemicals during fast pyrolysis. Thus, if the chemical components are known, it may be possible to predict the yield of chemicals from fast pyrolysis of that biomass type.

2.1 WOOD

Biomass refers to plant matter which is renewable in the short term. The biomass type, which has been studied most is wood. The general chemistry and structure of wood is similar to that of other biomass types; therefore this chapter will deal mostly with wood. However, it is acknowledged that there are differences between different biomass types. The biomass types used in this work are discussed in Chapter 6.

Wood is made up of cells, which are laid down successively on the outside of the stem as the tree grows. On the outside of the tree is a layer of bark. Bark can be further subdivided into an outside layer of dead cells and an inner layer, which contains living cells. In between the bark and the wood is a layer of cambial cells; these subdivide during growth to form both wood and bark cells. The activity of the cambial zone is greater at certain times of the year [spring]; during this time springwood [earlywood] is laid down and as the season progresses summerwood [latewood] is laid down. Spring and summerwood have different chemical compositions and colourings and so are easily distinguishable, which accounts for the formation of growth rings (13). Although they are different, it is not physically possible to separate them [except for analysis on the scale of a few grams]. Thus the difference in chemical composition between spring and summer woods will be examined no further here.

Trees are classified into two groups, the angiosperms [hardwoods] and gymnosperms [softwoods]. Hardwood trees usually have broad leaves and are deciduous in the temperate zone. Softwood trees usually have needles, produce seed cones and are often coniferous or evergreen. The term hard or softwood does not relate to the physical hardness of the wood but to whether the wood has originated from an angiosperm or a gymnosperm.

A typical biomass feedstock could be forest refuse. This could contain a mixture of thinnings, branches, twigs and leaves and hence would contain a mixture of bark, spring and summer woods. Thus when dealing with biomass it is likely that the feed material may not be chemically consistent. Care should therefore be taken in selecting a biomass feedstock since biomass characteristics vary not only from species to species, but also from tree to tree and also regions within that tree. Thus unless a feedstock comes from a specified part of a biomass species the chemical composition will vary.

2.2 STRUCTURE OF BIOMASS

The purpose of this work is to influence the liquid yield and chemical composition from fast pyrolysis of biomass. This can be achieved, to a certain extent, by pre-treatment of the feedstock, which is described in Chapters 4, 5 and 8. When investigating pre-treatment methods where the aim is to remove certain components, the location and structure of these components within the biomass structure should be known. The location and chemical bonding of a component will determine how easy or hard it is to remove.

Wood [biomass] is made up of the major components; cellulose, hemicellulose and lignin and minor components; ash and extractives. These components are chemically and physically bound together in a cellular structure, which is shown in Figure 2.1 below (14). The chemical content of each of these components is discussed later in Sections 2.3.2 through to 2.3.6, respectively.

The cross section of the cell [Figure 2.1] could typically have a diameter of approximately 40µm, however, this would depend on the wood and cell type. The components and properties that make up the wood cell are summarised in Table 2.1.

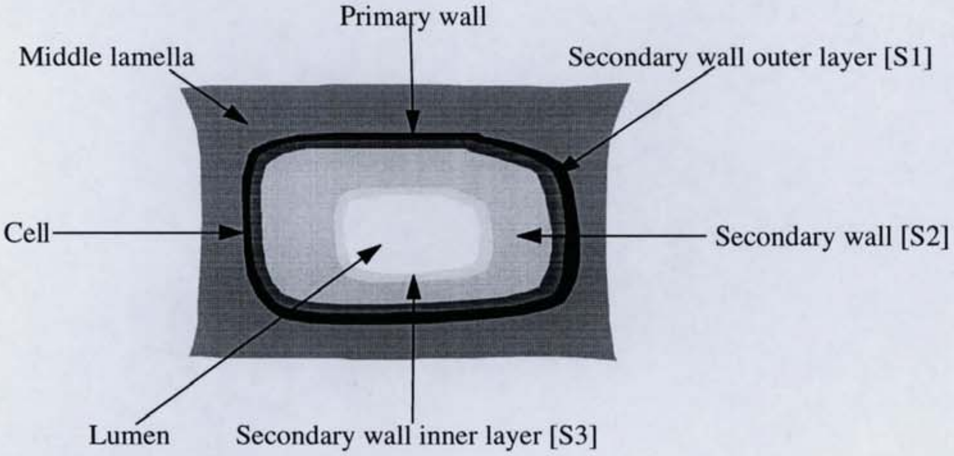


Figure 2.1: Simplified cross-section of a single wood cell and surrounding material

Table 2.1: Summary of cell components and properties

Cell Component	Composition	Properties
Middle lamella	mostly lignin	bonds the cells together
Primary wall	mostly lignin on outside, mostly cellulose on the inside	forms the surface of the cell
Secondary wall [S1] - transition lamella	mostly cellulose, some lignin	transient layer
Secondary wall [S2]	mostly cellulose, some hemicellulose	contains microfibrils giving strength to the cell
Secondary wall [S3] - tertiary lamella	cellulose, lignin and hemicellulose	hemicellulose contains xylans, which give chemical resistance to the cell
Lumen	water and minerals	contains the cells nutrients

From Figure 2.1, the middle lamella is not classified as part of the cell, but constitutes the intercellular bonding material between the individual cells; it contains a large proportion of lignin. Lignin is insoluble in a number of solvents [which is shown in Section 2.3.4] and therefore makes the separation of the individual cells inherently difficult.

During the production of a new cell the primary wall is laid down first. It has an intermediate composition, taking properties from the middle lamella [highly lignified] and the secondary wall [mostly cellulose]. The primary wall is on the outside of these fibres and therefore plays an important part in determining the surface properties, which are important for good quality paper. The pulp and paper making industry uses complex chemical treatment [Sulphite or Kraft processes (15, 16, 17)] to dissolve the lignin to leave long cellulose fibres.

The remainder of the cell is comprised of the lumen and the secondary wall. The lumen forms the interior passageway through which the sap runs. It makes up 25-50% of the cell volume. The sap carries nutrients and water around the plant. Thus sap contains minerals [which are classified in Section 2.3.6 as ash], which help the plant to grow. When biomass is dried these nutrients remain loosely held in the lumen.

The secondary wall consists mostly of cellulose and hemicellulose, but contains a small amount of lignin. It has three layers, the outer layer [S1] is termed the transition lamella and is more lignified than the middle layer [S2]. The middle layer can reach a thickness of 1-10 microns, contains 90% cellulose and has densely packed microfibrils organised in a parallel arrangement [i.e. in the z-plane, running into and out of the page]. The inner layer [S3] or tertiary lamella exhibits increased resistance to alkali, acid and to enzymatic degradation; this is caused by the presence of xylans in the hemicelluloses. The strength of the whole cell comes from the rigidity of the "cement-like" lignin and the densely packed fibre structure of the cellulose.

The pre-treatment methods, which will be described in Chapters 4 and 8, are largely concerned with the removal of the ash component. Ash is combined in the cell in three places. Primarily it exists as low levels of salts from the cytoplasm remaining in the lumen of the fibres [Figure 2.1 and Table 2.1]. Secondly ash comes from oxidation of the cell wall material [e.g. secondary wall S1-S3], which may produce acid groups holding inorganic ions. Finally, it may be contained with polyuronides, for example hemicellulose or pectate, which are sometimes present in biomass to fix inorganic counterions. The ash incorporated into the hollow lumen originates from the sap and is easily removed, since it is only loosely bound to the cell. The other ash is incorporated into the cell walls and therefore requires that reagents must actually penetrate the cell walls to remove the inorganic material. The primary wall and inner wall [S3] tend to contain high levels of lignin, which is resistant to a number of chemical reagents [as mentioned above]. This means that more concentrated reagents or more severe conditions [i.e. temperature and/or pressure] are required to penetrate through this lignin barrier. Therefore, some ash is easily removed from the cell [approximately 50%], while the remainder requires harsh treatment.

Since cellulose tends to be combined mainly into the secondary wall [S2] as long fibres, which often span through many cells, it is well protected by relatively insoluble lignin. This makes it inherently difficult to separate from the rest of the cell, again resulting in the use of stronger reagents or more severe conditions.

2.3 BIOMASS CHEMICAL COMPOSITION

In Chapter 3 the products obtained from the fast pyrolysis of the major biomass components will be reviewed. To a limited extent, this will illustrate how each biomass component when pyrolysed will result in the formation of a range of specific chemicals. Unfortunately, this is an over simplification, since when whole biomass is pyrolysed the separate components tend to interact. However knowing the composition of a biomass feedstock will help to predict its pyrolytic behaviour, pyrolysis product yields and chemicals. Thus the chemical composition of the cellulose, hemicellulose, lignin, extractives and ash components of biomass will be described in Sections 2.3.2 through 2.3.6.

2.3.1 Biomass Analysis

Figure 2.2 represents a guide to the composition of wood. The results of a recent round-robin analysis of wood test methods discovered that there were no uniform analytical methods for whole biomass for fuels, fibre, chemicals or other technical products (18). The documented method used to determine wood chemical composition is one of summative analysis [e.g. Wenzl (19), Puls (20), Farmer (21), Cote (22) and Milne (23)] in which the whole material is accounted for as the sum of the individual components [shown in bold in Figure 2.2]. There are a diverse number of tests, which can be used to analyse the biomass components. This is because there are many industries, which utilise biomass and thus require detailed analysis of their feedstocks [e.g. pulp and paper, wood, forage and food]. Each industry tends to have its primary focus on a particular region of the biomass; hence their method focuses primarily on that area.

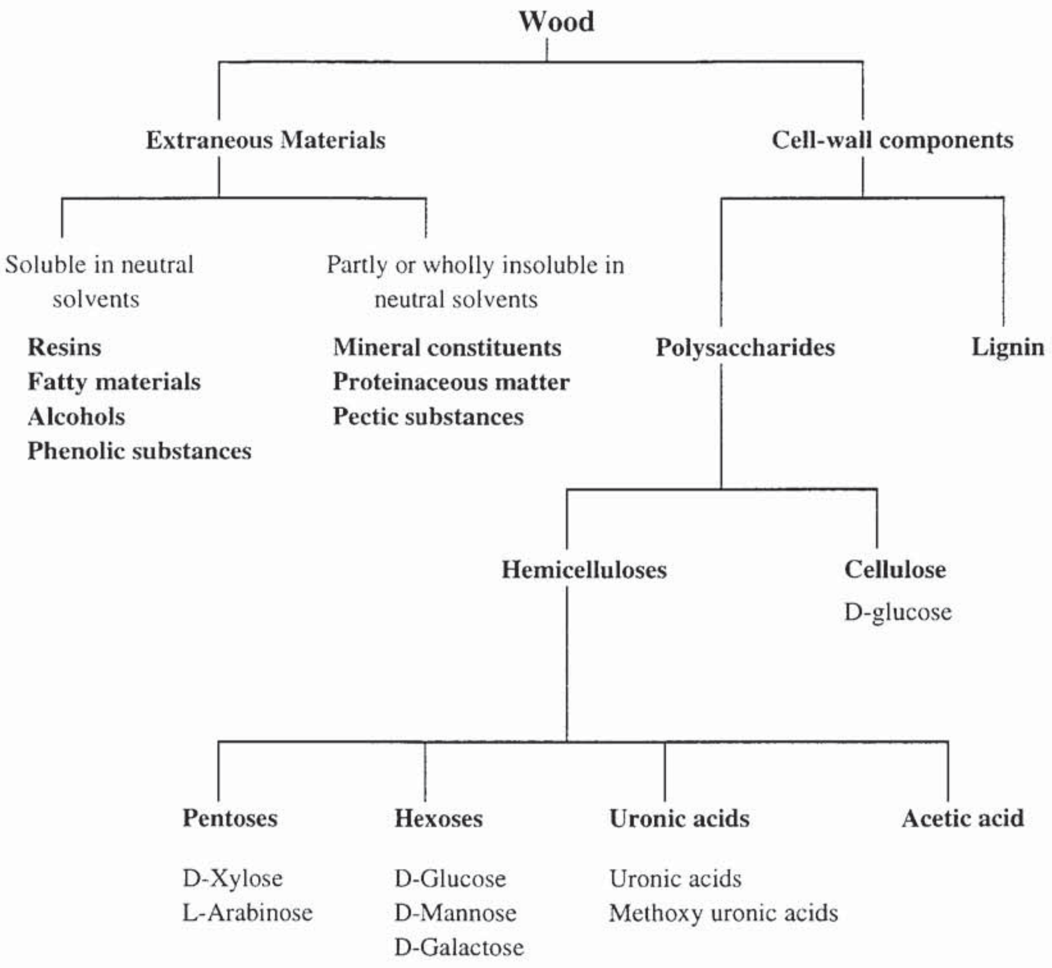


Figure 2.2: Composition of wood [biomass] (13)

The pulp and paper and wood industries use the TAPPI [Technical Association of Pulp and Paper Industry] and ASTM [American Society of Materials and Testing] methods. These methods are accurate for wood, but generally unsuitable for forage and other herbaceous materials due to the method used to determine the lignin component. Lignin is determined as the acid insoluble residue after hydrolysis with sulphuric acid. The presence of acid insoluble ash [e.g. silica] and proteinaceous material in forage and herbaceous feedstocks results in high apparent lignin values. The non-homogeneous nature of forage material also requires that large samples have to be used for analysis. This can be a disadvantage since often analysis equipment is designed for very small sample sizes [i.e. less than 1g].

In general, the summative analyses do not take into account the ash content of the wood since in most cases it is minimal [<0.5 mf wt.%]. The first step in any summative analysis is the removal of the extractives by suitable solvents. Some methods use organic solvents, for example extraction with 1:2 mix of ethyl alcohol and benzene followed by extraction with alcohol (24); others use aqueous or neutral solvents, e.g. detergent method (25). From the extractives free wood the lignin can be removed by a process called delignification. This can be carried out in a number of ways but the chlorite process is usually used (23). Following this, the remaining polysaccharides are classified as holocellulose [i.e. cellulose and hemicellulose combined]. Alkali treatment of the holocellulose dissolves the hemicelluloses and leaves α-cellulose.

The most widely used method of determination for forage characterisation is the detergent method (25). This method should be used primarily for analysis and comparison of individual species. Different species tend to behave differently in the detergent and so it is difficult to compare analyses between species. A neutral detergent is first applied to the sample to remove the extractives. An acid detergent is then used to determine the hemicellulose. The lignin component is then removed from the residue of the acid detergent by potassium permanganate degradation and the remainder is classified as cellulose. This method tends to overestimate the hemicellulose and cellulose components since both detergent washes tend to leave protein in the fibre.

From the above descriptions, it is evident that there is a degree of inaccuracy in all the biomass analysis methods. Accuracys of between ±1 to 10% have been found for most methods. The Uppsala method for biomass analysis has been developed using modern analytical chemistry techniques (26). The biomass is first hydrolysed using sulphuric acid, the hydrolysate is then passed into a gas liquid chromatography to analyse the individual sugar components. This method has been found to be accurate for both woody and herbaceous biomass but tends to have the same inaccuracies as TAPPI and ASTM methods for lignin determination.

It should be noted that all of the above methods bring about a chemical change in the wood. For example, the lignin isolated by delignification of the extractive free wood is chemically modified to that of the protolignin, or lignin that exists in the original wood; similarly the properties of native cellulose [or cellulose existing in the biomass] are different to those of extracted cellulose. Typically these changes result in shortened polymer chain lengths or changes to functional groups.

Some typical biomass compositions are given in Table 2.2 (27), in which all of the categories except ash correspond to Figure 2.2 above. As mentioned above, ash is not generally included in summative methods due to its low concentration. Ash is categorised as material remaining after the sample has been placed in a muffle furnace at 750°C for 6 hours. Water solubility is a measure of water soluble extractives [e.g. tannins, gums, sugars and colouring matter] and some ash. Alcohol/benzene solubility is also a measure of extractives [e.g. waxes, fats, resins, non-volatile hydrocarbons, low molecular weight carbohydrates and salts]. The lignin, hemicellulose and cellulose components will be described more fully in the following Sections.

Table 2.2: Analysis of typical biomass feedstocks (27)

Biomass All values are mf wt.%	Ash	Water soluble	Alcohol/ benzene soluble	Lignin	Hemicellulose	Cellulose
Sorghum bagasse	1.6	--	0.3	20.2	38.5	38.1
Beech wood	0.5	1.3	0.9	23.2	26.8	40.1
Hardwood	0.3	--	3.1	19.5	35.0	39.0
Softwood	0.4	--	2.0	27.8	24.0	41.0
Rice straw	16.1	13.3	11.9	4.6	24.5	30.2
Wheat straw	6.6	7.4	3.7	16.7	28.2	39.9

2.3.2 Cellulose

Cellulose forms the main component of the cell wall and comprises approximately 40% of dry wood [Table 2.2 (28)]. The elemental formula for cellulose is $(C_6H_{10}O_5)_n$. Chemical and physical analysis (28) indicate that cellulose consists of long chain molecules, as shown in Figure 2.3. This chain is composed of repeating units of two ß-D-glucopyranose, connected by a 1,4-glucosidic link between C1 and C4. The degree of polymerisation [i.e. the number of glucopyranose units in the cellulose polymer] can vary between 700 and 2000 units. The functional groups in the cellulose molecule have an appreciable effect on its chemical and physical properties, the principal functional group being the hydroxyl group [Figure 2.3].

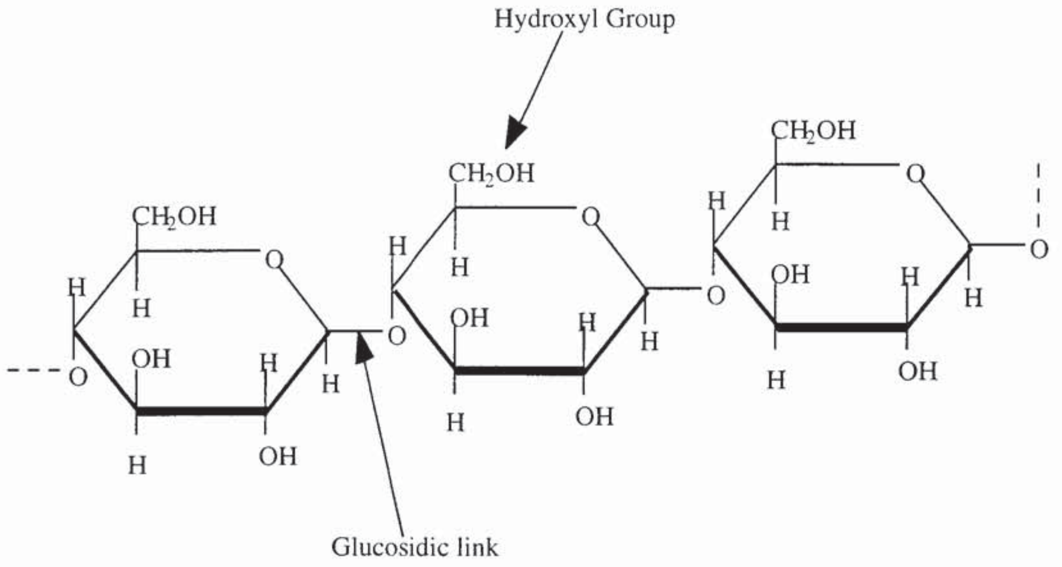


Figure 2.3: Cellulose polymer structure

To solubilise cellulose for analysis or prior to fermentation to alcohol, it is necessary to hydrolyse the glucosidic bonds. Cellulose is not soluble in water, due to its regularity and large number of hydrogen bonds (22). However, it is soluble in compounds that will form a complex with it, for example cadmium ethylenediamine complex [commercially known as cadoxen]. Glucosidic bonds can also be broken by aqueous alkalis at ambient temperatures and in the presence of oxygen. At higher temperatures oxygen is not required and alkali alone can attack the glucosidic bonds. Cellulose is hydrolysed in strong acids, for example 72% sulphuric, 41% hydrochloric or 85% phosphoric acid can be used to form soluble complexes (29). Further hydrolysis will yield the monomer D-glucose; however with concentrated acids some reversion will take place resulting in the production of oligosaccharides. Hydrolysis by concentrated acids is usually carried out at low temperatures to keep the degradation of sugars to humic substances to a minimum. The decomposition reaction rate increases rapidly with temperature (29).

2.3.3 Hemicellulose

All non-cellulosic polysaccharides and related substances are classified as hemicellulose (30). Hemicellulose is much less chemically specific than cellulose and, therefore, will result in more diverse and less predictable chemical yields during pyrolysis. Unlike cellulose, which has a linear chain, hemicellulose has a more branched structure with a degree of polymerisation of about 200; it does not pack together in regular bundles, like cellulose; and therefore does not possess marked fibre forming properties. It is comprised of a mixture of polyuronides, which can be characterised further as pentosans [5 carbons per ring, e.g. xylan and arabinan] and hexosans [6 carbons per ring, e.g. mannan and galactan] (31). In coniferous [soft] woods mannan, is the prevalent polymer [Figure 2.4] and xylan the prevalent polymer in deciduous [hard] woods [Figure 2.5] (14). Hemicellulose constitutes 20-35% of the weight of most woods. Hemicellulose is mostly soluble in hot water, alkali, and is readily hydrolysed by acids to simple sugars and / or sugar acids.

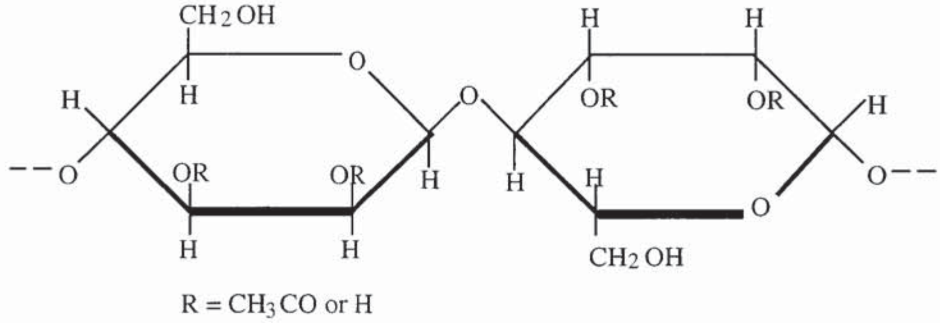


Figure 2.4: Mannan hemicellulose structure

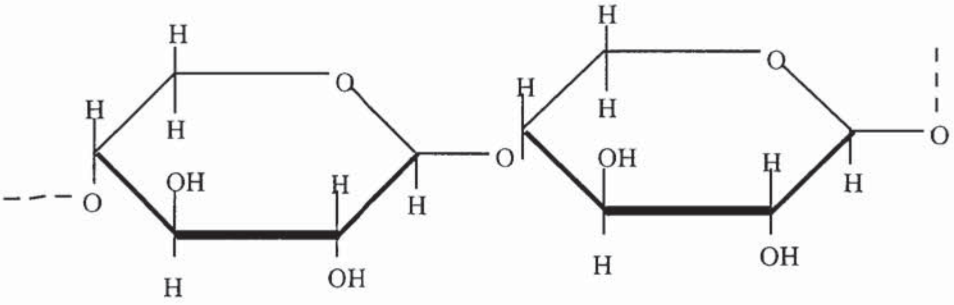


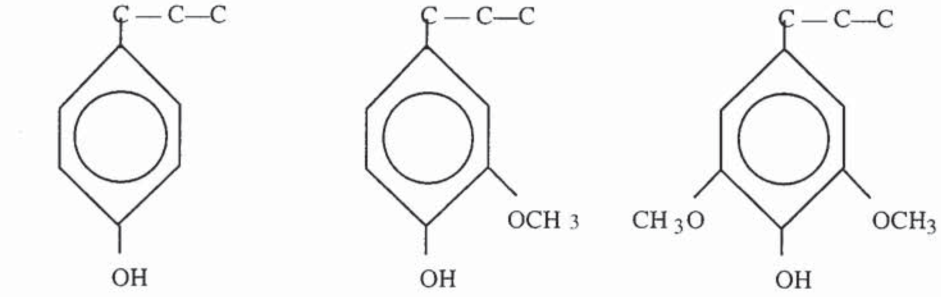
Figure 2.5: Xylan hemicellulose structure

2.3.4 Lignin

Lignin is a three-dimensional polymer of phenylpropane units, which can be hydroxyl, guaiacyl or syringyl. Gymnosperms [coniferous or soft] wood lignins are comprised exclusively of guaiacyl-propyl units, whereas angiosperms [deciduous or hard] wood lignins contain both guaiacyl- and syringyl-propyl units. Gramineae [grasses] and some angiosperm have the p-hydroxyphenyl unit as a major constituent, [see Figure 2.6] (32).

Lignin appears as an amorphous substance, cementing the cellulose together [described earlier in Section 2.2]. It can be isolated by 3 methods:

1. Isolation by extraction - using a neutral solvent [usually organic, e.g. ethanol] that does not react with the lignin, a small fraction of some lignin can be removed. After purification this fraction is called native lignin. The amount of lignin removed can be increased by ball milling or microbial attack on the wood.
2. Isolation as a residue - the polysaccharides are dissolved [usually by acid hydrolysis], thus leaving the majority of the lignin components as the residue. The remaining lignin is changed and no longer exhibits many of the chemical properties of the protolignin. Examples of lignin residues are Klason [sulphuric acid] and Willstatter [hydrochloric acid] lignin.
3. Isolation as derivatives - using a solvent that does react with lignin, the soluble products can be separated from the polysaccharides by chemical or physical behaviour.



p-Hydroxylphenylpropane Guaiacylpropane Syringylpropane

Figure 2.6: Lignin Monomers

2.3.5 Extractives

These are mostly located in the heartwood, and consist of terpenes, wood resins, polyphenols [e.g. flavanols, lignans and tannins], fatty acids and inorganic constituents (33). The extractives give to the wood properties, such as, colour, natural durability and resistance to fungal and insect attack. The nature and amount of extractives varies from one specie to another and they are present in only very small amounts, thus making characterisation difficult. The extractives can be removed from the wood matrix using organic solvents or hot water; however, this can also lead to the removal of some hemicelluloses and ash.

2.3.6 Ash

The inorganic content of plant fibres is known as ash (34). The ash content of wood is usually between 0.2-2.0% [e.g. pine 0.23%, poplar 0.46% and pine bark 1.94%]. The most common elements in ash are calcium, potassium and magnesium; and these are contained as carbonates, phosphates, silicates and sulphates (33). As discussed in Section 2.2, ash is located in the biomass in three places but primarily it exists as low levels of salts in the lumen of the fibres [Figure 2.1 and Table 2.1]. Secondly, ash comes from oxidation of the cell wall material [e.g. secondary wall S1-S3]. Finally, it is chemically bound to the hemicellulose in the secondary wall. The first type of ash mentioned above is removable by water washing, the second and third types of ash are chemically combined to the biomass and therefore can only be removed by rigorous acid washing or complete ion exchange.

The proportion of elements contained in the ash from a variety of biomass feedstocks is shown in Table 2.3 (35). The ash was determined by heating samples under oxidising conditions in a furnace at 575°C. The ash levels are higher in comparison to those quoted in Table 2.2, which is probably because they were produced at 575°C rather than at 750°C as recommended by British Standards (36).

Table 2.3: Ash composition of straws, waste residues and wood (35)

	Rice straw	Wheat straw	Switch grass	Sugar cane trash	Sugar cane bagasse	Douglas Fir wood
Ash [mf wt.%]	19.60	13.00	8.97	5.04	2.44	0.45
Cl [mf wt.%]	0.74	2.02	0.10	0.22	0.03	0.01
Oxide [% Ash]						
SiO_2	74.31	35.84	65.18	57.38	46.61	12.26
Al_2O_3	1.40	2.46	4.51		17.69	2.83
TiO_2	0.02	0.15	0.24		2.63	0.08
Fe_2O_3	0.73	0.97	2.03	1.74	14.14	4.24
CaO	1.61	4.66	5.60	13.05	4.47	37.08
MgO	1.89	2.51	3.00	4.30	3.33	5.86
Na_2O	1.85	10.50	0.58	0.27	0.79	3.16
K_2O	11.30	18.40	11.60	13.39	4.15	17.00
SO_3	0.84	5.46	0.44	7.31	2.08	11.20
P_2O_5	2.65	1.47	4.50	2.27	2.72	1.86
Undetermined	3.40	17.58	2.32	0.29	1.39	4.43

As far as pyrolysis is concerned, the ash component catalyses some reactions during pyrolysis, thus affecting the product yields. This phenomenon will be discussed in more detail in Chapter 3.

2.4 BIOMASS SELECTION

In Chapter 3 the pyrolysis products which are derived from certain biomass components will be discussed. From this it will become evident that the selection of a feedstock containing a high proportion of a particular biomass component, for example cellulose, will result in the production of a pyrolysis liquid containing mostly cellulose derived products. Thus by careful selection of a particular feedstock it should be possible to tailor the pyrolysis process to produce certain chemical products.

The chemical composition of biomass can also be modified by pre-treatment. The removal of certain chemical groups within a component can have a profound effect on the yield of pyrolysis products from a given feedstock. The area of pre-treatment and additives is discussed in Chapters 4 and 5.

The chemical composition of biomass is known to change during growth. This has been illustrated to a limited extent by examining the growth pattern of a tree [Section 2.1], especially the production of spring and summer wood. It therefore may be possible to increase the concentration of certain components in the biomass by harvesting at a different time of year. Another possible method for producing a feedstock with high or low levels of a particular component may be genetic engineering. The variation of biomass chemical composition during the growing season and genetic engineering of biomass are beyond the scope of this thesis. However, it is possible that these methods could be employed in the future to produce better fast pyrolysis feedstocks for chemicals production.

2.5 BIOMASS SUMMARY

This thesis examines the pre-treatment and pyrolysis of biomass for the production of liquids for fuels and speciality chemicals. This chapter illustrates the way in which biomass is physically and chemically held together. This will have an influence on how easy or hard it is to break the biomass apart, both during pre-treatment [removal of components] and fast pyrolysis. The methods used to analyse biomass have also been discussed, which will make it easier to understand subsequent chapters which contain analyses of a range of biomass types.

The composition of biomass has been investigated by a number of workers and is discussed above. It is hoped that by understanding some of the underlying chemistry of wood it may help to simplify the chemistry of fast pyrolysis. The chemistry of fast pyrolysis is discussed in Chapter 3. Also, by knowing the chemical pre-cursors in the biomass it will give a better indication about which component the chemicals in the pyrolysis liquids have come from. Hence, better pre-treatment methods have been developed [Chapters 4, 5 and 8] to make the pyrolysis reaction more selective towards the production of specific chemicals.

3. FAST PYROLYSIS

Fast pyrolysis uses moderate temperatures [400-600°C] to break down biomass into liquid, char and gas. The yields of these products are controlled by process and feedstock parameters. This Chapter describes the fast pyrolysis process and investigates the parameters which control it. The parameters which have the greatest influence are reviewed in more detail. This Chapter forms the basis for the experimental work described in Chapter 6, 7 and 8.

3.1 INTRODUCTION

Fast pyrolysis is the thermal degradation of a substance in the absence of oxygen. It is an established method for producing a liquid product in yields of 40-70 wt.% and char and gas in yields of 10-30 wt.%, on a dry material fed basis.

Graham et al. reviewed the literature up to 1984 on flash and fast pyrolysis and made a distinction between the two based on heating rates, reactor temperatures and residence times (37). However, since 1984 the distinction between flash and fast pyrolysis is in name only, the two regimes are now interchangeable and are described by the following process parameters:

- reactor temperatures of 450-600°C,
- high heating rates >1000°C/s,
- pyrolysis vapour residence times <2 seconds,
- pyrolysis vapour temperatures >400 but <500°C,
- rapid quenching of the product vapours.

Fast pyrolysis can be carried out in a number of reactor types [e.g. bubbling and circulating fluidised bed, ablative and rotating cone]. It is not the intention to review reactors or operating methods here, since excellent reviews already exist (38, 39). However, most workers are in agreement that, providing the above criteria are met, fast pyrolysis can be carried out in any type of reactor.

The parameters, which affect the fast pyrolysis process can be divided into three categories:

- feedstock related parameters,
- operation of the pyrolysis reactor and associated equipment,
- liquid product recovery.

Each of these parameters is considered by most researchers to significantly affect the yields and composition of the pyrolysis products; however, some parameters affect the yields more than others. The following is a description of all the parameters which affect the product yields.

3.1.1 Feedstock Parameters

Feedstock parameters have been grouped into the following categories for ease of explanation:

- composition,
- pre-treatment,
- physical and thermal properties.

Composition

Biomass composition relates to two areas, the amount of each of the biomass chemical components [i.e. cellulose, hemicellulose and lignin] and the chemicals contained in those components for a particular biomass type or anatomical part. This has largely been addressed in Chapter 2, which discussed the chemicals contained in biomass and biomass components. Each biomass type [e.g. poplar, pine, straw etc.] will have different amounts of each of the biomass components, as will different parts of the plant [i.e. poplar bark will be different to poplar heartwood]. Each component will also differ from species to species [i.e. lignin from poplar will be different to that from pine]. Every biomass type when fast pyrolysed could produce different yields of liquids, char and gas and also different chemicals in the liquid. Since the fast pyrolysis of a range of biomass types is one of the objectives of this work, the effect of feedstock on product yields will be shown in Chapter 7.

Pre-treatment

Pre-treatment covers both the physical preparation of the biomass [i.e. drying, comminution, screening] and the chemical modification [i.e. removal of components or addition of substances]. Comminution and screening are methods used to reduce the particle size and change the particle shape. Both particle size and shape can have a significant effect on the yield of fast pyrolysis products; therefore, they will be addressed in Section 3.2.3. The moisture content of the feedstock has been found by a number of workers to affect the yield of pyrolysis products and the chemical yields in the liquids; this is reviewed in Section 3.2.4..

Ash and extractives also have a significant effect on the yield of fast pyrolysis products. It is possible to change the chemical composition of the biomass by pre-treatment. Pre-treatment can be carried out in two ways, firstly by removing components, such as ash, from the biomass and secondly by introducing other chemicals [e.g. catalysts] into the biomass. Both methods are known to have significant effects on the pyrolysis product yields as well as the chemicals contained in the pyrolysis liquids. Component removal will be reviewed and discussed in Chapter 4 and additives will be reviewed and discussed in Chapter 5.

Physical and thermal properties

Physical and thermal properties include specific heat capacity, thermal conductivity, thermal diffusivity, grain structure, permeability, density, particle size and shape. They have a diverse range of values depending on biomass type, which is illustrated in Table 3.1 below (40, 41, 42, 43).

Table 3.1: Typical properties of wood (40, 41, 42, 43)

Property	Typical	Literature Values	Units
Wood heat capacity	1500	1100-2800	[J/Kg K]
Density	500	340-1100	[kg/m^3]
Thermal diffusivity	8×10^{-8}	10^{-6}-10^{-8}	[m^2/s]
Thermal conductivity	0.1	0.1-0.3	[W/mK]
Permeability		0.005-5	[darcy]

The effects of physical and thermal parameters have been reviewed extensively by Peacocke in his design of a novel ablative reactor (44). He concluded that for a particular biomass feedstock most physical and thermal parameters are fixed. Physical and thermal properties are essential when designing a new reactor; however, in this work they are of little relevance since the reactor has already been designed, built and operated. They would be of use in predicting how novel feedstocks might behave in the reactor. However, for most novel feedstocks physical, thermal and chemical properties are generally unavailable.

Peacocke found that the most significant physical and thermal parameters affecting fast pyrolysis was thermal conductivity. Biomass has low thermal conductivity, which means that it takes time for heat to travel into the centre of a particle. Therefore the size and shape of the particle will have an effect on how well a particle will pyrolyse. This effect will be discussed in more detail in Section 3.2.3.

3.1.2 Reactor Parameters

The operating parameters of the reactor are largely controllable [much more so than feedstock parameters]. They are listed below:

- Reactor temperature,
- Gas/vapour product reactor residence time,
- Gas/vapour product temperature,
- Biomass heating rate,
- Pressure,
- Gaseous environment.

Reactor temperature

The temperature at which biomass is pyrolysed is difficult [if not impossible] to measure. The best approximation to the true temperature of pyrolysis will be the average reactor temperature. It is acknowledged that the biomass particle will take a period of time to heat up to reactor temperature, which will be a function of its size and shape.

Reactor temperature is the reactor parameter, which most affects the pyrolysis product yields and composition of the liquids. Due to the significant effect which reactor temperature has, this is reviewed and discussed in Section 3.2.1.

Residence time

The gas/vapour product residence time is the ratio of net empty reactor volume to total gas/vapour volumetric throughput [i.e. the sum of the carrier gas and product gas/vapour]. The longer the gas/vapours remain in the hot reactor the more opportunity they have to react or continue reacting. Thus in conjunction with gas/vapour product temperature, residence time is seen as having a significant effect on product yields.

Change in products due to residence time could be due to the influence of primary/secondary pyrolysis reactions. Primary/secondary reactions come under the group name of pyrolysis fundamentals and have received much attention over the past decade. For the most part the debate is whether biomass forms either a primary "active" liquid product, which volatilises to form pyrolysis vapours or vaporises to form pyrolysis vapours directly. A recent paper by Lede et al. suggests that the former occurs (45). Much of the evidence in the paper is from experimental observation and does strongly suggest the presence of an "active" liquid.

From the primary products the "active" liquid or primary vapours degrade by secondary reactions into secondary products. The secondary products typically have lower molecular weights. The implications of this are that the longer the product vapours remain in the hot reactor zone the more likely it is that secondary reactions will occur. Therefore, since gas/vapour product residence time influences the chemicals, which are produced from pyrolysis, gas/vapour residence time will be reviewed in more detail in Section 3.2.2.

Heating Rate

High biomass heating rate is recognised by many researchers as a key feature for minimisation of char formation (46, 47, 41, 48). Maniatis and Buekens showed that heating rate had little effect on the yield of products above 100K/s (49). Fast pyrolysis is often quoted with high heating rates. These rates of the order of 10^4-10^5 K/s, Scott et al. (64), $4.5*10^5$ K/s, Diebold (50) and $>1*10^6$ K/s, Lede (51), can only refer to the high temperature gradients at the thin reaction layer or for very small particles [<100μm]. A fluidised bed pyrolysis reactor similar to that used by Scott et al. was used by this author [described more fully in Chapter 6]. Since all experiments will be carried out at similar conditions to Scott and within the fast pyrolysis regime described in Section 3.1 heating rate will not be a significant parameter in changing pyrolysis product yields.

Pressure

Mok and Antal have reviewed the effects of high pressure on biomass fast pyrolysis (52). Their general conclusion was that increasing pressure increased char formation with a subsequent decrease in volatiles. This conclusion is widely supported by a number of other workers, although high pressure work often tends to be carried out in reactive atmospheres at higher temperatures than are normally used for fast pyrolysis (53, 54, 48, 55, 56). The effect of high temperature [i.e. higher than 600°C, the upper limit defined for fast pyrolysis] is to promote the formation of gas. Thus many of the high pressure experiments have resulted in increased char yields but with mostly gas as the remainder of the products.

Low pressure fast pyrolysis [i.e. under vacuum] has been reported to give increased yields of volatile products (57, 58, 59). This could be due to the low pressure removing the products from the reactor faster than would normally happen with a similar reactor at atmospheric pressure. Conversely fast pyrolysis by Scott et al. carried out in a fluidised bed at 21kPa absolute gave increased yields of gas and char at the expense of liquids relative to yields obtained at atmospheric pressure (60). Agrawal also demonstrated this effect, by pyrolysing newspaper at 340°C (61). Possible reasons for lower liquid yields at low pressure are lower heat transfer in the more dilute gas phase and also lower heating rates.

It would appear that maximum liquid yields are obtained by operating a fluidised bed at atmospheric pressure. Providing gas/vapour residence times are kept low [i.e. less than 2s] then there should not be a problem with vapours remaining in the hot reactor space for too long; also, the lower heating rates and added cost of vacuum operation is avoided. By operating at slightly above atmospheric pressure additional fire risk problems of air ingress into the reactor can also be avoided.

Gas environment

The gas environment is the gas/vapour phase in the reactor, which the pyrolysis products are released into after volatilisation/decomposition from the biomass. Steinberg studied the effects of biomass flash pyrolysis in hydrogen, nitrogen, argon, helium and methane atmospheres (53). Pyrolysis in hydrogen resulted in methane being the major product, whereas carbon monoxide was the major product with the other gases. However, these experiments were carried out at 600-1000°C, which is above the fast pyrolysis upper limit. Scott et al. using recycle gas in place of nitrogen found little difference in overall liquid yields and considered the effects of reactive gases to be minimal below 600°C (73). Evans and Milne (62) agreed with the findings of Scott (73) that primary pyrolysis is not significantly influenced by the reactor gaseous environment at temperatures less than 600°C. Thus over the fast pyrolysis conditions employed for this work [temperatures of 400-600°C] reactor atmosphere will have very little effect on product yields.

3.1.3 Product Recovery Parameters

Most workers use some system of rapid cooling of the vapours in order to collect the pyrolysis liquids. Graham specifies rapid cooling of the product vapours [<40ms] to preserve speciality chemicals (63). The rate of cooling will depend on the system employed, with direct cooling offering the best heat transfer characteristics, but possible problems in subsequently removing the coolant. Pyrolysis liquid can be used as a direct coolant and hence avoids all subsequent separation problems. Indirect heat exchange will give low temperature gradients and could fractionate the larger molecular weight components, which collect first. It is likely that the way in which the pyrolysis liquids are collected will have a large effect on the liquid quality, especially for fuel applications. However, it is not in the scope of this work to design or test new collection systems or the impact that they might have on the liquid quality, although this could be a topic for further work. The collection system used in this work is described in Chapter 6.

3.1.4 Parameters Summary

The main feedstock, reactor and product recovery parameters have been briefly discussed above. It has been found that only a number of them will have a significant effect on the pre-treatment and pyrolysis experiments carried out in this project. Therefore only the parameters, which have a significant effect on the scope of this work will be reviewed and discussed in more detail. These are:

Reactor process parameters

- Reactor temperature,
- Gas/vapour residence time,
- Particle size and shape,
- Moisture content.

Feedstock parameters

- Feedstock type,
- Feedstock chemical composition,
- Pre-treatment - component removal [Chapter 4],
- Pre-treatment - chemical addition [Chapter 5].

3.2 PROCESS PARAMETERS

The reactor process parameters have a significant effect on the yields of pyrolysis products. Unlike the feedstock parameters, which are essentially fixed, the selected reactor parameters are much simpler to change and control. Reactor temperature is shown to have the biggest influence on pyrolysis product yields and liquid chemical products. However, the effect of temperature requires that the gas/vapour residence time, particle size and shape and moisture content are within certain limits. Thus these parameters will also be reviewed.

3.2.1 Reactor Temperature

Reactor temperature is the only measurable variable giving an indication of the temperature at which pyrolysis is being carried out. It is seen by most fast pyrolysis workers to be the main controlling factor on product yields and also the yield of chemicals in the pyrolysis liquid.

Reactor temperature influences the enthalpy of pyrolysis, the kinetics of biomass decomposition and the temperature at which biomass decomposes. However, these factors have been reviewed extensively by Peacocke (44). They are only of relevance when designing a new reactor. Since the scope of this work is concerned with operating an existing reactor with new feedstocks [both untreated and pre-treated] they will have little bearing on the results obtained. Also the equipment used in this work is not sensitive enough to be able to measure or assess enthalpy of pyrolysis, pyrolysis kinetics or biomass decomposition temperatures.

3.2.1.1 Pyrolysis Product Yields

The influence of reactor temperature on the fast pyrolysis of various biomass types has been investigated by most researchers in fast pyrolysis and it is widely supported that the maximum organic liquid yield is obtained at 400-600°C, depending on feedstock type (64, 65, 66, 67). Fast pyrolysis product yields are illustrated in Figure 3.1 (68).

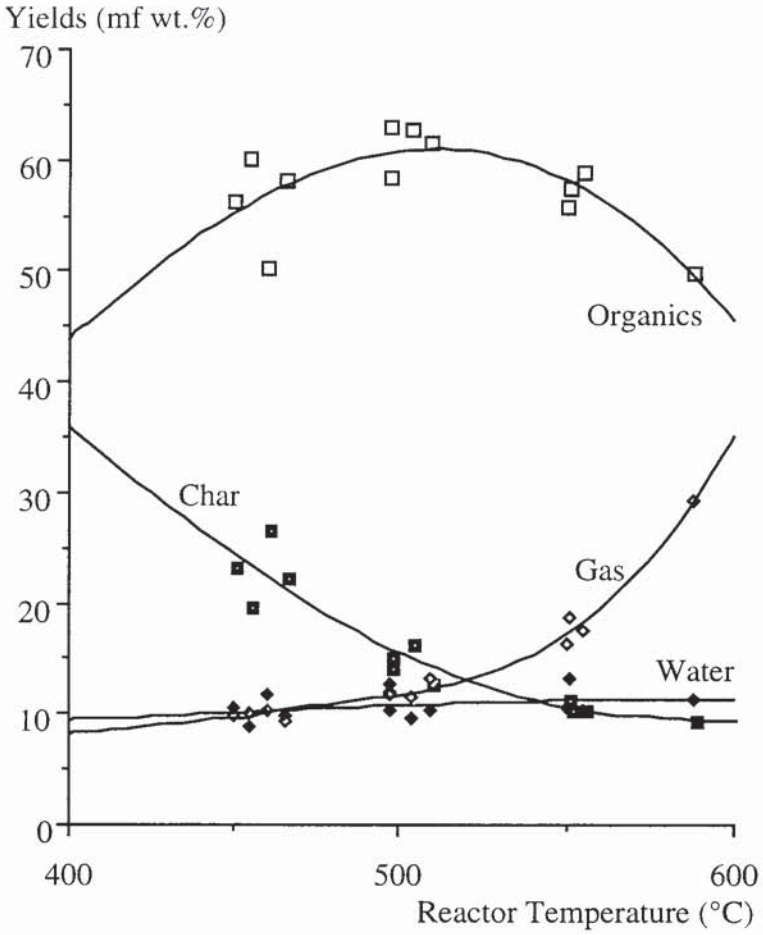


Figure 3.1: Fast pyrolysis product yields versus temperature (68)

Similar shaped curves are obtained from fast pyrolysis of any biomass type; however, the shape of the curve may change [i.e. flatter or more pronounced] and yields may be higher or lower depending on the biomass species. The temperature at which the maximum yield of organic liquids is produced can vary from 85 mf wt.% at 450°C for cellulose (64), to 85mf wt.% for sweet gum hardwood at 627°C (69). The char yield decreases as temperature increases, which is due to the slower reaction rates obtained at lower temperatures resulting in the formation of char. Gas and water yields remain relatively stable up to around 500°C. Above 500°C, gasification and secondary reactions tend to increase, which leads to increased cracking of the larger molecules resulting in the production of smaller molecules such as water and gas.

Toft analysed the product yields from a number of biomass feedstock types (70). He also confirmed that each biomass feedstock will have a maximum yield of organics [see Figure 3.2] and that the temperature at which this occurs depends on the feedstock type.

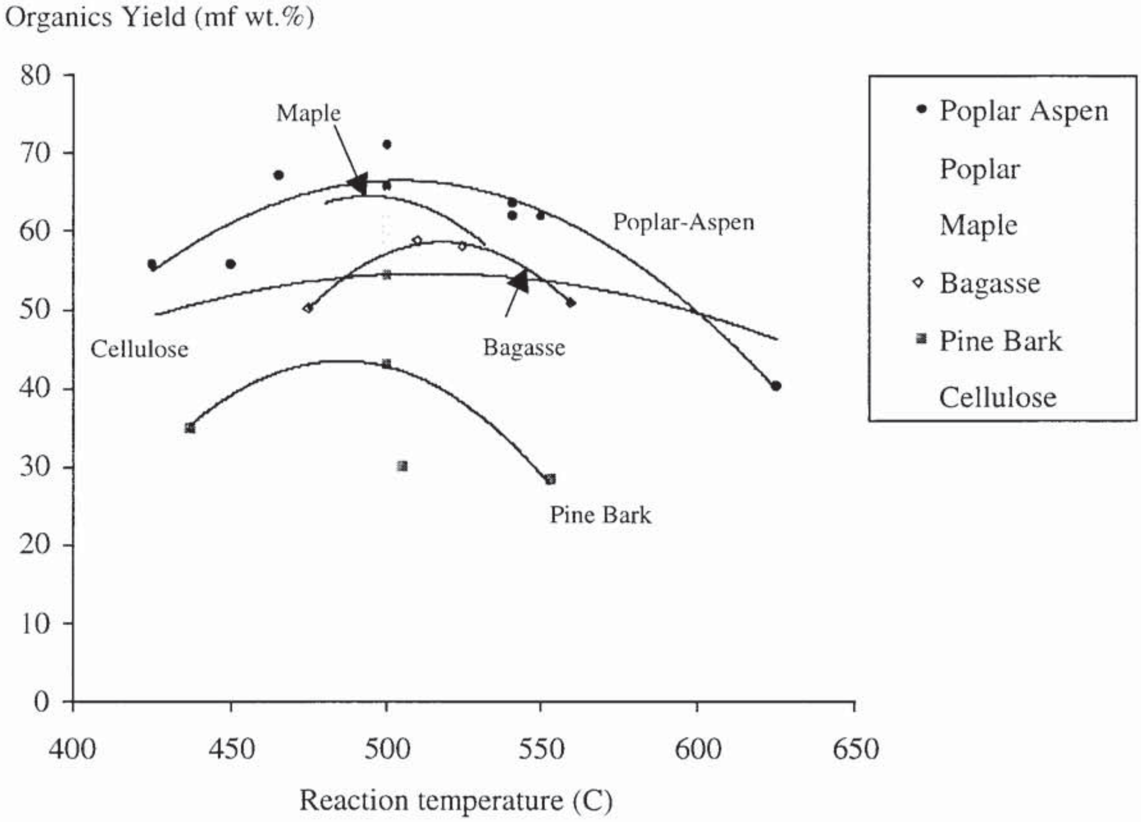


Figure 3.2: Variation of organics yield with feedstock type (70)

Toft modelled the pyrolysis products for a generic wood type, i.e. designed a model, which was applicable to any biomass type over any fast pyrolysis temperature. He compiled data for many feedstock types over the temperature range 400-650°C and derived relationships by regression analysis as shown in equations 3.01 to 3.04, which are plotted in Figure 3.3.

$$\text{Organics }\% = -16.4\times 10^{-6}(T)^2 + 0.0164(T) - 3.47 \quad (3.01)$$

$$\text{Gas }\% = 8.06\times 10^{-6}(T)^2 - 0.0071(T) + 1.64 \quad (3.02)$$

$$\text{Char }\% = 8.60\times 10^{-6}(T)^2 - 0.0099(T) + 2.95 \quad (3.03)$$

$$\text{Water }\% = 4.70\times 10^{-6}(T)^2 - 0.0049(T) + 1.20 \quad (3.04)$$

where T = Reactor temperature, °C

These equations adequately model any wood type; however, care should be taken in their use since some feedstocks may perform significantly worse [or better] than the equations and therefore could produce poorer [or better] results than expected. It would appear that there is a mistake in equation 3.04, since analysis gave negative yields of water. However, correspondence with Toft has found that the equation is correct for the data that he used. It should be noted that, in subsequent modelling work, Toft found that it is best to calculate the water by difference; this also has the advantage that 100% closure is always achieved. The water yields shown in Figure 3.3 are calculated by difference.

Toft differentiated the organics equation [3.01] to determine the temperature at which the maximum yield of organics occurred. He found the maximum yield of organics was 63.0 mf wt.% at 500°C.

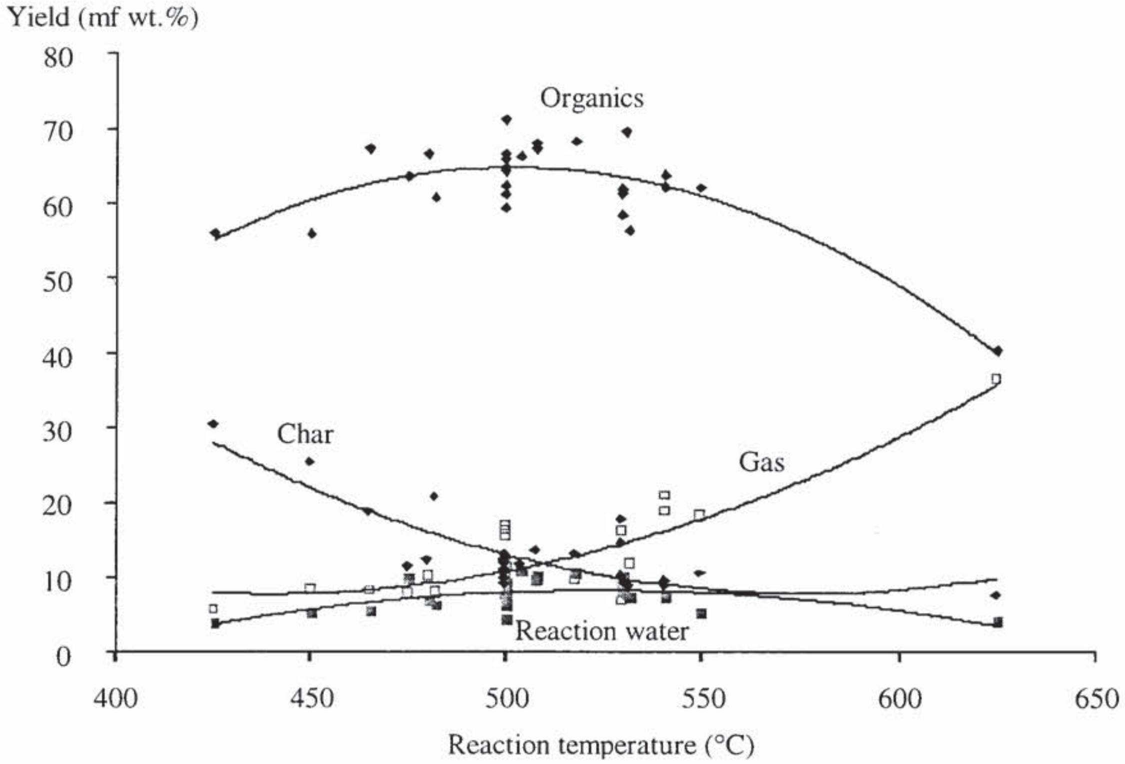


Figure 3.3: Fast pyrolysis yields from generic wood (70)

Scott et al. pyrolysed cellulose and eastern red maple using two different reactor configurations at two institutions to assess the influence of temperature on the yield of products (64). Good agreement was achieved between both reactor systems for both feedstocks. Their conclusions were that, if less than 10% of the particle weight was lost before the particle temperature reached 450°C, then the yields of char, oil and gases will be determined by the reactor temperature. Scott calculated, using kinetic and heat transfer modelling of Lidén (71) and kinetic data produced by Thurner and Mann (72), that for a 2mm diameter hardwood particle in a fluidised bed reactor the above criterion would be satisfied.

Thus for any reactor, providing the gas residence times [see Section 3.2.2] are the same, the product distribution will be a function of reactor temperature alone. For fluidised bed reactors, providing particles of less than 2mm are used, the pyrolysis temperature will determine the product yields. The final product distribution and composition will then depend on the history of the vapour phase and secondary vapour kinetics.

3.2.1.2 Liquid Chemical Composition

The chemicals, which are obtainable in reasonable yields [defined as >1 wt.%, wet oil basis] from fast pyrolysis of biomass, were compiled in a comprehensive review by Milne et al. (91). The review was compiled from literature published by ten laboratories investigating fast pyrolysis. It is complicated by the fact that each institute used its own feedstock type, fast pyrolysis system, collection system and method of analysis. However, 108 components are listed and of these 32 are reported by four or more laboratories. These are gathered into functional groups and are shown in Table 3.2.

Of the 54 fast pyrolysis experiments compiled by Milne only the following chemicals were obtained in yields higher than 3 wt.% [wet oil basis]; acetic and formic acids, levoglucosan, cellobiosan, ethanal, isoeugenol, pyrolytic lignin, glyoxal, hydroxyacetaldehyde and acetol. Most of these chemicals are derived from the cellulose component of the biomass [see Section 3.3.1]. Hemicellulose and lignin do form certain chemicals when pyrolysed [see Sections 3.3.2 and 3.3.3], but due to their chemical inconsistency they form many different chemicals in low yields [i.e. <1 wt.% wet oil basis]. Thus it is evident that the majority of chemicals present in high concentrations in the pyrolysis liquid come from the cellulose component. From this it follows that there are three possible options for potential chemical production research.

Firstly, since such a wide range of feedstocks have been pyrolysed over a wide range of conditions, it seems likely that the most common chemicals have been produced and analysed [i.e. the ten listed above in yields greater than 3 wt.% wet oil basis]. It may be possible to optimise the yields of one or more of these chemicals by feedstock selection or by utilising a previously untested feedstock. This is the aim of the experimental work described in Chapters 6 and 7.

Table 3.2: Most frequently detected chemicals contained in fast pyrolysis liquids (91)

Acids
Methanoic [Formic]
Ethanoic [Acetic]
Propionic [Propanoic]

Sugars
1,6-Anhydroglucofuranose
Levoglucosan [1,6-Anhydro-β-D-Glucopyranose]
α-D-Glucose [α-D-Glucopyranose]
Fructose
Cellobiosan

Alcohols
Methanol
Ethanol

Aldehydes
Methanal [Formaldehyde]
Ethanal [Acetaldehyde]

Phenols
2-Methyl Phenol o [o-cresol]
3-Methyl Phenol m [m-cresol]
4-Methyl Phenol p [p-cresol]
2,6-Dimethylphenol [2,6-Xylenol]

Guaiacols
Guaiacol [2-Methoxyphenol]
4-Methyl Guaiacol
4-Ethyl Guaiacol
Eugenol [Phenol, 2-Methoxy-4-(2-Propenyl)]
Isoeugenol [Phenol, 2-Methoxy-4-(1-Propenyl)]
4-Propylguaiacol
Pyrolytic lignin - water insoluble

Syringols
Syringol [2,6-Dimethoxyphenol]
Syringaldehyde

Furans
Furfural [2-furaldehyde]
5-Methylfurfural

Mixed oxygenates
Glyoxal [Ethanedial]
Hydroxyethanal [Hydroxyacetaldehyde; Glycolaldehyde]
1,2-Dihydroxyehane [Ethylene glycol]
1-Hydroxy-2-Propananone [Acetol]
4-Hydroxy-3Methoxybenzaldehyde [Vanillin]

Secondly, pre-treatment of biomass has been found to significantly increase the yield of some chemicals, especially levoglucosan by acid washing/hydrolysis. Pre-treatment [component removal] tends to remove components, hence moving biomass towards a pure cellulose composition. Therefore is it better to pre-treat biomass or start with cellulose ? This is the question that Chapter 4 investigates leading up to the experimental work described in Chapters 8 and 9 and the techno-economic assessment described in Chapter 10. The addition of substances to the biomass is also known to have an effect on the chemical composition of pyrolysis liquid. These substances may have a catalytic effect on the pyrolysis reaction or may shift it from one reaction [i.e. depolymerisation] to another [i.e. fragmentation]. This will be the focus of Chapter 5 and experimental work in Chapters 8 and 9.

Thirdly, it may be that one or more chemicals have been overlooked [unlikely] or that some potentially valuable chemicals are present in small amounts [i.e. <0.1 wt.% wet oil basis]. However, chemicals, which are present in such low concentrations may be difficult to extract and purify. Therefore the focus of this work will be on the known chemicals, which are present in concentrations of >1 wt.% [dry feedstock basis] or can be selectively increased by the use of pre-treatment.

3.2.2 Gas/Vapour Residence Time

Gas/vapour residence time is a measure of how long the pyrolysis vapours remain in the hot reactor environment. Although the yield of pyrolysis products is a function of reactor temperature, the history of the vapour phase will also influence the amount of secondary reactions which occur. Secondary reactions lead to the production of low molecular weight products and gas and should be avoided for the production of speciality chemicals [e.g. levoglucosan]. To avoid secondary reactions the pyrolysis vapours should be removed from the reactor environment as quickly as possible.

The effect of vapour residence time was shown conclusively by Scott and Piskorz (73), who studied the organic liquid yield from fast pyrolysis of poplar wood. The wood had a particle size of less than 595μm and was pyrolysed at 500°C. The results, shown in Figure 3.4, show that as vapour residence time increases the yield of organic liquids decreases. This corresponds to an increase in yields of gas and water, but this is not shown here.

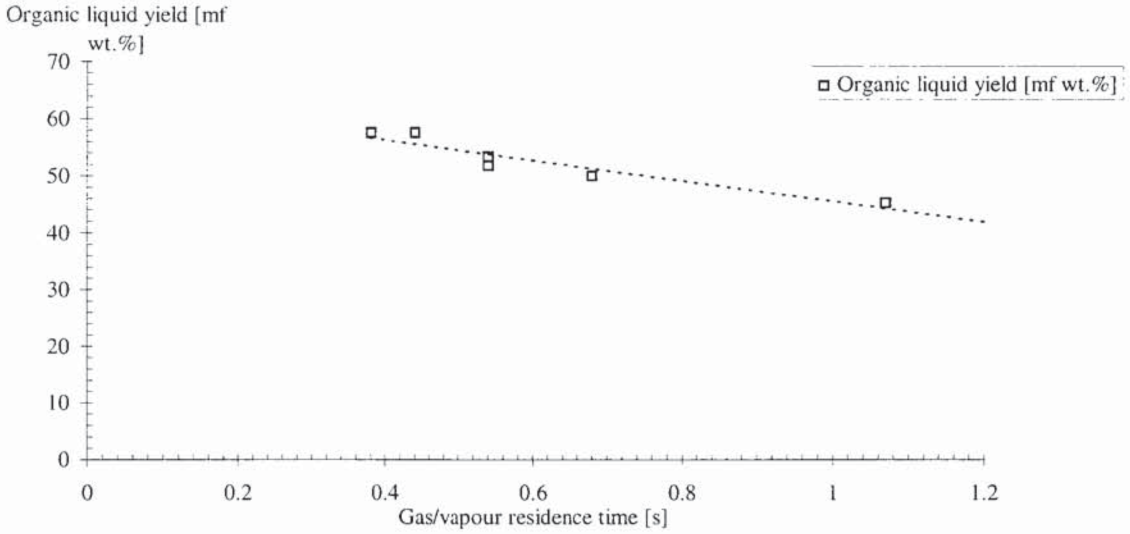


Figure 3.4: Organic liquid yield with gas/vapour residence time (73)

Peacocke investigated the effect of gas/vapour residence times from 1 to 10s on the yields of organics and water from ablatively pyrolysed pine wood (44). He found that as the gas/vapour residence time increased, the yields of water increased up to an asymptotic maximum of 24 mf wt.% after 10s [shown in Figure 3.5]. He also suggested that the yield of organics reached an asymptotic minimum of 47 mf wt.%. It may be that the high yields of water are due to the low gas vapour temperatures [280-420°C] present in his reactor, which may have initiated condensation reactions before the products left the reactor. Peacocke does suggest that in future work the temperature of the product gas/vapour should be increased by preheating the carrier gas and increasing the flowrate to reduce gas/vapour residence time and hence water yields.

Thus the residence time should be kept as low as possible to avoid lowering of organic liquid yield. Most fluidised bed reactors tend to operate on high gas throughputs to maintain fluidisation; this also helps to maintain low residence times. Thus it is unlikely that high gas/vapour residence times will be a problem in this work since all pyrolysis reactions are carried out using a fluidised bed reactor [see Chapter 6].

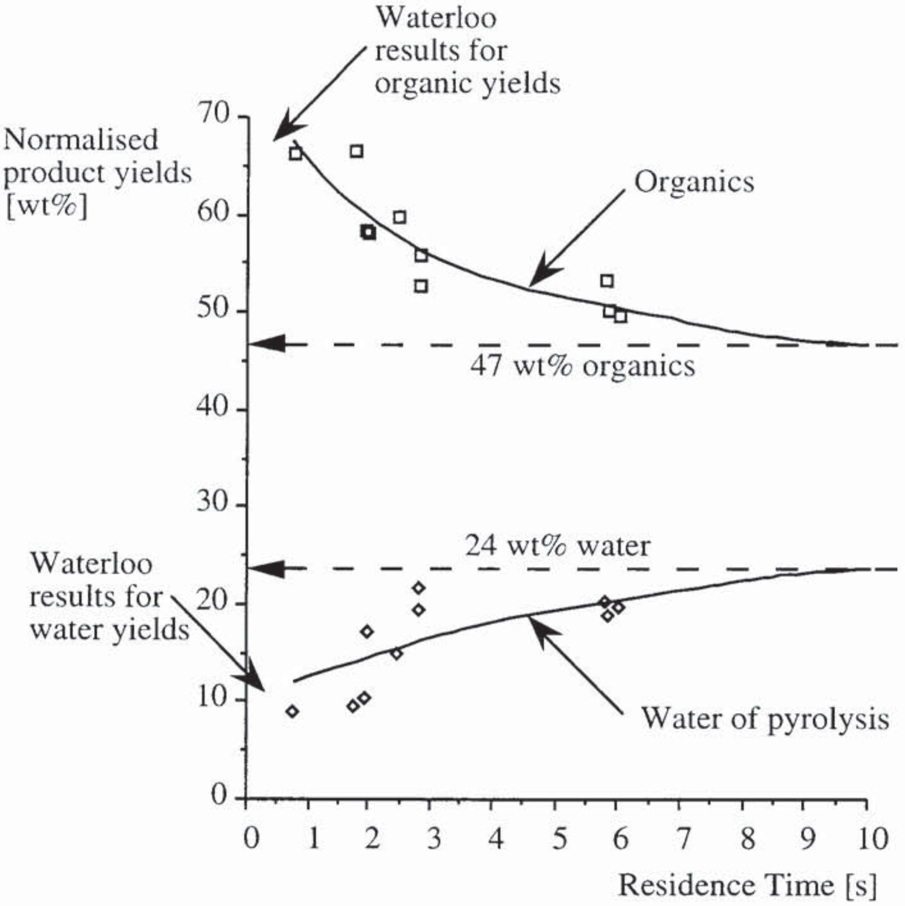


Figure 3.5: Yields of organics and water[mf wt.%] versus gas/vapour residence time [s] (44)

3.2.3 Particle Size and Shape

Although particle size and shape refer to the conditions of the biomass, grinding or milling before entering the pyrolysis reactor generally changes them. They are therefore discussed as part of process parameters.

Biomass has a low thermal conductivity [shown previously in Table 3.1]; thus as the particle size gets bigger the time it takes for the centre of the biomass particle to reach reaction temperature will increase. As a biomass particle is pyrolysed it tends to form an outer char layer. This char has a lower thermal conductivity than biomass and so can resist the flow of heat into the particle. For fluidised bed pyrolysis a particle diameter limit of 2mm has been suggested (64).

Scott et al. investigated the effect of particle size on organic liquid yields from a 100g/h fluidised bed reactor at 500°C (94). Using aspen poplar of particle sizes 44-105μm, 105-250μm and 250-500μm, they found that the best organic liquid yield was obtained using 105-250μm. Organics yields of 51.0, 58.9 and 53.0 mf wt.% were obtained for each size fraction respectively. Unfortunately char yields were not accurate due to the char being blown out of the reactor, before complete reaction. Thus the char could have been a mixture of unreacted wood, partially reacted wood and char. It may be that higher organic liquid yields would have been obtained if all of the wood had reacted. Results obtained by Scott et al. reported later have organic liquid yields of 66 mf wt.% for poplar at 500°C.

The geometry of the biomass particle has been assessed by a number of workers. Saastamoinen used spherical, flat and cylindrical particles, all with the same surface area to volume ratio, to assess the effects on particle weight loss. He found, in line with expectations, the mass loss to be fastest for flat particles and slowest for spheres. Maniatis and Buekens used a square [1.4 x 1.4mm], a cylinder [1.4mm diameter] and a rectangle [0.5 x 1.4mm] at temperatures between 600 and 900°C; they found that the highest organics yields were obtained with cylindrical particles and the lowest with rectangular particles (49). Since the temperatures used for these experiments were above those defined for fast pyrolysis [Section 3.1] it is expected that the higher organic liquid yields were obtained from the sphere due to reduced heat transfer and cracking of vapours. It is expected that if the experiments were repeated at lower temperatures the highest organic liquid yield would be obtained from biomass with the shortest distance from centre to outer edge [i.e. the rectangle, 0.25mm]. Vacuum pyrolysis carried out by Roy at 450°C using particle sizes from wood flour to 10mm chips found that the organics yields were much higher for flour [60.8 mf wt.%] than chips [50.7 mf wt.%] (74).

In commercial applications of fast pyrolysis, the largest biomass particle, which can still be pyrolysed with acceptable product yields [i.e. pyrolysis liquid or chemicals], should be used. The size reduction equipment used to produce it will determine the shape of the biomass particle. However, for this project, it is only possible to feed particles less than 600μm in size into the reactor, so any problems associated with large particles will be avoided. The details of how this small feedstock is produced will be discussed in Chapter 6 along with the evaluation of how the shape of the particles affects the pyrolysis experiments.

3.2.4 Moisture Content

The presence of water in the biomass will influence how the biomass behaves in the reactor, the physical properties and the heating value of the recovered pyrolysis liquid. In most laboratory experiments and commercial processes the feed is normally dried to less than 10% moisture content on a wet basis. This is because higher pyrolysis liquid yields are obtained from dryer feedstock [as will be illustrated below]. Since moisture content is altered by processing prior to entering the pyrolysis reactor it is discussed as part of process parameters.

Kelbon studied the effect of moisture content by pyrolysing feedstocks of 10, 60 and 110% [dry feedstock basis]. She found that the increase in water content delayed the onset of pyrolysis, due to moisture vaporisation, by as much as 150 seconds (75). Evans and Milne noticed a similar delay in pyrolysis of 75s when they investigated the effect of moisture on pyrolysis. Gray et al. investigated the effect of moisture on ash free Woodex (76). He found that, compared to dry ash free Woodex, the char yield increased from 31 to 36 mf wt.% and that the organics yield increased marginally from 26 to 28 mf wt.% when ash free Woodex with a 16% moisture content was pyrolysed.

Maniatis and Buekens compared the results from pyrolysis of a dry sample to pyrolysis of a sample containing 10% moisture (77). They found that pyrolysis of the moist sample resulted in about 10% more water in the product. This concurs with a statement by Piskorz, reported in work by Peacocke (44), that the unwritten rule of thumb for fast pyrolysis conditions on a dry basis is 12 mf wt.% water with a 1 mf wt.% increase in feedstock moisture contributing 1 mf wt.% to the final water yield (78).

Little work has been done on the effects of water content on the stability and physical properties of pyrolysis liquids. By increasing the moisture content of the feedstock it will be possible to produce liquids with higher water contents; however, although the increased water content lowers the viscosity of the liquid it also lowers the heating value. This is certainly a topic which should warrant some further attention.

Since the presence of water in the biomass delays the onset of pyrolysis this will result in the biomass taking longer to reach pyrolysis temperature. This could result in increased secondary reactions, which would lead to a reduction in the yield of some chemicals, for example levoglucosan. Therefore it would seem likely that feedstock moisture contents in excess of 15mf wt.% [dry feedstock basis] should be avoided for the production of chemicals and maybe also for the production of pyrolysis liquids.

3.3 FEEDSTOCK PARAMETERS

The selection of feedstock will have a profound effect on the yield of pyrolysis products and the chemicals contained within them. Most research on chemicals production has focused on chemicals from the cellulose component, since these chemicals are often present in the highest concentrations, water soluble and easier to analyse than water insoluble lignin derived chemicals. It is evident that if chemicals from the cellulose component of biomass are required then either commercial cellulose, a feedstock which is rich in cellulose or a feedstock modified to have a high cellulose concentration should be used.

By investigating the pyrolysis reactions of the individual biomass components it may be that a better understanding of whole wood pyrolysis will be achieved. Unfortunately this is an over simplification, since cellulose is relatively easy to purify and pyrolyse. However, hemicellulose and lignin are more difficult to separate and even harder to pyrolyse. Hemicellulose and lignin are also specific to a particular biomass type, so even if they could be separated and pyrolysed this would have to be carried out for every biomass investigated.

The following Sections review the pyrolysis of cellulose and also the small amount of literature available on the pyrolysis of hemicellulose and lignin. This is then related to the pyrolysis of whole biomass feedstocks.

3.3.1 Cellulose Derived Chemicals

Many of the individual chemicals, which are present in high yields [i.e. greater than 3 wt.% wet oil basis] from whole biomass pyrolysis liquids, come from the cellulose component of the biomass. Antal and Varhegyi have reviewed the current state of knowledge of cellulose pyrolysis (79). They found that new equipment and analytical methods have recently allowed much better understanding of chemical forming mechanisms.

The mechanisms, which are currently used to explain the range of chemicals contained in the pyrolysis liquids from cellulose were investigated by Halling (80) under the supervision of Scott. Halling carried out a thorough investigation into the effect of temperature on the yields of the predominant products of cellulose fast pyrolysis. Using statistical analysis on experiments performed using Avicel cellulose over the temperature range 375-800°C, it was concluded that two major pathways exist, one for low temperature products, and one for high temperature products. Both pathways have a formation range in which the yield of the product is increasing, and a decomposition range where the product yield is decreasing; these are shown in Table 3.3.

Table 3.3: Effect of temperature on the predominant products of cellulose fast pyrolysis

	Low Temp. Products		High Temp. Products	
Products	Formation Range	Decomposition Range	Formation Range	Decomposition Range
Levoglucosan	370-400	450-600		
Cellobiosan	370-400	400-600		
Glucose	350-400	500-650		
Fructose	350-400	450-500		
Hydroxyacetaldehyde			410-470	600-720
Acetic acid			420-520	600-730
Formic acid			440-520	600-730
Glyoxal			420-480	580-710
Methyl glyoxal			400-480	580-710
Acetol			430-530	560-760
Formaldehyde			450-620	760-800

This is illustrated more clearly by examining the variation in yields of the four major cellulose fast pyrolysis chemicals, which come from the two competing reactions. The major products from the high temperature pathway are hydroxyacetaldehyde [HA] and acetic acid and from the low temperature pathway are levoglucosan [LG, 1,6-anhydro-β-D-glucopyranose] and cellobiosan. Figure 3.6 shows how the variation in yield of these products changes as the pyrolysis reactor temperature is increased (151).

The yields of low temperature products [levoglucosan and cellobiosan, denoted by triangles in Figure 3.6] reach a maximum at temperatures lower than 500°C and the yields gradually decrease as temperature increases beyond 500°C. At temperatures above 500°C the yields of high temperature products [hydroxyacetaldehyde and acetic acid, denoted by squares in Figure 3.6] increase. It is also interesting to note that the maximum pyrolysis liquid yield [shown to be approximately 500°C in Figure 3.1] is typically obtained at the maximum point of the total line [i.e. the sum of all four chemical yields].

From Figure 3.6 it seems possible that hydroxyacetaldehyde is a degradation product of levoglucosan since cellulose must pass through 400°C to reach 500°C. However studies on the pyrolysis of levoglucosan have found that hydroxyacetaldehyde is not a product (81). Thus both hydroxyacetaldehyde and levoglucosan are formed directly from the pyrolysis of cellulose or possibly through some previously undiscovered intermediate [e.g. primary "active" liquid mentioned in 3.1.1].

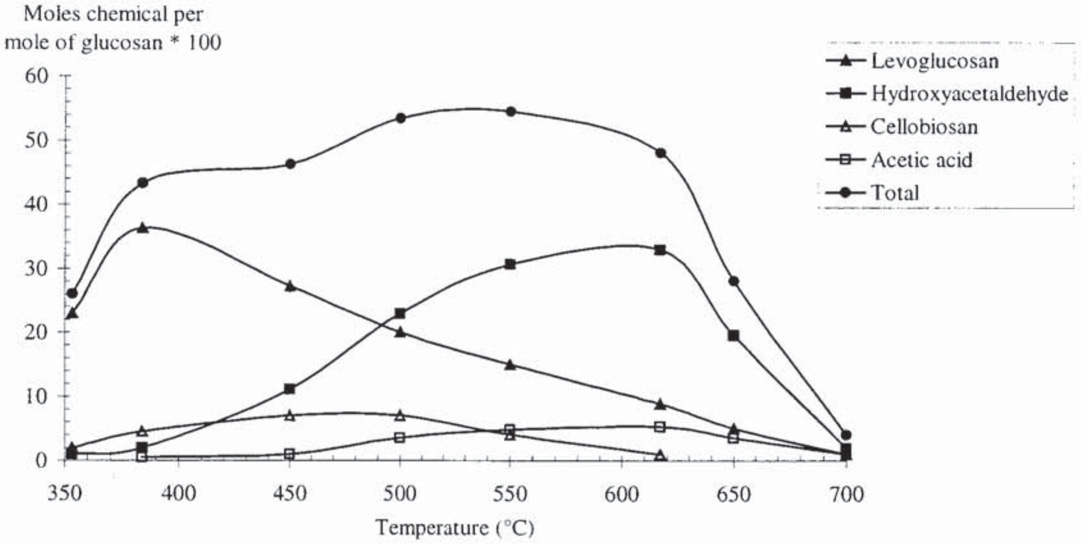


Figure 3.6: Variation in yields of chemicals from fast pyrolysis of Avicel cellulose (82)

From the above work of Halling, Scott et al. developed a model for the decomposition of cellulose during fast pyrolysis [Figure 3.8] (82). This model is currently regarded as the best way of describing the overall pyrolysis reaction for cellulose; however, as analytical techniques become more sophisticated it may be improved. The model has two competing pathways, fragmentation and depolymerisation [shown in Figure 3.7]. Fragmentation is the breaking apart of the glucose monomer in the cellulose polymer, whereas depolymerisation leads to the breaking of the bonds holding the monomers together [i.e. "unzipping" the 1,4 glucosidic link].

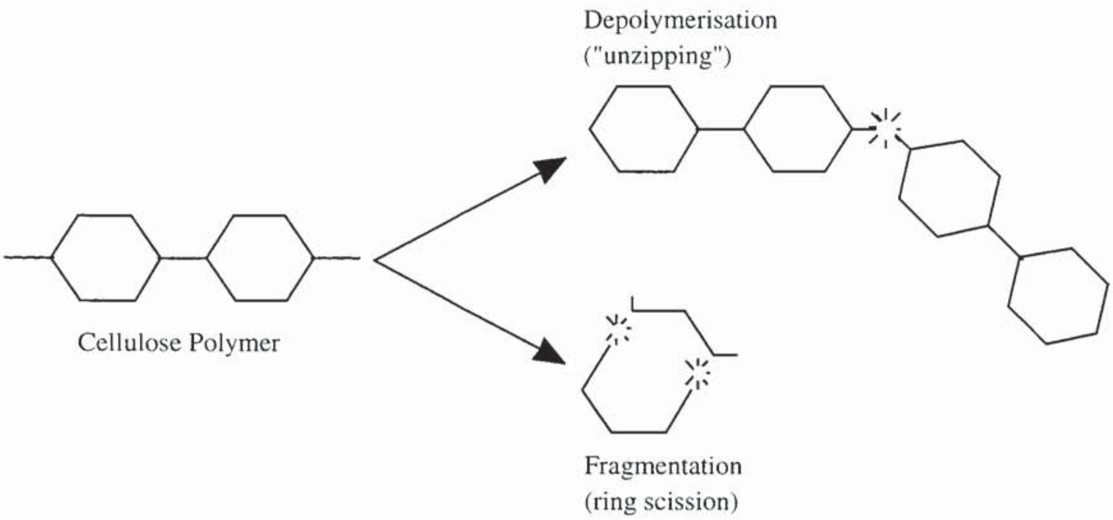


Figure 3.7: Depolymerisation and fragmentation of cellulose monomer

Both feedstock parameters and process parameters determine the choice of pathway. The main feedstock parameters are the morphology of the cellulose, its degree of polymerisation [DP] and the presence of alkali metal cations associated with the cellulose polymer. The morphology of the cellulose and degree of polymerisation are only altered when the wood has been chemically modified or altered by effects such as heating in a vacuum [Waterloo (60)].

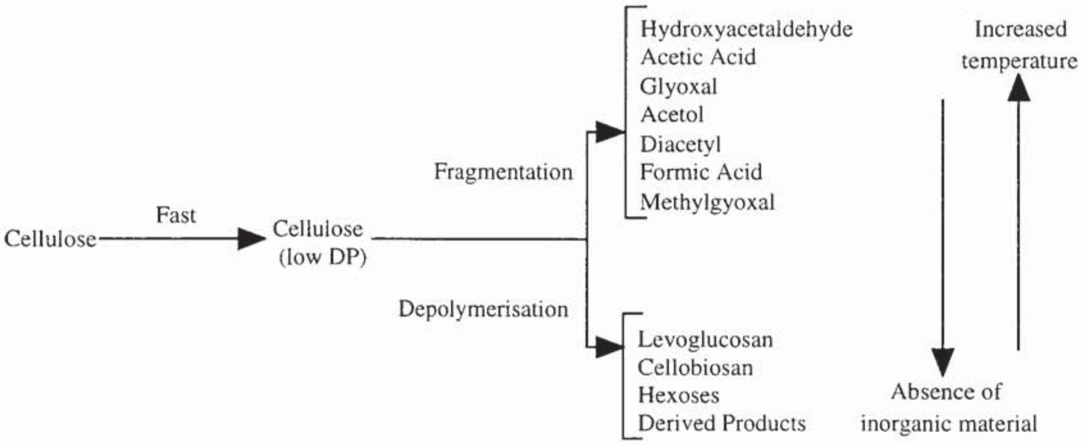


Figure 3.8: Waterloo model of cellulose decomposition by fast pyrolysis

From Figure 3.8 it is evident that the pyrolysis reaction tends to produce more depolymerisation products in the absence of inorganic material [i.e. ash]. Therefore this section will be addressed in Chapter 4, which deals with component removal [i.e. ash and other biomass components]. Conversely, higher temperatures and the presence of inorganic material tend to produce more fragmentation products. Therefore this will be addressed in Chapter 5, which assesses the effect of chemical additives on pyrolysis liquid chemical yields.

The main process parameter which has influence over the pyrolysis pathway is temperature. As temperature increases more fragmentation products tend to be produced. Vapour residence time [Section 3.2.2] also has a major influence on how far the fast pyrolysis reaction progresses, the longer the products remain in the reactor zone the more likely the production of secondary products.

Shafizadeh pyrolysed a range of cellulose types under vacuum with reaction times of 5-9 minutes [therefore not true fast pyrolysis]. He found that the tar [i.e. organics and water] and levoglucosan yield increased with the purity of the cellulose used (59). He obtained liquid yields of 46 mf wt.% for cotton fabric [90% cellulose] and 85 mf wt.% for cotton hydrocellulose [almost pure cellulose]. The yield of levoglucosan was 14 and 58 mf wt.% dry feedstock basis for the above cellulose types.

Similar effects were observed in the work of Scott et al., who carried out true fast pyrolysis on a crude cellulose of properties given in Table 3.4 (140). This was produced by the Iotech company using a steam process followed by an alkaline extraction process. Fast pyrolysis was carried out at a range of temperatures and the results are shown in Table 3.5 (140).

Table 3.4: Feedstock properties of feedstocks used by Scott et al. (140)

	Avicel cellulose	crude cellulose	poplar-aspen	aspen bark	wheat straw
Lignin	0.0	8	16.2	13.7	16.7
Hemicellulose	0.0	0	31.0	18.0	41.8
Cellulose	99.0	92	42.3	34.3	32.4
Ash [%]	<0.01	0.75	0.39	4.38	4.6
C		41.90	49.6	51.0	48.5
H		5.48	6.11	6.40	5.13
N		0.46	0.56	0.53	0.50
O [by difference]		52.16	43.7	42.1	41.3
S				nil	nil

The aim of this crude cellulose work was to analyse how the individual biomass components behaved during fast pyrolysis. The cellulose used was commercially produced and contained approximately 8% lignin [see Table 3.4]; this means that the liquid products contained some chemicals derived from the lignin component of the biomass. It was also their intention to pyrolyse commercially produced hemicellulose and lignin; however, these feedstocks proved too thermally sensitive and reacted in the feed tube prior to entering the reactor.

Table 3.5: Results of fast pyrolysis of Iotech cellulose

Temperature [°C]	426	532	625	741
Moisture content [mf wt.%]	4.02	4.02	4.02	4.02
Residence Time [s]	0.445	0.445	0.445	0.445
Ash [mf wt.%]	0.75	0.75	0.75	0.75
Yields [mf wt.%]				
Organics	47.3	52.2	44.3	33.1
Water	12.6	18	20.9	13
Char	18.9	9.7	10.9	8
Gas	12.1	18.3	21.1	44.1
Closure	90.9	98.2	97.2	98.2

The shape of the curves in Figure 3.9 are typical compared to those shown in Figure 3.1, with organics reaching a maximum between 500 and 550°C, char decreasing with temperature and gas increasing with temperature. The organics yields are lower than expected because of the high sodium content of the ash [13% ash basis] from the alkali production of the cellulose. Scott believed that sodium acts as a catalyst promoting secondary reactions. It was also found by Shafizadeh and Stevenson, that, even in small quantities, sodium can act as a significant pyrolysis catalyst (83).

The fast pyrolysis of cellulose can be related in many aspects to fast pyrolysis of whole biomass [see Section 3.4]. Biomass can be pretreated to remove mineral matter [as will be demonstrated in Chapter 4] and in the subsequent pyrolysis of the pretreated biomass the cellulose component behaves in a similar fashion to pure cellulose.

For the purpose of chemicals production, where the chemicals are derived from the cellulose component of biomass, it is justified to use assumptions based on cellulose chemistry. On an analytical level [as far as this work is concerned] it is only currently possible to analyse the aqueous fraction [using HPLC] of the pyrolysis liquid, which again is derived mostly from cellulose. Using more sophisticated analytical techniques, such as GC-MS the aqueous insoluble fraction of pyrolysis liquids can be analysed.

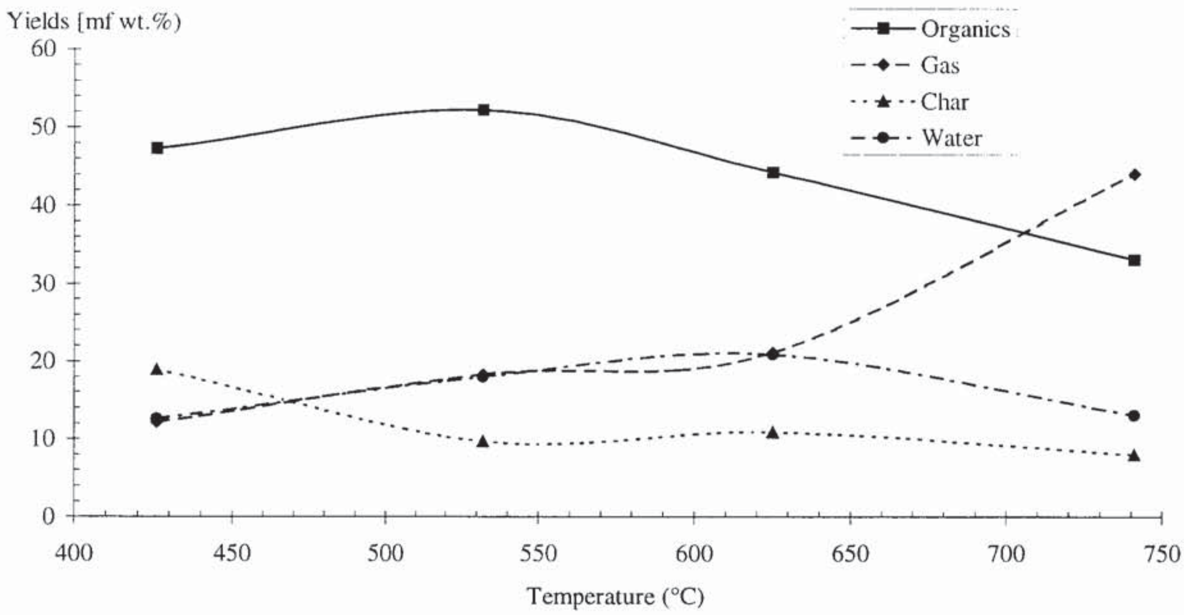


Figure 3.9: Product yields from fast pyrolysis of Iotech commercial cellulose

3.3.2 Hemicellulose Derived Chemicals

Hemicellulose is not as chemically consistent as cellulose [Sections 2.3.1 and 2.3.2 describe the chemistry of cellulose and hemicellulose]. It contains a number of pentosans and hexosans, which are probably the most unstable of the principal wood components towards heat. Because of this instability they are converted to low molecular weight compounds and furfural during fast pyrolysis. However, furfural is highly reactive so it is likely that much of it is converted to lower molecular weight products [e.g. furan or hydrocarbon gases] by secondary reactions (84). This is the most likely reason why there are low yields of furfural and furan decomposition products found in most pyrolysis liquids [see later experimental work, Chapters 7 and 9]. Another product from the hemicellulose component is acetic acid. Decomposition of the acetyl groups often results in the formation of acetic acid. The pentosans also decompose to form formic and acetic acids (84).

3.3.3 Lignin Derived Chemicals

Lignin is largely formed from phenylpropane units [previously discussed in Section 2.3.4]. The basic structures of lignin chemicals are largely retained through fast pyrolysis, with the majority of reactions being carried out on the side chains. Thus the characteristic decomposition products are phenolic ethers, guaiacol and pyrogallol 1,3-dimethyl ether and their derivatives.

The methoxyl groups of lignin are partially converted to methanol. However, the yields of methanol obtained are always much lower than the theoretical maximum obtained if all methoxyl groups were converted to methanol [typically less than 10%] (84). The decomposition products of lignin are prone to further decomposition and interactions resulting in the formation of a wide range of phenolic products.

Gardner et al. (85) investigated the effects of pyrolysis on a range of lignin preparations using thermogravimetry and pyrolysis gas chromatography. The thermogravimetric behaviour was found to vary depending on the way in which the lignin was prepared and was also found to be dependant on lignin species even when the same preparation method was used. This confirms that separation from the original biomass does modify the lignin and also that the lignin differs from species to species. The authors report the yields of guaiacol, methyl guaiacol, syringol and syringaldehyde from pyrolysis gas chromatography of all 15 of their lignin preparations. However, the total yields reported are only 3.0 mf wt.% of the feed material. The authors were unable to find suitable columns to analyse many of the products.

Samolada found that fluidised bed pyrolysis of fir and poplar woods gave different yields of pyrolysis products and the phenolic fraction of the pyrolysis liquids [lignin derived chemicals] (86). The total yield of phenols was found to be only affected by temperature [similar to total liquid yields]. The kind of biomass mainly affected the yields of phenol, ethylphenol and trimethylphenol. The yields of phenol and ethylphenol were higher from hardwood [poplar] whereas the yield of trimethylphenol was increased from softwood [fir]. Samolada attributes some of the higher trimethylphenol yields to the presence of extractives [9.1 maf wt.%] in the poplar wood compared to 4.7 maf wt.% in the fir. Samolada states that extractives contain a considerable amount of phenols, which can be contained in the pyrolytic lignin of pyrolysis liquids.

Table 3.6: Quantitative GC analysis of pyrolysis liquids (87)

Compound	Aston Pine	BTG Softwood cones	IWC Beech wood
All yields mf wt.% [water free liquid basis]			
Cellulose derived			
Hydroxyacetaldehyde	12.62	12.92	7.78
Levoglucosan	5.42	5.29	3.52
Formic acid	*	*	*
Acetic acid	3.22	3.04	4.65
Acetol	7.02	4.24	3.90
1,2-Ethanediol	*	*	*
1-Hydroxypropanol	*	*	*
3-Hydroxypropanal	*	*	*
Hemicellulose derived			
2,5-Dimethoxytetrahyrofuran (cis)	0.14		0.52
3-furaldehyde		*	
Butanedial		*	
2,5-Dimethoxytetrahyrofuran (trans)	*		*
2-Furaldehyde		0.41	
2-Furfuryl alcohol		0.01	
1-Acetyloxypropane-2-one		*	
2-Acetylfuran		*	
(5H)-Furan-2-one	0.77	0.40	0.67
Methyl-(5H)-furan-2-one			*
4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one	*	*	*
2-Hydroxy-1-methyl-1-cyclopentene-3-one	0.27	0.15	0.16
Lignin derived			
Phenol	0.06	0.15	0.03
Guaiacol	0.53	0.24	0.15
o-Cresol	0.05	0.09	*
m-cresol	0.31	0.10	*
p-cresol	0.02	0.09	*
4-Methyl guaiacol	0.88	0.36	0.14
2,4 and 2,5-Dimethyl phenol	0.05	0.08	0.41
4-Ethyl guaiacol	0.14	0.09	0.08
4-Vinyl guaiacol	0.06	0.03	0.05
Eugenol	0.22	0.16	0.06
5-Hydroxymethyl-2-furaldehyde	0.45	0.33	
Syringol			0.32
Isoeugenol (cis)	0.25	0.15	0.07
Isoeugenol (trans)	0.67	0.24	0.30
4-methyl syringol			0.30
Vanillin	0.26	0.34	0.10
Homovanillin	0.20	0.15	0.09
Acetoguaiacone	0.19	0.20	0.08
Syringaldehyde			0.25

* - indicates chemical identified but not enough to quantify

Meier has carried out extensive work on the classification of lignin and lignin derived pyrolysis products. In a recent paper, analysis by gas chromatography of three liquids produced at different institutes using different feedstocks and reactors is reported (87). The liquids were produced at Aston, BTG and IWC. Aston liquid was produced from pine in a 1kg/h fluidised bed reactor, BTG liquid from softwood cones in a rotating cone reactor and IWC liquid from beech wood in a fluidised bed reactor. The quantitative results are shown in Table 3.6. The cellulose derived chemicals make up the largest proportion of the analysed liquids. The hemicellulose and lignin derived chemicals make up only a small proportion of the total analysed liquid. There are a large number of different chemicals but they are only present in small concentrations. The chemicals derived from the cellulose component are present in high concentrations and are also present in the liquids from all biomass species.

From Table 3.6 it is evident that the hemicellulose and lignin derived chemicals are present in small concentrations. Also, since three different wood types were used there is a difference in the chemicals, which have come from each component. For example, softwoods [e.g. pine and pine cones] contain cresol, whereas hardwood [beech] does not. Also hardwood liquid contains syringol and softwood does not. This is due to the differences between hardwood and softwood lignin, as discussed in Chapter 2.

3.3.4 Natural Catalysts

The term natural catalysts refer to inorganic matter contained in the biomass, which is believed to have a catalytic effect. Due to the small quantities of mineral matter which are required to induce a profound change in product yields, it is concluded that this effect must be due to catalysis (88). The effects of demineralisation have been investigated by a number of researchers. In particular, Scott et al. (89) and Richards et al. (90) both found that removal of the metal ions gave increased yields of levoglucosan and subsequent re-introduction of small amounts of these salts gave much reduced yields.

The removal of ash from biomass is dealt with in Chapter 4, which deals with pre-treatment of biomass. Chapter 4 will also review results where ash has been removed from the biomass and subsequently re-introduced. The introduction of non-ash chemicals into biomass will be discussed and reviewed in Chapter 5.

3.4 WHOLE BIOMASS PYROLYSIS

Section 3.2.3 addressed the feedstock parameters which affect the fast pyrolysis product and chemical yields. The pyrolysis of individual biomass components was investigated in the hope that the sum of the individual parts would equal the whole. The analyses which are available for the individual components are most detailed for cellulose. The components which come from hemicellulose appear to be highly reactive and quickly degrade to lower molecular weight products. The products which come from lignin tend to be diverse and in low concentrations. Thus for the sum of the parts to be equal to the whole the individual parts must be accurately determined prior to pyrolysis.

Thus if it were possible to determine the chemical composition of a particular biomass accurately then it may be possible to predict the chemicals contained in the pyrolysis liquid. From Chapter 2, it would appear that at present there are no techniques sensitive enough to determine the exact chemical composition of biomass. Also, since each biomass type tends to have a different chemical composition, which may vary within the plant, this could result in a large number of analyses to be carried out before a feedstock is used.

At the optimum fast pyrolysis temperature, which has been determined as approximately 500°C for generic wood, there is an abundance of energy to initiate chemical reactions. Thus it is likely that many chemical reactions are taking place and the likelihood is that these reactions are to a certain extent random and therefore unpredictable. Thus even though pure cellulose will pyrolyse to give levoglucosan as the major product [i.e. 40-50 mf wt.% dry feed basis], in the presence of other components this yield can fall as low as 0.5-3.0 mf wt.%.

Thus, although the pyrolysis products obtained from the individual biomass components do help to understand some of the underlying reactions and mechanisms, the product yields cannot [at present] be accurately predicted from the composition of the biomass feedstock. This means that each biomass type should be assessed by fast pyrolysis experiments to determine the product and chemical yields. This is the focus of work reported in Chapter 7. As well as experimental results from this work relevant work from other institutes will also be reported and discussed.

3.5 SUMMARY

The feedstock and process parameters which affect the fast pyrolysis products and chemical yields have been reviewed and discussed. The parameters which have the largest effect on modifying the product and chemical yields will form the basis for the experimental work described in Chapters 7, 8 and 9.

The process parameter which has the largest influence on product and chemical yields is reactor temperature. It has been found by most fast pyrolysis workers that fast pyrolysis of any biomass feedstocks will result in a maximum yield of liquids between 400 and 600°C. Thus any new biomass feedstocks should be pyrolysed over this range of temperatures to determine the maximum liquids yield. This forms the basis for the work described in Chapter 7.

The composition of biomass can be altered by selecting a particular feedstock type, selecting a particular feedstock but at a different time in the growing season, genetic modification and pre-treatment [i.e. component removal]. The selection of novel biomass types to improve pyrolysis liquid yields or produce novel chemicals is the basis of experimental work described in Chapter 7. The seasonal selection of biomass and genetic engineering of biomass species is beyond the scope of this work; however, it is recommended that this study be taken up in the future. The modification of biomass by chemical pre-treatment is reviewed in Chapter 4 and forms the basis for the experimental work described in Chapters 8 and 9.

The presence of mineral matter [ash] in the biomass has a profound effect on the pyrolysis product and chemical yields. The effect of ash will be reviewed and discussed in Chapter 4. It is believed that ash modifies the pyrolysis product yields by some form of catalysis. Hence "catalytic" additives other than ash will be reviewed and discussed in Chapter 5.

4. PRE-TREATMENT

This chapter reviews past and current work in the area of biomass pre-treatment. Pre-treatment is defined as a chemical process carried out prior to pyrolysis, which either modifies the biomass lignocellulose polymers or adds substances, for example catalysts, into the lignocellulose complex.

This chapter deals specifically with the removal of parts of components or complete biomass components from the feedstock material. The purpose of this is to modify the pyrolysis reaction and hence increase the yield of some specific chemicals.

4.1 INTRODUCTION

Pre-treatment of biomass can be divided into two main areas, the removal of components from the biomass matrix and the addition of substances to the biomass. The removal of components, typically by a washing or leaching process, is the focus of this chapter. The addition of substances can be carried out by a number of means and is reviewed and discussed in Chapter 5.

The removal or separation of biomass components prior to fast pyrolysis has several potential applications and benefits. Firstly, if the number of biomass components are reduced this will reduce the number and diversity of biomass chemical pre-cursors entering the pyrolysis reactor and hence the number of chemical products contained in the pyrolysis liquid. It was shown in the previous chapter that particular biomass components tend to form specific chemicals when pyrolysed.

The removal of one or more biomass components will result in a reduction in total yield. For example, if the hemicellulose component [approximately 20% of the biomass] of a biomass feedstock was removed by pre-treatment this would result in 20% less material being fed into the pyrolysis reactor, hence 20% lower yields. However, by removing the hemicellulose component the yield of levoglucosan may be increased from 2 mf wt.% [dry feedstock basis] to 20 mf wt.% [dry pre-treated feedstock basis] or 16 mf wt.% [dry original starting material basis]. Thus even though the amount of biomass being fed into the reactor has decreased, the yield of a potentially valuable chemical [levoglucosan] has increased. The improved chemical yield from pre-treated feedstock may make extraction and purification simpler and cheaper.

Secondly, the ash component [Section 2.3.6] is known to catalyse certain fast pyrolysis pathways [Section 3.2.5]; thus its removal will influence the pyrolysis reaction pathway and hence the yield of chemicals. During fast pyrolysis the ash tends to be incorporated into the char; also, there is usually a small amount of char in the pyrolysis liquid. The alkali metals contained in the liquid [incorporated into the char] could cause fouling and corrosion problems if the pyrolysis liquid is used in a fuel application.

Thirdly, it is believed that certain chemicals from the hemicellulose component [e.g. acetic acid and furfural derived products] cause much of the odour problems associated with pyrolysis liquids. Removal of the hemicellulose component may help to reduce this problem.

Whether pre-treatment is used depends on the application intended for the product. If a fuel is the primary product, then pre-treatment may be used to reduce downstream problems, for example to lower ash content or improve liquid properties. For the production of chemicals, pre-treatment will be used to either influence the pyrolysis reaction to produce a chemical not normally contained in the pyrolysis liquid or to increase the yield of a selected chemical or groups of chemicals in the pyrolysis liquid. If the former, then the pre-treatment forms an integral part of the process and cannot be avoided. However, in the latter case whether pre-treatment is used depends upon whether it is better to produce large quantities of pyrolysis liquid containing a low concentration of a particular chemical. Alternatively it may be better to pre-treat the biomass to have a higher concentration of the chemical contained in a smaller amount of pyrolysis liquid.

The economic assessment of an integrated chemical production process will be the focus of Chapter 10. This Chapter considers several examples and assesses the costs of plant equipment and production expenses for reception, physical preparation, pre-treatment [if required], pyrolysis and chemical extraction.

4.2 CHEMICAL SELECTION

In the previous chapter, the chemicals, which are obtainable in yields greater than 1 wt.% [wet oil basis] from fast pyrolysis of biomass were reviewed by Milne (91). He found that 108 chemicals have been found by a number of institutes in the liquid products from a variety of feedstocks. However, of these chemicals, less than 20 were found in liquids produced at four or more institutions. In fact only the chemicals listed in Table 4.1 below have been consistently found [i.e. three or more results from different institutes] in yields of greater than 3 wt.% [wet oil basis].

Table 4.1: Chemicals from untreated biomass fast pyrolysis liquids

Functional group	Chemical	Max. literature yield [% wet oil basis]	Feed	Ref.
Acids	acetic	12.0	poplar	92
	formic	9.1	white spruce	93
Sugars	levoglucosan	35.0	cellulose	82
	cellobiosan	3.2	white spruce	93
Aldehydes	ethanal	8.5	aspen-poplar	94
Guaiacols	pyrolytic lignin	47.0	hog-fuel	93
Mixed oxygenates	glyoxal	4.6	oak	95
	hydroxyacetaldehyde	13.0	IEA poplar	93
	acetol	7.4	wood	96

From this it is tentatively concluded that the chemicals that can be obtained from pyrolysis liquids in high yields [i.e. >3wt.% wet oil basis] have all been discovered. It is unlikely that a "new" chemical will be found from the pyrolysis of untreated feedstocks. Thus chemical production schemes should focus on improving the yields of the chemicals listed in Table 4.1. The two chemicals which have been consistently obtained in the highest yields are levoglucosan and hydroxyacetaldehyde. Pyrolytic lignin is obtained in high yields, but since it does not consist wholly of a single chemical it will not be considered further.

Levoglucosan is reported in yields of approximately 35 wt.% [wet oil basis] from Avicel [99% pure] cellulose. However, since cellulose is obtained by pulping wood it is not an untreated feedstock. For untreated wood, yields of 3.8 wt.% [wet oil basis] have been achieved for IEA polar and 5.1 wt.% [wet oil basis] for white spruce (93). This yield can be increased significantly by pre-treatment [component removal] to approximately

21 wt.% [wet oil basis] (89). Levoglucosan is an interesting chemical to produce for a number of reasons:

- it has a high value [Sigma - \$30/g (97)],
- it is present in low concentrations in pyrolysis liquids from a number of feedstocks,
- the concentration can be significantly increased by pre-treatment of the biomass prior to fast pyrolysis,
- it has a number of potential commercial applications [e.g. biodegradable polymer or plastic, high value speciality chemicals precursor or low calorie food filler (2)],
- it is recoverable from the pyrolysis liquid.

Thus, unlike the other chemicals listed in Table 4.1, levoglucosan offers the largest potential for improvement [i.e. increase in yields from 3.8 to 21 wt.% wet oil basis]. It has no commercial market at present and therefore no competition, unlike acetic acid or other bulk chemicals. It may be possible to further improve the yield of levoglucosan beyond the literature values quoted above. Or it may be possible to produce similar yields by a less severe pre-treatment technique. This chapter will therefore focus on pre-treatment methods which lead to an increase in levoglucosan yields.

Hydroxyacetaldehyde is the single chemical which is present in highest concentration from untreated biomass. Unlike levoglucosan, little work has been carried out to investigate methods to improve the concentration in pyrolysis liquids. As discussed in Chapter 3, hydroxyacetaldehyde is produced by the fragmentation pathway. This is a competing pathway to depolymerisation, which produces levoglucosan. Thus, pre-treatment methods which selectively improve the yield of levoglucosan will reduce the yield of hydroxyacetaldehyde. Since levoglucosan yields are improved by component removal [especially ash], it is likely that hydroxyacetaldehyde will be increased by addition of substances to the biomass. This is investigated in Chapter 5.

4.3 PRE-TREATMENT REVIEW FOR LEVOGLUCOSAN PRODUCTION

As discussed in Section 2.3.5, the minerals taken up and retained by plants when growing are classified as ash. The most common elements in ash are calcium, potassium and sodium [relative proportions of these elements for a range of feedstocks were given in Table 2.3]. These are contained as carbonates, phosphates, silicates and sulphates; and are combined into the cells in three ways. Firstly, ash is loosely held in the hollow lumen of the cell. Secondly, it is combined with the cell wall material and thirdly, it is chemically bound with hemicellulose.

As the term suggests the loosely bound ash is easily removed, typically using demineralised water to wash it from the cells. However, the ash, which is bound to the cell walls and the hemicellulose is much harder to remove. It requires chemical reaction to remove it from the biomass matrix and therefore requires more severe agents such as acid for its removal. Thus ash can only be completely removed if some of the hemicellulose is removed. Thus techniques such as water washing will only be able to remove approximately 50% of the ash.

When a feedstock has been pre-treated, for example by washing with dilute sulphuric acid, the chemical composition of the biomass will be changed. The ash component may have been removed, which is measurable by ashing the feedstock in a muffle furnace at 750°C [this technique is described in Section 6.2.4]; the acid may have removed other components, for example extractives; and the hemicellulose may also have been chemically modified or even partially removed. The analysis of the biomass components is costly and time consuming, but most importantly it is also only accurate to between ±1-10% [depending on the analysis method used, see Section 2.3.1]. Thus small changes in biomass composition will be virtually impossible to detect. Thus it is only feasible to test the effectiveness of a particular pre-treatment by pyrolysing the pre-treated material and looking at changes in the product and chemical yields.

The fast pyrolysis literature contains a range of treatments of increasing severity. The mildest chemical pre-treatment is water washing, which removes approximately 50% of the ash. The use of mineral acids in low concentrations and at ambient conditions is termed acid washing and tends to result in the complete removal of ash and extractives with some loss of hemicellulose component. More concentrated reagents [e.g. acid or alkali] can be used at elevated temperatures [i.e. in excess of 50°C] to hydrolyse the hemicellulose or remove the lignin as well as removing ash and extractives.

The most severe pre-treatment [for pyrolysis] would result in the production of cellulose. However, since this is the purpose of the pulping process it is unlikely that such a process would be used as part of a pyrolysis plant. Economies of scale suggest that it would not be possible to produce cellulose on a small scale cheaper than it is produced commercially. Thus the production of cellulose will not be examined.

The literature has been reviewed and is reported in order of increasing severity of pre-treatment [i.e. starting with water washing and finishing with acid hydrolysis]. Where possible the results from fast pyrolysis of the pre-treated feedstocks will be included and discussed.

4.3.1 Water Washing

Very little water washing experimentation has been carried out. From the literature the most relevant work was carried out by Jenkins et al. (35). Their intention was to reduce ash in the biomass [straw] in order to reduce fouling in the combuster when these materials were burned. The elements, which are believed to cause fouling in boilers are potassium, chlorine, silicon, sulphur, calcium, magnesium and sodium (98, 99, 100, 101, 102, 103).

Jenkins et al. focused on two types of straw, wheat and rice. Samples from two different sites were used, wheat straw from Imperial Valley, USA was grown with saline irrigation, while rice straw grown in Yolo County, USA was produced in low salinity conditions. The elemental composition of the straws is shown in Table 4.2. The effect of saline irrigation is evident from the much higher levels of chlorine in the wheat straw.

The washing experiments consisted of no washing [i.e. no treatment, whole straw was analysed as harvested], sprayed [100g whole straw samples were sprayed for 1 minute with tap water], soaked [100g whole straw was submerged in 7 litres distilled water for 24 hours] and rain washed [straw left in field and washed naturally by 65mm of rain].

From Table 4.2 it is evident that soaking reduced the overall ash content of rice straw to the lowest level. Soaking was also effective at removing the ash from the saline wheat straw; however, no other treatments were tested on this material. The overall level of ash reduction is low for rice straw, but the levels of chlorine, sodium and potassium were significantly reduced. The effect of soaking is more pronounced in wheat straw, with the overall ash being reduced by almost 50% and the levels of chlorine, sodium and potassium significantly reduced.

Table 4.2: Ash composition of straws (35)

	Rice straw low salinity				Wheat straw saline irrigation	
Treatment	none	water sprayed	water soaked	rain washed	none	water soaked
Ash [mf wt.%]	18.63	17.59	17.10	17.84	12.78	6.45
Cl [mf wt.%]	0.74	0.38	0.06	0.06	2.02	0.21
Oxide [% Ash]						
SiO_2	74.31	81.30	93.13	91.60	35.84	61.79
Al_2O_3	1.40	0.59	0.98	0.82	2.46	2.85
TiO_2	0.02	0.07	0.05	0.02	0.15	0.04
Fe_2O_3	0.73	0.74	0.46	0.50	0.97	1.62
CaO	1.61	2.36	2.12	2.09	4.66	5.84
MgO	1.89	2.17	0.86	1.32	2.51	2.37
Na_2O	1.85	1.57	0.18	0.19	10.50	3.48
K_2O	11.30	7.45	2.03	2.21	18.40	5.81
SO_3	0.84	0.86	0.32	0.36	5.46	1.68
P_2O_5	2.65	1.68	0.39	0.63	1.47	3.35
Undetermined	3.40	1.21	-0.52	0.26	2.76	10.37

The rice straw was also milled until it passed a 19mm screen and then a 100g sample was flushed with 20 litres of tap water. The overall effect on the ash was to reduce it to 18.3 mf wt.%. A similar experiment was conducted using distilled water instead of tap water, which only had the minimal effect of reducing ash to 18.2 mf wt.%. Finally the straw was milled until it passed a 20 mesh screen and then flushed with 7 litres of distilled water; this reduced the ash level to 17.9 mf wt.%.

From these experiments it is evident that the best ash removal using water at ambient conditions was obtained by soaking the biomass for 24 hours in distilled water. It could be that the prolonged soaking time allowed the biomass structure to swell, thus making it more accessible. Although only a small proportion of the ash was removed overall [i.e. 18.63 to 17.10 mf wt.%] all components except silica were significantly reduced. Ash from straws and grasses always have a high silica content, whereas wood ash contains much less silica, [12% for Douglas fir ash was reported in Chapter 2]. Hence water washing of woody biomass would have a more significant impact on the overall ash content and more importantly a reduction in the levels of sodium and potassium.

The authors do not report whether soaking straw in tap water was tested. If the effects were similar to those of distilled water [as were the flushing tests], soaking in tap water would have a significant economic advantage over soaking in distilled water.

The use of large volumes of water in this soaking technique [i.e. 7 litres of distilled water per 100g wood] suggests that on a commercial basis this could be a costly process, not just in terms of the cost of water, but of the subsequent disposal of the waste water after soaking. A commercial pyrolysis plant operating on a continuous 1000 kg/h basis would require storage vessels of at least 1680m^3 to cope with the 24 hour hold up. Also, the addition of large amounts of water to the biomass may have significant economic impact, since the feedstock is supposed to enter the fast pyrolysis reactor at approximately 10% moisture. However, this will be considered in more detail in Chapter 10, Techno-economic assessment.

Venn (104) found that the presence of inorganic impurities [1 mf wt.% ash content] in cotton linters and fabric samples reduced the pyrolytic yield of levoglucosan. Improved yields of levoglucosan were obtained when the cotton was first washed with distilled water prior to pyrolysis. However, the best yields were obtained after dilute alkali then dilute acid washing of the cotton, which reduced the ash content to 0.04 mf wt.%. This reinforces the earlier statement that approximately 50% of the ash is held loosely in the lumen and is therefore easily removed. The remainder of the ash is bound to the hemicellulose and therefore requires more severe treatment for complete removal.

4.3.2 Dilute Acid Washing

Browning conducted experiments on acid washing of cellulose in columns (105). The experiments found that contact times in excess of 2 weeks were necessary for the complete removal of cations. However, most of the cations appeared to come from salts occluded in or absorbed by the fibres and only a small fraction were actually bound to the cellulose. The paper does not specify what type of acid, concentration or temperature Browning used.

The removal of mineral acids from the biomass matrix after acid washing was reviewed by Browning (106). He found some inconsistency between reported results; some investigators found acid was completely removed with just a small amount of water [e.g. HCl can be removed with 100ml water per gram of fibre] (106, 107, 108).

Conversely, other investigators have found that mineral acids are tenaciously retained by cellulose fibres and are only completely removed by an extended period of repetitive washing (109, 110). Clearly both statements cannot be true; it seems most likely that the bulk of the mineral acid is removed easily from the matrix, but the remainder is difficult to remove. Distilled water saturated with carbon dioxide was recommended for removal of cations and stronger acids to avoid the reintroduction of cations from the wash water (106). An alternative could be to use de-ionised water.

Shafizadeh et al. investigated the chemicals produced by the fast pyrolysis of cellulose (59). A number of cellulose types were used, but those which gave the worst yields of levoglucosan were produced by methods which did not involve acid treatment. From this, it also follows that the substrates, which gave the best yields of levoglucosan were produced by acid washing.

Table 4.3 shows the results of pyrolysis of two cellulose types. It can be seen that boiling the cellulose in de-ionised water [or ethanol and then de-ionised water] gave marginally increased yields of tar [i.e. organics and water] and levoglucosan. A mild acid wash carried out at room temperature followed by rinsing with de-ionised water to neutrality brought about a significant increase in the levoglucosan yield.

Table 4.3: Effect of washing prior to vacuum pyrolysis of cellulose (59)

		Percentage yield from cellulose		
Substrate	Pre-treatment	Char	Tar	LG
Whatman CF11				
	Untreated [a]	7	58	29
	Water wash [b]	4	70	33
	1% H_2SO_4 wash [c]	5	79	48
Cotton fabric				
	Untreated [a]	10	46	14
	Boiling EtOH then water wash [b]	9	59	28
	1% H_2SO_4 wash [c]	5	73	42
	5% H_2SO_4 wash [c]	3	76	50

[a] - as supplied [b] - water 97°C, 2h [c] - 2h, room temp.

Shafizadeh suggests that it is unclear whether the changes are due to removal of inorganic impurities, addition of trace amounts of acid or changes in structure/crystallinity of the cellulose due to the acid washing pre-treatment. It is feasible that all of these factors will have an effect. However, it is believed that, since cellulose contains very small amounts of ash, then removal of ash will only have a small effect. The use of acid seems to have a much more pronounced effect, perhaps suggesting some sort of catalysis or promotion of reactions.

This effect was later confirmed by Shafizadeh (88) when he found that transglycosylation reactions are catalysed by trace amounts of inorganic acids. Transglycosylation reactions are believed to be part of the mechanism for formation of levoglucosan during fast pyrolysis. The presence of inorganic acid lowers the temperature of pyrolysis and increases the yield of volatile pyrolysis products. Higher concentrations of acid and the presence of inorganic materials tend to catalyse dehydration and condensation reactions resulting in increased yields of char.

The effect on the pyrolysis products of the addition of small amounts of sulphuric acid to Douglas fir without washing to remove the acid was investigated by Shafizadeh (59). From Figure 4.1 it is evident that the introduction of low concentrations of sulphuric acid [i.e. less than 0.01%] has little effect on the yields of tar, char and levoglucosan. As the concentration is increased to 0.1% there is an increase in the yield of tar and levoglucosan due to the above mentioned catalysis. Once the concentration of acid is increased beyond 1.0%, dehydration of the sugar units results leading to the production of levoglucosenone, furan derivatives and the condensation of intermediate compounds resulting ultimately in increased yields of char and gas.

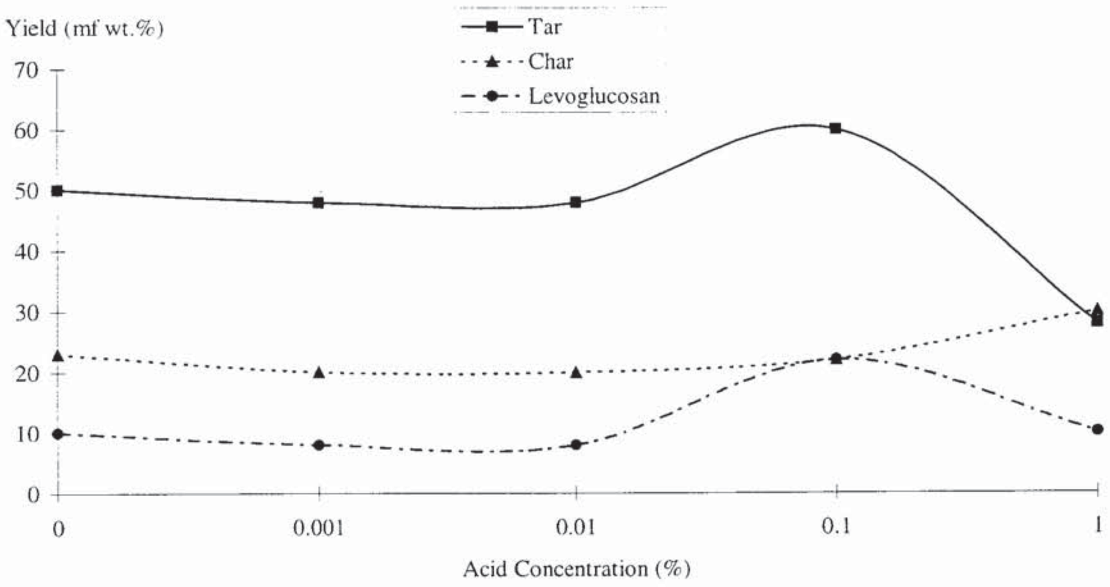


Figure 4.1: Products from pyrolysis of Douglas fir treated with sulphuric acid

These results have also been confirmed using other feedstocks, such as cellulose (111) and phenyl glucoside as a model compound (112). The effect of other inorganic materials on the formation and reactivity of chars, with reference to the problems of flaming combustion, has also been extensively investigated by Shafizadeh. However, the addition of substances to biomass is reviewed in Chapter 5.

Shafizadeh et al. (59) also investigated the effects of water and mild acid washing on a low grade hardwood and a sample of newsprint. The aim of the investigation was to see if pre-treated feedstocks could perform as well as cellulose. Western Cottonwood [populus trichocarpa] was selected because it was a typical low grade hardwood. Newsprint was selected because it had low value and high availability. The yields of pyrolysis products from both untreated and pre-treated cottonwood and newsprint samples are shown in Table 4.4.

The extracted and water washed cottonwood, which contained 0.59% inorganic material [ash], gave quite high yields of tar [47% in comparison to 58% for Whatman cellulose, Table 4.3]; however, the yield of levoglucosan was considerably lower [3% compared to 29%]. Dilute acid washing considerably reduced the ash and gave increased yields of tar and levoglucosan, but the levoglucosan yields [9 mf wt.%] are still not close to those of cellulose.

Table 4.4: Effect of washing prior to vacuum pyrolysis of cellulose at 400°C

	mf wt.% dry feed basis, mf wt.% cellulose basis in []			
Substrate	Ash	Char	Tar	LG
Cottonwood				
Extracted and water washed	0.59	16	47	3 [6]
1% H_2SO_4 wash	<0.05	12	52	9 [20]
Cottonwood lignocellulose				
H_2SO_4 washed, filtered, washed to pH7	<0.05	18	71	34 [57]
Cottonwood holocellulose				
water washed	0.87	21	21	1 [1]
1% NaOH, then 1% H_2SO_4 washes	<0.05	9	65	29 [51]
Newsprint				
Untreated	--	12	39	2
1% H_2SO_4 wash	--	19	43	15
1% HCl wash	--	14	56	19

Cottonwood lignocellulose [56% cellulose] was produced by hydrolysing cottonwood with dilute sulphuric acid to remove xylan [part of the hemicellulose component]. The resultant lignocellulose was then washed with sulphuric acid to ensure removal of inorganic material and washed with water to neutrality. Pyrolysis of this resulted in increased yields of char, tar and levoglucosan, which was caused by the absence of inorganic material. The yield of levoglucosan was comparable to that of water washed CF11 cellulose [Table 4.3].

Cottonwood holocellulose [59% cellulose] was produced by removing the lignin from the lignocellulose using an acid chlorite treatment. It is possible that some of the chlorite remained in the substrate, hence the increased ash content. Since this holocellulose was produced from cottonwood which had already had the xylan component removed, it is likely that it is almost pure cellulose. The isolated holocellulose had an ash content of 0.87% and so pyrolysis resulted in lower yields of tar and levoglucosan than untreated cottonwood.

Pre-treatment of the holocellulose was carried out by first alkali washing and then acid washing, which reduced the ash content to less than 0.05%. Pyrolysis of pre-treated holocellulose resulted in increased yields of tar and levoglucosan compared to untreated holocellulose. Yields of tar are higher than for untreated CF11 cellulose, but levoglucosan yields are the same.

It is interesting to note that cottonwood treatments which used sulphuric acid at some stage resulted in pyrolysis liquids containing high concentrations of levoglucosan. It would appear that sulphuric acid hydrolysis of cottonwood followed by washing with sulphuric acid is the most effective treatment [of those tested above] for the production of levoglucosan.

Pyrolysis of untreated newsprint resulted in low yields of tar and levoglucosan. Pre-treatment using sulphuric or hydrochloric acid washes resulted in increased yields of tar and levoglucosan. This again suggests that the increase in levoglucosan is affected by the presence of acids as well as the mineral content. The results do not mention the ash content of the newsprint, either untreated or pre-treated.

Richards et al. (90) have also investigated the presence of natural ash on the products of cellulose pyrolysis. Using cellulose from a variety of sources and with a range of chemical treatments and additives they investigated the chemical forming mechanisms in cellulose. All experiments were conducted using vacuum pyrolysis (113). Richards notes that the formation of volatile products occurs from two competing pathways, which produce high yields of levoglucosan [LG] or glycolaldehyde [GA also known as hydroxyacetaldehyde, HA] respectively. The pathway selection is influenced by temperature [as described in Section 3.4.1] and also by the presence of metal salts. The formation of levoglucosan typically occurs at low temperatures [400-500°C] while the production of hydroxyacetaldehyde occurs at higher temperatures [500-600°C] and is promoted by the presence of metal salts.

From Table 4.5 it is evident that both Whatman 41 and CF11 cellulose, pyrolysed at 400°C, gave very similar yields of levoglucosan and glycolaldehyde. Therefore they must be of similar quality and contain similar amounts of inorganic elements. Vacuum pyrolysis of CF11 at three different temperatures produced little change in the yield of levoglucosan or glycolaldehyde. The removal of virtually all metal salts by acid washing resulted in a large increase in the yield of levoglucosan and a subsequent decrease in the yield of glycolaldehyde.

Table 4.5: Table of major volatile products from vacuum pyrolysis of low ash celluloses

Sample	ppm Na	ppm Ca	Temperature [°C]	Yield [mf wt.%] Tar	LG	GA
Whatman 41	30	5	400	68	38	1.9
Whatman CF11	28	15	500	76	42	2.3
Whatman CF11	28	15	400	70	37	1.9
Whatman CF11	28	15	350	71	41	1.4
Acid washed CF11	d	d	350	84	55	<0.5
Cotton Hydrocellulose	d	d	350	89	61	<0.1

d - some detected, but on limits of detectability of ICAPS

Work carried out by Raveendran et al. at the Indian Institute of Technology specifically investigated the effect of ash on the products of pyrolysis from 13 Bombay feedstocks (114). The feedstocks, which were used are shown in Table 4.6 along with component analysis. The study had 2 phases, the first was to demineralise the biomass and the second was to produce a synthetic biomass. Both demineralised and synthetic types were then assessed by thermal analysis [TGA - thermogravimetric analysis and DTG. - differential thermogravimetric analysis] and pyrolysis.

The demineralised biomass was produced using a two stage process. In the first stage biomass particles in the range 100 to 250mm were treated with 10% HCl at 60°C for 48h with constant stirring. The second stage used 5% aqueous NaOH for 1h at 90°C to further remove minerals, specifically those with a high silica content.

The use of such large particles [100 to 250mm] may have hindered the removal of mineral matter from the biomass. It is most likely that a mistake was made during publication and particle sizes of 100-250μm were used. It is unlikely that a 48 hour soaking period, even at 60°C, would have been long enough for the dilute acid to permeate into the large biomass particles and react with the ash component.

Table 4.6: Component analysis of biomass [mf wt.% basis] (114)

	Holocellulose	Cellulose	Hemicellulose	Lignin	Extractives	Ash	K [ppm]
Bagasse	65.0	41.3	22.6	18.3	13.7	2.9	2682
Coconut coir	67.0	47.7	25.9	17.8	6.8	0.8	2438
Coconut shell	67.0	36.3	25.1	28.7	8.3	0.7	1965
Coir pith	40.6	28.6	15.3	31.2	15.8	7.1	26283
Corn cob	68.2	40.3	28.7	16.6	15.4	2.8	9366
Corn stalks	63.5	42.7	23.6	17.5	9.8	6.8	32
Cotton gin waste	90.2	77.8	16.0	0.0	1.1	5.4	7094
Groundnut shell	55.6	35.7	18.7	30.2	10.3	5.9	17690
Millet husk	50.6	33.3	26.9	14.0	10.8	18.1	3860
Rice husk	49.4	31.3	24.3	14.3	8.4	23.5	9061
Rice straw	52.3	37.0	22.7	13.6	13.1	19.8	5402
Subabul wood	65.9	39.8	24.0	24.7	9.7	0.9	614
Wheat straw	55.8	30.5	28.9	16.4	13.4	11.2	28930

Synthetic biomass was prepared by mixing individual biomass constituents, that is cellulose, lignin, xylan, extractives and ash in the proportions shown in Table 4.6. Extractives were isolated from each biomass type by standard methods [TAPPI T 11m]. The ash was isolated from each biomass type by burning in a muffle furnace. It is unclear whether the other individual components were isolated from the specific biomass type or were supplied from a stock of cellulose, hemicellulose, lignin and xylan. Hemicellulose and lignin are specific to their biomass type and even isolation from that biomass type would produce a component that was different to the original proto-hemicellulose or proto-lignin.

Thermal analysis of feedstocks, which were untreated, demineralised, synthetic and synthetic without ash, was carried out using dynamic thermogravimetric analysis [TGA] at a heating rate of 50K/min in nitrogen flow. From these studies it was found that in most cases the removal of the mineral matter increased the yield of volatile matter, the maximum rate of devolatilisation and the initial decomposition temperature. With the feedstocks rice husk, groundnut shell and coir pith these effects did not occur. It was found that these biomass types had a high lignin content and high mineral matter [notably potassium] before demineralisation. Wheat straw also had a high potassium content, but because of the lower lignin content the effect was less significant. Thermal analysis of original biomass compared to synthetic biomass gave good matches, the

TGA and DTG. curves matching closely. A similar comparison between de-ashed and synthetic biomass without ash also gave a good correlation.

Pyrolysis was carried out on untreated and deionised samples of coir pith, corn cob, groundnut shell, rice husk and wood in a packed bed pyrolyser at 773 K. Nitrogen gas was used as carrier gas and volatiles were collected and quenched in a train of ice water cooled flasks. The non-condensable gases were measured in a gas meter. After cooling the char remaining in the reactor was weighed and the volatiles obtained by difference. The liquid was weighed directly from the flasks.

Table 4.7: Influence of ash on pyrolysis of de-ashed feedstocks

		Yield [mf wt.%]			
	State	Volatiles	Char	Liquid	Gas
Coir pith	U	70.5	29.5	29.4	41.0
	D	68.7	31.3	36.2	32.5
Groundnut shell	U	72.9	27.1	40.5	32.5
	D	72.5	27.5	45.9	26.6
Rice husk	U	82.7	17.3	41.2	41.5
	D	75.6	24.4	57.4	18.2
Corn cob	U	79.9	20.1	37.4	42.5
	D	87.1	12.9	43.4	43.6
Wood	U	80.7	19.3	22.6	58.0
	D	86.4	13.6	40.1	46.4
Relative change caused by demineralisation					
Coir pith		-2.4	5.5	23.1	-20.8
Groundnut shell		-0.5	1.5	13.4	-9.1
Rice husk		-8.6	41.3	39.3	-56.2
Corn cob		8.9	-35.6	16.0	-3.2
Wood		7.1	-29.8	76.9	-20.1

U - Untreated D - Demineralised

The results of the pyrolysis experiments are shown in Table 4.7. As shown in the TGA experiments, coir pith, groundnut shell and rice husk gave increased char yields after demineralisation. With other feedstocks the char yields decreased with demineralisation. This is more evident from the relative change. Demineralisation gave an increase in liquid yields in all cases.

The above experiments produced some interesting results, which are relevant to this work. Firstly, thermal analysis has shown that de-ashed feedstocks produce higher yields of volatile products than untreated feedstocks. Exceptions to this are feedstocks containing high levels of potassium and/or zinc in conjunction with high lignin contents. Although no previous work has been found relating to zinc, it seems likely that feedstocks containing high yields of potassium would be prone to secondary reactions. Even though de-ashing may have removed most of the potassium, only a small amount is required to significantly affect pyrolysis yields [or thermal analysis results].

Secondly, combining cellulose, hemicellulose, lignin and ash has produced synthetic feedstocks. These behaved similarly to natural feedstocks in thermal analysis. Unfortunately, pyrolysis experiments do not appear to have been conducted on synthetic biomass. The pyrolysis experiments that were conducted appear to be slow pyrolysis in a furnace and not true fast pyrolysis reported in Chapter 3 and used in this work [Chapters 7 and 9]. It would be interesting to compare more detailed analysis of the true fast pyrolysis products from natural biomass against those from synthetic biomass. Although this is beyond the scope of this work it is recommended that this type of study is repeated in the future using fast pyrolysis to assess the effectiveness of synthetic and de-ashed biomass types.

4.3.3 Acid Hydrolysis

The difference between acid washing and acid hydrolysis is that acid washing usually involves less concentrated acids [typically less than 5 mf wt.%] at ambient conditions [i.e. room temperature and pressure] whereas acid hydrolysis usually involves more severe conditions [i.e. more concentrated acid, boiling and sometimes pressure]. Acid hydrolysis tends to dissolve [hydrolyse] some of the biomass components [i.e. all hemicellulose, extractives and ash], whereas acid washing will generally remove less of the components [i.e. some hemicellulose, but all ash and extractives]. This definition is typical for pre-treatment methods carried out prior to fast pyrolysis.

The pulping and enzymatic hydrolysis industries utilise chemical methods to remove/dissolve certain biomass components. However, the conditions utilised are much more severe than would be required for fast pyrolysis. The pulping industries method of component removal is summarised in Section 4.3.3.1. and the most common pre-treatment methods used in the enzymatic hydrolysis industry described in Section 4.3.3.2.

4.3.3.1 Pulping

There are two main types of chemical pulping in operation today, the sulphite process and the Kraft process. The sulphite process uses an acidic process to dissolve the lignin and carbohydrates associated with the cellulose while leaving the cellulose fibres intact. This is thought to occur in two steps, first the lignin is sulphonated to form a solid lignosulphonic acid, which is then rendered soluble by hydrolysis and extracted from the wood structure. The degree of delignification is proportional to the acid concentration and the presence of cations (e.g. Ca, Mg or Na). The process typically lasts for 4-12 hours and is carried out at temperatures between 135 and 150°C, at pressure and pH in the range 1.5-2.5. Further details can be found in Farmer (16) and Wenzl (15). The sulphite process can only be applied to hardwoods since some of the extractives present in softwoods inhibit the process.

The Kraft process is an alkaline process and can be applied to all species of wood, since the extractives in softwoods, which cause problems in the sulphite process, are dissolved in the alkaline sulphate liquor as sodium salts and do not interfere with the delignification reaction. The active ions in the Kraft [or sulphate] process are the hydroxyl ion and the hydrosulphide ion. Ether groups in the lignin are hydrolysed by the alkali to smaller groups, which have are reactive with the hydrosulphide ion. Alkalis have a strong swelling effect on the wood, and consequently the liquor penetrates into the wood faster than in the sulphite process. The process is usually carried out at temperatures greater than 160°C, as below this the delignification reactions are too slow. At higher temperatures the lignin is solubilised more rapidly, but there is also solubilisation of the cellulose. At 270°C both lignin and cellulose are believed to solubilise at the same rate (17). It is therefore important to run at as low a temperature as is economically feasible to prevent degradation of the cellulose.

4.3.3.2 Enzymatic Hydrolysis

Enzymatic hydrolysis is a biochemical process which utilises enzymes to break down selected biomass components to sugar. The process is restricted by three factors. Firstly, it is a surface reaction and so requires that the biomass has a large surface area; this invariably means reducing the particle size as much as is economically possible. Secondly, the crystallinity of the cellulose reduces susceptibility to enzymes. Finally, the presence of a lignin-hemicellulose shield surrounding the cellulose fibres restricts the action of enzymes (115). Therefore pre-treatment is often applied to the biomass to reduce these restrictions prior to enzymatic hydrolysis.

A typical enzymatic pre-treatment to remove the lignin/hemicellulose shield and reduce the cellulose crystallinity would use sulphuric acid, temperatures of 140-180°C and pressures up to 13.5bar. Low solid to liquid ratios are normally used [typically 10% by volume] so that mechanical stirrers can be used (116, 117).

4.3.4 Hydrolysis as a Pyrolysis Pre-treatment

It will be shown in the following section that hydrolysis as a fast pyrolysis pre-treatment method is used partly to remove some of the components [ash, extractives and hemicellulose], but mainly to condition the cellulose towards the production of sugars [especially levoglucosan]. Hydrolysis may also improve the accessibility of cellulose by reducing its crystallinity [degree of polymerisation] and also by removing hemicellulose, which may be protecting cellulose from some of the chemical reactions.

Work carried out by Piskorz et al. using two types of cellulose found that 5% sulphuric acid at 90°C had a significant effect on the pyrolysis product and chemical yields. The treatment removed all the ash from an already low ash feedstock, but more importantly did not reduce the degree of polymerisation (82). This is important since it has been suggested previously that the status of the cellulose may have an effect on the chemical yields. Results from fluidised bed fast pyrolysis of these pre-treated celluloses are shown in Table 4.8.

The fast pyrolysis of cellulose produces high yields of organics and chemicals. Acid hydrolysis of the cellulose increased the yield of organics and also decreased the yields of char and gas. Piskorz suggests that the acid hydrolysis was responsible for suppressing some of the decomposition modes. This is evident, since the yields of hydroxyacetaldehyde, formic and acetic acids have been severely reduced. The pre-treatment appears to have brought about increased yields of all sugar components.

Table 4.8: Product and chemical yields from fast pyrolysis of untreated and acid hydrolysed cellulose

	Cellulose SS144	Pre-treated SS144	Cellulose Avicel	Pre-treated Avicel
Temperature [°C]	500	502	500	503
Ash	0.062	0.00	<0.01	0.00
DP	164	186	227	222
Yields [mf wt.%]				
Organics	72.5	83.5	87.1	86.3
Water	10.8	6.1	3.1	
Char	5.4	1.3	2.5	0.7
Gas	7.8	3.9	8.9	3.3
Hydroxyacetaldehyde	15.3	6.2	8.6	0.43
Levoglucosan	7.0	31.8	26.9	38.41
Cellobiosan	4.0	11.5	10.1	5.6
Glucose	1.0	1.8	2.1	2.0
Fructose	2.0	3.0	4.7	2.7
Glyoxal	3.5	5.5	6.5	2.1
Methylglyoxal	0.8	1.3	0.23	0.30
Formic acid	5.5	1.9	3.8	1.5
Acetic acid	4.9	0.1	1.4	0.03
Ethyleneglycol	1.7	0.02	0.56	0.00
Formaldehyde	1.2	0.94	0.72	0.24
Acetol	2.2	0.12	0.04	0.02
Anhydroglucofuranose		5.5		7.0
Oligosaccharides		5.3		5.7

The untreated cellulose shown in Table 4.8 has very low levels of ash [virtually zero for avicel]. Following acid hydrolysis there is no ash in either cellulose. The yield of levoglucosan has been significantly increased at the expense of hydroxyacetaldehyde. However, due to the low levels of ash contained in the untreated cellulose it seems more likely the hydrolysis has brought about a change in the cellulose structure or that residual acid remains in the cellulose to catalyse reactions. This behaviour is similar to that observed by Shafizadeh with pyrolysis of Douglas fir wood containing sulphuric acid (59).

A similar acid hydrolysis treatment to that used above on cellulose was tested with IEA poplar wood. The results are shown in Table 4.9. This treatment was severe enough to remove most of the hemicellulose [evident from the increased cellulose concentration] and ash. Similar results can be seen to those of cellulose, increased yields of organics and sugars, most notably levoglucosan and decreased yields of low molecular weight aldehydes, ketones and acids.

Table 4.9: Product yields from fast pyrolysis of untreated and acid hydrolysed IEA poplar

	Untreated	Pre-treated
Temperature [°C]	497	501
Vapour res. Time [s]	0.46	0.45
Moisture content [%]	3.3	16.5
Ash	0.46	0.04
Cellulose [%]	49.1	62.8
Yields [mf wt.%]		
Organics	65.8	79.6
Water	12.2	0.9
Char	7.7	6.7
Gas	10.8	6.4
Hydroxyacetaldehyde	10.03	0.37
Levoglucosan	3.04	30.42
Cellobiosan	1.3	5.68
Glucose	0.4	1.89
Fructose	1.31	3.89
Glyoxal	2.18	0.11
Methylglyoxal	0.65	0.38
Formic acid	3.09	1.42
Acetic acid	5.43	0.17
Ethyleneglycol	1.05	
Formaldehyde	1.16	0.8
Acetol	1.40	0.06
Anhydroglucofuranose	2.43	4.50
Oligosaccharides	0.7	1.19
Lignin [aromatics]	16.2	19.0

Scott et al. continued with this work by examining the effect of using different acids (94). From Table 4.10, both HCl and H_2SO_4 were effective in removing ash from the samples. Poplar wood was boiled in sulphuric acid at 100°C for pre-treatment 1. It is evident from the increase in cellulose concentration [compared to no pre-treatment] that approximately 35% of the biomass must have been removed. Thus it is likely that the hemicellulose component has been removed. The pre-treatment increased the yield of levoglucosan and decreased the yield of hydroxyacetaldehyde. This is most likely an effect of the reduced ash level, but may also be due to the catalytic effect of residual sulphuric acid [as suggested by Shafizadeh (59)].

Table 4.10 Effects of pre-treatment on pyrolysis yields from poplar wood using a range of acids, 475-490°C, 0.5 s gas/vapour product residence time (94)

Pre-treatment	none	1 5% H_2SO_4, 100°C, 2h	2 3.7% HCl 100°C, 2h	3 0.5% HCl 165°C, 6min	4 3, then 1 100°C, 2h
Ash, [mf wt.%]	0.46	0.04	0.05	0.85	0.30
Moisture	4.6	6.0	15.9	25.4	16.9
Cellulose	49.1	67.0	67.8	65.4	69.2
Yields,[mf wt.% feed]					
Gas	10.8	6.4	8.7	7.6	6.4
Char	7.7	6.3	5.5	10.1	10.5
Water	12.2	6.3	--	2.9	5.2
Organic liquids	65.8	73.6	85.4	78.4	75.0
Closure	96.5	92.6	99.6	98.9	97.1
Hydroxyacetaldehyde	10.0	0.9	6.5	9.1	0.9
Levoglucosan	3.0	28.7	17.5	4.5	30.1
Other sugars	8.3	12.5	17.1	5.1	18.8
Pyrolytic lignin	16.2	19.2	25.7	18.8	17.9
HA/LG ratio	3.33	0.03	0.37	2.02	0.03
LG cellulose basis	6.11	42.84	25.81	6.88	43.50

Poplar was boiled in hydrochloric acid for two hours for pre-treatment 2. It is evident that the hemicellulose fraction has been removed. In this case, the yields of levoglucosan have increased in comparison to those obtained from untreated poplar, but not as much as in the case of pre-treatment 1. This again implies that sulphuric acid has a catalytic effect, which is supported by Scott. The feedstock was more than 2.5 times wetter than pre-treatment 1, which may have resulted in slower heating of the poplar and possibly more secondary reactions resulting in the lower yield of levoglucosan.

Pre-treatment 3 was carried out in a semi-commercial pilot plant using a plug flow reactor with a residence time of 6 minutes. Again, much of the hemicellulose component appears to have been removed. It is possible that some of the hydrochloric acid has remained in the wood since the ash content has increased. The yields of levoglucosan and hydroxyacetaldehyde are similar to those of untreated poplar. The moisture content of the feedstock was 25.4%, which may have again resulted in slower heating and possibly secondary reactions.

Pre-treatment 4 was a combination of pre-treatments 3 and 1. The hemicellulose component has been removed and the ash content has been decreased but not by as much as pre-treatment 1. The moisture content was similar to that of pre-treatment 2, but does not appear to have had any adverse effect since the yield of levoglucosan is 30.1 mf wt.%. It would appear that the initial high temperature hydrochloric acid treatment may have loosened the cellulose structure thereby increasing the efficiency of the sulphuric acid treatment. It would be interesting to see other experiments with 2 or more pre-treatment stages.

Table 4.11: Product yields from fast pyrolysis of de-ionised IEA poplar (94)

	Untreated	De-ionised
Temperature [°C]	497	530
Moisture content [%]	3.3	0
Yields [mf wt.%]		
Organics	65.8	60.5
Water	12.2	18.25
Char	7.70	2.50
Gas	10.8	14.13
Hydroxyacetaldehyde	10.03	3.35
Levoglucosan	3.04	9.33
Cellobiosan	1.3	4.92
Glucose	0.4	0.94
Fructose	1.31	1.81
Glyoxal	2.18	2.86
Acetic acid	5.43	0.67
Anhydroglucofuranose	2.43	1.12
Lignin [aromatics]	16.2	17.8

Since the above pre-treatments all removed the hemicellulose component, Scott et al. continued their study of pre-treatment to see if it was necessary to remove the hemicellulose component or whether a milder treatment would be just as effective at improving sugar yields. The poplar was de-ionised by a continuous percolation of 0.1% sulphuric acid through a packed wood column (94). The wood was then washed until acid free using de-ionised water. The results shown in Table 4.11 show that de-ionisation gave significant increases in the yield of levoglucosan and other sugars with decreases in the yields of hydroxyacetaldehyde and other non-sugar chemicals. Thus similar results to acid hydrolysis were obtained by a much less severe technique, although in slightly lower yields.

Thus it would appear that the presence of hemicellulose is not detrimental to the pyrolysis of biomass, as was suggested by Shafizadeh and Stevenson (83). However, ash tends to be associated with the hemicellulose component; thus its complete removal will ensure that most of the ash is also removed.

4.4 CONCLUSIONS

Component removal by pre-treatment has been found to significantly improve the yield of sugars in pyrolysis liquids, most notably levoglucosan. The soaking of biomass in water for periods of 24 hours or more has been found to remove almost 50% of the ash component. Subsequent pyrolysis of cellulose and biomass containing little or no ash has shown that ash has a significant effect in suppressing the production of sugars. However, no pyrolysis experiments have been carried out on biomass which has only been washed in water. Therefore this has been investigated and the results and conclusions reported in Chapters 8 and 9.

Pure cellulose containing very low levels of ash has been pyrolysed and produced high yields of organics. Acid hydrolysis to remove this low level of ash resulted in higher yields of organics, but more importantly a shift in liquid products from low molecular weight aldehydes, ketones and acids to the production of sugars.

Acid hydrolysis of IEA poplar has resulted in similar effects to those observed in cellulose. That is to say, increased yields of sugar at the expense of aldehydes, ketones and acids. It has also been found that less severe techniques [de-ionisation], which only remove ash and leave hemicellulose intact, can be almost as effective as complete hemicellulose hydrolysis in improving product yields. Therefore the influence of the de-mineralising process, mineral acid type, concentration, temperature and contact time have been investigated and the results and conclusions reported in Chapters 8 and 9.

Two stage pre-treatment processes gave improved pyrolytic yields, especially levoglucosan. It is believed that two stage processing may allow less severe conditions to be used to achieve the same level of component removal or improved levoglucosan yields. Experiments have been conducted using two-stage processing and are reported in Chapters 8 and 9 along with results and conclusions.

5. ADDITIVES

This chapter reviews the effect of biomass additives on pyrolysis products with particular reference to selectively increasing the yields of specific chemicals in the fast pyrolysis liquid.

Much of the literature involving the addition of substances to biomass investigates the effects by thermogravimetric [TGA] studies involving slow heating rates. Only a few of the literature sources investigate the effects of additives on the yields of chemicals in the pyrolysis liquid; hence, these will be the primary focus.

5.1 INTRODUCTION

Elements or compounds which are introduced into the biomass matrix by a variety of means are categorised as additives. Additives can be further divided into four groups, acidic, basic, neutral and inorganic. The individual effects of these additives are not clearly defined, since in the literature experiments [usually pyrolysis, TGA, or others] have been conducted over a wide range of conditions [i.e. slow and fast heating rates, vacuum and high pressure and temperatures from 300-900°C]. In all cases it was found that the introduction of additives typically led to a reduction in pyrolysis liquid yields and an increase in char.

Table 5.1 is a summary of additives that are included in this literature review. Table 5.2 is a summary of the effects of these additives and also a brief description of the conditions that the experiments were carried out under. More detailed explanation of each entry in Table 5.2 will be given later in this Chapter.

Table 5.1: Summary of additives

Acidic additives	Basic additives	Neutral additives	Inorganic additives
$(NH_4)_2HPO_4$	NaOH	NaCl	Ca
$(NH_4)H_2PO_4$	K_2CO_3		K
H_3PO_4	KOH		Li
$ZnCl_2$	$Ca(OH)_2$		$CuAc_2$
$SbCl_3$	$Ca(Ac)_2$		$CuCl_2$
$FeCl_3$			$FeAc_2$
HCl			$FeCl_2$
HNO_3			$FeSO_4$
H_2SO_4			
NH_4SO_4			
$CoCl_2$			

Table 5.2: Summary of effects of additives on pyrolysis

Additive	Ref.	Conditions	Effects
H_3PO_4	(81)	350-840°C	Good LGO yields, thought to lower cellulose decomposition temperature.
$(NH_4)_2HPO_4$	(81)	350-840°C	as H_3PO_4
$(NH_4)H_2PO_4$	(120)	Vac	as H_3PO_4
$SbCl_3$	(121)	Vac	Increase char, decrease volatiles, promotes dehydration, thus forms water to hydrolyse glucosidic bonds.
$ZnCl_2$	(121)	Vac	as $SbCl_3$
	(122)	TGA	Increase furfural
$FeCl_3$	(118)	350°C	Promotes dehydration and char, increase furfuraldehyde, decrease levels of furfurylic alcohol and hydroxypropanone.
	(123)	500°C	Promotes dehydration and char, decrease in acetic acid.
$CoCl_2$	(123)	500°C	Promotes dehydration and char, decrease in acetic acid.
HCl	(124)	Vac	In high conc. reduce LG, increase HA, in low conc. Promote LG
HNO_3	(124)	Vac	Improve LG any conc.
H_2SO_4	(124)	Vac	as HCl
	(89)	495°C	Following de-ionisation improved LG yield.
NH_4SO_4	(89)	530°C	Following de-ionisation improved LG yield.

NaOH	(118)	350°C	Promotes dehydration and char, increase hydroxypropanone and gas, decrease furaldehyde.
K_2CO_3	(125)	400-700°C	Increase char
	(128)	500°C	Increase HA [up to 17%]
	(126)	High T	Higher H_2/CO ratio, decrease HC's
KOH	(128)	500°C	Increase HA.
$Ca(Ac)_2$	(128)	500°C	Increase HA
$Ca(OH)_2$	(89)	450-600°C	Liquids at lower temp. similar comp., increase gas, ethylene and methane, char contained more C, less O.
NaCl	(129)	Vac	Using cellulose gave increase char and low MW prods, esp. HA, hydroxyacetone and formic acid, decrease LG.
Ca-exchange	(129)	Vac, 250°C	Reduced rate of wt. loss, decrease volatiles CO_2 and formic acid.
K-exchange	(129)	Vac, 250°C	Increase in CO_2 and methanol, K catalyses lignin reactions ?
K	(130)	Vac, 250°C	Increase char, decrease tar, low LG yields.
Li	(130)	Vac, 250°C	similar to K
Ca	(130)	Vac, 250°C	similar to K
$CuAc_2$	(130)	Vac, 250°C	Reduced rate of wt. loss, decrease volatiles CO_2 and formic acid. With acid washing increase LG, decrease char.
$CuCl_2$	(130)	Vac, 250°C	With acid washing increase LG, decrease char.
$FeAc_2$	(130)	Vac, 250°C	Increase char, LG as AW
$FeCl_2$	(130)	Vac, 250°C	Increase char, LG half AW
$FeSO_4$	(130)	Vac, 250°C	Increase char, LG half AW, >2% LGO. With AW and cellulose feed gave higher LGO.

HC's - hydrocarbons AW - acid washed LG - levoglucosan Vac - vacuum
HA - hydroxyacetaldehyde LGO - levoglucosenone TGA - thermogravimetric analysis

5.2 ACIDIC ADDITIVES

Overall, Beaumont and Schwob (118) and Shafizadeh (88) are in agreement that acidic additives promote dehydration and charring reactions during fast pyrolysis. More specifically, trace amounts of acidic additives catalyse the transglycosylation reaction of cellulose, resulting in the formation of levoglucosan [1,6-anhydro-ß-D-glucofuranose]. Thus feedstocks which have been acid pre-treated may contain some residual acid and behave in this way. In larger concentrations, acidic additives can bring about dehydration of the anhydro sugar accompanied with hydrolysis and rearrangement reactions producing levoglucosenone, 5-hydroxymethyl-2-furaldehyde, 2-furaldehyde, levulinic acid and other dehydration products.

5.2.1 Phosphates

The role of phosphoric acid or compounds containing the phosphate group has been found by a number of researchers to produce interesting yields and novel chemicals in the liquids from fast pyrolysis. Levoglucosan is normally expected from the fast pyrolysis of pre-treated biomass or cellulose; however, pyrolysis of biomass treated with phosphoric acid tends to produce levoglucosenone rather than levoglucosan.

Fung pyrolysed cellulose [Whatman no. 1 filter paper] over the temperature range 350-840°C (81). Untreated cellulose gave good yields of levoglucosan, whereas cellulose treated with H_3PO_4 gave a maximum yield of 34% levoglucosenone [LGO] at 430°C; a similar effect was observed with the pyrolysis of cellulose treated with ammonium dihydrogen ortho phosphate [$NH_4H_2PO_4$]. Fung expected the phosphoric group to catalyse the degradation of levoglucosan to levoglucosenone. However, when pyrolysed, levoglucosan was found to decompose almost completely to give char, water, CO, CO_2 and only a small amount of levoglucosenone. From this, Fung concluded that phosphoric acid lowers the decomposition temperature of cellulose and changes the decomposition reaction path to give levoglucosenone instead of levoglucosan. Thus it would appear that levoglucosenone is a direct decomposition product of cellulose.

The impregnation of phosphoric acid and ammonium hydrogen phosphate [$(NH_4)_2HPO_4$] into cellulose was also investigated by Shafizadeh (119). Shafizadeh concluded that addition of an acidic catalyst or slow heating promotes the dehydration and charring reactions, favouring the production of char, water and CO_2. Shafizadeh's work was conducted at relatively slow heating rates and also under vacuum. These conditions could have lead to different products compared to fast pyrolysis at atmospheric pressure.

5.2.2 Chlorides

The effects of 5% $SbCl_3$ on the vacuum pyrolysis of cellulose were investigated by Shafizadeh (120). It was found to increase the yield of D-glucose and char and to decrease the yields of tar and levoglucosan. $SbCl_3$ acts as a Lewis acid promoting the hydrolysis of the glucosidic bonds; hence, the increase in the cellulose monomer, D-glucose. More free sugar is formed as $SbCl_3$ generates water by dehydration reactions; it also promotes the decomposition of the molecule over an extended temperature range. Shafizadeh also found similar results for $ZnCl_2$ (119, 121).

Pavlath and Gregorski also examined the effects of $ZnCl_2$, using thermogravimetric analysis [TGA] on untreated and treated carbohydrates (122). They concluded that acidic additives gave furfural as the most prevalent product. From these conclusions it would appear that the carbohydrate feedstock contained high levels of hemicellulose, since this is generally the source of furfural.

The impregnation of acidic additives was also examined by Beaumont and Schwob (118). Beech wood was impregnated with 5% $FeCl_3$ and flash pyrolysed at 350°C. The additive was found to promote water formation and increase char yield. The pyrolysis liquid contained increased yields of furaldehyde and decreased yields of hydroxypropanone and furfurylic alcohol. These experimental results concur with the research of Shafizadeh, Pavlath and Gregorski, who are in agreement that an acid catalyst promotes dehydration and furaldehyde formation, whereas a basic catalyst favours gasification and charring.

In order to assess the effects of a number of acidic additives, Font et al. flash pyrolysed almond shells at 500°C using $CoCl_2$ at concentrations of 3% and 6.4% and $FeCl_3$ at 3% (123). Acidic additives produced an increase in char and water [see Table 5.3], especially 3% $CoCl_2$, which produced an increase in water from 17.0 to 23.6%. These additives also increased the yields of furfural and acetic acid. The key pyrolysis products [i.e. levoglucosan, hydroxyacetaldehyde and levoglucosenone] were not analysed or detected. These chemicals are probably one of the best indications of the type of pyrolysis reaction occurring. If levoglucosan or levoglucosenone yields are high it is an indication of depolymerisation reactions; high yields of hydroxyacetaldehyde indicate fragmentation reactions. The gas yields are lower in all cases, which could indicate that fragmentation reactions are not promoted since they tend to result in higher gas yields.

Table 5.3: Effect of acidic additives on products from fast pyrolysis of almond shells

Additive	none	3% $FeCl_3$	3% $CoCl_2$	6.4% $CoCl_2$
Temperature [°C]	495	500	500	500
pyrolysis liquid	58.3	46.9	54.6	45.9
char	26.3	43.0	28.1	37.9
gas	14.8	10.4	13.9	12.7
Closure	99.4	100.3	96.6	96.5
Liquid composition				
water	17.0	17.8	23.6	21.1
methanol	0.95	0.54	0.50	0.70
acetaldehyde	0.18			
acetone	0.07	0.11	0.36	0.15
2-propanol	0.05	0.19	0.78	0.37
acetic acid	9.9	2.2	7.4	6.5
hydroxyacetone	1.9			
propionic acid	0.14	0.09	0.13	0.13
3-methyl-1-butanol	0.69	0.01	0.04	
1-hydroxy-2-butanone	1.3			
2-furaldehyde	0.57	3.3	3.3	5.2
dry residue [@ 120°C]	26.0	22.0	15.4	
Gas composition				
CO_2	10.2	6.1	9.1	8.1
CO	4.0	3.3	4.0	4.1
CH_4	0.60	0.93	0.80	0.54

5.2.3 Sulphates

From an investigation of the effects of demineralisation and hydrolysis pre-treatments on the products of pyrolysis, Scott et al. found that residual acid in the biomass had a profound effect on chemical yields. To examine this effect further, they introduced 0.1wt.% ammonium sulphate and 0.1wt.% sulphuric acid into poplar, which had been de-ionised in a packed wood column by a continuous percolation of 0.1wt.% sulphuric acid (89). The results shown in Table 5.4 show that de-ionisation gave significant increases in the yield of levoglucosan and other sugars with decreases in the yields of hydroxyacetaldehyde and other non-sugar chemicals. Both additives gave further increases in the yields of levoglucosan and other sugars compared to de-ionised and untreated wood. However, ammonium sulphate proved slightly better than sulphuric acid. From this it would appear that the sulphate ion does play a catalytic role in fast pyrolysis for the production of levoglucosan.

Table 5.4: Product yields from fast pyrolysis of IEA poplar containing additives

	Untreated	De-ionised	De-ionised + $(NH_4)_2SO_4$	De-ionised + H_2SO_4
Temperature [°C]	497	530	530	495
Moisture content [%]	3.3	0	3.0	7.0
Yields [mf wt.%]				
Organics	65.8	60.5	66.07	66.10
Water	12.2	18.25	16.20	17
Char	7.70	2.50	4.33	6.13
Gas	10.8	14.13	7.35	3.22
Hydroxyacetaldehyde	10.03	3.35	3.36	1.65
Levoglucosan	3.04	9.33	18.73	15.52
Cellobiosan	1.3	4.92	2.46	1.68
Glucose	0.4	0.94	0.98	1.00
Fructose	1.31	1.81	1.54	1.84
Glyoxal	2.18	2.86	2.96	2.26
Acetic acid	5.43	0.67	1.41	1.17
Anhydroglucofuranose	2.43	1.12	2.76	2.72
Lignin [aromatics]	16.2	17.8	21	23.1

5.2.4 Mineral Acids

The influence of acid impregnation on slow vacuum pyrolysis of cellulose was investigated by Julien et al. (124). Starting with α-cellulose, three batches were treated with 0.5N sulphuric, hydrochloric and nitric acids for two hours at room temperature. After this time the cellulose was washed with HPLC grade water. Throughout the washing, samples of cellulose were removed at various pH's. The amount of acid remaining in the cellulose from each of these samples was determined by direct titration.

Analysis of the pre-treated cellulose found that most of the ash in the original cellulose [0.2%] was removed by the pre-treatments [i.e. H_2SO_4 - 0.06%, HCl - 0.07%, HNO_3 - 0.02%]. Sulphuric and hydrochloric acid pre-treatments were found to incorporate sulphate and chloride ions into the cellulose. The authors do not state whether nitrate ions were detected in the cellulose from nitric acid treated cellulose. It may be that the method used for testing removed the volatile nitrate ions.

Slow vacuum pyrolysis of the samples does give an indication of the way these treatments are likely to perform under atmospheric fast pyrolysis conditions. Generally it was found that higher concentrations of acid [i.e. removed from the washing process while the pH was low] resulted in low yields of pyrolysis liquid and levoglucosan, with high yields of water, char, gas, hydroxyacetaldehyde, acetic and formic acids. Thus as the pH increased [i.e. the concentration of acid in the cellulose decreased] the yields of pyrolysis liquid and levoglucosan increased and the yields of water, char, gas, hydroxyacetaldehyde, acetic and formic acids decreased.

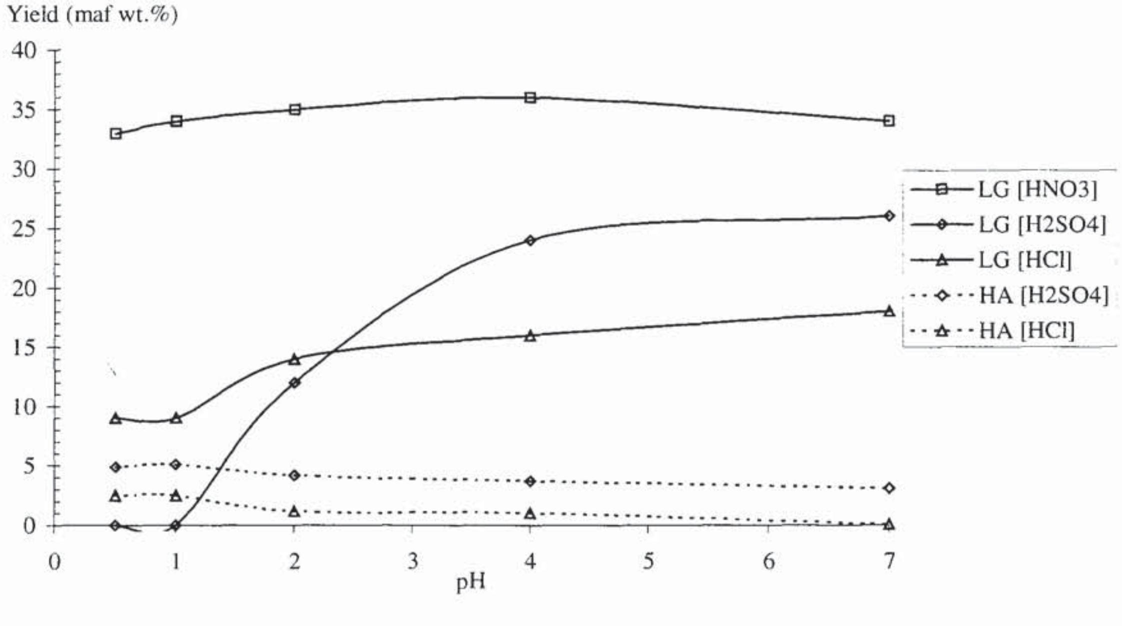


Figure 5.1: Yield of levoglucosan and hydroxyacetaldehyde as a function of pH (124)

From Figure 5.1 it can be seen that nitric acid produced the highest yields of levoglucosan. Nitric acid concentration had the least effect on the yield of levoglucosan since the yield remains relatively constant throughout. For sulphuric and hydrochloric acids the levoglucosan yield decreased with increasing concentration. Julien believes that this may be due to the residual nitric acid decomposing at low temperatures and therefore not causing undesirable side reactions, presumably because it leaves the reactor before pyrolysis begins. However, this would not be the case in a continuous fast pyrolysis reactor, since the continuous addition of fresh material into the reactor would result in the presence of volatile nitric acid or nitrate ions in the reactor vapour space.

The variation in the yield of hydroxyacetaldehyde also supports the above argument. Since cellulose containing nitric acid produced no hydroxyacetaldehyde, this suggests that the residual acid had left the reactor before pyrolysis occurred [i.e. during heating up]. Whereas with sulphuric and hydrochloric acid treated cellulose the yield of hydroxyacetaldehyde decreased as the concentration of residual acid decreased [i.e. as pH increased]. This can be seen in Figure 5.1.

5.3 BASIC ADDITIVES

Beaumont and Schwob claim that basic additives promote gasification and charring (118). Shafizadeh also found that basic additives had a profound effect on the properties and quantity of char.

5.3.1 Sodium Compounds

Pavlath and Gregorski (122) and Beaumont and Schwob (118) tested the effect of NaOH on fast pyrolysis products. Both found that unlike acidic additives [i.e. $ZnCl_2$ and $FeCl_3$], NaOH prevented the formation of furfural and increased the yields of furfuryl alcohol, hydroxypropanone and gas.

5.3.2 Potassium Compounds

The addition of basic salts to cellulose was investigated by Radlein (128). It is evident from Figure 5.2 that all of the additives tested [i.e. K_2CO_3, KOH and $Ca(Ac)_2$] increased the yields of hydroxyacetaldehyde compared to untreated cellulose. Using 0.01% K_2CO_3 increased the yield of hydroxyacetaldehyde up to 17% when fast pyrolysed at 500°C. The yield of hydroxyacetaldehyde was not increased further by increasing the concentration of K_2CO_3 to 0.1%. The anion clearly plays an important role, since hydroxyacetaldehyde yields were further reduced when the additive was changed to 0.01% KOH [in comparison to 0.01% K_2CO_3]. It is also evident that 0.1% $Ca(Ac)_2$ behaved in a similar manner to KOH. Although the anion clearly has an effect on the hydroxyacetaldehyde yield, it is unclear whether this is a direct effect or whether it modifies the action of the cation.

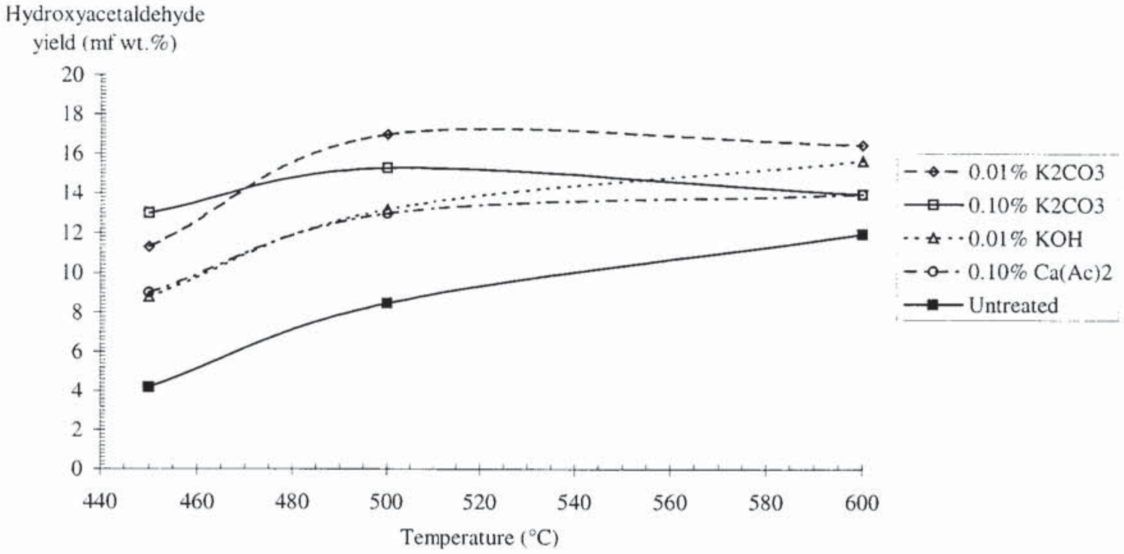


Figure 5.2: Yields of hydroxyacetaldehyde from cellulose containing additives (128)

The effect of potassium carbonate on fast pyrolysis of reed was tested by Barbooti (125). The untreated reed was analysed and was found to contain a relatively high concentration of natural catalyst [Na - 1850ppm, K - 900ppm]. The reed was soaked in K_2CO_3 solution to give a 10% concentration in the biomass. It was then flash pyrolysed over the temperature range 400-700°C, products were passed through a cyclone and collected in a water condenser, after which the gases were collected in a sampling bulb for gas analysis. Most attention was paid to the analysis of the gases rather than the liquid product. The additive resulted in the production of a larger amount of hydrogen in the form of ethane at the expense of ethylene. It is expected that the addition of potassium in such high concentrations would give high yields of hydroxyacetaldehyde similar to the above results of Radlein (128). However, such high concentrations of potassium would probably promote char formation.

Utioh et al. pyrolysed grain screenings at high temperatures [600-800°C] (126). Due to the high temperatures, the reactions occurring are more likely to be gasification rather than fast pyrolysis. Grain screenings impregnated with 15 wt.% K_2CO_3 gave an increased yield of syngas with a H_2/CO ratio of 4.1. The additive was also found to lower the yields of hydrocarbons. Mass balance closures for these experiments were only 65-77%. This is probably due to the products being collected in water, which is known to be an inefficient product collection method.

5.3.3 Calcium Compounds

Scott et al. investigated the effects of lime addition [$Ca(OH)_2$] to the products of pyrolysis using various feedstocks (145). Their findings were that similar pyrolysis liquid yields were obtained as untreated feedstocks, but at a 50°C lower temperature. Gas yields were found to have increased, with the yield of ethylene doubling and the yield of methane increasing by 50%. The char was analysed and contained more carbon and less oxygen than char from untreated material.

5.4 NEUTRAL ADDITIVES

5.4.1 Sodium Chloride

Richards et al. vacuum pyrolysed cellulose with varying amounts of sodium chloride [NaCl] (34). Their findings were that addition of NaCl increased char and low MW products especially glycolaldehyde, hydroxyacetone and formic acid; it also decreased the yield of levoglucosan.

Table 5.5 shows the effect of small quantities of sodium chloride additive on the volatile pyrolysis products (90). The introduction of a low level [0.01%] of sodium chloride was enough to reduce the levoglucosan yield and give a subsequent increase in GA yield. Richards states that this level of salt addition is equivalent to one formula unit of salt per 3640 anhydroglucose units. Increase in concentration beyond 0.05% has little effect on the products given below; however, it should be noted that higher levels [around 10%] of sodium chloride have induced the formation of dihydroxy and trihydroxy benzenes (127).

Table 5.5: Percentage yield of volatile products from vacuum pyrolysis of acid washed CF11 cellulose at 350°C with sodium chloride additive

Sodium Chloride [%]	0	0.01	0.05	0.10	0.50	1.00
Tar	84	66	26	26	15	13
Distillate	9	15	29	32	32	40
Levoglucosan	55	36	9	9	2	1
Glycolaldehyde	<0.1	1.8	4.0	4.0	4.9	4.1
Hydroxyacetone	trace	0.2	0.9	0.9	1.6	1.6
Formic Acid	trace	trace	0.9	0.6	0.6	0.6
Acetic Acid	trace	0.1	0.2	0.3	0.4	0.6

From Table 5.5 it can be seen that the introduction of sodium chloride has a detrimental effect on the yield of levoglucosan. From Table 5.6 it can be seen that the anion appears to have little influence under these conditions, since both the chloride and carbonate salts of sodium gave similar yields. Thermogravimetric analysis of other sodium salts also gave similar results to those of sodium chloride.

Table 5.6: Influence of different salts in 1% concentration on vacuum pyrolysis of acid washed CF11 cellulose at 350°C

Salt	Tar [%]	Levoglucosan [%]	Glycolaldehyde [%]
None	84	66	2.1
NaCl	13	1	4.1
Na_2CO_3	14	1	6.1
$MgCl_2$	42	25	1.8

5.4.2 Magnesium Chloride

In the above work, Richards (90), found that magnesium chloride behaved differently to sodium salts; it did reduce levoglucosan yield and the author quotes an increased glycolaldehyde yield, but this is not evident from Table 5.6. The author concludes that it may tentatively be suggested that the behaviour of alkali and alkaline earth metals have major differences in their mode of influence of cellulose pyrolysis. This seems feasible since in most other forms of chemistry the alkali and alkaline earth metals behave differently.

5.5 INORGANIC ADDITIVES

The effect of inorganic additives is complicated by the fact that untreated wood contains a residual amount of inorganic compounds [e.g. K, Na, Ca, Mg, P, and Zn]. Thus for a true investigation of the effects of inorganic additives the original cations should be removed.

5.5.1 Alkali and Alkaline Earth Metals

Radlein et al. (128) used a range of basic potassium salts to investigate the effect of potassium on cellulose pyrolysis. The potassium ion catalysed the formation of hydroxyacetaldehyde, but the use of different anions resulted in differing hydroxyacetaldehyde yields. From the work of Radlein it remains unclear whether the anion plays a direct role or whether it indirectly affects the action of the cation. This contradicts the work of Richards (129) who found that the anion in conjunction with sodium had very little effect on the yields of hydroxyacetaldehyde.

The effect of residual and sorbed metal ions on the products of pyrolysis was investigated by Pan and Richards (129). Cottonwood and treated cottonwood were analysed using ICAPS [inductively coupled argon plasma spectrometry] for metal ion content, see Table 5.7.

Table 5.7: Metal ion content [ppm dry wt. basis]

	Ca	Mg	P	K	Na	Zn
Original wood	1500	200	140	1000	30	9
Acid Washed	12	1	8	5	7	0
Ca-Exchanged	1399	4	11	45	43	11
K-Exchanged	12	2	8	2122	0	0

All of the samples were heated at 250°C. Acid washed wood [i.e. removal of all metal ions] gave a reduced rate of weight loss, reduced yields of all volatile products compared with the original wood and the yields of CO_2 and formic acid reduced to one third of the untreated wood value. Wood, which was Ca-exchanged, behaved similarly to acid washed wood. This is as expected as calcium is only a weak cation.

Wood, which was K-exchanged, behaved similarly to untreated wood, but CO_2 was increased by 50% of its peak value and methanol was increased by 70% of its peak value. This suggests that potassium specifically catalyses the pyrolysis reactions of lignin to produce methanol and also catalyses the pyrolytic decarboxylation of uronates to produce CO_2.

Richards also incorporated metals into cottonwood samples by ion exchange. Potassium, lithium, and calcium induced high char formation and low tar yields. Potassium, being the strongest alkali metal, had the greatest influence, giving low levoglucosan yields.

5.5.2 Transition Metals

Richards sorbed transition metals and their salts into untreated and acid washed samples of cottonwood and then pyrolysed them under vacuum; the results are shown in Table 5.8 (130).

Table 5.8: Vacuum pyrolysis of cottonwood sorbed with various salts

Sample	Char yield	LG	LGO
Original Wood	15	0.4	--
acid washed [AW]	19	5.4	--
AW + $CuAc_2$ [0.45 % Cu]	29	11.2	not determined
$CuAc_2$ [0.43 % Cu]	15	5.9	--
AW + $CuCl_2$ [0.46 % Cu]	27	13.2	--
$FeAc_2$ [3.18 % Fe]	28	5.2	--
$FeCl_2$ [1.21 % Fe]	27	7.2	--
AW + $FeSO_4$ [1.69 % Fe]	38	6.1	3
$FeSO_4$ [1.69 % Fe]	36	7.5	2.3
Cellulose + $FeSO_4$ [1.1 % Fe]	37	2.8	2.4
AW + $FeSO_4$ [1 bar pressure]	47	1.4	4.9
newsprint + $FeSO_4$ [0.77 % Fe]	20	16.6	4.2

Ac - acetate salt AW - acid washed LGO - levoglucosenone

In contrast to the alkali metals, transition metals gave increased yields of levoglucosan. This behaviour is believed to be caused by transition metals forming complexes with the lignin fraction of the biomass feedstock and hence decreasing the interference of lignin in the conversion of cellulose to levoglucosan. The combined effect of acid washing to remove metal cations followed by sorbing transition metal elements into the sample should give the best yields of levoglucosan.

The effect of the anion is also interesting. Samples sorbed with transition metal acetate salts behaved similarly to ion exchanged wood; this is because the acetate is lost from the sample at approximately 350°C leaving the metal behind. All chlorides behaved in a similar manner and both copper and iron II had beneficial effects on the levoglucosan yield. Sulphate is believed to remain in the sample and act as a Lewis acid, promoting the formation of levoglucosan and / or levoglucosenone.

5.5.3 Flame Retardants

Much of the early additives research was carried out in order to find effective flame retardants to make wood frame buildings safer. This type of work does not have the same aims as the fast pyrolysis experiments, which are carried out today, but some of the results are still of use. The selection of a flame retardant was typically based around how little weight was lost when a sample with an additive was exposed to a measured heat source. Thus, for the purpose of improving the yield of certain chemicals in the fast pyrolysis liquid, an additive which is a poor flame retardant may prove to be a "good" pyrolysis additive.

A number of inorganic additives in pyrolysis reactions have been investigated by Shafizadeh (121). These experiments were usually conducted under vacuum, with low heating rates and at low temperatures. Inorganic materials in general lower the temperature of decomposition and enhance char formation at the expense of volatiles and smouldering or glowing combustion. To determine the effectiveness of these additives, Shafizadeh treated cellulose with the additives and used thermogravimetric analysis to rank them in terms of increasing the formation of char. The results of the TGA study are shown in Table 5.9.

From Table 5.9 the weight loss range shows the points at which the weight loss starts and finishes. The fast rate is the range where the rate of sample weight loss was quickest, the maximum rate is the temperature at which the rate of weight loss was at a maximum, and the weight loss at 500°C is the percentage of the sample, which has been volatilised. Compounds which are more effective flame retardants have a low rate of heat release, and produce more char and less volatiles. The volatiles produced contain more carbon dioxide and water, and therefore have lower heats of combustion.

From Table 5.9 the compounds that had the least effect as flame retardants and do not contain alkali metals are ammonium carbonate, ammonium chloride and ammonium sulphate. These compounds may be useful additives to promote key fast pyrolysis reactions.

Table 5.9: Effect of flame retardants on thermogravimetric analysis of cellulose

Flame retardant	Range [°C]	Fast rate [°C]	Max. rate [°C]	Weight loss @ 500°C [mf wt.%]
H_3PO_4	170-500	170-290	265	61
$(NH_4)_2HPO_4$	170-500	225-310	290	66
$NH_4H_2PO_4$	190-500	250-325	300	66
$ZnCl_2$	200-500	200-500	265, 320	74
NaOH	50-500	150-350	300	79
H_3BO_3	275-500	275-400	335	81
NaCl	275-500	275-400	375	82
$CaCl_2$	260-500	260-400	355	83
$NaHSO_4$	150-500	150-400	300	84
$SbCl_3$	75-500	275-350	320	84
$NaVO_3$	225-500	300-380	355	85
$SbCl_3$ hydrate [90%H_2O]	100-500	275-390	330	86
$(NH_4)_2SO_4$	200-500	200-400	310	86
Na_2CO_3	225-500	225-380	355	87
$NaH_2PO_4.H_2O$	255-500	255-350	325	87
$Na_2B_4O_7.10H_2O$	245-500	300-370	350	89
$Na_2WO_4.2H_2O$	240-500	300-380	360	90
Na_3PO_4	220-500	300-380	360	91
$NaHCO_3$	250-500	290-380	335	92
NH_4Cl	150-500	300-375	350	93
$(NH_4)_2CO_3$	260-450	300-380	340	93
Untreated	290-500	290-370	345	93

5.5.4 Hydrogen Donors

The use of pyrolysis liquid as a fuel has several problems, primarily due to the difference between the physical and chemical properties of pyrolysis liquid and petroleum fuel, illustrated in Table 5.10 (131). It is evident that pyrolysis liquid does not compare well to a conventional petroleum fuel. Pyrolysis liquids have higher water, micro-carbon, oxygen, density, viscosity, pH and ash contents and lower carbon, hydrogen, nitrogen, sulphur and HHV.

One of the main problems associated with the low heating value and physical/chemical instability of pyrolysis liquids is the high oxygen content. Much research has been carried out on reducing the oxygen content of pyrolysis liquid by full catalytic hydrotreating (132, 133, 134, 135) or mild catalytic hydrotreating (136, 137, 138).

However, these processes utilise hydrogen [in large quantities for full hydrotreating and lesser quantities for mild hydrotreating] to eliminate unstable molecules in the pyrolysis liquid. Any form of hydrotreating will add extra cost onto the production of pyrolysis liquid as a fuel for two reasons. Firstly because hydrogen is expensive and secondly because extra processing stages invariably increase production costs.

Table 5.10: Typical properties of pyrolysis liquid and petroleum fuel (131)

Characteristic	Fast pyrolysis liquid	Petroleum fuel
Water content [mf wt.%]	15-25	0.1
Micro-carbon [mf wt.%]	0.5-0.8	0.01
C [mf wt.%]	44.14-46.37	85.2
H [mf wt.%]	6.60-7.10	11.1
O [mf wt.%]	47.03-48.93	1.0
N [mf wt.%]	0	0.3
S [mf wt.%]	<0.05	2.3
HHV [MJ/kg]	16.5-17.5	40
Density [kg/dm3]	1.23	0.94
Viscosity [cP@25°C]	400-1200	180
pH	2.4	
Ash	0.01-0.14	

It may be possible to pyrolyse biomass with additives containing hydrogen in order to reduce the amount of oxygen in the pyrolysis liquid. This has two advantages over hydrotreating. Firstly hydrogen can be replaced with an additive, which may be less dangerous, easier to handle and possibly cheaper. Secondly, since the reaction is carried out during fast pyrolysis the need for extra processing stages is eliminated.

Little work has been done on the addition of additives containing hydrogen to biomass. It is possible that compounds of ammonia may liberate some hydrogen at fast pyrolysis temperatures. Shafizadeh (121) investigated the flame retarding properties of some ammonia compounds [and other inorganic additives, see Section 5.5.3]. His work was carried out using TGA [i.e. not true fast pyrolysis]. He found that ammonium carbonate, ammonium chloride and ammonium sulphate were all poor flame retardants and therefore may make good pyrolysis additives.

5.6 SELECTION OF ADDITIVES FOR FAST PYROLYSIS

From the above review of additives it is evident that a great deal of work has been carried out. This work covers a number of additives over a wide range of conditions.

However, in many cases the results do not contain information from fast pyrolysis or do not contain satisfactory chemical analysis of the pyrolysis liquid. Nevertheless, three possible uses have been identified for additives:

1. Influence the pyrolysis reaction to produce a specific chemical,
2. Minimise the effects of secondary reactions,
3. Improve the liquid quality.

Thus three additives have been selected to carry out one of these specific tasks.

Specific Chemical Production

It has been established that the chemicals which are present in pyrolysis liquid in the highest concentrations are derived from the cellulose component of biomass. The two chemicals which can be influenced the most by a combination of pre-treatment and reactor process parameters are levoglucosan and hydroxyacetaldehyde.

Levoglucosan from biomass pyrolysis liquids can be increased by component removal pre-treatment [as reviewed in Chapter 4]. It is widely believed that the absence of ash in biomass leads to improved yields of depolymerisation products, most notably levoglucosan. However, the removal of ash is generally carried out by an acid washing/hydrolysis process. The presence of mineral acids or ions from acids [e.g. sulphate, chloride and nitrate] in small concentration have increased the yield of levoglucosan from both cellulose and biomass. Therefore the yield of levoglucosan can be increased by the removal of ash by acid washing/hydrolysis providing that the majority of the acid is removed from the biomass.

Hydroxyacetaldehyde is a product from a competing pyrolysis pathway to levoglucosan. It has been found that levoglucosan yields are improved by the removal of ash. From this it follows that the yields of hydroxyacetaldehyde can be increased by increasing the active ash content. In biomass species such as wood, potassium is usually the ash component which is present in the highest concentrations. It is also believed to be the most "active" of the ash elements [work by Radlein has shown this (128)].

Increasing the concentration of potassium in the biomass should increase the yield of hydroxyacetaldehyde. Therefore a potassium additive has been selected so that further investigation into the role of potassium in influencing the fast pyrolysis reaction can be carried out. Potassium chloride has been selected since it has not been tested previously, is soluble in water, relatively harmless and easy to handle.

Minimise Secondary Reactions

It was reported in Section 5.5.2 that transition metals are believed to form complexes with the lignin fraction of the biomass feedstock during fast pyrolysis. This behaviour may decrease the interference of lignin in the conversion of cellulose to levoglucosan. In particular, iron sulphate was found to have a large effect on the production of levoglucosan and levoglucosenone (130).

Since iron has been proved to be an effective additive for improving levoglucosan yields it has been selected for further assessment. Iron chloride will be used so that the same anion is used as the experiments to increase hydroxyacetaldehyde yield [i.e. KCl]. Thus comparison may be drawn between the two additives.

Hydrogen Donors

An area, which has received a great deal of attention is the upgrading of pyrolysis liquids by hydrotreating. The introduction of hydrogen makes a more stable liquid containing fewer carbonyl groups [C=O bonds]. The use of a hydrogen donor as an additive during fast pyrolysis might produce a more stable liquid possibly of more commercial value.

Shafizadeh (121) investigated the flame retarding properties of a large number of inorganic compounds. His work was conducted using TGA and the best flame retardants gave the lowest total weight loss as they produced more char and less volatile compounds. Thus in the selection of an inorganic nitrogen compound to produce higher yields of chemicals it will be important to increase the yield of volatiles. The suggested compounds are ammonium carbonate, ammonium chloride and ammonium sulphate.

It may be that ammonia will liberate some of its hydrogen to stabilise C=O bonds during the fast pyrolysis reaction. Since chloride salts are being used for the above experiments ammonium chloride will be used so that the effect of the anion can be compared in all cases.

5.7 CONCLUSIONS

The literature covering pyrolysis of material containing additives has been reviewed. Despite the diverse conditions used to assess additives three promising areas for investigation have been determined. These are:

- Increase the yield of hydroxyacetaldehyde using potassium chloride,
- Investigate the effect of iron chloride in reducing the influence of lignin in the pyrolysis reaction,
- Investigate the effect of ammonium chloride addition in improving the chemical stability of the pyrolysis liquid.

In all cases the chloride anion has been chosen to allow the effect of the anion to be investigated. The effects these additives have will be assessed in Chapters 8 and 9.

6. EXPERIMENTAL

One of the objectives of the project was to evaluate and compare different feedstocks. The feedstocks, which have been tested are described and characterised in this Chapter. The received condition of the feedstock and any preparation methods used prior to pre-treatment or pyrolysis are also described.

The pyrolysis experiments used to evaluate the feedstocks were carried out in a 150g/h reactor system. The equipment is described and procedures for operating the pyrolysis system, analytical equipment and obtaining mass balances are described. A critical assessment of the mass balance and analytical procedures is included.

6.1 FEEDSTOCKS INVESTIGATED

The following section characterises the feedstocks used during the course of this work.

6.1.1 Poplar

IEA poplar was originally grown so that a number of institutions would be able to conduct research using a very consistent feedstock. It was chosen by the IEA Committee specifically because of its high cellulose content and good chemical consistency. Samples of IEA Poplar used in this experimental work were sent to ADAS Wolverhampton laboratories on the 16th January 1995. The samples were tested using the detergent analysis method for cellulose, hemicellulose, lignin, oven dry matter and a range of metal cations. The results are shown in Table 6.1:

Table 6.1: Analysis of IEA poplar

Component	Content [mf wt.%]
Moisture content	6.7
Cellulose	59.4
Hemicellulose	19.0
Lignin	18.4
Metal Cations	[mg/kg dry wood]
Potassium	1120
Calcium	1120
Magnesium	250
Sodium	37.1
Phosphorous	132
Zinc	16.2
Manganese	4.3
Copper	3.74

The IEA poplar was received as dry wood chips in the size range 600-1000μm. To prepare them for the 150g/h reactor some size reduction and screening was required; details of the methods employed are described in Section 6.2.

6.1.2 Pine

This feedstock was the same material used by Peacocke in his ablative pyrolysis work (44). The material was received in a dry [i.e. less than 10mf wt.% moisture] sawdust form and had to be ground and screened to the size fraction 355-500μm. This particular size range was easy to feed and produced consistent feedrates. This will be discussed in more detail in Section 6.2.

6.1.3 Pine Bark

The pine bark used in the experiments was supplied by the New Zealand Forest Research Institute and was received in June 1995. The bark had been pretreated using methyl bromide to comply with Customs and Excise regulations with regards to the import of bark. The bark was received prepared for the 1kg/h fluid bed reactor [average particle size 0.5-2.0 mm]. However, initial screening runs [this work] were carried out on the 150g/h unit [described later]; therefore, the size was reduced to 355-500μm. The sample as received had a moisture content of 14.1 mf wt.% and an ash content of 1.79 mf wt.% determined using ASTM D1762 - 84, both on a moisture free [mf wt.%] basis.

Elemental analyses were carried out to British Standard BS 5750 with oxygen calculated by difference as given in Table 6.2.

Table 6.2: Pine bark elemental analysis [mf wt.%]

Element	Pine bark	Pine Bark (139)	Aspen Bark (140)
Carbon	53.31	55.9	48.86
Hydrogen	5.43	5.3	6.13
Nitrogen	0.14	0.4	0.51
Chlorine	0.39		
Bromine	< 0.1		
Sulphur	< 0.1	0.02	0.00
Ash	1.79	1.3	4.38
Oxygen	38.9	37.1	40.3

The bark has similar ash content to VTT pine bark (139) but much lower ash content than Waterloo Aspen bark (140) [see Table 6.2]. As discussed in Chapter 3, ash, in particular sodium and potassium salts, is known to catalyse fragmentation reactions. These reactions tend to lead to the formation of low molecular weight chemicals, water and increased gas yields. The high level of chlorine [shown in Table 6.2] in the bark was unexpected and combined with the level of alkali metal and alkali earth metal salts had a very significant effect on the pyrolysis results obtained and the product quality. This will be discussed later in [Chapter 7].

Detailed ash analysis for the pine bark and comparative values for wood are given in Table 6.3. The potassium and calcium levels are much lower than those of wood ash. However, the sodium is approximately twice that of wood ash.

Table 6.3: Pine bark and wood ash elemental analysis

	Pine bark ash [mf wt.%]	Pine bark [ppm]	Wood [ppm]
Potassium	5.97	223	1100-1500
Calcium	11.60	422	1100-1500
Sodium	1.01	64	20-100
Phosphorus	1.56	73	100-200
Sulphur	< 0.1	-	
Bromine	< 0.1	-	

6.1.4 Miscanthus

Miscanthus sinensis, or elephant grass is a species of the monocotyledoneae group and the gramineae family and originates from East Asia. Miscanthus is a plant which adapts easily to its environment. It is resistant to low temperatures and has a C4 metabolism, which allows it to photosynthesise and use water more efficiently than C3 plants (141). It is a perennial crop, which means it does not require replanting every season but grows from the same plant. It reaches full development after 3 growing years. It grows to approximately 4m in height and can produce yields of 40 ton/hectare under European growing conditions. A measure of its typical chemical breakdown is given in Table 6.4 below.

Table 6.4: Chemical composition of miscanthus sinensis [mf wt.% dry basis] (141)

Component	Amount	Description
Ash	5.7	inorganic component of biomass remaining after heating to 750°C
Solubility in EtOH/Toluene	3.2	a measure of waxes, fats, resins, non-volatile hydrocarbons, low MW carbohydrates, salts and other water soluble substances
Cold water solubility	6.3	a measure of tannins, gums, sugars and colouring matter
Hot water solubility	9.6	as cold water plus starches
1% NaOH solubility	44.9	extracts low MW carbohydrates, mostly hemicellulose and degraded cellulose
Klason Lignin	23.7	substance remaining after boiling with strong sulphuric acid
Total Polysaccharides	65.8	polysaccharide content

The miscanthus used for this study was produced by ADAS in a growing study carried out in Cambridgeshire. The plants used were harvested at the end of their third growing season and so had reached maturity. The miscanthus was received as a "straw" bale and was ground using a cutting mill and then screened to 355-500μm. The long stems, as received, were difficult to process. For future work it would be beneficial to receive feedstocks pre-ground and sized, or at least chipped to a size amenable to a cutting mill aperture [<2mm].

6.1.5 Rape Straw

Oil seed rape has been a popular crop since the introduction of set aside quotas. The attraction with oil seed rape is that the plant is grown mainly for the production of rape oil, which can be used for cooking or fuel. The residue from oil production is straw [i.e. that part of the plant remaining after threshing to remove the seeds] and the rape seed pressings or rape meal. Originally these residues were used as cattle feeds; however, the terms of set aside state that none of the land should be used for food use and so an alternative use for the residues had to be found. Hence pyrolysis trials were commissioned by ETSU (142).

Rape straw was received in a poor condition; it had been stored in a field and had become very wet. It had also been shipped in polythene bags, which reduced its quality further. It was first removed from the bag and was then left to air dry in the laboratory for a number of days. After a week it was dry and was broken into small enough pieces to fit into the cutting mill. It was then cut down and screened to 355-500μm. Table 6.5 shows the elemental analysis, ash and moisture contents of the rape straw and rape meal used. The ash content was determined using ASTM D1762-84. Elemental analyses were carried to British Standard BS 5750 with oxygen calculated by difference. Bulk density was measured by tapped density in a 100ml measuring cylinder.

Table 6.5: Analysis of rape meal and rape straw

Feedstock	**Rape meal**	**Rape straw**
Elemental Analysis		
Carbon	46.4	47.2
Hydrogen	6.4	6.2
Oxygen [by difference]	32.7	40.3
Nitrogen	6.8	1.1
Ash and Moisture Content [mf wt.%]		
Ash	7.7	5.2
Moisture	1.0	8.5
Densities [as fed]		
Absolute Density [g/cm^3]	1.33	0.83
Bulk Density [g/cm^3]	0.59	0.22

6.1.6 Rape Meal

Rape meal was received as a broken up cake, which had been scraped from the press/extruder after rape oil extraction. It was screened for large particles [i.e. greater than 5mm] and was then ground to 355-500μm using the cutting mill. In addition to this screening the rape meal was also oven dried to overcome feeding problems [see later experimental Section 7.1.7]. The physical properties of rape meal are described in Table 6.5 above.

6.2 FEEDSTOCK PREPARATION

As described in Section 6.1 above, feedstocks are usually received in a ground and sized form; however, some additional size reduction, screening and/or drying may be carried out in order to make the feedstock suitable for the feeder and pyrolysis reactor. The important feedstock properties are that it is of a suitable particle size, particle range and dry. It is acknowledged that other properties may have an influence on the results of pre-treatment or pyrolysis experiments [e.g. particle shape, regularity, surface area and surface area/volume ratio]. However, by using a small particle size [less than 600μm] with a reasonably narrow range [355-500μm] it is hoped that these other factors will be negligible.

For all pre-treatment and pyrolysis experiments the feedstocks were prepared to the following conditions:

- Ground and screened to a given particle size range [for pyrolysis typically 355-500μm]
- Moisture content measured and where necessary reduced to a value less than 10% mf wt.%.

6.2.1 Size Reduction

From experience it has been found that the feedrate can be maintained at optimum levels [100-150g/h] by using particle sizes in the range 355-500μm. Unless the feedstock was already in this particular size range then size reduction was used. This was carried out on a number of feedstocks, especially miscanthus and rape straw, which were received as stalks in a bale. The first stage of size reduction was to reduce the size of the feedstock to less than 75mm to allow it to fit into the cutting mill.

A Fritsch cutting mill with an interchangeable screen was used to reduce the feedstock particle size. Screen sizes of 100, 250, 500μm and 1cm were available. In all cases a screen size of 500μm was used, since this was found to produce the majority of particles in the 355-500μm range. Some undersized particles were produced, but these were removed by screening.

6.2.2 Screening

After size reduction the feedstock was in a powder form with a particle size less than 500μm. As mentioned above, it is desirable to have a particle size distribution as narrow as possible. Thus in order to maintain a narrow particle size distribution, but also minimise the amount of feedstock wastage [i.e. undersized feedstock], a size distribution of 355-500μm was chosen. This was achieved by sieving the feedstock using standard test sieves of mesh size 500μm and 355μm. Oversized fractions were reground using the cutting mill and undersized fractions were saved in case further work required smaller particles.

Some feedstock materials occasionally caused blocking in the feed tube aperture [Section 6.3.1] and the feed tube in the reactor [Section 6.3.2]. It was found that this occurred due to the nature of the size reduction and screening, which allowed particles through, which were bigger than the selected screen size. This can occur since the sieve will allow particles through, which have a smaller dimension, in a particular orientation, than the mesh size. Thus a rectangular particle could pass through a screen in a particular orientation, but may not in another orientation [Figure 6.1]. This problem was eradicated by double grinding of the feedstock, to remove long thin rectangular or "pin like" particles. It is purely a matter of chance, which way a particle is orientated; by double grinding the feedstock the probability of pin-like particles remaining is reduced. Feedstock that had been ground once was found to occasionally block; however, double ground feedstock did not block the feeder aperture or reactor feed tube.

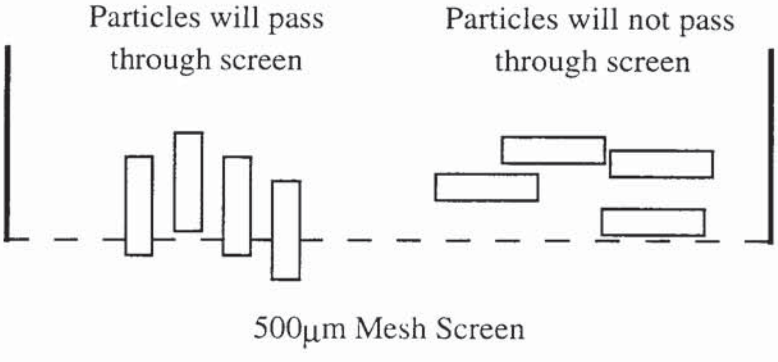


Figure 6.1: Particle orientation on a sieve

6.2.3 Moisture content

The method used for measuring the feedstock moisture content was drying (36). After the feedstock was prepared to the correct size distribution, approximately 1g was weighed [to 4 decimal places] and then placed in a pre-dried and weighed crucible; this was then placed in an oven at 105°C for at least 24 hours. From previous experiments involving repeated weighing of drying wood samples this has been found to be an adequate time period to achieve constant weight. The crucible and sample were then re-weighed and the moisture content of the sample was calculated on a dry feedstock basis. This technique is always carried out in triplicate and an average taken.

6.2.4 Ash content

Ash content measurement was carried out in accordance with the ASTM method (36). Approximately 1g was weighed [to 4 decimal places] and then placed in a pre-dried and weighed crucible; this was then placed in an oven at 105°C for at least 24 hours. The crucible and sample were then re-weighed and the moisture content of the sample was calculated on a dry feedstock basis. The crucible is then placed in a muffle furnace at 750°C for a minimum of 6 hours before it is removed and cooled in a dessicater for 1 hour before weighing [to 4 decimal places]. The ash content was then calculated on a dry feedstock basis. The ash content measurement of a feedstock was usually carried out directly after the moisture content measurement, since the same crucible and pre-dried sample can be used.

6.2.5 Drying

Fast pyrolysis requires feedstocks in a relatively dry state [i.e. less than 10mf wt.% moisture as measured by the method in Section 6.2.3 above]. Feedstocks were dried where necessary by storing in a fan oven at a constant 105°C for 24 hours. Most feedstocks were received in a dry state and so did not require drying. However, rape straw and rape meal both had to be dried before being pyrolysed, as discussed previously in Sections 6.1.5 and 6.1.6 respectively.

6.3 PYROLYSIS SYSTEM

The 150g/h fluidised bed system [see Figure 6.2] consists of three sections: feeder, reactor and products collection. The approximate dimensions and operating methods are described in the following sections.

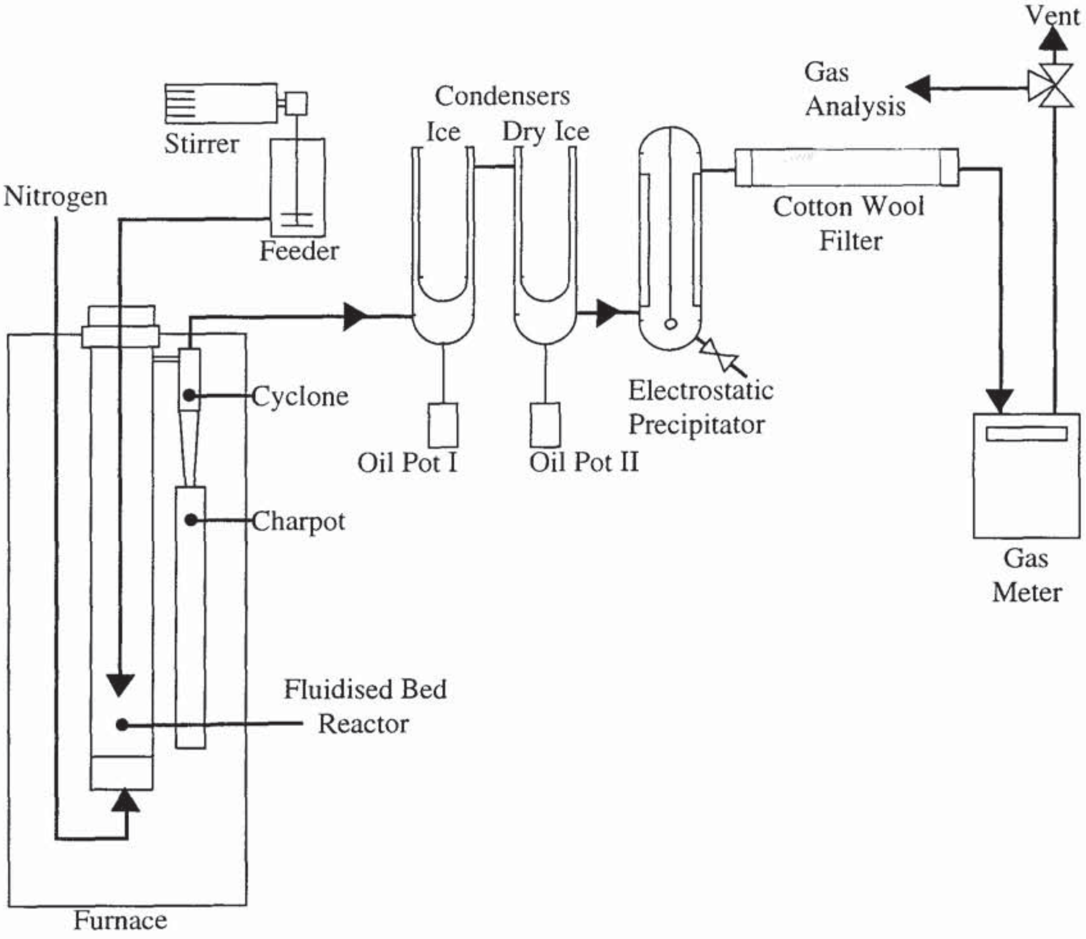


Figure 6.2: 150g/h reactor and products collection system

6.3.1 Feeder

A diagram of the feeder is shown in Figure 6.3. The feeder consists of a tubular storage hopper, which is blanketed with nitrogen and slowly stirred by two paddles. Biomass is entrained through the feed aperture by a continuous flow of nitrogen into the biomass entrain tube, which crosses the hopper at the bottom. The biomass is entrained along the entrainment tube where it then passes into a flexible tube linking it to the feed tube in the reactor.

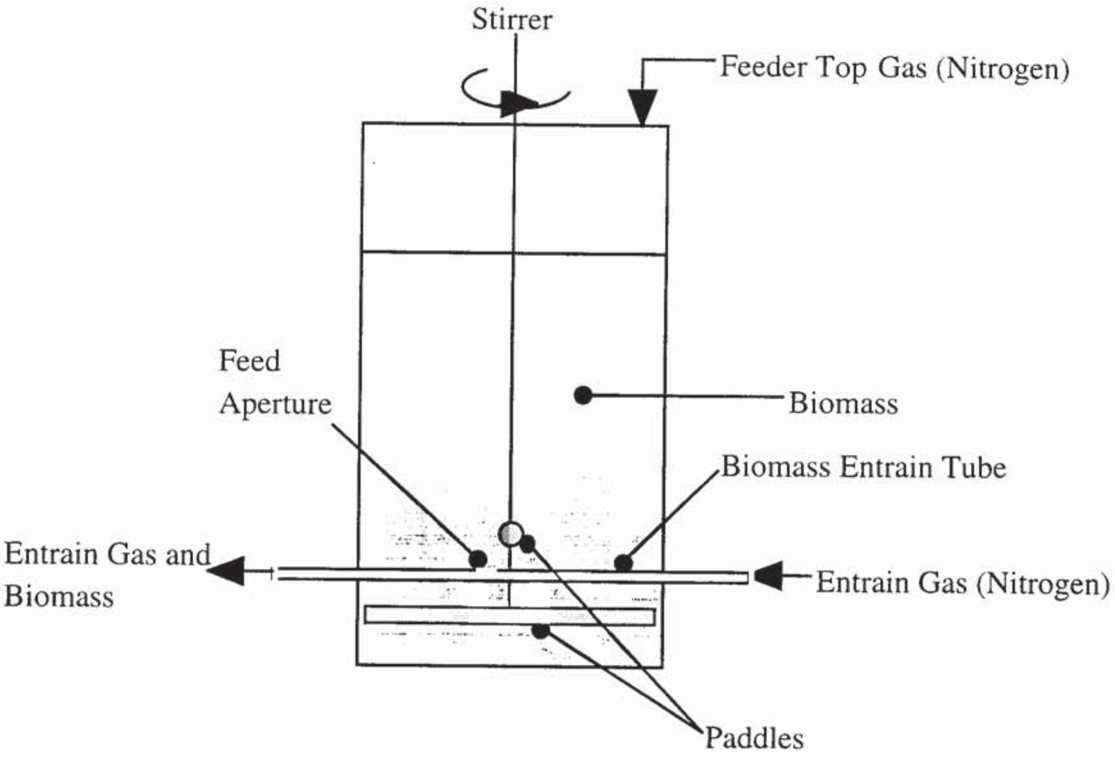


Figure 6.3: Schematic diagram of biomass feeder

The main body of the feeder is constructed from clear perspex for a number of reasons. Firstly perspex is a strong and robust material, which is easy to machine, thus allowing modifications or new designs to be quickly implemented. Since the perspex is clear it is easy to observe the behaviour of the feedstock during a run; thus problems such as bridging or low feedstock levels can be observed and corrected. Perspex is an easy material to clean and therefore it is easy to change feedstocks after a series of tests have been completed.

The factors which affect the biomass feedrate are size, moisture content, shape, preparation method and the feeder variables [entrain tube aperture size, paddle speed, entrainment flow and feeder top pressure]. For a given biomass prepared by the methods described in Section 6.2, the size, moisture content and shape will all be fixed. Therefore the feedrate of biomass is controlled by the feeder variables.

Calibration

Every time a new feedstock is used, calibration of the feeder is carried out. A feedrate of 100-150g/h is desirable since this is the design rating of the equipment. It may be possible to run at higher or lower feedrates but this is not recommended. At rates higher than 150g/h the feed tube in the fluidised bed is prone to blocking and at very low feedrates [<50g/h] the dilution of the pyrolysis vapours by the nitrogen gas makes gas analysis difficult [this is discussed in Section 6.5.1].

The feedrate is a function of biomass type as well as feeder variables. Thus it is necessary to calibrate the feeder each time a new biomass type is used. The entrain tube aperture has the most significant effect on feedrate for a given stirrer speed and nitrogen flow. For most feedstocks the 1.7mm aperture is suitable, but for some feedstocks [i.e. dry and powdery or more dense] a smaller aperture is required to reduce the feedrate to acceptable limits [i.e. less than 150g/h]. Once a suitable aperture has been found [trial and error] the feedrate can be fine tuned by altering the feeder top flow [changes pressure in feeder] or paddle speed [increases fluid behaviour around the entrainment aperture making it easier to entrain the biomass].

The feeder has mechanical paddles which slowly rotate to prevent bridging of the feedstock and also to maintain accurate and continuous flow of the feedstock. The speed of the feeder paddles can be adjusted, which allows the feedrate to be altered during a run.

The top of the feeder is pressurised with a small flow of nitrogen which forces the feedstock through the feed aperture into the feed tube. This flow can be changed during a run to either increase or decrease the biomass feedrate. By increasing the gas flowrate the pressure in the feeder is increased, thus increasing the feedrate.

From Figure 6.4 using IEA poplar [295-600μm] as feedstock, it is evident that for a 1.7mm feed tube aperture and an entrain gas flowrate of 1.5l/min, the feedrate is approximately twice as sensitive to stirrer speed than to feeder top flowrate. Figure 6.4 is a specific relationship for IEA poplar prepared according to the specifications described in Section 6.2. However, the general principle can be applied to other feedstocks. The influence of paddle speed and feeder top flowrate are useful since they can be altered during a run to increase or decrease the flowrate. Entrainment gas flow can also be altered during a run but is not recommended since this makes up part of the fluidising gas and therefore should be kept constant.

The feedrate calibration was developed when the feeder was full. It is expected, and experimental observation suggests, that the feedrate reduces with the height of biomass in the feeder. Thus, as a run progresses the rate at which the biomass enters the reactor reduces. During a run the pyrolysis vapours can be observed in the glass collection system. How dense the vapours look gives an indication of feedrate. During a run the apparent density of the vapour does not appear to change significantly. Therefore it is theorised that the feedrate does not alter by a significant amount during a run [i.e. less than 10%]. This will not affect the overall feedrate since that is calculated as an average over the run.

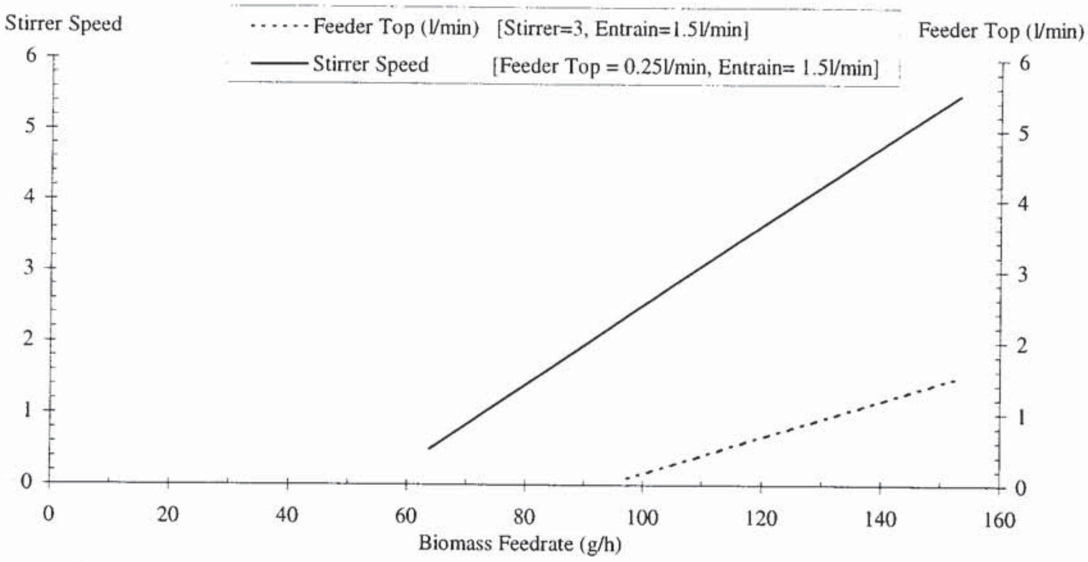


Figure 6.4: Calibration relationship for feeder

6.3.2 150g/h Reactor

The reactor [shown in Figure 6.5] consists of a 40mm internal diameter 316 stainless steel tube with a length of 260mm. The top of the tube is threaded allowing the top of the reactor to be removed for weighing, cleaning and to add/remove the heating/fluidising medium [sand]. The top of the reactor has three apertures, one is for a thermocouple to measure the reactor internal bed temperature and the second and third are for the feed tube and air cooling line. The feed tube transports the feedstock into the centre of the fluidised bed. It can be air cooled by a pressurised flow of air, which prevents temperature sensitive feedstocks from being pyrolysed before they reach the fluidised bed.

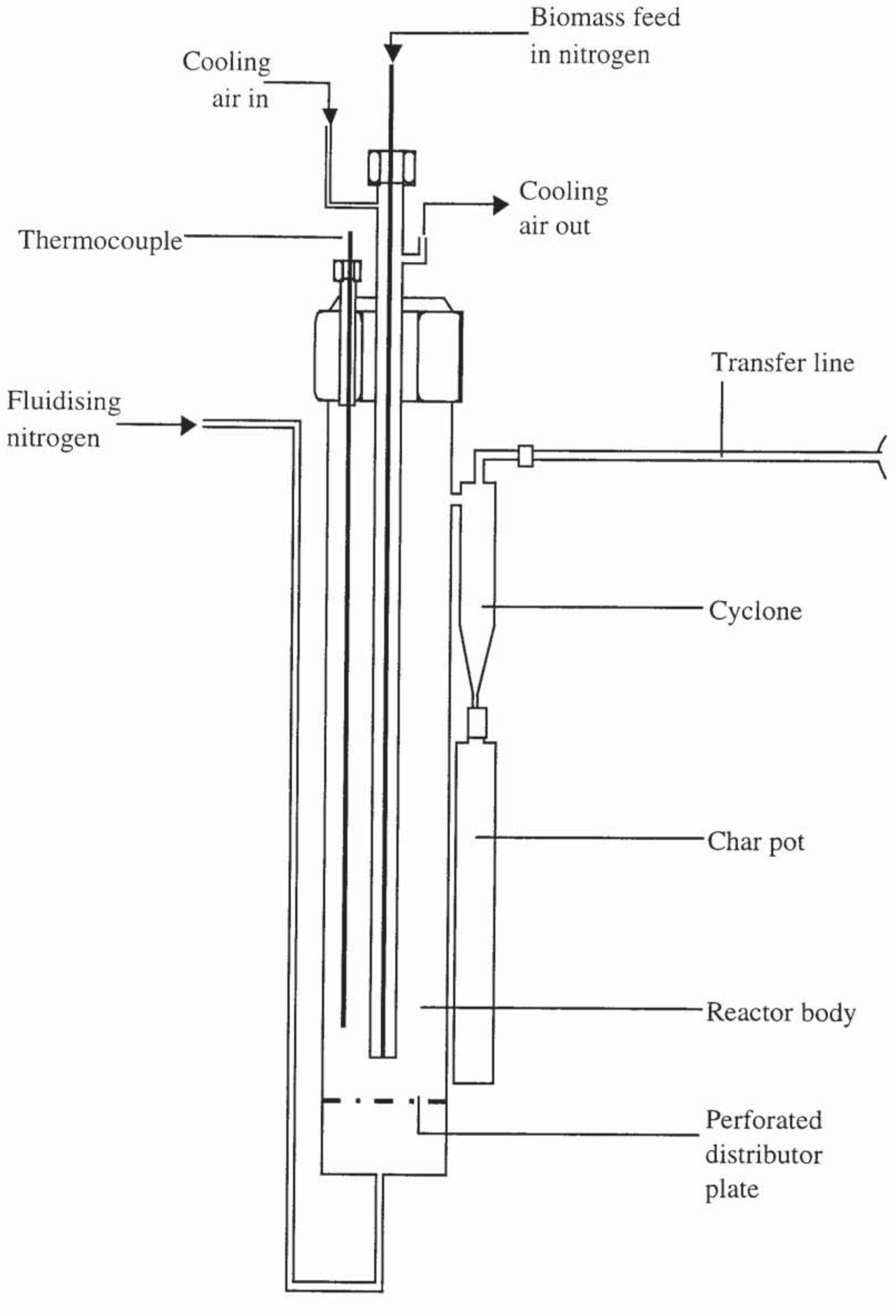


Figure 6.5: Schematic diagram of 150g/h fluidised bed reactor

The heating medium in the reactor is inert sand with a particle size of 355-500μm. This particle range is used so that the reactor operates on blow-through mode. This means that the fluidising velocity of the sand is enough to blow the pyrolysed biomass [char and vapours] completely out of the bed while the sand remains in the bed. The sand fills the reactor to a depth of approximately 8cm and expands during fluidisation to 12cm. The sand is fluidised using nitrogen, which is preheated by the furnace in the line prior to entering the base of the reactor. The nitrogen then passes into the base of the reactor and is distributed by a sintered inconel plate with a 100μm pore size. The reactor is fluidised using 10-18l/min nitrogen [0.5bar 20°C]; this means that the bed is operating at approximately 5 times the minimum fluidising velocity [U_{mf}] [i.e. U_{mf}=8cm/s, U_{op}=40cm/s (143)].

The biomass is carried down the reactor feed tube in a stream of entertainment nitrogen into the centre of the fluidised bed. Once it leaves the tube it begins to pyrolyse almost instantaneously producing pyrolysis vapours and ultimately char. Once the biomass has reacted completely it forms char particles having similar dimensions to the original biomass, but having only approximately 10% of the original weight. This char is then carried out of the fluidised bed by the fluidising gas flow.

The vapours and char then pass into the first stage of product collection, which is the cyclone and char pot. The cyclone is used to separate the char from the pyrolysis vapours. The pyrolysis vapours pass out of the cyclone via an outlet in the top and the char falls to the bottom of the cyclone where it passes into the char pot.

The reactor, cyclone and char pot sit in a vertical tube furnace which maintains the temperature of the furnace at a set-point, which can be controlled to a fixed point between 400 and 600°C. The temperature of the reactor is measured by a K-type thermocouple placed directly into the fluidised bed. The furnace set-point is approximately 20°C higher than the desired reactor temperature; this is because energy is constantly required by the reactor to heat up the nitrogen and biomass and perform the pyrolysis. Thus to maintain a constant reactor temperature there must be enough excess heat available from the furnace to overcome the nitrogen and biomass specific heats and the pyrolysis heat of reaction. The furnace uses a proportional controller linked to a thermocouple, which is independent from the reactor to maintain the set-point to within ±5°C. The furnace thermocouple is mounted in the furnace wall at approximately 100mm from the top.

The top of the furnace and hence the top of the reactor, cyclone and char pot is lagged to prevent heat loss. The outlet from the top of the cyclone to the second stage of the products collection system is also lagged to maintain pyrolysis vapour temperatures above 400°C. This is very important, since below 400°C the pyrolysis vapours start condensing. Vapour condensation can result in blockage of the transfer pipe between cyclone and second stage products collection, which would result in an early termination of the run.

6.3.3 Vapour Residence Time

Vapour residence time is the time that the pyrolysis vapours spend in the reactor or reactor system. It is therefore an indication of secondary reactions [discussed in Chapter 3]. There are two methods of vapour residence time measurement, reactor only residence time and total hot space residence time. The reactor, cyclone and char pot all sit in the furnace and are exposed to the temperature of the furnace. Thus the vapours are kept at a constant temperature [which is that of the furnace or slightly lower] and could undergo secondary reactions. The reactor only residence time is not a realistic view of the time/temperature exposure of the vapours, since once the vapours leave the reactor they are still exposed to the furnace temperature. In all cases the residence time reported will be the total hot space residence time since this represents a more realistic view of the time/temperature, which the vapours are exposed to.

The volumetric throughput of the reactor is the volume of gas at the average reactor temperature passing through the reactor system in a given time. The total hot space of the reactor system is the volume of the reactor [above the distributor], cyclone and transfer line, discounting the volume taken up by sand. The total hot space residence time is calculated from the volumetric throughput of the reactor system divided by the total hot space of the reactor. Once the pyrolysis vapours leave the hot space and enter the liquids collection system [first condenser], condensation starts and the liquid products will start to collect.

6.3.4 Liquids Collection System

The liquid products collection consists of two cooled condensers, an electrostatic precipitator and cotton wool filter [shown previously in Figure 6.2]. All of the liquids collection system is constructed from glass for easy cleaning and also so that the behaviour of the condensing pyrolysis vapours can be observed. The first cooled condenser has a cold finger filled with ice [0°C]; this cools the pyrolysis vapours from around 400°C to 50°C and starts the condensation process. The heavy ends are condensed by the first condenser, collect on the inner wall and drip down to collect in oil pot I [OPI]. The second condenser has a cold finger filled with dry ice and acetone [approximately -80°C]; this further cools the pyrolysis vapours from around 50°C to 5°C. The light ends and water are condensed by the secondary condenser, collect on the inner wall and drip down to collect in oil pot II [OPII].

The electrostatic precipitator [EP] was not installed until run SFB13; thus, for the first twelve runs the next stage in product collection was the cotton wool filter. The filter is a glass column, which is densely packed with around 40g of dry cotton wool. This forms a dense filter, which the pyrolysis vapours coalesce on. However, during a run, as the vapours condense on the cotton wool the pressure drop over the cotton wool increases [starting off at approximately 50 inches H_2O and often rising as high as 150 inches H_2O]. As the pressure increases there is a danger that the oil pots could be blown off; thus, if the pressure reached 150 inches H_2O the run would be stopped. Although the cotton wool is efficient at collecting the vapours it is difficult to remove the pyrolysis liquid from the cotton wool after the run; only by using a solvent [ethanol] can the pyrolysis liquids be completely removed. In order to analyse the chemicals in the pyrolysis liquids the solvent must be removed. However, even low pressure distillation of the pyrolysis liquid and solvent mixture leads to losses of volatile components from the pyrolysis liquid; therefore, it is better to use a liquid collection method that does not require solvent washing.

The EP was commissioned on run SFB13. It is very effective at removing the remaining aerosols, which are present in the gas after the second condenser. It uses a 15,000V negative charge on a thin stainless steel wire suspended in the centre. This charges the aerosols, which are then attracted to the positively charged plate on the walls of the EP. The pyrolysis liquid runs down the walls of the EP and collects in the bottom, where it can be drained off during or after the run. The introduction of the electrostatic precipitator [EP] has meant that the cotton wool collects only a small fraction of the total pyrolysis liquids [less than 2% liquid basis] and is now mostly used as a fail-safe to protect downstream equipment [i.e. gas meter and gas analysis equipment]. Hence much less cotton wool is required and the pressure drop over the cotton wool is much lower, at the start of a run and during. It also ensures that only clean non condensable gases enter the gas meter and gas sampling/analysis system.

After the cotton wool filter is a gas meter. The gas meter measures the total volumetric throughput of gas through the system and is required to allow the gas to be analysed volumetrically for mass balance purposes [see Section 6.4].

6.4 MASS BALANCE

The products of pyrolysis are separated and collected into three distinct categories, char, pyrolysis liquid and gas. These three categories will be defined, for mass balance purposes, in the following Sections [Char 6.4.2, Liquids 6.4.3, and Gas 6.4.4].

6.4.1 Mass Balance Reporting

Table 6.6 shows a typical table, which is used for mass balance reporting. The experiment number has the prefix SFB [small fluidised bed] followed by a number. The temperature is that of the reactor and is the average recorded temperature from the in-bed thermocouple. The temperature is taken manually at 1 minute intervals throughout the course of a run; the temperature reported is the average reactor temperature for a particular run. The total hot space residence time is shown next, this is calculated by the method described in Section 6.3.3.

The rate at which the feedstock is fed into the reactor is shown in grams per hour [g/h]. As discussed in Section 6.3.1, the feedrate should be kept between 50 and 150g/h to maintain consistency and accuracy during a run. Low feedrates can result in poor gas analysis and high feedrates can result in overloading the reactor and collection system leading to blockages. The feedrate is calculated by weighing the feeder [±0.01%] before and after the run. The feedstock is not weighed alone since the small particle size means it is difficult to handle, which could introduce inaccuracies. The feedrate is the difference in feeder weights [before and after] divided by the total run time in hours. The moisture and ash content of the feedstock are calculated by the methods described in Section 6.2.3 and Section 6.2.4 respectively.

The yields of pyrolysis products are reported on a moisture free feedstock basis. The char is calculated as per Section 6.4.2; the organics are calculated as described in Section 6.4.3; the gas yield is calculated by the method described in Section 6.4.4; and the water of pyrolysis is calculated by analysis of the organics as per Section 6.5.2.1. The total liquids is measured by weighing [details in Section 6.4.3] and this contains both organics and water of pyrolysis. The closure is the percentage of the original feedstock, which has been recovered. It gives a measure to assess the quality of the experiment, since a poor closure [i.e. less than 90mf wt.% or in excess of 100%] indicates that something has not been measured or accounted for correctly. In most cases the closure is in the region of 95-100mf wt.%. Reasons for incomplete closure are discussed in Section 6.6.

Table 6.6: Example of mass balance reporting

Run No.	SFB##
Temp. [°C]	Fluid bed in-bed average temperature
Res. Time [s]	Average total hot space residence time
Feedrate [g/h]	Average rate at which feedstock is fed into the reactor
Moisture [mf wt.%]	Moisture content of feedstock
Ash [mf wt.%]	Ash content of feedstock
Yields [mf wt.%]	Major product yields on a dry feedstock basis
Char	Analysis method Section 6.4.2
Organics	Analysis method Section 6.4.3
Gas	Analysis method Section 6.4.4
Water	Analysis method Section 6.5.2.1
Total Liquids	Sum of organics and water
Closure	Percentage of feed/input recovered as products
Gas [mf wt.%]	Gas yields on a dry feedstock basis
Carbon Monoxide	Yield of carbon monoxide
Carbon Dioxide	Yield of carbon dioxide
Methane	Yield of methane
C2's	Yield of ethane and ethylene
C3's	Yield of propane and propylene
Gas [nitrogen free, vol. %]	Gas yields on a volume basis not including nitrogen
Carbon Monoxide	Volume of carbon monoxide
Carbon Dioxide	Volume of carbon dioxide
Methane	Volume of methane
C2's	Volume of ethane and ethylene
C3's	Volume of propane and propylene

The gas yields are further sub-divided into the uncondensable gases carbon dioxide, carbon monoxide, methane, C_2's [e.g. ethane, ethylene] and C_3's [e.g. propane, propylene]. Other gases [e.g. hydrogen, n-butane and n-butylene] are analysed but are rarely detected so are not included in the mass balance reporting. All gas yields are given on a weight percent dry feedstock basis and also on a nitrogen free volume basis.

6.4.2 Char

Char is a black substance that is collected in the char pot, as a residual coating on the sand, reactor, char pot and cyclone and in the pyrolysis liquids, as some char is blown through the collection system. The reactor, cyclone and sand are assumed to remain at a constant weight, so any increase in weight will be due to char. It is feasible that the sand will be worn away by attrition but this effect has been assumed to be minimal.

The reactor and cyclone are weighed before and after a run [±0.01%] and the difference is assumed to be char. The coating on the sand is quantified by weighing the sand before and after a run, the difference again being char. The contents of the char pot are also classed as char and again are weighed. In both cases the weighing is to 2 decimal places and is accurate to ±0.01g. It is possible that some of the sand is blown into the cyclone and hence char pot, but, since the sand is weighed before and after it would be accounted for.

The char, which is blown through the cyclone and into the liquids collection system, tends to stick to the glass walls and can be filtered from the pyrolysis liquid washings [see section 6.4.3]. However, any char which gets into the liquids is very difficult to remove, since the pyrolysis liquids must be diluted with a suitable solvent [ethanol, methanol or acetone] before they will pass through a filter. As discussed in Section 6.3.3 dilution of the pyrolysis liquids by solvents will result in loss of volatile components when the solvents are removed. It should be noted that the pyrolysis liquids contain a small amount of microfine char [less than 20μm]; this char is too fine to remove by filtration and therefore has to remain in the liquid.

6.4.3 Liquids

The collection of the liquid products begins in the first [ice] condenser. They are collected on the walls of the first and second condensers, where they run down the walls into oil pots I and II. They are also collected in the EP, where again they run down the walls to be collected in the base. The oil pots are weighed [to an accuracy of ±0.01g] before and after the run and the difference is pyrolysis liquid. The condensers and the EP are weighed before and after the run [to an accuracy of ±0.1g]. The liquids from the oil pots I, II and the EP are placed into separate storage containers for subsequent water and chemicals content analysis. Any liquids remaining on the glassware are washed off using ethanol; this is then filtered to remove char using pre-dried and weighed Whatman No. 1 qualitative filter paper. The filtered liquids have their water content analysed using Karl Fischer coulometry [Section 6.5.2] and are then stored as washings.

The pyrolysis liquids are further sub-categorised into organics and water. The organics are classified as the total liquids [difference in weight of the glassware and cotton wool] less the weight of char and water. The water comes from the feedstocks original moisture content and also from water of pyrolysis [formed as a product of the pyrolysis reaction]. The total water content of each of the pyrolysis liquid samples [OPI, OPII, EP and wash] is measured by Karl Fischer coulometry [see Section 6.5.2]. The total water from the pyrolysis liquids [i.e. the sum of water from the four samples] has the original feedstock water content subtracted from it; thus, the water product quoted in the mass balance is the water of pyrolysis.

6.4.4 Gas

The total volumetric throughput of the fluidised bed reactor system is measured using a Schlumberger Remus3 G1.6 total gas meter [shown in Figure 6.2]. This measures the total gas throughput in cubic metres, to three decimal places, and is accurate to ±2.0% of the total hourly flowrate. After the gas meter a gas pump is used to take representative samples throughout the course of the run; usually three or more samples are taken for subsequent gas chromatographic analysis [see Section 6.5.1]. The samples are analysed for their volumetric content of the major pyrolysis gases, which are carbon monoxide, carbon dioxide, hydrogen, methane, ethane, ethylene, propane, propylene, n-butane and n-butylene. It is assumed that the remainder of the pyrolysis gas is made up of nitrogen. From this analysis the volumetric constituents of the pyrolysis gas can be calculated and hence the weight of gas produced.

6.5 PRODUCT ANALYSIS

Accurate measurements and analysis are essential to any experimental based project. The following section describes analytical techniques used to quantify the major pyrolysis products and produce good quality reproducible mass balances.

6.5.1 Gas Analysis

Gas samples are taken periodically during the course of a run. These samples are analysed for pyrolysis gases using gas chromatography. Three separate systems are used to detect the full range of gases. Hydrogen, oxygen, nitrogen and carbon monoxide are detected using a molecular sieve column [for complete equipment detail refer to Appendix B]; carbon dioxide is detected using a Poropak Q column and C_1-C_4 gases are detected using a picric acid column.

Gas chromatography is an analytical technique which relies on the comparison of gas concentrations. Thus for every gas analysed a standard gas, with a known concentration and of similar concentration to that expected in the pyrolysis system exit gas, has to be injected into the column and the peak residence time and area noted. This residence time will then correspond to that particular gas under the specific conditions for that GC system and column. Thus when a gas sample is injected only the gases, which have been previously analysed and calibrated, can be identified and quantified. By using several standard gases the concentrations of all of the major pyrolysis gases can be identified and quantified. From the total volume measured by the gas meter the mass of pyrolysis vapours produced can then be calculated.

The pyrolysis vapours are dilute because the fluidised bed reactor requires a high throughput of gas [6-18 l/min. nitrogen was typically used] to keep the sand fluidised. Extra gas is also required to entrain the biomass from the feeder and into the reactor [2-5 l/min]. This extra gas means that the pyrolysis vapours only make up approximately 2% [volume basis] of the total volume output of the reactor system, as measured by the gas meter.

The main problem with the gas chromatography systems described above is that the sensitivity has to be turned up to detect the low concentrations of gas. The concentrations of gas, which the GC's detect, is usually in the range of 1.00% [total gas volume basis] for abundant gases such as carbon monoxide and dioxide, down to concentrations as low as 0.02% [total gas volume basis] for minor gases such as n-butane and n-butylene.

Other problems are specific to particular detection systems. Thus the molecular sieve column uses helium as a carrier gas, but unfortunately this tends to mask most of the hydrogen it is detecting so only concentrations greater than 1.0% can be detected. As mentioned above it is unlikely that any minor product gas would be found in such concentrations; thus, the small volume of hydrogen which is produced in every run is an unquantifiable loss. This loss could be estimated; however, this has not been done since all mass balances are reported in a format where everything has been measured directly.

6.5.2 Pyrolysis Liquid Analysis

The pyrolysis liquids are collected as 4 discreet samples from the pyrolysis system, oilpots I and II, electrostatic precipitator and washings. All 4 of these samples have to be analysed for water content [using Karl Fischer coulometry, Section 6.5.2.1] and also chemicals content [using HPLC, Section 6.5.2.2].

6.5.2.1 Karl Fischer Coulometer

A Mitsubishi, model CA-20, KF coulometer is used for quantitative determination of water in pyrolysis liquids. Due to the relatively high water content and sometimes high viscosity of the pyrolysis liquids and the sensitivity of the coulometer, the pyrolysis liquids are diluted using methanol before being analysed. If the liquids were not diluted they would require much more reagent [hence increased cost], would take more time or may not dissolve in the coulometer properly and give low [false] readings].

To find the water content of a pyrolysis liquid, a small amount is first weighed into a vial; this is then diluted [by at least 1:10] with a known weight of methanol with a known moisture content. A known weight [±0.02%] of the combined liquid is injected through a septum directly into the meter. The meter then determines the amount of water contained in the injected sample and since the weight of the combined liquid is known the percentage water can be calculated. The moisture content of the original liquid can then be back calculated. The coulometer gives a moisture content, which is reproducible and accurate to ±0.01mf wt.%.

6.5.2.2 HPLC Analysis

HPLC [High Performance Liquid Chromatography] is used to determine the concentration of some of the chemicals contained in the pyrolysis liquids. HPLC is a similar technique to GC, in that the analysis is achieved by comparison to previously identified chemicals with known concentrations. Thus, as for GC analysis, a standard is required which contains the chemicals which are expected to be in the pyrolysis liquid in similar concentrations. The standard contains the following chemicals in specified concentrations [typically 0.1-2.0 mf wt.%]: glyoxal, xylitol, levoglucosan, hydroxyacetaldehyde, formic acid/formaldehyde, acetic acid, acetol, methanol, 2-furoic acid, cyclotene, cellobiosan, glyceraldehyde, ethanol, fructose and glucose.

HPLC uses a 0.05wt.% sulphuric acid solution as mobile phase. The mobile phase is constantly pumped through the column and carries the sample to be analysed. Hence only water soluble compounds in the pyrolysis liquids can be analysed. The samples are prepared by weighing out an amount of pyrolysis liquid into a pre-weighed plastic vial. A known weight of mobile phase is then added to the vial to dilute the pyrolysis liquids [about 4 part mobile phase to 1 pyrolysis liquid]. The sample is shaken and the water insoluble fraction forms a precipitate known as pyrolytic lignin. The plastic vial is centrifuged for 5 minutes at 4000rpm to remove all the precipitate. The water soluble pyrolysis liquid fraction is poured out of the vial and filtered using a Gelman Acrodisc PTFE filter [0.2μm pore size] to remove any remaining lignin. The filter is used as a precautionary measure to prevent lignin entering the HPLC system and damaging the analytical columns. The precipitate remains in the sample vial and after several hours drying the remaining fraction is weighed and is classified as pyrolytic lignin.

The HPLC system uses a Bio-rad column, which is linked to a refractive index detector [for complete equipment detail refer to Appendix C]. The filtered water soluble sample is injected into the column and after approximately 30 minutes a trace showing the chemicals detected and their areas is produced. The software package then integrates these areas and compares them with the standard; thus, the chemical concentrations can be found.

6.6 EXPERIMENTAL ACCURACY

The experimental results presented are believed to be the best achievable from the equipment available at Aston. However, this does not necessarily mean that they are 100% accurate. In all stages there is an element of error, inaccuracy or non-quantification of a product or products resulting in incomplete closure. The point of this section is to highlight the areas of the mass balance that are believed to be incomplete or less accurate, suggest possible reasons and predict the effect on the mass balance.

Table 6.6 [previously] detailed all areas of mass balance reporting; however, this can be summarised into four categories:

- Feedstock parameters,
- Reactor parameters,
- Mass balance yields,
- Product analysis.

6.6.1 Feedstock Parameters

The major feedstock parameters are moisture content and ash content. The moisture content is measured by the method described in Section 6.2.3, which is a reliable method accurate to ±0.1mf wt.% [dry feedstock basis]. However, due to the hygroscopic nature of biomass, it will naturally absorb moisture from the air. The likelihood of this is increased if the moisture content is reduced [i.e. by drying in an oven]. Thus, although the moisture content of a feedstock may be correct at the time of measurement, if left open to the atmosphere, improperly stored or stored for a long period of time, then the moisture content may change [typically increase to the equilibrium moisture level]. Thus the moisture content should be measured at the time of performing the experiment.

The moisture content of the feedstock plays an important role in the mass balance since the original moisture is discounted from the water in the pyrolysis liquids [to leave water of pyrolysis]. Over measurement of the feedstock moisture content could result in reduced closure, or even a seemingly negative water yield [this has not occurred in any runs to date, although in some cases the water yield has been low]. Under measurement of the feedstock moisture content could result in increased closure, possibly beyond 100%, since the water in the pyrolysis liquid would be water of pyrolysis and the extra feedstock moisture.

The ash content is measured after the moisture content and is calculated on a dry basis; thus inaccuracies in the moisture content could have a compound effect on the ash content. Unlike the moisture content the ash content does not have such a significant effect on the mass balance. Ash does have a significant effect on the pyrolysis reaction and in later sections [Chapter 9] pre-treatment methods have been used to reduce the ash level and significantly increase the yields of certain chemicals.

The feedrate is measured as the difference in the feeder weight [before and after a run] divided by the total run time; hence it is an average. It may seem less accurate to weigh the total feeder rather than the feedstock. However, due to the nature of fine biomass particles [i.e. sawdust] it is difficult to pour and tends to become charged with static from the stirrer; thus is very difficult to weigh separately. So although the feeder is only weighed to ±0.01%; this is more accurate than trying to pour the biomass into and out of the feeder to weigh to ±0.001%.

6.6.2 Reactor Parameters

The key reactor parameters are temperature and residence time. The reactor temperature is measured directly from a K-type thermocouple located in the fluidised sand. The temperature is maintained by a furnace, which surrounds the reactor, cyclone and char pot. The reactor temperature is measured manually at set time intervals throughout a run and noted. At the end of a run the average reactor temperature is calculated. The average reactor temperature may not adequately describe the temperature of the reactor, since the run could have consisted of 30 minutes at 450°C followed by 30 minutes at 550°C, which is an average of 500°C. However, in most cases it is felt that the average reactor temperature provides a fair indication of the temperature the reactor was maintained at during a run.

It is important to know the total hot space residence time as this measures the amount of time the pyrolysis vapours are exposed to the reactor temperature. This gives an indication of the amount secondary reactions, which may have occurred. The total hot space residence time [shown in Equation 6.1] is a function of the volume of the total hot space, weight of sand in the reactor, density of the sand, total volumetric throughput of the reactor, temperature of volumetric measurement, total run time and average reactor temperature. Thus any error in the measurement of these variables will result in errors in the residence time.

$$\text{Residence Time}_{\text{Total Hot Space}} = \frac{\left(Volume_{TotalHotSpace} - \frac{W_{sand}}{\rho_{sand}}\right) * \ T_{Measurement} * Time}{1000 * T_{\mathrm{Re}actor} * Volume_{TotalThroghput}}$$

Equation 6.1: Total hot space residence time

Where:

$Volume_{TotalHotSpace}$ = Volume of reactor, cyclone and exit tube in cm^3 [$377.86cm^3$],
W_{sand} = Weight of sand used in g [150g],
ρ_{sand} = Particle density of sand in g/cm^3 [$2.67g/cm^3$],
$T_{measurement}$ = Ambient temperature in K [273K],
$T_{reactor}$ = Average reactor temperature in K [873K],
Time = Total run time in seconds [1800s],
$Volume_{TotalThroughput}$ = Total volumetric output of system in litres [300 l].

The volume of the total hot space and the density of the sand are constants. The weight of sand is accurate to ±0.01g and so is unlikely to introduce errors into the residence time calculation. The volumetric throughput of the reactor is assumed to be measured at 0°C. It is possible that the gases passing through the gas meter are hotter or colder than this since they are heated in the reactor and then cooled in ice and dry ice condensers. The reactor temperature is an average, so could also be a potential source of error. However, in this calculation, it is used to calculate the total volume of gas at the reactor temperature and, since an average volumetric throughput is calculated, it is best to use the average reactor temperature. The total run time is measured ±1s and since a run usually lasts at least 30 minutes there is virtually no error from this variable.

Analysis of the possible error in residence time measurement produced the results shown in Table 6.7. To estimate the minimum value of the residence time the variables on the top line of Equation 6.1 should be less than the typical values [except W_{sand} which should be greater than typical] and the values on the bottom line should be greater than typical values. To estimate the maximum value of the residence time the reverse should be applied. Thus using the expected highest and lowest values for each variable the deviation from the typical calculated result was calculated.

Table 6.7: Residence time error analysis

Variable	Typical	Minimise	Maximise	Deviation
Sand [g]	150.00	150.01	149.99	±0.01
$T_{measurement}$ [°C]	0	-5	5	±5
Time [s]	1800	1799	1801	±1
$T_{reactor}$ [°C]	500	505	495	±5
$Volume_{Total\ Throughput}$ [dm^3]	400	408	392	±2%
$Residence\ Time_{Total\ Hot\ Space}$ [s]	0.51	0.49	0.53	
Percentage Error		4.43	4.65	

6.6.3 Mass Balance Yields

Mass balance yields are categorised into char, liquids [including organics and water] and gas. The closure is the sum of the categories. The way in which each category is calculated has already been discussed in Sections 6.4.2 [Char], 6.4.3 [Liquids] and 6.4.4 [Gas].

Char is collected in the char pot and as a coating on the sand and inside the reactor and can therefore be weighed directly making it simple to quantify. However, the small microfine char tends to be blown through the cyclone and into the liquid collection system where it collects in the pyrolysis liquids. This char is very difficult to remove from the liquids except by solvent dilution followed by filtration, but as discussed in Section 6.3.3 this is not practical. The level of char in the liquid is generally very low [typically less than 2% on a pyrolysis liquid basis] so does not present a large increase in liquids. However, the calculated level of char could be lower than expected as some of the char may have entered the liquids. Since this char in the liquids will be classed as liquids then it will not lead to reduced closure only to incorrect classification.

The liquids are collected in the oilpots [OPI and OPII] and the EP as described in Section 6.4.3. Similar to the char, the liquids can be weighed directly [either to 1 or 2 decimal places], thus it is unlikely that any error is introduced here. As mentioned above, some char may have blown into the liquids, thus giving a slightly inflated liquids yield; however this is minimal. As discussed in Section 6.5.2.1, water content measurement of the liquids is accurate to ±0.01 wt.% so it seems unlikely that this could introduce errors into the organic/water categories.

The most likely source of error in pyrolysis liquids yield estimation is the possible loss of water and/or volatile organics from the liquids collection system. Since large volumes of fluidising and entrainment gas [nitrogen] are used, the gas will act as a carrier and could carry a small percentage of the more volatile components out of the collection system and into downstream equipment. It is difficult to quantify on a general basis, since each feedstock and reactor temperature will result in the production of a certain yield of volatile components. Thus for any run it is uncertain how much volatile organics will be produced and hence lost. If it were possible to analyse the gas more accurately then perhaps these losses could be quantified. Until more sensitive gas analysis is possible then the loss of water and/or volatile organics must remain an unquantified loss.

Unlike the char and liquids, the gas cannot be measured directly. Although the total volumetric throughput is known the amount of fluidising and entrainment nitrogen is not measured. This could be estimated from the rotameters, which are used to measure the nitrogen flows. However, sometimes these flows are altered during a run. In the future a gas meter could be placed on the nitrogen inlet to give an indication of the nitrogen consumption. Even if both the nitrogen input and total gas outputs where known this would, only give an indication of total gas volume; the gas composition and therefore weight would still have to be determined.

Determination of gas composition is carried out by chromatography, which has been described in Section 6.5.1. Possible inaccuracies were only briefly mentioned there; they will be assessed more fully in Section 6.6.4.

6.6.4 Product Analysis

The product analyses are split into 2 categories; gas analysis and liquids analysis. The liquids analysis can be sub-divided into water [Karl Fischer] and chemicals [HPLC] analysis.

The gas analysis is probably the weakest part of the mass balance. When closure is low, it is usually due to poor detection of the uncondensable gases due to the high dilution. Also it is possible that some water and/or volatile organics escape undetected as vapour, which could also lead to poor closure in the mass balance. The closure is not low for every run; thus it would be incorrect practice to estimate vapour losses for runs with low closures and not for runs with good [95-100%]. The loss of vapour can be estimated from the total volumetric throughput and partial pressures of components, which are believed to be lost [i.e. water and volatile organics].

Although the gas analysis is the weakest part of the analysis, this is not due to poor equipment. The problem is that the equipment has to be turned up to its limits of detectability and hence is performing at its upper most range. However, in the absence of any other method of gas analysis this method must remain. In the future a new system may be developed; this will be discussed in Chapter 12.

The Karl Fischer system and method has been described previously in Section 6.5.2.1. It is accurate to 0.01wt.%; thus it is not believed that this is a source of inaccuracy or poor closure.

The method and system used to carry out HPLC analysis of the pyrolysis liquids was described in Section 6.5.2.2. Since the major part of the HPLC analysis work concerns the analysis of pre-treated pyrolysis liquids, the accuracy of the technique will be discussed in Chapter 8.

7. PYROLYSIS OF UNTREATED FEEDSTOCKS

A number of previously untested feedstocks have been fast pyrolysed over a range of temperatures [450-600°C]. In all cases the maximum yield of organics has been determined along with the temperature at which this maximum occurs. The results are compared, where possible, to work by other institutes carried out on similar feedstocks at similar conditions. In all cases chemical analysis of one or more of the pyrolysis liquid samples from each feedstock has been carried out. The results are presented and critically compared.

7.1 UNTREATED FEEDSTOCKS

The production of a liquid fuel from fast pyrolysis of biomass will require that the maximum quantity of good quality liquid is produced from a particular biomass feedstock. This Chapter attempts to solve half of the above statement. By knowing the maximum liquid yield and the temperature at which it occurs, the maximum amount of pyrolysis liquid can be produced. However, this does not necessarily mean it is the best quality for use as a fuel. The quality of the pyrolysis liquid as a fuel depends on its stability, viscosity and energy value. It is recommended that these properties are assessed in the future and some correlation established between feedstock, reactor temperature, product collection system and fuel quality.

The yields of organics obtained from fast pyrolysis of a range of untreated biomass feedstocks are shown in Figure 7.1. The results shown in Figure 7.1 have been obtained in this work using a 150g/h reactor system [described in Section 6.3.2]. It is evident that the yield of organics depends on feedstock type and temperature. Thus for every feedstock type there will be a temperature at which the maximum yield of organics occurs.

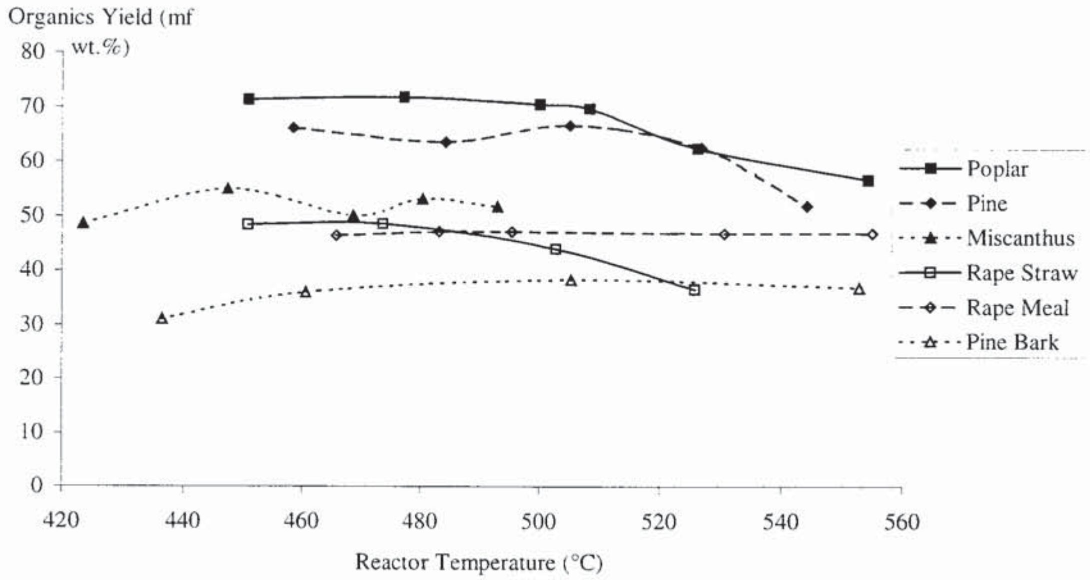


Figure 7.1: Yield of organics from pyrolysis of a range of feedstocks

Table 7.1 shows the maximum yields of organics and the temperature at which they were produced for a range of feedstocks pyrolysed at a number of institutions using different reactor systems. From Table 7.1 it is evident that woods give the best organics yields and barks give the worst. The temperature at which this maximum occurs varies from 429 to 582°C due to the type of feedstock used.

Table 7.1: Table of maximum organic yields and pyrolysis temperatures

	Maximum organics	Temperature	Source	Reference
IEA Poplar	**72**	**485**	**This work**	**[Section 7.1.1]**
IEA Poplar	70	500	Waterloo	[94, 73]
Pine	**68**	**477**	**This work**	**[Section 7.1.3]**
White spruce	65	512	Waterloo	[154]
Pine	60	549	Aston ablative	[153]
Pine	60	504	Aston 1kg/h FB	[153]
Sweet sorghum bagasse	58	515	Waterloo	[144]
Sugar cane bagasse	58	498	Waterloo	[82]
Miscanthus	**55**	**458**	**This work**	**[Section 7.1.5]**
Rape straw	**48**	**457**	**This work**	**[Section 7.1.6]**
Rape meal	**47**	**429**	**This work**	**[Section 7.1.7]**
Wheat straw	43	582	Waterloo	[82]
Poplar bark	43	500	Waterloo	[82]
Pine bark	**38**	**505**	**This work**	**[Section 7.1.4]**
Average	56	498		

The following sections present the results from the mass balances obtained in this work and discuss any experimental points specific to a particular feedstock. Where possible, comparison has been drawn between the feedstocks pyrolysed at Aston and the same or similar feedstocks pyrolysed at other institutes.

7.1.1 IEA Poplar

IEA poplar has been chosen as the base case. Poplar was chosen because it is chemically consistent, has low ash content, high cellulose content, is widely available and has been used by a number of other institutions (145, 146, 147, 148, 93, 149, 150, 94, 73). Also from Figure 7.1 and Table 7.1 it is evident that it gives the highest yield of organic liquids compared to any other feedstock.

IEA poplar feedstock has been pyrolysed over the temperature range 430-550°C, the mass balance reporting [as per Section 6.4.1] is shown in Table 7.2 and the major products plotted in Figure 7.2. The same feedstock material was used for all runs, hence the identical moisture and ash contents. Since the same feedstock was used throughout, the effects of particle size/shape will be the same in all cases and therefore can be ignored. The pyrolysis temperatures were chosen to cover this range in approximately 25°C steps.

In Chapter 3, it was found that as vapour residence time increased the liquid yields decreased. Therefore in this work the vapour residence times have been kept low [less than 1 second] to minimise secondary reactions. In most cases vapour residence times of 0.5 s have been achieved.

Table 7.2: IEA poplar, mass balance results

Run No.	SFB65	SFB25	SFB24	SFB28	SFB21	SFB23
React. Temp. [°C]	434	451	477	508	526	554
Vap. Res. Time [s]	0.71	0.57	0.53	0.51	0.59	0.49
Length of run [min]	60.5	38.0	45.5	40.8	30.1	41.4
Feedrate [g/h]	69.2	98.7	119.9	88.8	130.2	103.8
Moisture [mf wt.%]	7.25	7.25	7.25	7.25	7.25	7.25
Ash [mf wt.%]	0.46	0.46	0.46	0.46	0.46	0.46
Yields [mf wt.%]						
Char	11.88	9.80	8.73	8.23	8.36	8.03
Organics	66.10	71.38	71.78	69.69	62.37	56.57
Gas	13.83	15.00	11.98	15.62	21.24	22.11
Water	3.20	3.02	3.08	1.47	4.12	3.27
Total Liquids	69.30	74.40	74.86	71.16	66.49	59.84
Closure	95.01	99.20	95.57	95.01	96.09	89.89
Gas [mf wt.%]						
Carbon Monoxide	6.31	6.58	4.83	7.31	9.49	10.80
Carbon Dioxide	7.31	7.93	6.69	7.32	9.82	9.04
Methane	0.21	0.49	0.45	0.55	1.13	1.26
C2's	0.00	0.00	0.00	0.29	0.53	0.68
C3's	0.00	0.00	0.00	0.98	0.28	0.33
Gas [nitrogen free, vol. %]						
Carbon Monoxide	55.89	52.86	49.08	55.07	51.67	55.13
Carbon Dioxide	40.87	40.25	42.87	34.80	33.77	29.12
Methane	3.24	6.89	8.05	7.21	10.73	11.26
C2's	0.00	0.00	0.00	2.18	2.84	3.42
C3's	0.00	0.00	0.00	0.75	0.98	1.07

The experimental data from the runs are arranged in order of increasing temperature. SFB65 was carried out at the lowest temperature [434°C]. The residence time is slightly higher than for other runs. This may be due to the lower feedrate [and hence lower nitrogen inputs] or could be due to the fact that less gas is produced at lower temperatures resulting in slightly longer residence times. The longer residence time may have a slight effect on the liquids yield. Work by Scott (73), discussed in Chapter 3, indicated that increasing the gas/vapour residence time from 0.5 to 0.7 seconds reduced the organic liquid yield from 55 to 52 mf wt.%. Thus if the organic liquid yield was changed proportionally the yield for SFB65 may be 69.7 mf wt.%.

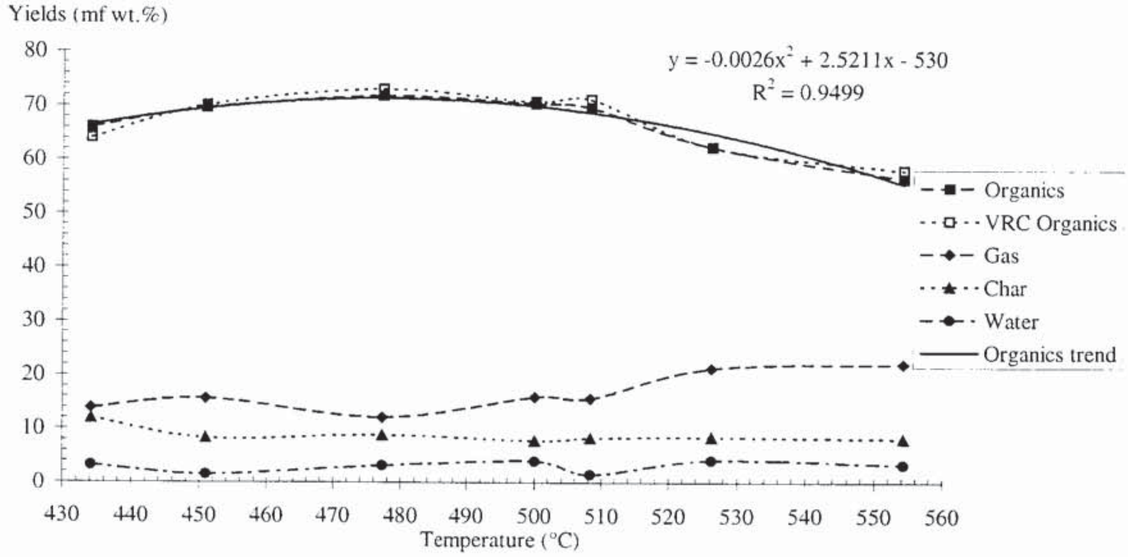


Figure 7.2: IEA poplar, product yields

The organic liquid yields from Table 7.2 have been corrected using a correlation developed from work by Scott (73) and the effect shown as VRC Organics [Vapour Residence Corrected Organics] in Figure 7.2. By comparing organics to VRC organics it is evident that there is very little difference between results. The organics trend shows that there is some experimental variation in product yields. This experimental variation shown by the corrected and uncorrected organics is no worse than that of the uncorrected organics trend. Therefore for all subsequent feedstocks the vapour residence correction will not be carried out.

The yield of pyrolysis products follows similar trends to those described in Chapter 3. The yield of organic liquid reaches a maximum at a temperature between 400 and 600°C; gas yields increase with temperature; char yields decrease with temperature and water remains relatively constant throughout.

The organics yield was found to follow a quadratic trend [the equation is shown in Figure 7.2, y is the yield of organics, mf wt.% and x is the temperature, °C]; differentiation of this trend gave the maximum organics yield at 485°C. The gas yields increase with temperature. However the gas analysis [as discussed in Section 6.5.1] is probably the weakest part of the mass balance. Hence the variability of the line. The water yields remain relatively constant through the temperature range investigated, although the levels seem lower than for other feedstocks [see proceeding sections for other Aston feedstocks]. This lower water yield could be due to the low water content in the starting material or may just be an intrinsic part of fast pyrolysis of poplar.

Figure 7.3 shows fast pyrolysis product yields for IEA poplar carried out at the University of Waterloo. The solid symbols and lines are the yields of products from their pilot plant scale [3kg/h] (73), while the outline symbols are the results of experiments carried out on their bench scale [15 g/h] pyrolysis reactors (94). It is evident that while the yield of organics is slightly higher in the pilot plant unit, both units obtain a maximum yield at approximately 500°C [520°C for 15g/h]. Similar shape curves are obtained for all products and this compares favourably with the results obtained for a similar feedstock at Aston [Figure 7.2].

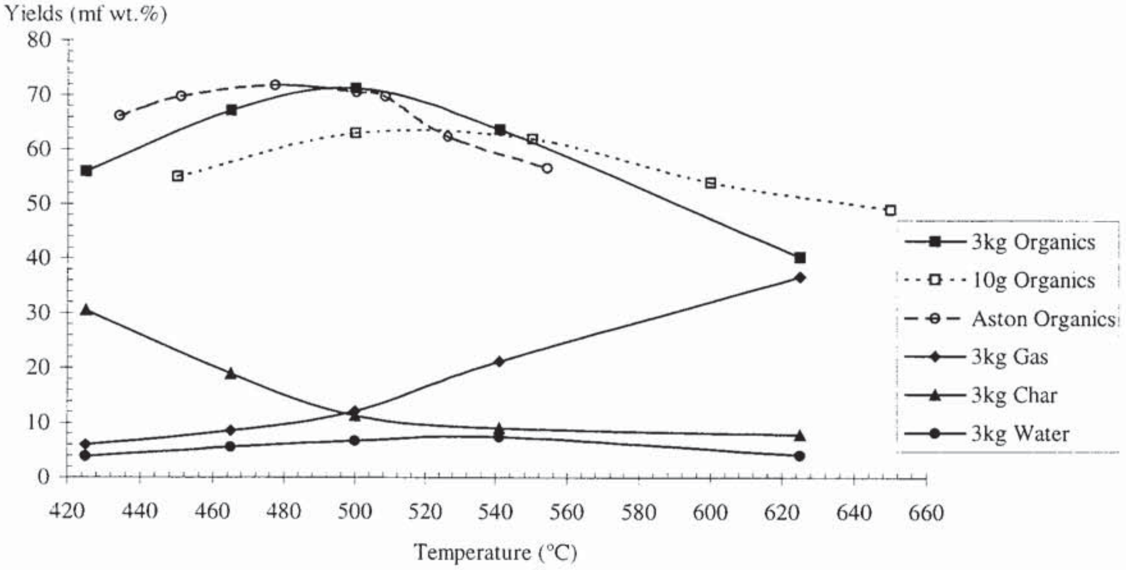


Figure 7.3: Waterloo product yields for IEA Poplar (94, 73)

As discussed in Chapter 6, the gas yields are probably the weakest part of the mass balance; thus detailed analysis of the gas components is difficult due to the suspected large errors involved. From Table 7.2 the yield of all gases on a dry feedstock basis increases with temperature; this is expected since as temperature increases reaction rates increase and the pyrolysis reactions can progress much further before leaving the reactor.

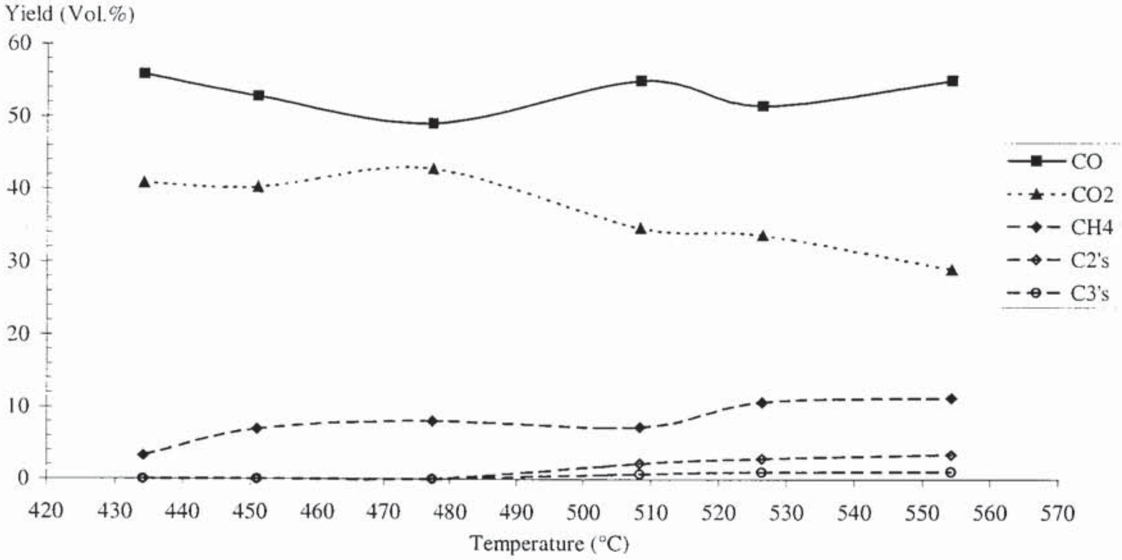


Figure 7.4: IEA poplar, gas component yields [volume basis]

The general trends of the gas yields are slightly more evident from Figure 7.4, which shows gas product percentage volumes on a nitrogen free basis. The volume percent of carbon monoxide [CO] produced remains relatively constant; however, the volume percent of carbon dioxide [CO_2] reduces. This is an indication that more secondary reactions are taking place as temperature increases, resulting in the formation of more carbon monoxide and more higher hydrocarbons [e.g. methane, ethane, ethylene, propane and propylene]. This is expected, since gas yields were found [Chapter 3] to increase with temperature.

7.1.2 IEA Poplar Pyrolysis Liquid Chemicals

The pyrolysis liquids from the above runs have been analysed by HPLC according to the method described in Section 6.5.2.2. The key reactor parameter [temperature] and mass balance yields [gas, organics, char, water, total oil and closure] are shown in Table 7.3. The yields of the chemical products detected by HPLC in concentrations greater than 1mf wt.% [dry feed basis] are shown in Table 7.3. The other chemicals have been grouped together since they were only detected in yields of less than 1 mf wt.%.

From Table 7.3 there are some interesting trends in chemical yields. The yield of fructose decreases quite rapidly, from 1.84mf wt.% at 434°C to 0.06 mf wt.% at 554°C. From this, it would appear that fructose is degraded to secondary products and gas at higher temperatures, or that at higher temperatures a different product is formed in preference to fructose. The yield of acetol shows 2 major peaks for runs SFB65 [434°C] and SFB21 [526°C]; this is due to the HPLC analysis column being changed, which has altered the sensitivity and the yields of products. Because of this, runs SFB65 and 21 are not shown in Figure 7.5.

Table 7.3: IEA poplar, chemicals analysis

Run No.	SFB65	SFB25	SFB24	SFB28	SFB21	SFB23
Temp. [°C]	434	451	477	508	526	554
Yields [mf wt.%]						
Gas	13.83	15.00	11.98	15.62	21.24	22.11
Organics	66.10	71.38	71.78	69.69	62.37	56.57
Char	11.88	9.80	8.73	8.23	8.36	8.03
Water	3.20	3.02	3.08	1.47	4.12	3.27
Total Liquids	69.30	74.40	74.86	71.16	66.49	59.84
Closure	95.01	99.20	95.57	95.01	96.09	89.89
Chemicals [mf wt.%]						
Hydroxyacetaldehyde	10.19	8.69	8.38	7.26	8.13	5.63
Levoglucosan	3.81	2.52	2.73	2.45	2.84	2.01
Formic acid	5.49	4.69	5.28	4.76	6.64	3.07
Acetic acid	8.35	7.41	7.56	6.73	9.06	6.34
Fructose	1.84	1.62	1.28	0.92	0.24	0.06
Acetol	2.35	0.35	0.48	1.04	2.24	0.16
Others	0.61	2.08	2.25	1.81	0.68	2.22
Pyrolytic Lignin	18.80	19.03	19.29	17.09	21.91	17.19
Total	51.43	46.39	47.24	42.08	51.73	36.68

The four chemicals [hydroxyacetaldehyde {HA}, levoglucosan {LG}, acetic acid {HOAc} and formic acid/formaldehyde {FC/FD}] are shown in Figure 7.5 in a graph of yield versus temperature. The yields of organics, total chemicals detected and pyrolytic lignin are also shown on the second [right hand] Y axis. The yield of HA appears to reach a maximum at 450°C, which is slightly different to previous work done by the University of Waterloo on cellulose (151). HOAc and FC/FD show a slight increase at 480°C. The yield of LG shows a slight peak at approximately 475°C; this concurs to a limited extent with cellulose work done by Waterloo (151).

It was demonstrated in Chapter 3 [Figure 3.5] that for the pyrolysis of cellulose there are two distinct reactions. Depolymerisation is the splitting of the long chain cellulose polymer into the monomeric units [D-glucose] and results in the primary pyrolysis product of levoglucosan [LG]; the maximum LG yield occurs at approximately 370°C for pyrolysis of cellulose (82). Fragmentation is the breaking apart of the monomeric units and results in the primary pyrolysis product of hydroxyacetaldehyde [HA]; the maximum HA yield for cellulose occurring at approximately 590°C.

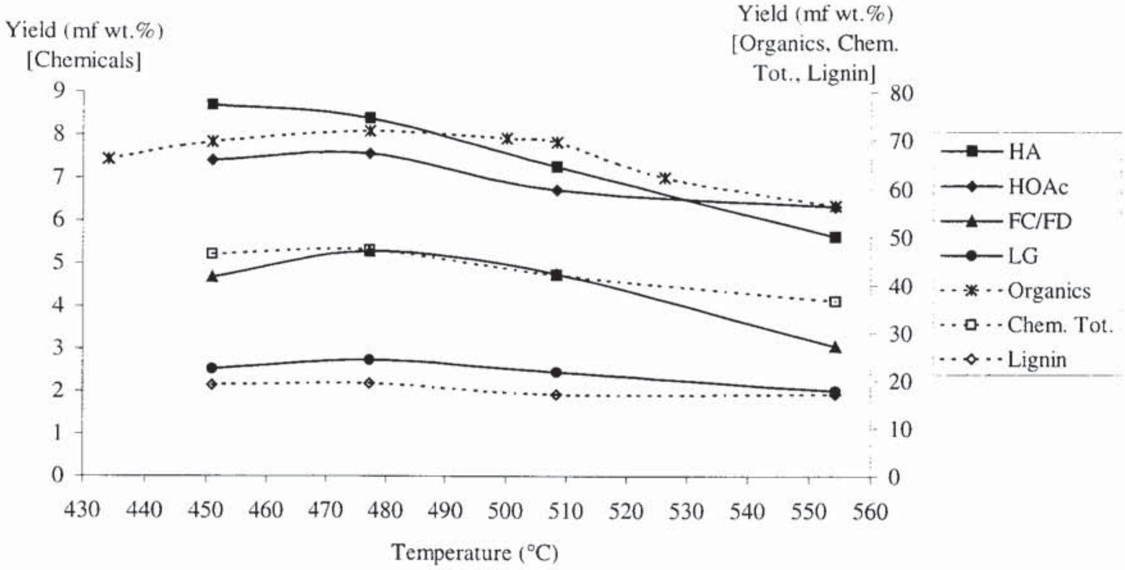


Figure 7.5: IEA poplar, chemical products

Since IEA poplar wood contains cellulose as its major chemical component [59.4 mf wt.%] it would be expected that similar behaviour to that of pure cellulose should be observed. This does not appear to be the case, as can be seen in Figure 7.6.

It is evident that much higher yields of chemicals [especially LG, HA and HOAc] are obtained from fast pyrolysis of cellulose. Since poplar [and other biomass types] contain much less cellulose than pure cellulose this is to be expected. If the yields are corrected for the reduced cellulose content [i.e. divide all values by 0.5] then an increase in yields for all components is observed [i.e. a scaling effect]. However, this does not change the shape of the curves. Thus as was suggested in Chapters 2 and 3, the chemicals produced from fast pyrolysis of biomass are not merely a sum of the chemicals from the individual chemicals. The other biomass components must interact and have therefore produced a marked change in the liquid chemical products.

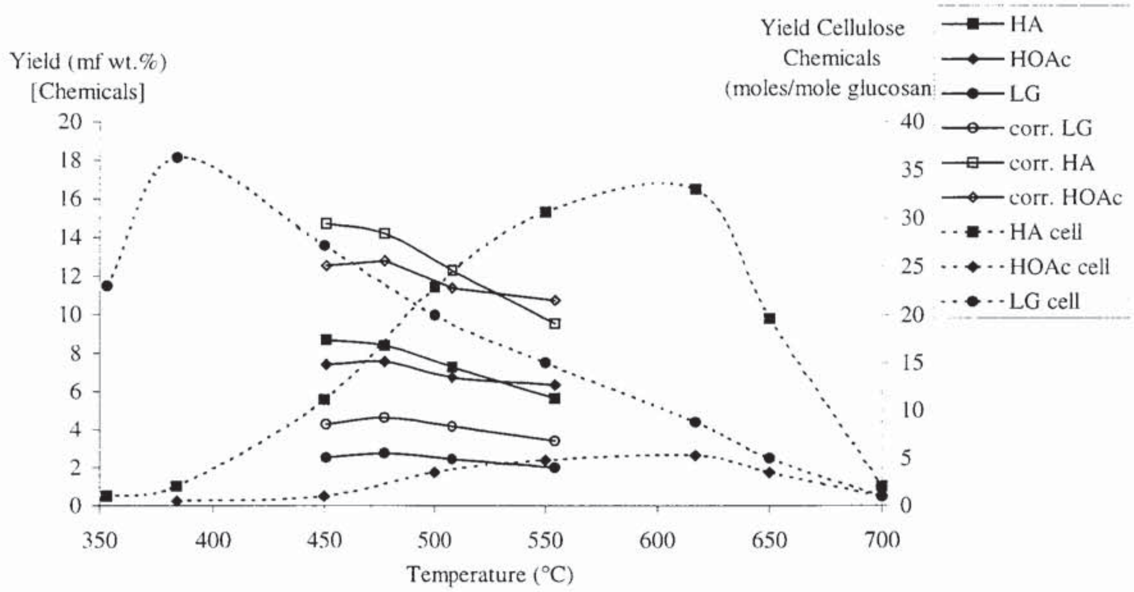


Figure 7.6: Aston IEA poplar liquid chemical yields compared to cellulose

It would also appear that the presence of other biomass components [i.e. hemicellulose, lignin and ash] can have an influence not only on the yields of chemicals, but on the temperature profile over which they are produced. This is also illustrated in Figure 7.7, for chemical pyrolysis products from Western hemlock (152) and sweet sorghum bagasse (144). It is only sweet sorghum bagasse hydroxyacetaldehyde which exhibits any clear peak.

Unlike cellulose, which has clearly defined regimes of depolymerisation [LG] and fragmentation [HA], IEA poplar would appear to have an optimum temperature for chemicals production between 450 and 500°C. From this it is tentatively concluded that the production of chemicals from untreated biomass should be attempted at fast pyrolysis temperatures of 500°C or less.

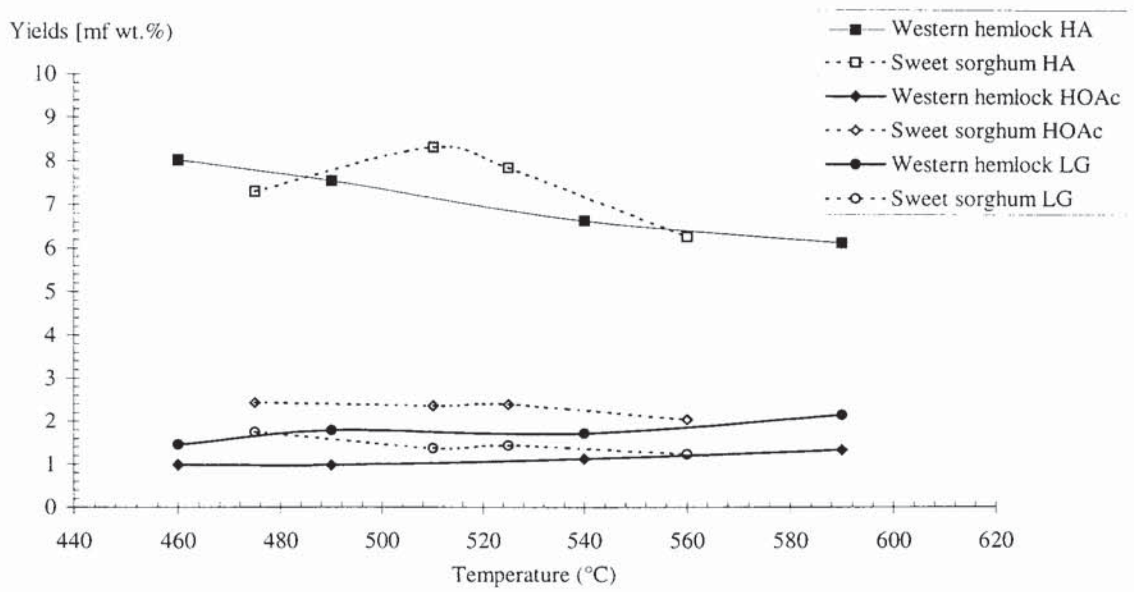


Figure 7.7: Chemical yields from western hemlock (152) and sweet sorghum bagasse (144)

7.1.3 Pine

Pyrolysis experiments were conducted on pine over the temperature range 450-550°C. The mass balance reporting [as per Section 6.4.1] is shown in Table 7.4. A total of nine experiments were carried out on pine. However only the best results have been included in Table 7.4. All nine experiments are included in the graph of the major products plotted in Figure 7.8 and all nine results are used for the curve fit. The same feedstock material was used for all of the experiments, hence the identical moisture and ash contents. A similar experimental plan was adopted as with IEA poplar [Section 7.1.1]; thus temperatures were chosen at 25°C intervals to span the range and residence times were kept low to reduce secondary reactions.

Table 7.4: Pine, mass balance results

Run No.	SFB08	SFB07	SFB12	SFB10	SFB11
Temp. [°C]	458	484	505	527	544
Res. Time [s]	0.75	0.78	0.65	0.61	0.60
Feedrate [g/h]	78.4	47.7	80.0	66.4	64.0
Moisture [mf wt.%]	10.04	10.04	10.04	10.04	10.04
Ash [mf wt.%]	0.23	0.23	0.23	0.23	0.23
Yields [mf wt.%]					
Char	18.47	11.58	11.03	10.59	13.66
Organics	66.14	63.55	66.64	62.51	51.79
Gas	7.89	8.27	8.76	17.71	16.64
Water	10.49	9.87	6.80	7.87	6.54
Total Liquids	76.63	73.42	73.44	68.38	57.33
Closure	94.53	93.26	93.08	98.68	88.62
Gas [mf wt.%]					
Carbon Monoxide	3.27	3.38	3.03	10.37	7.82
Carbon Dioxide	4.42	4.66	5.32	5.94	6.95
Methane	0.20	0.23	0.41	0.56	0.78
C2's	0.00	0.00	0.00	0.26	0.41
C3's	0.00	0.00	0.00	0.87	0.25
Gas [nitrogen free, vol. %]					
Carbon Monoxide	51.05	50.35	42.62	66.26	54.55
Carbon Dioxide	43.62	43.76	47.34	23.96	30.59
Methane	5.33	5.88	10.05	6.26	9.50
C2's	0.00	0.00	0.00	1.67	2.87
C3's	0.00	0.00	0.00	0.67	1.09

As mentioned in Section 6.3.3, the electrostatic precipitator [EP] was only introduced into the secondary products collection after run SFB12. These early runs were carried out using 2 ice water cooled condensers, which may account for some of the poorer closures.

The char yield at 458°C [SFB 08] is approximately 19%. As the temperature increases the char yield decreases; at 544°C [SFB11] there is an unexpected increase in char. This run was extremely problematical, had some feeding problems, only lasted for 19 minutes and only 20g of wood were fed. It is likely that the results from this run should not be used. The organics yield is adequately described by a second order polynomial [shown as hashed line in Figure 7.8, y is the organics yield and x is the temperature]. The maximum organics yield was found to occur at 477°C., this is slightly lower than IEA poplar [485°C] and this is believed to be due to the lower ash content of the pine [0.23mf wt.% pine compared to 0.46mf wt.% IEA poplar].

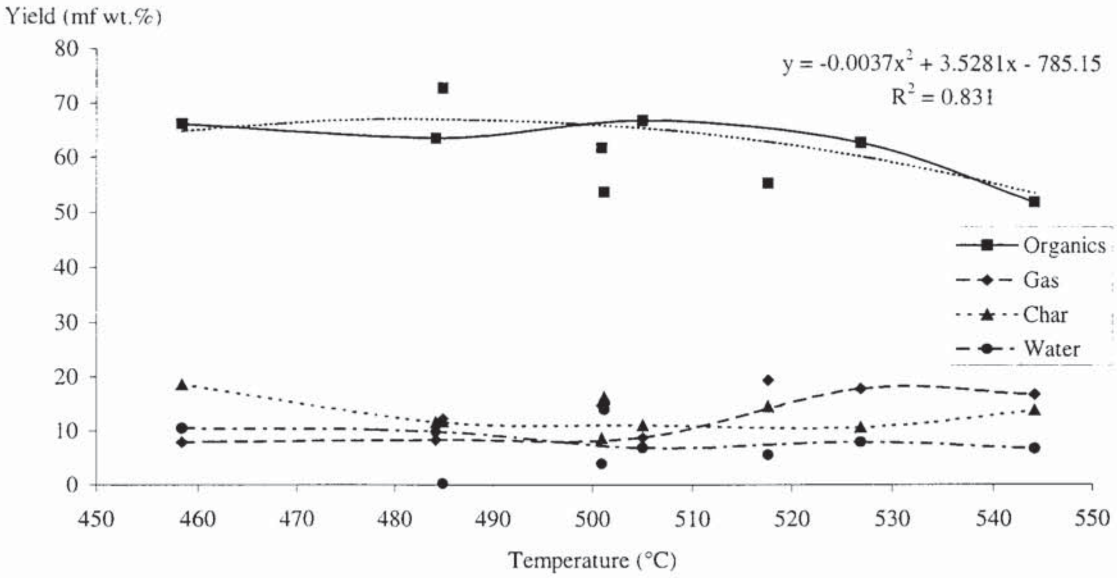


Figure 7.8: Pine, product yields

The gas yields increase with temperature until 544°C [SFB11] at which point the yield decreases slightly. SFB11 had a poor closure [88.62], which is due to blockages in the reactor during the run, which required the reactor to be restarted. The yield of water remained relatively constant throughout these experiments, which is comparable to the yields obtained from IEA poplar.

The product yields from the ablative fast pyrolysis of pine [Aston University] (153) and fluidised bed pyrolysis of white spruce [University of Waterloo] (154) are shown for comparison in Figure 7.9. The results for ablative pyrolysis are shown in solid black, fluidised bed pyrolysis of pine is shown as unfilled squares with dotted lines, fluidised bed pyrolysis of white spruce is shown as unfilled triangles with dotted lines and the above pine work [SFB pine] is shown as unfilled circles. Regression of the organics yields gave maxima at 504°C for fluidised bed pine, 549°C for ablative pine and 512°C for fluidised bed white spruce. These maximum temperatures are slightly higher than those found in this work.

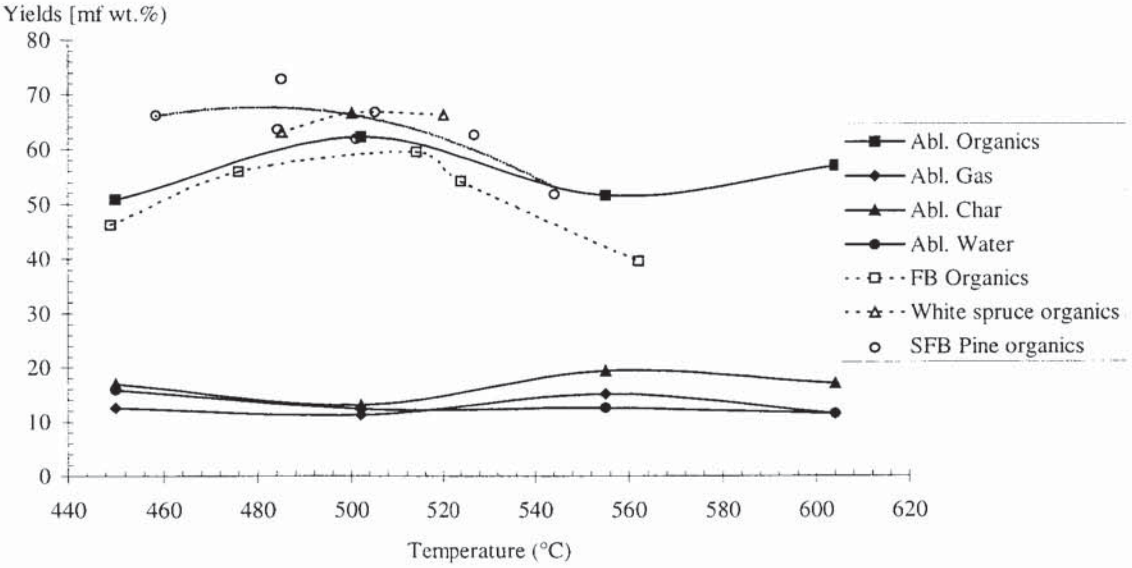


Figure 7.9: Yields of products from pine (153) and white spruce (154)

7.1.4 Pine Bark

Pyrolysis of pine bark was carried out over the temperature range 430-560°C. Mass balances were carried out and reported [as per Section 6.4.1] in Table 7.5. The yield of major pyrolysis products is shown in Figure 7.10. The same feedstock was used for all runs, hence the identical moisture and ash contents. Char yields were much higher than IEA poplar or pine [almost double the yields]. Pine bark organics yields were considerably lower than woods such as poplar and pine.

The gas yields do not appear to behave typically [i.e. similar to IEA poplar or pine] since it is expected that the gas yield increases with temperature. However gas analysis for these runs appears to be less reliable than usual, since SFB04 had a particularly high gas yield and SFB05 had a low yield, which may have been due to the subsequent breakdown of the GC analysis system. Due to this breakdown a new analysis method using mass spectroscopy was utilised for SFB06. This required the fluidising gas to be changed from nitrogen to argon to avoid masking carbon dioxide [both nitrogen and carbon dioxide have a molecular weight of 28]. This technique proved unsuccessful, hence the gas yield for SFB06 is low. It was expected that the gas yield would be closer to 20mf wt.% [as was found for poplar and pine], which would considerably improve the closure.

The water yield remained relatively constant throughout these experiments. It should also be noted that these experiments were carried out before the EP was installed, but this does not appear to have affected the results. The poor closures are believed to be due to the quality of the gas analysis.

Table 7.5: Pine bark, mass balance results

Run No.	SFB03	SFB04	SFB05	SFB06
Temp. [°C]	436	461	505	553
Res. Time [s]	0.51	0.36	0.56	0.66
Feedrate [g/h]	86.0	89.3	134.7	131.5
Moisture [mf wt.%]	14.94	14.94	14.94	14.94
Ash [mf wt.%]	1.94	1.94	1.94	1.94
Yields [mf wt.%]				
Char	34.14	32.70	29.30	27.75
Organics	31.04	35.99	38.25	36.80
Gas	14.31	19.20	13.72	11.13*
Water	10.55	12.34	11.93	11.52
Total Liquids	41.59	48.33	50.18	48.32
Closure	90.05	100.23	93.19	87.20
Gas [mf wt.%]				
Carbon Monoxide	4.17	5.57	5.12	4.15
Carbon Dioxide	9.43	12.61	8.16	6.62
Methane	0.22	0.29	0.31	0.25
C2's	0.50	0.66	0.13	0.11
C3's	0.00	0.07	0.00	0.00
Gas [nitrogen free, vol. %]				
Carbon Monoxide	38.04	37.92	46.77	46.77
Carbon Dioxide	54.34	54.18	47.08	47.08
Methane	3.44	3.43	4.96	4.96
C2's	4.19	4.17	1.19	1.19
C3's	0.00	0.30	0.00	0.00

* mass spectroscopy used for gas analysis rather than gas chromatography

Figure 7.10 shows the distribution of the major pyrolysis products with temperature. As mentioned above the organics yield has a typical shape compared to IEA poplar or pine but shifted down due to the lower yields. From the second order polynomial curve fit of the organics yield [Figure 7.10] the maximum organics yield is predicted at 505°C; this is approximately 25°C higher than IEA poplar or pine and is believed to be due to the higher ash content. As expected, the char yields decrease with temperature and the water yield remains relatively constant throughout.

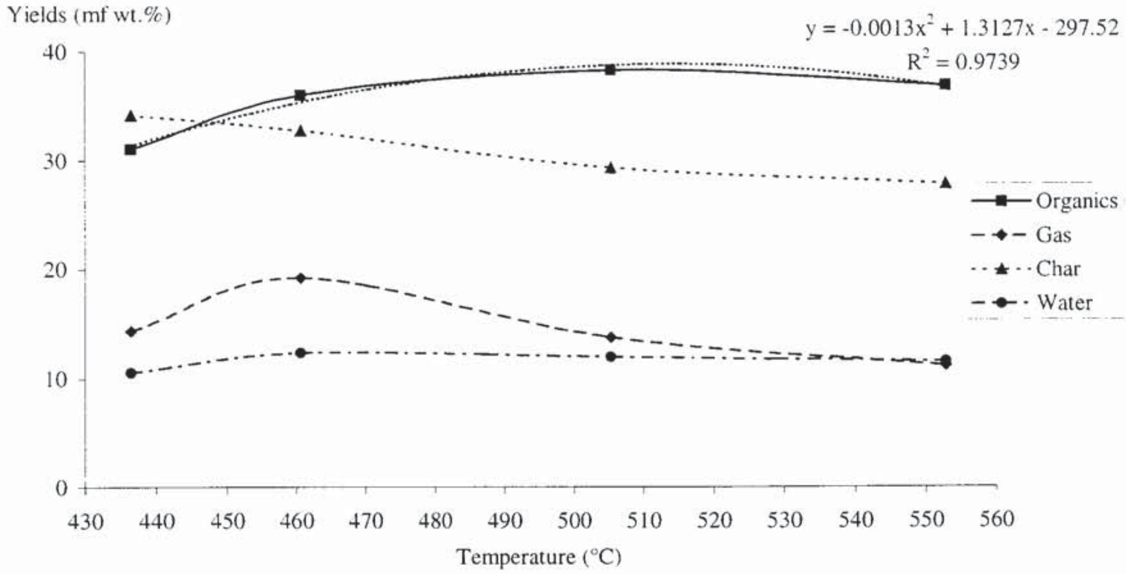


Figure 7.10: Pine bark, product yields

Scott et al. pyrolysed poplar bark, which was taken from the outside of the same tree used for the poplar wood experiments [shown in Figure 7.3] (140). The results for poplar bark are shown in Figure 7.11 along with results from the above pyrolysis of pine bark [SFB PB organics + water] (140). Waterloo found that the maximum tar yield [43%] occurred at the same temperature as for poplar [i.e. 500°C], but the yield was noticeably lower.

Aston pine bark gave maximum organic yields of 38% at 505°C, which is the same temperature as the Waterloo poplar bark results. Unlike Waterloo's findings, pine bark used at Aston did not have the same temperature for maximum yield as pine [477°C]. However, the pine bark came from a different source to the pine and so is probably a completely different species of pine, which may account for the difference.

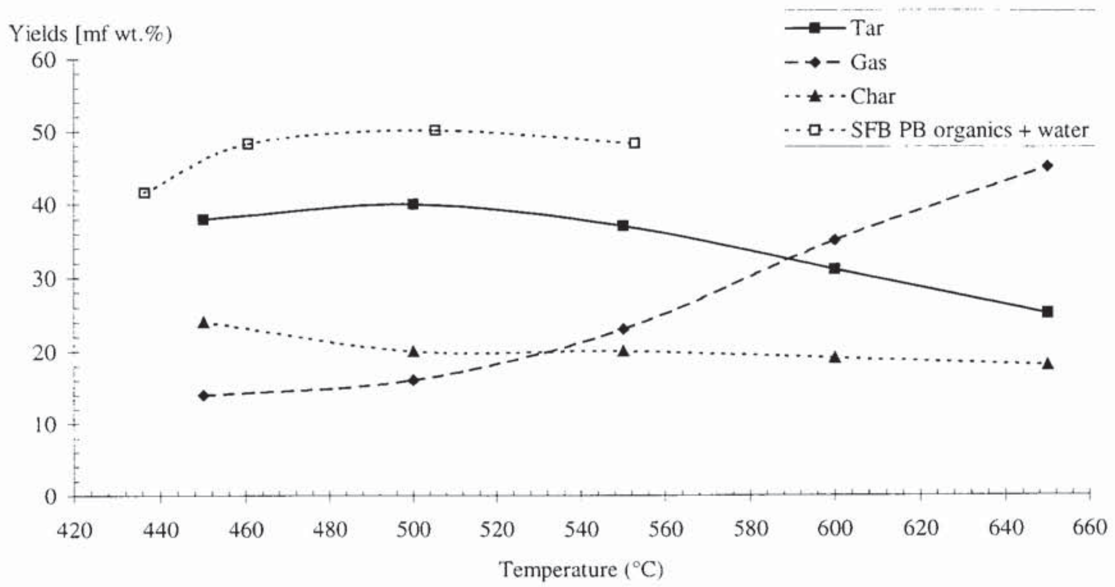


Figure 7.11: Waterloo pyrolysis products from poplar bark (140)

Scott et al. found the poplar bark contained high levels of ash and extractives, notably tannin like materials. Pyrolysis of tannins tends to lead to the formation of polyhydroxyphenols and carbon dioxide, hence the high gas yields at elevated temperatures. This was expected for the Aston pine bark, but due to equipment problems gas yields were low.

7.1.5 Miscanthus

Pyrolysis experiments were conducted on miscanthus over the temperature range 420-500°C in a similar manner to all other pyrolysis experiments previously reported. Miscanthus yields followed typical trends [e.g. IEA poplar, pine] but at lower temperatures. The char content seemed to remain relatively constant over the temperature range investigated. It started off at approximately 19.5 mf wt.% [423°C] and the yield decreased initially [down to 17.3 mf wt.% at 447°C]; it then increased to finish at 19.4 mf wt.% [493°C].

The maximum yield of organics [55 mf wt.%] was calculated from the second order polynomial shown in Figure 7.12 and occurred at 458°C. The organics yield is lower than for poplar or pine at around 50 mf wt.% compared to 60-70 mf wt.% for IEA poplar and pine. This lower organics yield is thought to be due to the high levels of ash in the miscanthus, 3.16 mf wt.%, compared to 0.46 mf wt.% for IEA poplar and 0.23 mf wt.% for pine. The gas yields increased with temperature and the char yields decreased with temperature. Water yields remained relatively constant at around 8 mf wt.% throughout.

Table 7.6: Miscanthus, mass balance results

Run No.	SFB30	SFB19	SFB31	SFB18	SFB17
Temp. [°C]	423	447	469	480	493
Res. Time [s]	0.54	0.55	0.52	0.53	0.56
Feedrate [g/h]	80.5	97.6	85.4	108.0	89.0
Moisture [mf wt.%]	8.46	8.46	8.46	8.46	8.46
Ash [mf wt.%]	3.16	3.16	3.16	3.16	3.16
Yields [mf wt.%]					
Char	19.51	17.32	17.73	18.85	19.40
Organics	48.55	54.93	50.06	53.08	51.68
Gas	14.71	14.49	12.67	18.45	17.97
Water	8.54	6.98	9.01	6.31	7.61
Total Liquids	57.09	61.92	59.07	59.39	59.29
Closure	91.31	93.73	89.47	96.69	96.66
Gas [mf wt.%]					
Carbon Monoxide	4.08	5.16	3.80	7.22	5.98
Carbon Dioxide	10.40	8.81	8.65	10.58	11.40
Methane	0.24	0.34	0.22	0.50	0.45
C2's	0.00	0.17	0.00	0.14	0.15
C3's	0.00	0.00	0.00	0.00	0.00
Gas [nitrogen free, vol. %]					
Carbon Monoxide	36.91	44.96	39.43	48.45	42.40
Carbon Dioxide	59.35	48.42	56.57	44.81	51.04
Methane	3.74	5.23	4.00	5.90	5.60
C2's	0.00	1.38	0.00	0.84	0.95
C3's	0.00	0.00	0.00	0.00	0.00

This is a completely novel feedstock, no fast pyrolysis research on a comparative energy crop has been found. The growth of energy crops [i.e. crops which have no food use] are currently being promoted in the UK. Miscanthus has proved a reasonable fast pyrolysis feedstock which produces "average" pyrolysis liquid yields [i.e. not as good as wood but better than forest residues such as pine bark].

Miscanthus is a perennial crop, which matures after 3-4 seasons growing and can be harvested every season thereafter. This cycle is much faster than trees or coppiced wood and therefore it may prove more economic to grow this type of crop rather than wood, even with reduced pyrolysis liquid yields. The pyrolysis liquid may also contain high yields of novel chemicals, which could provide more incentive to potential growers. The analysis of the pyrolysis liquid has been carried out and is reported in Section 7.3 along with comparison of the chemicals obtained from the other feedstocks tested as part of this work.

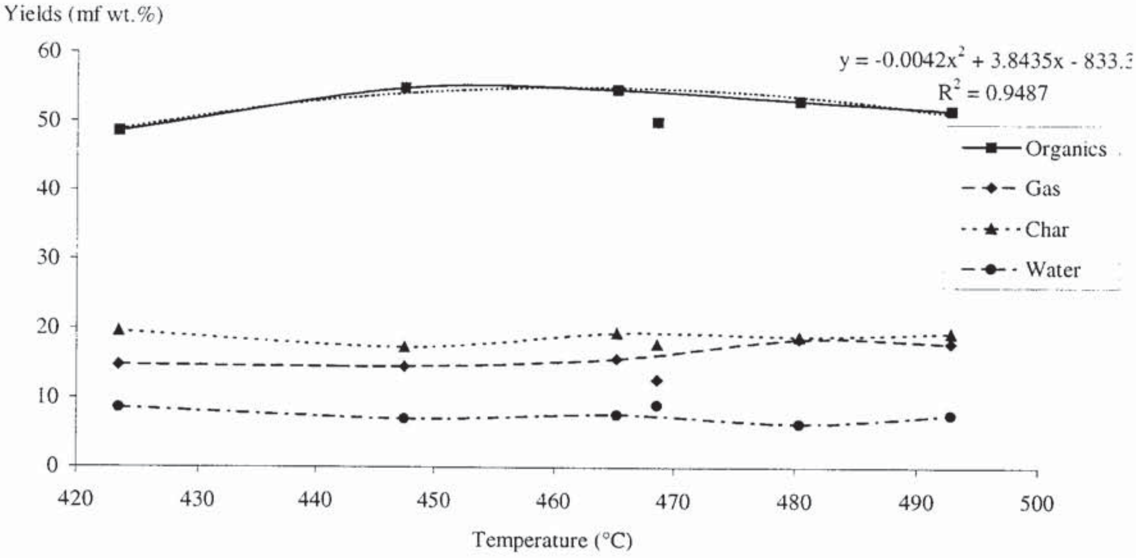


Figure 7.12: Miscanthus, product yields

7.1.6 Rape Straw

Rape straw was pyrolysed over the temperature range 450-525°C; temperatures were chosen at 25°C intervals, as per earlier experimental procedure. Detailed mass balance results [as per Section 6.4.1] are shown in Table 7.7 below. A graphical representation of product yield results is shown in Figure 7.13 below.

Rape straw behaved very similarly to miscanthus. This is to be expected since they will most likely have similar chemical compositions. The char yield remained relatively stable at around 20 mf wt.%. The organics yield as determined from the second order polynomial curve [Figure 7.13] has a peak of approximately 48mf wt.% at 457°C, which is almost identical to miscanthus [458°C]. The gas yield increases with temperature as does the water yield. Slight variations in the shape of the curve are most likely caused by lower mass balance closures. In the case of SFB44 only a 90% closure was achieved, which may be due to gas analysis problems.

Table 7.7: Rape straw, mass balance results

Run No.	SFB47	SFB43	SFB44	SFB48
Temp. [°C]	451	474	503	526
Res. Time [s]	0.59	0.51	0.49	0.52
Feedrate [g/h]	69.9	73.9	83.7	68.9
Moisture [mf wt.%]	8.51	8.51	8.51	8.51
Ash [mf wt.%]	5.18	5.18	5.18	5.18
Yields [mf wt.%]				
Char	22.28	19.19	21.27	20.77
Organics	48.42	48.54	43.95	36.52
Gas	18.19	17.87	14.89	23.19
Water	10.22	10.36	10.78	14.56
Total Liquids	58.64	58.90	54.73	51.08
Closure	99.11	95.96	90.90	95.04
Gas [mf wt.%]				
Carbon Monoxide	5.85	5.45	4.05	7.93
Carbon Dioxide	11.78	11.83	10.13	13.68
Methane	0.32	0.59	0.57	0.88
C2 s	0.14	nd	nd	0.45
C3 s	0.59	nd	0.14	0.24
Gas [nitrogen free, vol. %]				
Carbon Monoxide	41.63	39.11	35.13	42.39
Carbon Dioxide	52.94	53.54	55.44	46.16
Methane	4.03	7.36	8.68	8.22
C2 s	0.90	0.00	0.00	2.40
C3's	0.50	0.00	0.74	0.83

Figure 7.13 shows the variation in major product yield with pyrolysis temperature. The char yield is relatively stable over the range, but does decrease slightly. The organics yield shows the typical curve exhibited by IEA poplar and pine. The water yields remained stable at around 10 mf wt.% until the reactor temperature was increased beyond 510°C; after this the water increased to around 15 mf wt.%.

Pyrolysis of wheat straw was carried out at Waterloo and the results shown in Figure 7.14. The organics yields from miscanthus and rape straw have also been included. It is evident that the wheat straw produced different results to those of miscanthus and rape straw. Wheat straw produced maximum organic liquid yields of 43 mf wt.% but at a much higher temperature than either miscanthus or rape straw. From Figure 7.14 it is interesting to note that miscanthus gave much higher organic yields than rape straw. This may be because the product from a rape plant is rape seed; therefore, much of the plants energy goes into the production of the seed. However, miscanthus is purely an energy crop and therefore all of the energy goes into producing the stem, which was used for these experiments.

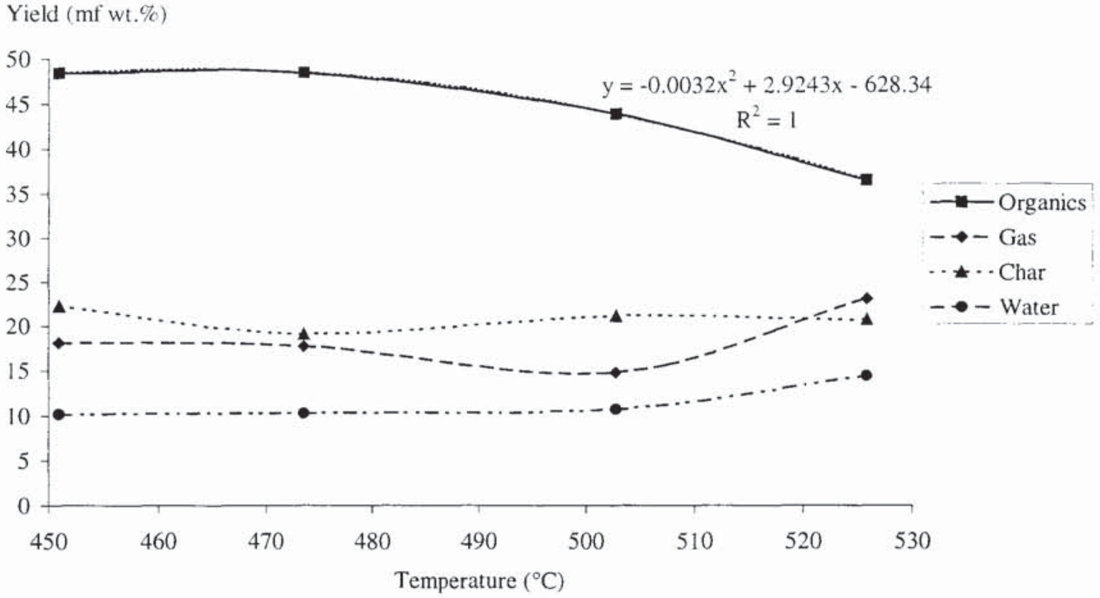


Figure 7.13: Rape straw, product yields

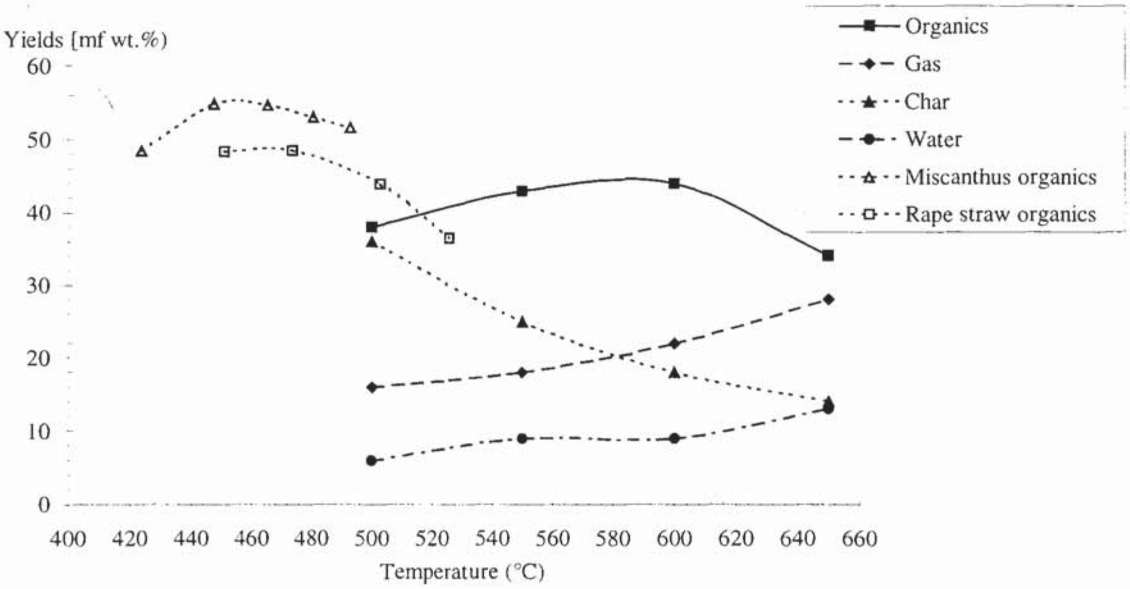


Figure 7.14: Waterloo pyrolysis products from wheat straw (82)

7.1.7 Rape Meal

Initial rape meal pyrolysis runs were unsuccessful due to reactor blockages caused by the feed forming a cake almost as soon as it was blown into the hot fluidised bed. As previously mentioned [Section 6.1.5] rape meal has a high bulk and absolute density

[1.33 and 0.59 g/cm^3 respectively] in comparison to wood or straw [absolute and bulk densities of approximately 0.6 and 0.4g/cm^3 respectively].

Table 7.8: Rape meal, mass balance results

Run No.	SFB42	SFB39	SFB38	SFB37	SFB41
Temp. [°C]	466	483	495	531	555
Res. Time [s]	0.48	0.46	0.47	0.48	0.41
Feedrate [g/h]	77.7	86.8	72.2	37.0	144.5
Moisture [mf wt.%]	1.00	1.00	1.00	1.00	1.00
Ash [mf wt.%]	7.68	7.68	7.68	7.68	7.68
Yields [mf wt.%]					
Char	24.03	24.86	25.78	22.26	20.32
Organics	46.35	47.11	47.04	46.71	46.72
Gas	11.98	12.06	12.47	16.14	15.09
Water	9.81	10.62	9.63	11.98	12.15
Total Liquids	56.16	57.73	56.67	58.69	58.87
Closure	92.16	94.66	94.92	97.09	94.28
Gas [mf wt.%]					
Carbon Monoxide	3.12	1.89	1.92	4.99	5.24
Carbon Dioxide	8.73	9.40	9.91	10.39	8.80
Methane	0.13	0.35	1.92	0.25	0.33
C2's	nd	0.25	0.11	0.27	0.38
C3's	nd	0.18	0.23	0.24	0.34
Gas [nitrogen free, vol. %]					
Carbon Monoxide	35.22	21.51	21.44	40.22	43.76
Carbon Dioxide	62.21	67.66	70.03	52.86	46.44
Methane	2.57	6.89	5.79	3.54	4.85
C2's	0.00	2.65	1.11	2.15	3.13
C3's	0.00	1.29	1.63	1.23	1.82

The 150g/hr reactor was commissioned using poplar wood, which has a bulk density of around 0.4g/cm^3 and an absolute density of around 0.6g/cm^3. The feeder described in Section 6.31. operates on a volume basis, since only a fixed volume of particles can get through the entrainment tube per unit time. Therefore, since rape meal is much more dense than wood the mass flowrate was almost double that of wood. The rotameters, which control this flowrate could not be set at a low enough level for rape meal to be fed at less than 150g/h, which resulted in overloading of the reactor. The rotameters were changed to alleviate this problem and allow much lower flows of nitrogen to the feeder. It was also felt that the moisture content of the rape meal [9.3 mf wt.%] may have been causing agglomeration problems so the feedstock was also oven dried to improve its pyrolysis characteristics.

Rape meal was successfully pyrolysed over the temperature range 465-555°C, temperatures chosen at 25°C intervals, as per earlier experimental procedures. Detailed mass balance results [as per Section 6.4.1] are shown in Table 7.8 above. A graphical representation of product yield results is shown in Figure 7.15.

The results from early runs, which had feeding problems, are not shown. The entrainment gas flow had to be doubled to feed the rape meal into the reactor and prevent the end of the feed tube from becoming blocked. Hence residence times were kept low and secondary reactions were kept to a minimum.

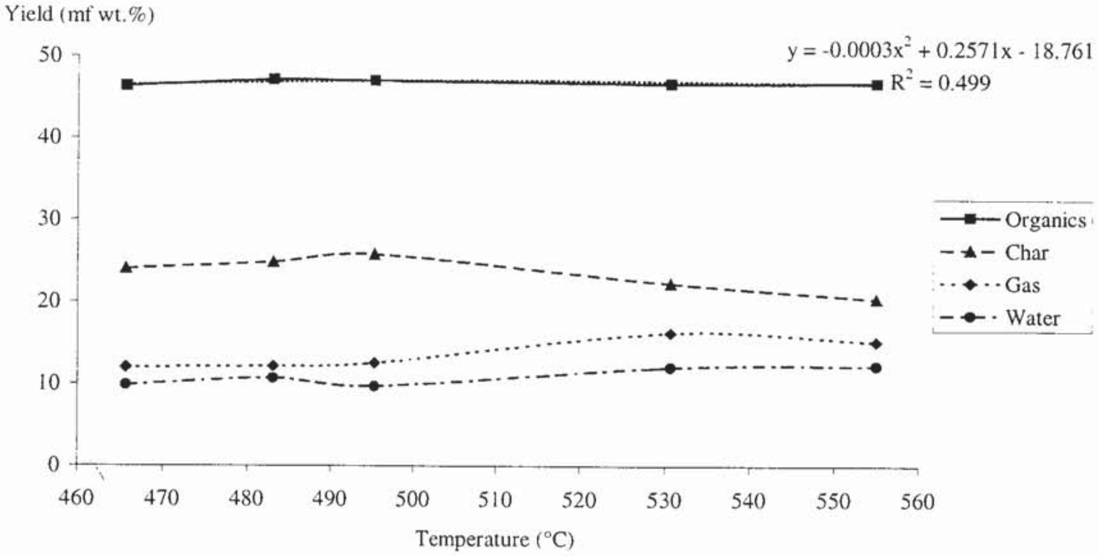


Figure 7.15: Rape meal, product yields

The char yields remained relatively constant [approximately 25 mf wt.%] until the pyrolysis temperature reached 500°C; above this temperature the yields decreased. The yields of organics remained stable at around 47 mf wt.% over the temperature range. A second order polynomial curve [Figure 7.15] was used to estimate the temperature at which the maximum organics yield was obtained; this curve did not fit particularly well [due to the organics yield being practically a straight line]; this is evident from the low R^2 value of 0.499. The maximum organics yield of 48 mf wt.% was predicted to occur at 429°C; however, no reactions were carried out at such a low temperature. This possibly suggests that reactions should have been carried out at lower temperatures. The processed nature of the rape meal [i.e. pressing/extruding to remove rape oil] may have weakened the cellular structure and made it more susceptible to thermal attack.

The gas yields followed typical trends observed in other feedstocks [e.g. IEA poplar and pine] and increased with increasing temperature. The yield of water remained relatively constant at around 10 mf wt.%, although levels did rise once the temperature increased above 500°C.

The major pyrolysis products are shown in Figure 7.15. As discussed above, the yields are similar to those of other feedstocks, but the yield of organics has a much flatter curve. The yields of carbon monoxide are low and the yields of carbon dioxide are high, which are similar trends to those observed in rape straw and wheat straw [Waterloo]. Perhaps this is due to the high lignin content of barks and straws. It is certainly possible that since rape meal has already undergone extensive processing [to remove the rape seed oil] that the cellular or molecular structure has been weakened and this has made it easier to pyrolyse. The low temperature for the maximum yield of organics is also evidence of this.

7.2 FEEDSTOCK COMPARISON

Table 7.9 shows a compilation of results from the above feedstocks pyrolysed at 500°C. The results are arranged in ascending order of organics yield. To allow direct comparisons to be made the yields have been normalised.

Pyrolysis of pine bark produced the lowest yield of organics and the highest yield of char. This is surprising since it does not have the lowest cellulose content or the highest ash content. However, analysis of pine bark in Chapter 6 reported a chlorine content of 0.39mf wt.%. Chlorine is believed to catalyse char forming reactions, which may well account for the low organics yield.

Table 7.9: Comparison of pyrolysis products from a range of feedstocks at 500°C

Feedstock	Pine Bark	Rape Straw	Rape Meal	Miscanthus	Pine	Poplar
Run No.	SFB05	SFB44	SFB38	SFB17	SFB13	SFB28
Temp. [°C]	505	503	495	493	501	508
Res. Time [s]	0.56	0.49	0.47	0.53	0.75	0.51
Feedrate [g/h]	134.7	83.7	72.2	89.0	113.5	88.8
Moisture [mf wt.%]	16.89	8.51	1.00	8.46	10.94	7.25
Ash [mf wt.%]	1.94	5.18	7.68	3.16	0.23	0.50
Ref. for composition	(140)	(28)	(155)	Section 6.1.4	(156)	Section 6.1.1
Cellulose [mf wt.%]	34.3	32.4	5	41.4	37.4	59.4
H.cell. [mf wt.%]	18.0	41.8	28	24.9	32.2	19.0
Lignin [mf wt.%]	13.7	16.7	59*	23.7	27.2	18.4
Yields [mf wt.%]						
Char	29.99	21.27	25.78	19.40	8.57	8.23
Organics	39.15	43.95	47.04	51.68	61.75	69.69
Organics [maf wt.%]	39.90	46.40	51.00	53.40	61.90	70.00
Gas	14.04	14.89	12.47	17.97	14.60	15.62
Water	9.86	10.78	9.63	7.61	3.88	1.47
Total Oil	49.01	54.73	56.67	59.29	65.63	71.16
Closure	93.03	90.90	94.92	96.66	88.80	95.01
Normalised yields [mf wt.%]						
Char	32.24	23.40	27.16	20.07	9.65	8.66
Organics	42.08	48.35	49.56	53.47	69.54	73.35
Organics [maf wt.%]	42.89	51.05	53.73	55.25	69.71	73.68
Gas	15.09	16.38	13.14	18.59	16.44	16.44
Water	10.60	11.86	10.15	7.87	4.37	1.55
Total Oil	52.68	60.21	59.70	61.34	73.91	74.90
Closure	100.00	100.00	100.00	100.00	100.00	100.00

* rape meal lignin calculated by difference, will contain protein

Rape straw is a previously untested feedstock for which no compositional information was available. It has been assumed that it has similar composition to that of wheat straw investigated at Waterloo (82). Rape straw is believed to have a slightly lower cellulose content and higher ash content than pine bark. However, it also contains more hemicellulose than pine bark, which also forms pyrolysis liquid. This may account for the slightly higher yield of organics and lower yield of char compared to pine bark. Straw ash often contains high proportions of silicon [e.g. rice straw - 74.31%, wheat straw - 35.84%], which is relatively inert in terms of influencing pyrolysis reactions. From this it might be tentatively concluded that the ash in the rape straw contained less char forming components than the pine bark.

Rape meal is also a previously untested feedstock; however, limited compositional data was found (155). It has a low cellulose content, but much of the remainder is made up of protein [residue from rape seed oil extraction], which it is believed forms pyrolysis liquid. Rape meal also has the highest ash content of all of the feedstocks studied in this work. It is likely that much of the rape meal ash is made up of "pyrolysis inert compounds", which did not promote char forming reactions.

From the compositional data available on miscanthus it is evident that it has a similar cellulose content to that of pine wood. However, the yield of pyrolysis liquid is much lower than yields obtained from pine. It is expected that this is due to the higher ash content, which also account for the higher char yield.

The yields from pyrolysis of pine and poplar wood are similar. Poplar has a much higher cellulose content than pine; however, this is probably due to different analysis methods being used [the detergent method was used for poplar and the method used for pine is not known]. It is evident that woody biomass with low ash and high cellulose content produces the highest yields of pyrolysis liquid.

Calculating the organics yield on a moisture and ash free basis does very little to change the yield and does not change the rank order of the feedstocks. Thus the low organic yields for high ash feedstocks appear to be due to the catalytic effect of the ash. This is illustrated in Figure 7.16 by a plot of the maximum organic yields versus ash content of the feedstock. Both results obtained at Aston in the course of this work and results obtained by the University of Waterloo (82) have been included. It is evident that as ash content of the feedstock increases the yield of organics decreases.

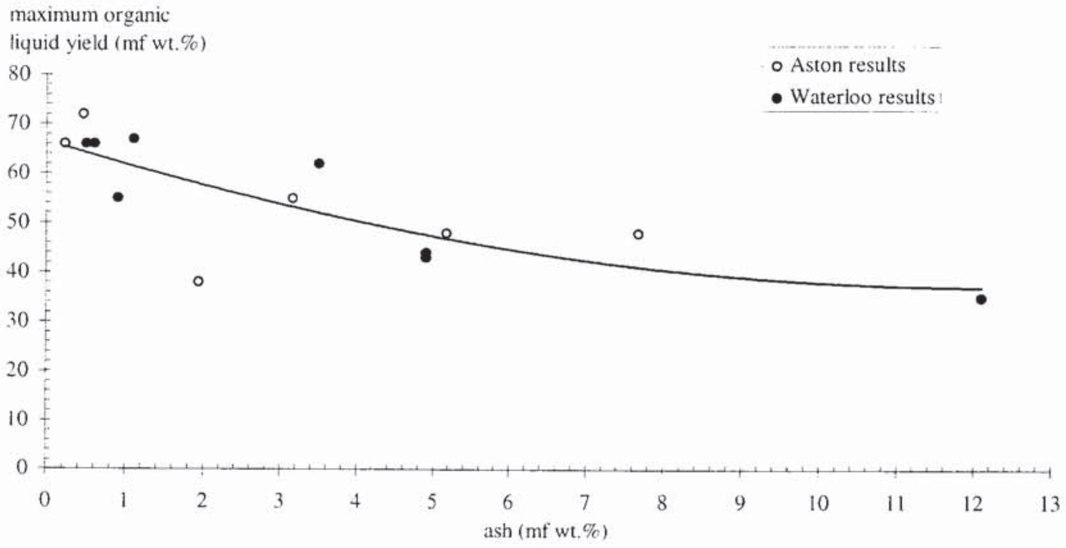


Figure 7.16: Maximum yield of organics versus ash content

7.3 CHEMICAL PRODUCTS COMPARISON

Table 7.10 and Table 7.11 contain chemical analyses of the organics fraction of the feedstocks pyrolysed in this work and also relevant literature analyses for similar feedstocks. The liquids produced at temperatures close to 500°C have been analysed since much of the published literature on the chemicals in fast pyrolysis liquids is obtained at 500°C. It is acknowledged that the yield of chemicals is a function of reactor temperature and feedstock type. However, for a particular feedstock there may be one temperature to maximise the yield of levoglucosan, one to maximise the yield of hydroxyacetaldehyde and one temperature for the maximum organic liquid yield. Therefore 500°C has been chosen arbitrarily to allow all of the Aston data to be compared with that available in the literature.

Table 7.10: Comparison of chemicals from different feedstocks at 500°C

Feedstock	Pine Bark	Rape Straw	Miscanthus	Rape Meal	Hog fuel	Sunflower hulls
Reference					(157)	(157)
Run No.	SFB05	SFB44	SFB31	SFB38	PP 126	PP 122
Temp. [°C]	505	503	469	495	500	500
Res. Time [s]	0.56	0.49	0.52	0.47	0.44	0.5
Moisture	14.94	8.51	8.46	1.00	12.0	11.1
Ash [mf wt.%]	1.94	5.18	3.16	7.68	2.20	4.0
Cellulose [mf wt.%]	34.3	32.4	41.4	5		
H.cell. [mf wt.%]	18.0	41.8	24.9	28		
Lignin [mf wt.%]	13.7	16.7	23.7	59*		
Yields [mf wt.%]						
Gas	14.04	14.89	12.67	12.47	13.1	18.7
Organics	39.15	43.95	50.06	47.04	46.6	44.4
Char	29.99	21.27	17.73	25.78	31.8	26.3
Water	9.86	10.78	9.01	9.63	12.1	9.4
Total Oil	49.01	54.73	59.07	56.67	58.7	53.8
Closure	93.03	90.90	89.47	94.92	103.6	98.8
Chemicals [mf wt.%]						
Hydroxyacetaldehyde	1.21	3.03	6.78	0.00	3.75	0.78
Levoglucosan	0.90	0.94	1.93	0.50	2.16	0.33
Formic acid	0.81	1.21	3.07	0.26	1.06	1.01
Acetic acid	0.75	4.57	7.48	0.66	2.63	2.12
Fructose	0.25	0.13	0.42	0.00	0.39	0.12
Glyoxal	0.14	0.23	0.00	0.00	0.53	0.07
Acetol	0.75	2.07	2.56	0.02	1.56	1.16
Others	0.51	0.24	0.80	1.08	1.87	0.33
Pyrolytic Lignin	0.93	15.54	19.60	29.50	27.70	38.40
Total Chemicals	**5.62**	**27.74**	**42.63**	**32.02**	**43.52**	**44.32**

* rape meal lignin calculated by difference, will contain protein

Pine bark

The yield of chemicals for pine bark is very low. This is because the majority of the pyrolysis liquid was collected in a cotton wool filter. Ethanol was used to solubilise the liquid to remove it from the cotton wool. Hence the liquid was very dilute and many of the chemicals were virtually undetectable by HPLC. Experiments for the other feedstocks used cold traps in conjunction with an electrostatic precipitator resulting in improved collection and analysis of chemicals.

Scott found that poplar bark contained tannin-like compounds, which when pyrolysed will form polyhydroxyphenols (82). It is likely that pine bark will also contain a similar tannin like material and therefore there should have been higher yields of pyrolytic lignin. Thus it is likely that had a better collection system been used, much of the chemicals would have been pyrolytic lignin. Hog fuel is lumber mill waste containing 80% bark, thus the results from pyrolysis of hog fuel should be similar to those of pine bark. The yield of pyrolytic lignin from hog fuel makes up over 60% of the total chemicals, with 7% sugars and the remainder acids and mixed oxygenates.

Rape straw and miscanthus

Rape straw was earlier compared to wheat straw; however, no chemical analysis of wheat straw liquids is available. The yields of rape straw and miscanthus have similarities. As expected, the organics yield is higher for miscanthus, as are many of the chemicals. This is probably due to miscanthus having a higher concentration of cellulose, which produces the majority of chemicals contained in the pyrolysis liquid in high yields.

Both rape straw and miscanthus produced high yields of formic and acetic acids, which may be due to the hemicellulose component of the feedstock. The yields of hydroxyacetaldehyde were quite high in both cases with correspondingly low yields of levoglucosan. As mentioned earlier, this may well be a function of ash content, since both miscanthus and rape straw have high ash contents [i.e. >3 mf wt.%]. Overall it was expected that miscanthus would produce better yields than rape straw because miscanthus is a dedicated energy crop devoting all of its energy to growth whereas rape straw is merely a conduit for moving nutrients up to the head of the plant for seed production.

Rape meal

Rape meal is the residual cake remaining after rape oil has been extracted. It consists mostly of seed casings and protein from the seeds. There is very little cellulose, which is why the chemicals normally contained in pyrolysis liquid [i.e. levoglucosan and hydroxyacetaldehyde] are only present in small concentrations. The majority of chemicals are contained in the pyrolytic lignin or were not detected by HPLC. The closest feedstock found in the literature to rape meal was sunflower hulls since both feedstocks are mostly seed casings. It is evident that both rape meal and sunflower hulls produced the majority of chemicals from the lignin portion of the biomass and a smaller amount from the hemicellulose [i.e. acetic and formic acids]. Both feedstocks produced mostly acids rather than sugars, which is probably due to the low cellulose content and high ash content.

Table 7.11 shows the chemical analysis for pine and IEA poplar pyrolysed at Aston [this work] and results from white spruce and IEA poplar pyrolysed at University of Waterloo for comparison.

Table 7.11: Comparison of chemicals from different feedstocks at 500°C

Feedstock	Pine	Pine	IEA Poplar	White Spruce	IEA Poplar
Reference				89	89
Run No.	SFB13	313	SFB28	43	A-2
Temp. [°C]	501	501	508	500	497
Res. Time [s]	0.75	0.31	0.51	0.65	0.46
Moisture	10.04	7.61	7.25	7.0	3.3
Ash [mf wt.%]	0.23	0.23	0.50	0.5	0.46
Cellulose [mf wt.%]	37.4	37.4	59.4		49.1
H.cell. [mf wt.%]	32.2	32.2	19.0		
Lignin [mf wt.%]	27.2	27.2	18.4		
Yields [mf wt.%]					
Gas	14.60	11.7	15.62	7.8	10.8
Organics	61.75	68.5	69.69	66.5	65.7
Char	8.57	10.5	8.23	12.2	7.7
Water	3.88	8.8	1.47	11.6	12.2
Total Oil	65.63	77.3	71.16	78.1	77.9
Closure	88.80	99.5	95.01	97.7	96.4
Chemicals [mf wt.%]					
Hydroxyacetaldehyde	7.94	6.86	7.26	7.67	10.03
Levoglucosan	2.84	1.67	2.45	3.96	3.04
Formic acid	2.44	3.27	4.76	7.15	3.09
Acetic acid	1.70	0.00	6.73	3.86	5.43
Fructose	1.03	0.00	0.92	2.27	1.32
Glyoxal	0.48	0.00	0.42	2.47	2.18
Acetol	0.71	1.28	1.04	1.24	1.40
Others	0.73	1.61	1.39	4.37	2.76
Pyrolytic Lignin	24.93		20.6	17.09	16.20
Total chemicals	**42.32**	**14.69**	**42.08**	**53.60**	**50.40**

Pine

Pine runs SFB13 and 313 were both carried out on the same feedstock. However, SFB13 was carried out at Aston using a 150g/h fluidised bed reactor and 313 was carried out at Waterloo using a 100g/h reactor. The chemical analysis was carried out using HPLC, with SFB13 analysed on the Aston equipment and 313 analysed using equipment at Waterloo.

It is evident that there are slight differences in the results from the chemical analysis, which should in theory be identical since it is the same feedstock at virtually identical conditions. However this is probably due to slight differences in HPLC systems. Pine contains approximately 37mf wt.% cellulose, hence cellulose derived chemicals [i.e. hydroxyacetaldehyde, levoglucosan, fructose and glyoxal] are present in reasonable concentrations. Chemicals derived from both the cellulose and hemicellulose components [i.e. acetic and formic acids] are also present.

White spruce is a softwood similar to pine, which was pyrolysed at the University of Waterloo. Similar chemical yields were obtained to those of Aston. However slightly higher yields of almost all of the chemicals detected were obtained from white spruce. This may be due to the white spruce having slightly different chemical composition [i.e. higher cellulose content].

IEA poplar

IEA poplar pyrolysed at Aston shows similar chemical yields to those from Waterloo. Aston appears to have higher yields of acids [formic and acetic], whereas Waterloo has higher yields of sugars [levoglucosan, fructose]. This may be due marginally to the slightly higher ash content in the Aston poplar.

The yields of hydroxyacetaldehyde and levoglucosan for IEA poplar are similar to those obtained from pine, despite the much higher cellulose content of IEA poplar. It is concluded from this that the detergent analysis method for biomass feedstocks may have resulted in an overestimation of the cellulose component. This may result in lower yields than expected if chemical yields were predicted purely on cellulose content.

7.4 CONCLUSIONS

A number of feedstocks have been successfully fast pyrolysed at Aston using a 150g/h fluidised bed reactor. Some of these feedstocks [poplar and pine] have been pyrolysed by other institutes who have obtained comparable results. Novel feedstocks, which had previously not been tested, have been pyrolysed and comparison between similar materials have been drawn where results are available. For the case of miscanthus and rape meal no fast pyrolysis results for similar feedstocks have been found.

The pyrolysis temperature has been varied for all feedstocks in order to investigate maximum organic yields. These have been found for all feedstocks and are shown in Table 7.1 along with comparative results from other institutions. It is believed that establishing the maximum organic yield and the temperature at which this maximum occurs is the first part to optimisation of the pyrolysis process for fuel production.

The yield of organics has been found to a limited extent to be a function of ash content in the feedstock. The higher the concentration of ash in the feedstock the lower the yield of pyrolysis liquid. The chemicals contained in the pyrolysis liquid are a function of cellulose and hemicellulose content for aqueous soluble chemicals and lignin for aqueous insoluble chemicals. Generally, the pyrolysis of agricultural residues tends to result in the lowest yield of organics, whereas wood tends to give the highest yield of organics.

The pyrolysis liquids produced at 500°C from all feedstocks have been analysed to determine the chemical content. The highest yield of aqueous soluble chemicals were produced from feedstocks containing the highest concentration of cellulose [i.e. wood]. The chemical yields tend to decrease as cellulose content decreases and ash content increases. The yield of chemicals obtainable from fast pyrolysis of untreated feedstocks has now been established. In the following chapter the effects of pre-treatment will be examined on the pyrolysis product and chemical yields for IEA poplar.

8. PRE-TREATMENT EXPERIMENTS

Pre-treatment methods were investigated in Chapters 4 and 5. From this the most promising areas of pre-treatment for the production of selected chemicals from fast pyrolysis have been selected.

This chapter describes the pre-treatment experiments which were used to assess how effective each pre-treatment was.

8.1 LITERATURE REVIEW CONCLUSIONS

Pre-treatment can be split into two areas, component removal [washing or leaching] and component addition [additives]. This section details the pre-treatment experiments carried out and the effects of each treatment on the feedstock. Mass balance results from subsequent pyrolysis of the pre-treated feedstocks and chemical analysis of the pyrolysis liquids will be the subject of Chapter 9.

Chapter 7 found that IEA poplar produced the highest yields of pyrolysis liquid and also contained the highest concentration of aqueous soluble chemicals. Therefore IEA poplar has been used for the majority of pre-treatment experiments. The only exceptions to this are pre-treatment and pyrolysis experiments carried out at the University of Waterloo, which were conducted using pine wood.

Leaching

From the literature review [Chapter 4] two key areas were suggested for investigation:

1. The effect of water alone on reducing ash content and the effects this has on pyrolysis products and chemical yields,
2. The investigation of the demineralisation process; investigation of mineral acid type, concentration, temperature and contact time. Variations along this theme will include the effect of two stage processing and the use of boiling acid.

Additives

Since ash plays such a major role in the selection of pyrolysis pathways [Chapters 3, 4 and 5] it is believed that other chemicals may also have a similar catalytic effect. This was reviewed in Chapter 5 and from this review three promising additives have been selected and tested:

1. increasing natural ash content [potassium]
2. increasing hydrogen availability [ammonium]
3. decreasing lignin effects [transition metal - iron]

8.2 PRE-TREATMENT EXPERIMENTS SUMMARY

The effect of water washing or leaching has been investigated by two experimental techniques. The first used boiling water in a soxhlet extractor to remove components from the biomass. This method is described in Section 8.3.1. The second method utilised water as part of a pre-wash. Following this, the pre-washed wood was washed in dilute acids of varying concentrations and a range of temperatures. This method is described in Section 8.3.3.

The de-mineralising process has been investigated using several experimental techniques. The first method used an acid percolation process at room temperature followed by water rinsing to remove the dissolved ash and excess acid [Section 8.3.2]. The results from pyrolysis of this material are shown in Section 9.1 along with results from the same wood, which was hydrolysed in acid. The effect of mineral acid type, concentration and pre-treatment temperature has been investigated and is reported in Section 8.3.4. A range of mineral acids was used to treat enough wood for pyrolysis experiments to be performed. Hence results from pyrolysis of different mineral acid treated woods are shown in Section 9.3.

The effect of two-stage processing on increasing the effectiveness of the washing process is investigated in Section 8.3.3. Wood samples were soaked in water prior to mild acid washing using sulphuric acid at a range of temperatures and concentrations. Again, large amounts of biomass were treated so that pyrolysis experiments could be carried out [Section 9.2].

Three additives were selected to catalytically influence the yields of pyrolysis products. The method used to incorporate these additives into the biomass is described in Section 8.5, along with the concentrations used. Results from pyrolysis of feedstocks containing additives are reported in Section 9.4.

It has already been mentioned [Chapter 2] that the compositional analysis of biomass is time consuming, costly and only accurate to between ±1-10% [dry biomass basis depending on the method used]. Thus it will prove difficult to analyse exactly what has been removed or affected by a particular pre-treatment method. Although every effort has been made to measure all possible variables this has proved far from successful as will become evident as this Chapter progresses. The author believes that the only true way to find out how effective a pre-treatment method has been in modifying the chemical yields from biomass fast pyrolysis is to actually pyrolyse the pre-treated biomass. Thus the "true" test of pre-treatment methods [i.e. fast pyrolysis] has been carried out on all pre-treated feedstocks [providing enough pre-treated biomass was available]. The results from fast pyrolysis of pre-treated feedstocks are presented, analysed and discussed in Chapter 9.

8.3 LEACHING

The removal of biomass components is carried out by washing [leaching] techniques. As previously discussed in Chapter 2, biomass is made up of 3 major components: cellulose, hemicellulose and lignin; and minor components: ash and extractives. As discussed in Chapters 3, 4 and 5, ash has a catalytic effect on the pyrolysis reaction and so its presence or absence can have a major effect on the chemicals contained in the pyrolysis liquid. Ash is comprised of salts of alkali metals of which some are held loosely in the biomass structure and some are bound more tightly.

Mild washing techniques [such as water washing] at low temperatures [i.e. less than 40°C] will remove some of the ash without affecting the other biomass components (35). For complete ash removal more severe techniques are required, for example acid washing or acid hydrolysis. However, the penalty of using more aggressive techniques is that some of the other biomass components are affected or removed [e.g. hemicellulose] (82). By reducing the levels of ash the yields of certain chemicals [notably levoglucosan] can be increased in the pyrolysis liquid.

Whether to pre-treat or not to pre-treat is then simply a question of economics. For example, from 100g wood, is it better to water wash, pyrolyse and extract 5% levoglucosan from 70g pyrolysis liquids or acid hydrolyse, pyrolyse and extract 30%

levoglucosan from 45g pyrolysis liquids ? The economics of pre-treatment [component removal] will be investigated in Chapter 10.

8.3.1 Water Washing Experiment

Water washing was carried out on ground [<1mm] pine wood by soxhlet extraction. Soxhlet extraction is a method for continuously cycling distilled water [or any other solvent] into a sample of wood and then removing the whole liquor. Each cycle introduces clean distilled water into the soxhlet and therefore could be viewed as a single step in a multi-stage washing process. The experimental conditions used in this method were taken from ASTM methods on the production of extractive free wood (24).

This technique involved a standard soxhlet into which a cellulose thimble filled with pine wood was placed. The soxhlet was fitted to a flask, which was filled with distilled water, which was then heated electrically to boiling point. The water vapours passed from the flask up into the soxhlet and condenser. They condense and then drop back to fill the soxhlet. Once full the soxhlet siphons back into the flask and the process begins again. The soxhlet was set to cycle [fill and siphon back] at its maximum rate, which was 3-4 times per hour.

The above procedure was carried out on a single sample of pine wood. It was extracted for approximately 5 hours at 3-4 cycles per hour. The thimble and wood were then removed and dried in a fan oven at 105°C until dry. The results are shown in Table 8.1. The wood lost 3.36 mf wt.% of its original mass by the extraction. Since pine wood was found to have an ash content of 0.23 mf wt.% only a fraction of this loss can be ash. The temperature of the distilled water in the soxhlet was approximately 50-75°C during the extraction. Thus it is expected that more components than ash were removed. Hence, some of the lost components must be extractives and/or hemicelluloses. The exact determination of what components were lost from the pine was never carried out since the method was abandoned.

Table 8.1: Results from soxhlet extraction of pine wood

Original wood [g]	81.87
Wood remaining after extraction [g]	79.12
Difference [g]	2.75
Percentage loss [mf wt.%, dry basis]	3.36

For a number of reasons the above procedure was only carried out once. Firstly, only a small amount of biomass can be treated at a time [typically 10g], which is not enough to carry out a fast pyrolysis experiment. Secondly, a thimble must be used to hold the biomass and it was difficult to remove the biomass from the thimble after extraction. Finally, the treatment was found to be too severe since more than just ash appeared to have been removed, although this has not been confirmed.

8.3.2 Demineralisation Percolation Experiments

Nitric acid

A percolation experiment using dilute acid was set up. By using percolation rather than soaking it was hoped that smaller volumes of acid would be required and hence smaller volumes of water would be required to remove the residual acid and solubilised ash. A percolation column also mimics the behaviour of a plug-flow reactor, which would give an alternative to stirred tank reactors on an industrial scale.

The apparatus shown in Figure 8.1 was used to percolate 0.1M nitric acid through milled pine. Low acid concentration was used to prevent solubilisation of biomass components other than ash [e.g. hemicellulose]. Nitric acid was chosen arbitrarily because the experiment was conducted at the University of Waterloo [by the author] and this acid had not been tested before. The equipment was set up for downward flow so that the pine forms a natural packed bed and it also prevents the wood from floating out of the column.

Approximately one litre of dilute acid was used per 50g of wood. The demineralisation reaction is slow and so the pump was set at a flowrate between 5 and 15 ml/min per square inch of column cross section. These values were calculated by Scott (89). After the acid had been pumped through, the pine was washed with two litres of de-ionised water to remove any residual acid from the pine and bring it back to around pH6. Previous experiments by Scott et al. found that wood was naturally slightly acidic and further washing beyond this point did not increase the pH any further. The treated pine was then dried, ready for pyrolysis. The loss in mass of the pine was around 5 mf wt.%. It is believed that this lost material consists of extractives and ash, although this was not analysed and so cannot be confirmed.

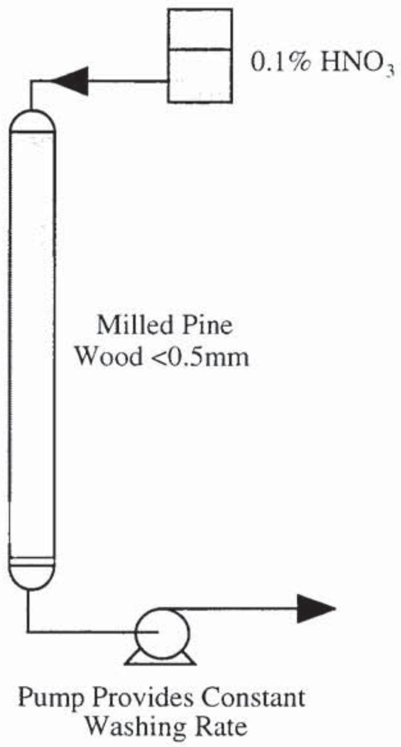


Figure 8.1: Demineralisation apparatus

The experiment was carried out at the University of Waterloo. Subsequent pyrolysis using a 100g/h reactor [courtesy of D.S. Scott and all personnel in the Pyrolysis Research Group at the University of Waterloo] was also carried out at Waterloo. Mass balance results for the pyrolysis of untreated pine [run 313], percolation demineralised pine [run 312] and nitric acid hydrolysed pine [run 314, pre-treatment method described in Section 8.4] are shown in Section 9.1.

Sulphuric acid

Following on from the above nitric acid experiment a series of experiments were devised in an attempt to assess the effectiveness of acid washing in the removal of metallic cations. This time sulphuric acid was used since it has been suggested by Shafizadeh (88) and Julien (124) that small amounts may have a catalytic effect in the production of levoglucosan. Demineralisation was carried out on samples of IEA poplar using sulphuric acid concentrations of 1.0 and 5.0 mf wt.%, and temperatures of 25, 45 and 60°C.

The wood was placed in a jacketed column, which could hold approximately 20g of wood. A volume of acid [typically one litre] was percolated through the wood column in a similar manner to that described above and shown in Figure 8.1. The column of wood was maintained at a fixed temperature by circulating water around the jacket surrounding the column. After the volume of acid had been percolated through the column, the column was washed out using two volumes of distilled water. After this treatment the wood samples were removed from the column and dried in a fan oven at 65°C for at least 24 hours. The lower oven temperature of 65°C, rather than 105°C normally used, was chosen as a precaution in case any residual acid remained on the wood. As the wood dries the acid becomes more concentrated and can cause charring. However, in all cases this did not occur.

The untreated and treated IEA poplar samples were sent to external laboratories [MEDAC] to be analysed for alkali and alkali earth metals by ICP-AES [Inductively Coupled Plasma Atomic Emission Spectrography]. The results of the analyses are shown in Table 8.2 below. Mass balances were carried on each experiment, but due to the small amounts of wood used the losses were prohibitively high and so the results have not been included here. Since only small amounts of wood were treated [20g] pyrolysis experiments could not be carried out.

Table 8.2: ICP-AES analysis of untreated and treated IEA poplar

	Acid Strength	Temp	Element [mg/kg)]								
Sample Name	[%]	[°C]	K	Ca	Na	Mg	S	P	Zn	Mn	Cu
Original Wood			1120	1120	37.1	250	122	132	16.2	4.3	3.74
Sample 01	1	25	3.8	60	19	4.6	109	30	5.0	1.0	1.13
Sample 02	5	25	0.1	76	0.1	4.4	110	27	5.0	1.0	1.72
Sample 03	5	25	0.1	50	0.1	2.6	106	29	5.0	1.0	1.22
Sample 04	1	45	0.1	29	0.1	2.6	116	27	5.0	1.0	1.60
Sample 05	1	45	0.1	43	0.1	3.4	116	28	5.0	1.0	1.84
Sample 06	5	45	0.1	29	0.1	2.4	127	21	5.0	1.0	2.37
Sample 07	5	45	0.1	17	0.1	1.2	105	21	6.1	1.0	1.22
Sample 08	1	60	0.1	45	0.1	3.6	96	22	5.0	1.0	1.45
Sample 09	1	60	0.1	42	0.1	1.9	97	23	5.0	1.0	1.87
Sample 10	5	60	0.1	32	0.1	2.7	148	17	5.0	1.0	1.22
Sample 11	5	60	0.1	30	0.1	1.0	122	12	5.0	1.0	1.0

From the Table 8.2 it is evident that the mildest treatment [i.e. that of 1.0% acid at 25°C] removed almost all of the alkali and alkali earth metal cations [K, Ca, Na, Mg]. The levels of potassium and sodium are virtually zero after the mildest pre-treatment; this indicates that they are loosely bound into the wood and are also easily dissolved into the aqueous acid. Calcium, magnesium and phosphorous appear to be the best indicators of severity of pre-treatment; as shown in Figure 8.2 the levels of calcium, magnesium and phosphorous in the wood are further reduced as temperature and acid concentration increase. The concentration of sulphur varies, which could indicate that in some cases there was incomplete washing of the wood and some acid remained. Alternatively, this sulphur could be due to natural variability in the wood. The transition metals zinc, manganese and copper are hard to detect, so although there appears to be good removal the concentrations are at the limit of detection for this analysis method.

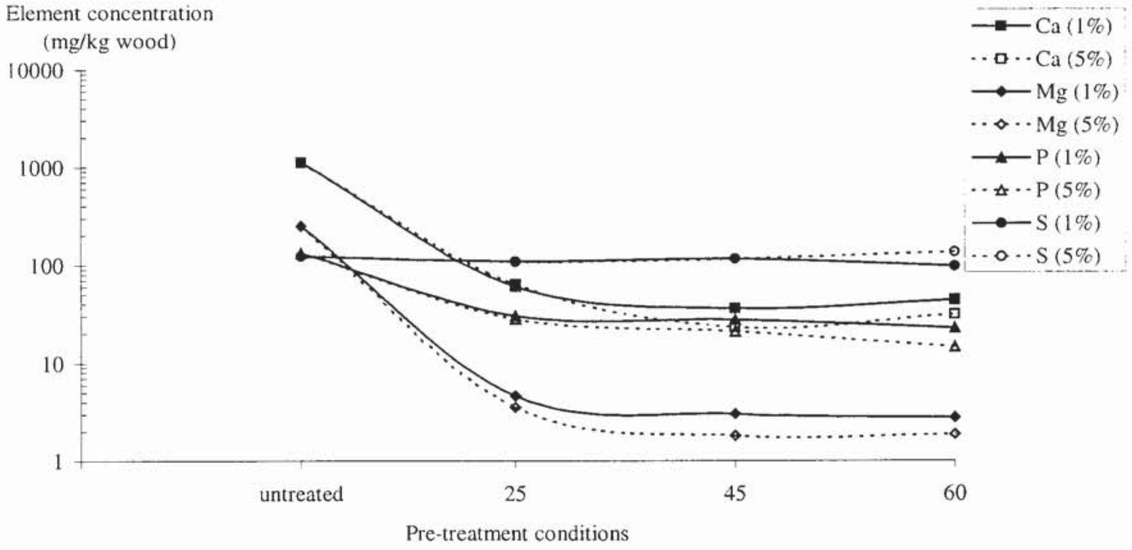


Figure 8.2: Element concentration with increasing severity of pre-treatment

This type of experiment mimics the effects of a plug-flow reactor and may well require much less acid and washing than other pre-treatment methods [e.g. soaking or hydrolysis]. However, similar to the soxhlet extraction process only small amounts of biomass can be treated at one time. Also the method requires a very slow rate of percolation, which requires a specific type of pump. Therefore this method was abandoned.

8.3.3 Experiments With Pre-Washing Followed By Mild Acid Washing

In Chapter 4 a number of pre-treatment experiments were reviewed, which utilised a two-stage process. It is believed that an initial water wash will open up the pore structure of the biomass and hence make it more susceptible to chemical treatment in the second stage. The use of an initial wash/soak may allow the severity of the second stage to be reduced [i.e. lower temperature or less concentrated reagent]. This could help to reduce process and waste treatment costs. As legislation becomes ever tougher it is more important than ever to minimise wastes.

The overall aim of the treatment is to demineralise the biomass using dilute acids at ambient conditions. By using mild conditions it is also hoped that the removal of non-ash components will be minimised, which will reduce wastage of biomass and also reduce the cost of treating the waste [on a commercial scale].

This treatment consists of a room temperature de-ionised water pre-wash followed by a dilute sulphuric acid wash over a range of concentrations and temperatures. Previous work [Section 8.3.2] has concentrated on continuous washing using dilute acid [nitric or sulphuric] followed by flushing the biomass with distilled water. In the previous study only small samples of biomass were used; consequently, the biomass could only be analysed for ash removal and could not be tested by fast pyrolysis. This study used much larger biomass samples, which produced enough pre-treated biomass to allow fast pyrolysis experiments to be carried out.

The pre-wash and acid wash experiments were carried out batchwise since 24 hour soak times were used. Such a long holding time would be too long for a continuous process. Analysis was carried out on the pre-wash liquor and the dilute acid wash liquor using flame photometry [instrument specification and operation described in Appendix D]. The ash content of the biomass was also analysed by ASTM methods (36).

In order to test the effectiveness of the pre-treatment a mass balance was carried out on the biomass and the key ash components [potassium and sodium] contained therein. The amount of biomass can be weighed throughout the course of the pre-wash and dilute acid wash. However, the key ash components [potassium and sodium] in the biomass were determined by ICP-AES and the concentration in the pre-wash and acid wash liquors determined using flame photometry.

Pre-washing procedure

The first step in the pre-washing procedure was to measure the water content of the biomass so the amount of dry biomass treated could be calculated. Following this a known mass [usually 250-500g, enough for 2-4 pyrolysis experiments] was placed in a large vessel with an exact quantity of de-ionised water. Approximately four litres of deionised water were used for every 250g biomass, since it was found that four litres adequately soaked the biomass and formed a slurry, which could be stirred by mechanical means. However, to avoid possible contamination with metal ions the slurry was not stirred. The biomass was left in the vessel to soak at ambient conditions for 24 hours since it was believed that all reactions would be complete after this time, even with no stirring. After the soaking period the water was removed from the biomass by vacuum filtration. A sample of the filtered pre-wash liquor was taken for elemental [flame photometry] and HPLC analysis. A small sample of the biomass was taken for moisture analysis to enable a mass balance to be carried out on the first stage.

Acid washing procedure

Following the filtration at the end of pre-washing the biomass was weighed [for mass balance purposes] and was then placed in another large vessel. An exact volume [usually 2 litres per 250g biomass] of sulphuric acid [the concentration was changed for each experiment] was then added to the biomass and the vessel was placed in a water bath to maintain its temperature. The biomass was left in the dilute acid for 24 hours, again without stirring.

After the 24 hour period the biomass was removed from the vessel and the liquid removed by vacuum filtration. A sample of the dilute acid liquor was taken for elemental [flame photometry] and HPLC analysis. The biomass was washed with additional de-ionised water until the filtrate from the biomass was greater than pH6. The biomass was then dried slowly in a fan oven at 65°C for approximately 48 hours. As mentioned earlier, biomass is normally dried at 105°C; however, following pre-treatments involving acid it is best to take extra care to ensure that no charring of the biomass occurs in the oven. 48 hours was found, by repeated weighings, to be ample time for the biomass to dry.

Pre-wash results

Table 8.3 shows the results from pre-wash experiments. The sample size is the amount of biomass used on a dry basis in the experiment. All pre-wash experiments were carried out at ambient conditions; the temperature in all cases was approximately 20°C. The percentage biomass lost was not calculated for the first 4 runs because intermediate weights and moisture contents were not taken. The last 3 runs were carried out with all necessary measurements; hence full results are shown. The levels of potassium and sodium in untreated IEA poplar as determined by ICP-AES [Table 8.2] are shown and have been used to determine the percentage potassium or sodium removal. The ash was determined by ASTM for samples labelled untreated and PreDi4H_2O, for all other experiments an intermediate ash content was not determined.

Table 8.3: Pre-wash results

Label	Sample size [g]	Temp. [°C]	%age biomass lost	%K removal	%Na removal	Ash [mf wt.%]
Untreated IEA poplar						0.42
PreDi1H_2O	577.46	ambient	n/a	61.8	93.6	
PreDi2H_2O	484.69	ambient	n/a	52.3	66.9	
PreDi3H_2O	534.86	ambient	n/a	98.8	161.7	
PreDi4H_2O	547.17	ambient	n/a	88.8	197.6	0.26
PreDi5H_2O	232.94	ambient	0.88	122.7	232.1	
PreDi6H_2O	232.07	ambient	2.00	123.1	372.7	
PreDi7H_2O	232.01	ambient	1.60	120.1	792.1	

n/a - result not available as intermediate readings not taken
%K and %Na removal based on IEA poplar containing 1120ppm - K and 37ppm - Na.

The percentage of potassium and sodium ions removed into the pre-wash liquor [determined by flame photometry] are shown in Table 8.3. This is calculated on the basis that the poplar wood contains 1120mg/kg K ions and 37mg/kg Na ions.

Thus 577.46g of poplar soaked in 4 litres of de-ionised water produced a concentration of 100ppm K ions. This is equivalent to a potassium ion removal of 61.8%.

Since $\frac{4*100*1000}{577.46*1120}*100\% = 61.8\%$

The percentage biomass lost for experiments 5, 6 and 7 is less than 2% in all cases. This loss could be due to loss of ash, loss of some hemicellulose, loss of biomass when transferring from vessel to filter and/or biomass remaining on the filter. Every care was taken to remove all biomass from the vessel and the filter; therefore, it is believed that losses are due to the loss of ash and hemicellulose.

HPLC analysis of the wash liquors was carried out to see if there was any degradation of biomass to sugars. HPLC found that sugars were present in both pre-wash and acid wash liquors. However, the sugars could not be identified or quantified due to the lack of proper standards. This does prove that some of the biomass was hydrolysed to sugars; unfortunately there is not enough detail to confirm which part of the biomass or how much.

The percentage removal of potassium and sodium ions does not appear to be an accurate assessment of pretreatment, since the removal levels go beyond 100%. This could indicate that the initial potassium and sodium levels measured in the poplar are low. Since wood is a natural material it is likely that there is some variation in the levels of potassium and sodium. It could also be that the ash is not evenly distributed in the wood. However, from a 500g sample it is likely that such effects would be minimised. It is certain that extra potassium or sodium did not come from the de-ionised water, since the de-ionised water used to soak the biomass was also used to provide the zero on the flame photometer and therefore would already be accounted for.

It is most likely that the measured level of potassium in the wood is not typical. If the ppm level of potassium is increased by 23% to 1260ppm then all removal figures are less than 100%. However, it is not feasible that the sodium level measured in the IEA poplar is 700% too low. Therefore, it is debatable whether this method of pre-treatment assessment is valid [especially for sodium].

Acid wash results

Table 8.4 shows the results from the dilute acid wash experiments. The experiments were carried out consecutively, so PreDi1H_2O was the pre-washing stage and PreDi1H_2SO_4 was the dilute acid washing stage. Thus the pre-wash was carried out first and then the wood from this wash was used in the dilute acid wash.

The dilute acid washing was carried out at the temperatures and acid concentrations shown in Table 8.4. The sample remains is the amount of material remaining after pre-wash and acid wash treatments have been carried out. From this the percentage wood lost can be calculated.

The potassium and sodium levels in the filtered dilute acid wash liquor were analysed by flame photometry, the same method used for the pre-wash liquor. The percentage removal of potassium and sodium ions was calculated, as above, and the results are shown in Table 8.4. The amount of ash in each sample has also been found by the ASTM method (36) and the results are shown on a dry weight basis.

Table 8.4: Dilute acid wash results

Label	Temp. [°C]	Acid Conc. [M]	Sample remains [g]	%age wood lost	%K removal	%Na removal	Ash [mf wt.%]
PreDi2H_2SO_4	30	0.1	470.40	3.02	18.1	66.9	0.10
PreDi3H_2SO_4	30	0.1	530.00	0.91	16.3	50.5	0.08
PreDi1H_2SO_4	30	0.15	560.23	2.98	29.1	56.2	0.12
PreDi5H_2SO_4	40	0.1	221.12	5.07	55.2	232.1	0.05
PreDi6H_2SO_4	40	0.2	217.38	6.33	44.6	186.3	0.07
PreDi4H_2SO_4	40	0.5	294.00	n/a	19.9	29.6	0.08
PreDi7H_2SO_4	40	0.5	218.96	5.62	40.0	326.2	0.03

The dilute acid wash experiments are ranked in order of treatment severity, lowest temperature and weakest acid first, highest temperature and strongest acid last. The percentage wood lost appears to increase with severity of conditions, although it is not a well defined increase.

From the results of the pre-wash ion removal it is certain that very little confidence can be placed in the absolute levels of potassium and sodium removal. However, from the values obtained from the dilute acid washing experiments it would appear as though most of the potassium and sodium was removed in the pre-wash.

Ash content of the dilute acid washed woods is highest for the mild treatments [approximately 0.1 mf wt.% for 30°C and 0.1-0.15M] and reduces as severity increases [approximately 0.5 mf wt.% for 40°C and 0.5M]. Thus, the more severe the pre-treatment the better the ash removal.

Overall results

From the above experiments it would appear that pre-washing IEA poplar can remove approximately half of the ash content [from 0.50 to 0.26 mf wt.%. ash by ASTM analysis]. In all cases an amount of wood greater than the ash content of the wood was lost during the washing. Dilute acid washing of pre-washed poplar further removed ash to levels from 0.26 down to between 0.12-0.03 mf wt.%. It is suspected that this ash was made up of components other than sodium and potassium [since these components have been found to be easily removed, see Figure 8.2].

The optimum conditions for a dilute acid wash are the mildest [PreDi3H_2SO_4, 30°C, 0.1M], since this gave good ash removal [down to 0.08 mf wt.%] and very little wood was lost [0.91 mf wt.%]. More severe conditions did not lower the ash content significantly [i.e. 40°C and 0.5M acid gave 0.03 mf wt.% ash] and so it is expected that this higher temperature and extra acid would not be justifiable. It is not conclusive from these results whether it is better to have a pre-wash followed by dilute acid wash, or whether a dilute acid wash by itself is sufficient to remove the ash. This will become more evident from the fast pyrolysis mass balance results and chemicals analysis of pyrolysis liquids from these pre-treated feedstocks shown in Section 9.2.

8.3.4 Experiments Investigating Mineral Acid Type

In order to investigate the effect of dilute mineral acids over a range of temperatures, reaction times and particle sizes and keep the number of experiments to a manageable level the plan shown in Table 8.5 was devised and utilised.

Table 8.5: Experimental plan

Acid	Molarity	Temperature	Particle Size	Experiments
Sulphuric	0.1, 1.0	20, 50, 70	Small, Large	12
Hydrochloric	0.1, 1.0, 3.0	20, 50	Small, Large	12
Nitric	0.1, 1.0, 3.0	50	Large	3
Phosphoric	0.1, 1.0, 3.0	50	Large	3
Particle size	[Small] = 300-600μm		[Large] = 600-1000μm	

A series of batch reactors were used. Each reactor contained 500ml of dilute acid and 50g of IEA poplar wood. The whole reactor was immersed in a water bath to maintain constant temperature. Samples of the reactor liquid were taken periodically to allow the levels of alkali metal cations [potassium and sodium] to be determined by flame photometry. The volume of reactor liquid removed was replenished with fresh acid. The reactors were operated for approximately 5-8 hours, after which time it was believed that all demineralisation reactions would be complete. After this time the contents of the reactor were filtered and the wood washed thoroughly with de-ionised water. The wood was then dried and ASTM moisture and ash analysis carried out. The samples were then stored in sealed bags until they were pyrolysed, the results of which are detailed in Section 9.3.

The results of ASTM analysis of the acid washed wood are shown in Table 8.6. It was expected that best ash removal would occur using the strongest acids at the highest temperature on the smallest particle sized woods. Based on the results of ash content the optimum conditions for de-ashing of poplar wood are:

- 1.0M sulphuric acid at 20°C on the small particle size wood.
- 1.0M hydrochloric acid at 20°C on the large particle size wood,
- 0.1M phosphoric acid at 50°C on the large particle size wood,
- 0.1M nitric acid at 50°C on the large particle size wood.

Table 8.6: Ash content of treated poplar by ASTM method

	Small biomass (300-600μm)			Large biomass (500-1000μm)		
	20°C	50°C	70°C	20°C	50°C	70°C
Sulphuric acid						
0.1M	0.09	0.15	0.13	0.10	0.13	0.13
1.0M	0.03	0.04	0.09	0.08	0.09	0.09
Hydrochloric acid						
0.1M	0.09	0.10		0.05	0.05	
1.0M	0.08	0.04		0.01	0.07	
3.0M	0.06	0.05		0.04	0.02	
Phosphoric acid						
0.1M					0.04	
1.0M					0.44	
3.0M					0.09	
Nitric acid						
0.1M					0.03	
1.0M					0.08	
3.0M					0.11	

Samples of the reactor liquid analysed by flame photometry produced results which were far from conclusive. A typical example of the results obtained is shown in Figure 8.3. It shows the calculated concentration of potassium ions from each of the small biomass sample batch reactors. It can be seen that for 0.1M sulphuric acid as the reactor temperature is increased the concentration of potassium ions in solution increases.

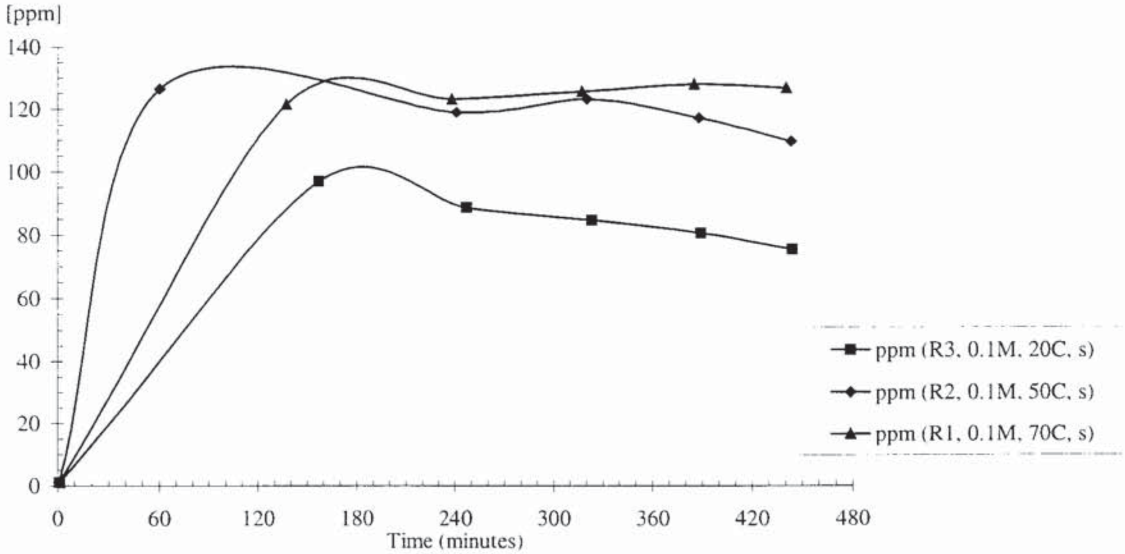


Figure 8.3: **Small biomass 0.1M sulphuric acid wash - potassium concentration in solution versus time**

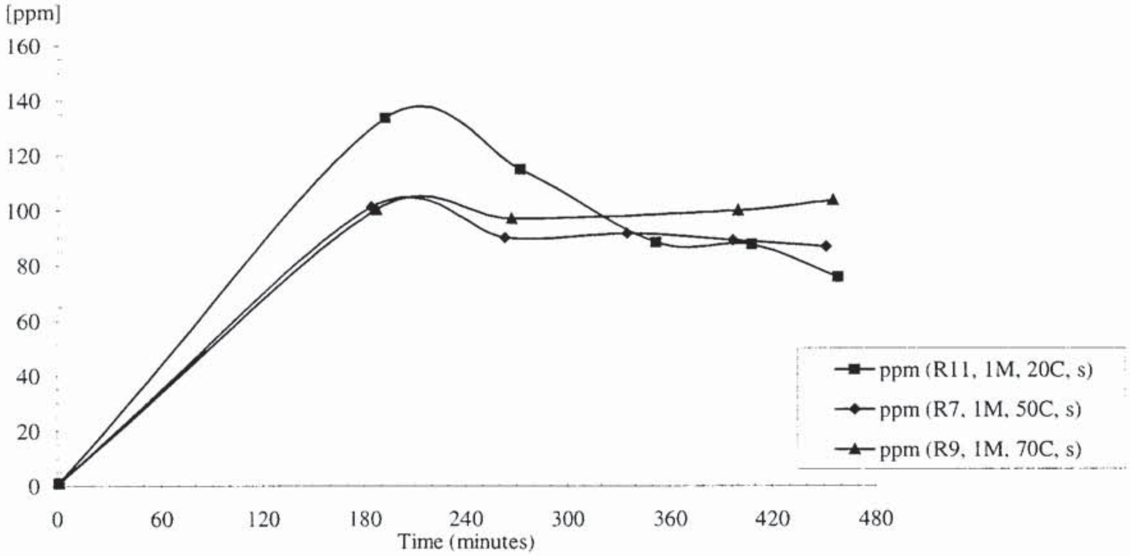


Figure 8.4: **Small biomass 1.0M sulphuric acid wash - potassium concentration in solution versus time**

Figure 8.4 shows the potassium concentration for 1.0M sulphuric acid with small biomass particles. With 0.1M sulphuric it is evident that as temperature increases the concentration of potassium in solution also increases. However, no similar trend is observed for the 1.0M sulphuric acid.

In both 0.1M and 1.0M systems a general downward trend in the concentration of potassium can be seen. It is believed that this is due to a dilution effect caused by the removal of liquid from the reactor and replenishment with fresh acid. This effect appears most significant at 20°C; perhaps at higher temperatures the potassium is still being removed from the biomass and therefore the potassium concentration is maintained.

Similar graphs to those shown in Figure 8.3 and Figure 8.4 have been plotted and are contained in Appendix E. The following is a list of figure numbers and results contained therein:

E.1: Small biomass, 0.1M sulphuric, potassium concentration in solution versus time
E.2: Small biomass 0.1M sulphuric, sodium concentration in solution versus time
E.3: Small biomass 1.0M sulphuric, potassium concentration in solution versus time
E.4: Small biomass 1.0M sulphuric, sodium concentration in solution versus time
E.5: Large biomass 0.1M sulphuric, potassium concentration in solution versus time
E.6: Large biomass 0.1M sulphuric, sodium concentration in solution versus time
E.7: Large biomass 1.0M sulphuric, potassium concentration in solution versus time
E.8: Large biomass 1.0M sulphuric, sodium concentration in solution versus time
E.9: Small biomass 20°C hydrochloric, potassium concentration in solution versus time
E.10: Small biomass 20°C hydrochloric, sodium concentration in solution versus time
E.11: Large biomass 20°C hydrochloric, potassium concentration in solution versus time
E.12: Large biomass 20°C hydrochloric, sodium concentration in solution versus time
E.13: Small biomass 50°C hydrochloric, potassium concentration in solution versus time
E.14: Small biomass 50°C hydrochloric, sodium concentration in solution versus time
E.15: Large biomass 50°C hydrochloric, potassium concentration in solution versus time
E.16: Large biomass 50°C hydrochloric, sodium concentration in solution versus time
E.17: Large biomass 50°C phosphoric, potassium concentration in solution versus time
E.18: Large biomass 50°C phosphoric, sodium concentration in solution versus time
E.19: Large biomass 50°C nitric, potassium concentration in solution versus time
E.20: Large biomass 50°C nitric, sodium concentration in solution versus time

For all results there is an initial peak [for the first sample] after approximately 60 minutes. From this it is tentatively concluded that the demineralisation reaction is complete in less than 60 minutes. Following this the levels generally decrease with time; however, this effect is most significant for reactions carried out at 20°C. For temperatures greater than 20°C the decrease in concentration is more gradual. There are no clear distinctions between any of the treatments; no one treatment significantly out performs any other.

It is concluded that the ASTM ash analysis method was not accurate enough to detect the small changes in ash content of the wood tested [i.e. from 0.50 down to 0.01]. It is therefore recommended that if this type of study is carried out again that the elemental concentration be measured in the treated biomass rather than the overall ash content.

The potassium and sodium ion measurements show that these ions are being removed from the biomass. It would appear that the demineralisation reaction could be better assessed by a continuous measurement of the dissolved ions. This may also allow reaction rates to be determined. However, from the equipment used in this study those types of calculation are not possible.

Pyrolysis of these feedstocks has been carried out and the results of pyrolysis and chemical analysis of the pyrolysis liquids are shown in Section 9.3. It is believed that the results from fast pyrolysis give a better indication of how effective a particular pre-treatment method was.

8.4 ACID HYDROLYSIS OF WOOD

During an exchange visit to the University of Waterloo a number of pre-treatment and fast pyrolysis experiments were carried out. The pre-treatments carried out were demineralisation [Section 8.3.2] and acid hydrolysis [this Section]. Pyrolysis experiments were carried out in a 100g/h system on untreated pine [run 313], demineralised pine [run 312] and acid hydrolysed pine [run 314]. The pyrolysis results are shown in Section 9.1. From these experiments it was possible to see the significant effect pre-treatment can have on increasing the yield of levoglucosan in the pyrolysis liquid.

Figure 8.5 shows the experimental set-up for acid hydrolysis. Any acid can be used, but in this case nitric acid was used because it is a strong oxidising agent and was expected to remove a large fraction of the hemicellulose as well as some lignin. Approximately 100g of wood was boiled under reflux for 4 hours in a 2 litre flask with 1 litre of 5 wt.% nitric acid. The remaining wood was then washed with distilled water to pH6.

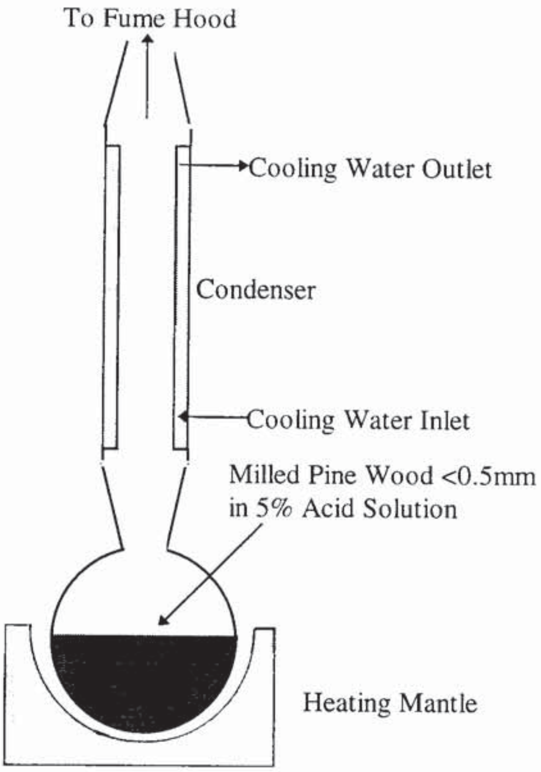


Figure 8.5: Acid hydrolysis equipment

From Table 8.7 it is apparent that approximately 50% of the biomass was hydrolysed by the nitric acid treatment. This means that as well as ash and hemicellulose some of the cellulose and lignin components must also have been hydrolysed from the biomass. However, the hydrolysis liquors were not analysed in any way so this cannot be determined for certain. It is also possible that some of these losses could be due to handling [i.e. small amounts of biomass remaining on filter papers etc.]. This experimental loss could be minimised by treating larger samples. With such severe treatment it is possible that it may be more economic to use commercial cellulose rather than pre-treating biomass. However, this will be assessed, along with other pre-treatments, in Chapter 10.

Table 8.7: Results from acid hydrolysis experiment

	Before hydrolysis (g)	After hydrolysis (g)	Loss in weight (%)
Mass of wood (mf wt.% basis)	96.3	50.7	47.6

8.5 ADDITIVES

From the literature review in Chapter 5, three areas of additives were selected:

- removal, addition or re-introduction of alkali and alkali earth metal cations,
- transition metal complexes,
- compounds containing hydrogen [e.g. hydrides, compounds of ammonia].

Thus three additives were selected:

- Potassium chloride [KCl, 2% on a K basis],
- Ferric chloride [$FeCl_3$, 2% on an Fe basis],
- Ammonium chloride [NH_4Cl, 2% on an NH_4 basis].

The chloride salts were chosen because they are all readily soluble in water and could thus be easily incorporated into the biomass by soaking. Although the effect of the anion cannot be completely discounted, by selecting the same anion in all cases it was expected that it would have the same effect in all cases.

The additives were introduced by soaking IEA poplar wood in a solution of the additive; the concentrations are shown in Table 8.8 below. The poplar was then air dried; it was not dried in an oven [at 105°C] in case the additives reacted with the wood causing it to char. The poplar samples containing additives have been pyrolysed and the results along with chemical analysis of the pyrolysis liquids are given in Section 9.4.

Table 8.8: Additive concentrations added to IEA poplar

Additive	KCl	$FeCl_3$	NH_4Cl
Active component	K	Fe	NH_4
Weight of additive	5.66	8.96	8.79
Weight of poplar	150.04	150.01	150.02
Concentration of additive	3.73	5.97	5.86
Concentration of "active" component	1.96	2.01	2.02

8.6 CONCLUSIONS

The demineralisation of biomass using leaching techniques has been investigated. A number of techniques have been used to assess how effective pre-treatment techniques were.

Water and acid percolation experiments were found to be limited, in that only small quantities of biomass could be treated at one time. At least 50-100g of biomass is required to carry out a single pyrolysis experiment. Therefore as many as ten pre-treatment experiments could be required for one pyrolysis experiment. The small quantities of biomass used in the percolation experiments also meant that small losses in handling were magnified into unacceptable mass balance closures. ICP-AES did prove that acid percolation was effective in removing almost all of the potassium and sodium contained in IEA poplar. Percolation treatments were rejected and replaced with batch washing treatments.

Two types of batch washing process were tested; pre-washing followed by dilute acid washing and dilute washing alone. It was expected that pre-washing would enable milder conditions [i.e. less concentrated acid and lower temperatures] to be used in the dilute acid washing stage. The dilute washing [with no pre-wash] were used to investigate the effects of a range of mineral acids at different concentrations and temperatures. The techniques were assessed by mass balance [to determine total biomass loss], ASTM [to determine ash removal] and flame photometry [to determine potassium and sodium levels in the wash liquors]. Since larger biomass samples were used in these tests than for percolation experiments, the mass balance closures were much better [i.e. between 95-100%]. ASTM analysis was accurate in determining ash content to ±0.01%. Analysis of the wash liquors by flame photometry was not as effective as had been planned. The results obtained from flame photometry are sometimes questionable.

Three types of additive have been introduced into samples of biomass. These samples have been fast pyrolysed to determine the effects on the fast pyrolysis products and chemical yields.

Attempts have been made to determine the effectiveness of particular pre-treatment techniques. However, in the most part these assessments have proved far from successful. It is concluded that the only true way to test the effectiveness of a pyrolysis pre-treatment method is to carry out fast pyrolysis and analyse the resulting products.

9. PYROLYSIS OF PRE-TREATED FEEDSTOCKS

Fast pyrolysis of pre-treated feedstocks has been carried out at 500°C using a 150g/h reactor. This temperature was found [in Chapter 7] to give the highest yield of organics for most feedstock types. The yields of pyrolysis products and chemicals are reported along with critical assessment and comparison with the results of similar experiments from other institutes. The following sections present the results from the pyrolysis experiments and also results from HPLC analysis of the pyrolysis liquids.

9.1 PYROLYSIS OF DEMINERALISED AND HYDROLYSED PINE

Pyrolysis experiments have been carried out at the University of Waterloo using a 100g/h fluidised bed reactor [by this author] on samples of untreated and pre-treated pine wood. The pre-treated pine was produced by two pre-treatment experiments also carried out at the University of Waterloo. The method used to demineralise pine was described in Section 8.3.2 and the method used to hydrolyse pine was described in Section 8.4. All runs were carried out at approximately 500°C and with low residence times to minimise secondary reactions. The mass balance results are shown in Table 9.1.

The yield of organics is high for all runs [i.e. >60mf wt.%] and the high yields of water for both pre-treated runs brings the total liquids up to 85 mf wt.%. The char yield decreases with increased severity of pre-treatment. The yields of gas for both pre-treated runs are almost half that of the untreated run, which could be due to reduced fragmentation reactions [since these tend to result in the formation of gas and low molecular weight compounds].

Table 9.1: Mass balance results from untreated and pre-treated pine

Run No.	313	312	314
Pre-treatment	none	demineralised	hydrolysis
Temp. [°C]	501	479	512
Res. Time [s]	0.31	0.32	0.33
Feedrate [g/h]	54.8	39.8	49.4
Moisture [mf wt.%]	7.61	5.81	1.21
Ash [mf wt.%]	0.23	0.05	0.05
Yields [mf wt.%]			
Char	11.7	9.4	8.4
Organics	68.5	63.7	66.4
Gas	10.5	5.4	6.3
Water	8.8	21.8	18.6
Total liquids	77.3	85.5	85.0
Closure	99.5	100.4	99.6
Gas [mf wt.%]			
Carbon Monoxide	4.13	2.21	1.79
Carbon Dioxide	5.00	2.87	3.82
Methane	0.37	0.37	0.11
C2 s	0.13	0.00	0.04
C3 s	0.05	0.00	0.00

The yield of aqueous soluble chemicals from the pyrolysis liquids, as determined by HPLC is shown in Table 9.2. The yields of hydroxyacetaldehyde and levoglucosan give the best indication of the effectiveness of the pretreatments. Untreated pine gave yields of 6.86 and 1.67 mf wt.% [hydroxyacetaldehyde and levoglucosan respectively]. Demineralised pine gave yields of 2.39 and 4.19 mf wt.% and hydrolysed pine gave yields of 3.86 and 22.94 mf wt.%.

It was expected that the yield of levoglucosan would increase and the yield of hydroxyacetaldehyde would decrease with increasing severity of pre-treatment. The yield of levoglucosan increases significantly for both demineralised and hydrolysed woods. However, the yield of hydroxyacetaldehyde is decreased for hydrolysed pine but is further decreased for demineralised pine. It is possible that because run 312 [demineralised pine] was carried out at a slightly lower temperature this has resulted in a lower yield of hydroxyacetaldehyde. Conversely since run 314 [hydrolysed pine] was carried out at 512°C this may have resulted in an increased yield of hydroxyacetaldehyde.

Table 9.2: Chemical analysis results from untreated and pre-treated pine

Run No.	313	312	314
Pre-treatment	none	demineralised	hydrolysis
Temp. [°C]	501	479	512
Yields [mf wt.%]			
Char	11.7	9.4	8.4
Organics	68.5	63.7	66.4
Gas	10.5	5.4	6.3
Water	8.8	21.8	18.6
Total Liquids	77.3	85.5	85.0
Closure	99.5	100.4	99.6
Chemicals [mf wt.%]			
Hydroxyacetaldehyde	6.86	2.39	3.86
Levoglucosan	1.67	4.19	22.94
Formic acid	3.27	3.55	8.41
Acetic acid	0.00	0.00	0.00
Fructose	0.00	0.00	0.00
Acetol	1.28	0.00	1.86
Others	1.61	4.61	10.61
Pyrolytic Lignin			
Chem. Total	14.69	14.73	47.67

The yield of formic acid increased with severity of pre-treatment; this is because formic acid is also a fragmentation product and so increased yields are expected at higher temperatures. However, the pre-treatment of the feedstock by nitric acid may also have lead to increased yields. There is no value for pyrolytic lignin because the preparation method for HPLC analysis differs slightly at Waterloo from that used at Aston.

The Chem. Total is the sum of all of the chemicals analysed/detected [mf wt.% dry feedstock basis]. In all cases the total chemicals are those contained in the liquid. If the whole of the pyrolysis liquid had been/could be analysed then the Chem. Total would approach the organics yield. However, in most cases only around 60% of the pyrolysis liquid is analysed, including the pyrolytic lignin fraction. Thus some of the chemicals must be present in yields too low for detection or are beyond the range of the analysis technique employed.

9.2 PYROLYSIS OF IEA POPLAR WITH PRE-WASH AND MILD ACID WASH

Table 9.3 and Table 9.4 show mass balance results from pyrolysis of the feedstocks pre-treated in Section 8.3.3 above. SFB28 has been included in the table for comparative purposes since it is the best experiment of untreated poplar at 500°C. In an effort to minimise the effect of temperature and residence time on pyrolysis product and chemicals yields all runs have been carried out at 500°C with a residence time of approximately 0.5s. All pre-treated feedstocks were dried [after pre-treatment] to moisture contents of less than 10 mf wt.%. Ash contents have been found by ASTM and are shown below; they are reduced [i.e. less than untreated poplar] because of the pre-treatments carried out.

Table 9.3: Pre-wash and dilute acid wash poplar mass balance results

Run No.	SFB28	SFB26	SFB27	SFB66	SFB67
Pre-treatment [PreDi]	none	$4H_2O$	$1H_2SO_4$	$2H_2SO_4$	$3H_2SO_4$
Temp. [°C]	508	506	498	496	503
Res. Time [s]	0.51	0.57	0.51	0.48	0.56
Feedrate [g/h]	88.8	89.2	90.5	63.0	56.6
Moisture [mf wt.%]	7.25	7.25	4.20	7.52	8.69
Ash [mf wt.%]	0.46	0.26	0.12	0.10	0.08
Yields [mf wt.%]					
Char	8.23	6.86	6.40	10.40	6.45
Organics	69.69	72.52	78.67	71.43	77.03
Gas	15.62	14.08	11.13	8.12	9.75
Water	1.47	1.16	0.86	1.78	0.19
Total Liquids	71.16	73.68	79.53	73.21	77.22
Closure	95.01	94.61	97.06	91.73	93.42
Gas [mf wt.%]					
Carbon Monoxide	7.31	7.92	6.27	4.21	4.98
Carbon Dioxide	7.32	5.26	3.96	3.61	4.23
Methane	0.55	0.47	0.51	0.30	0.53
C2 s	0.29	0.28	0.25	0.00	0.00
C3 s	0.98	0.14	0.13	0.00	0.00

For all pre-treated runs char yields are between 6-10mf wt.%, which was also obtained from untreated poplar [SFB28]. The organics yield ranges from 68-80mf wt.%, but in most cases pre-treated organics is more than 3mf wt.% higher than that obtained using untreated poplar. The yield of gas tends to be lower than that obtained for untreated poplar. The yield of water in all cases is very low, but the untreated poplar also gave low water yields. Overall it would appear that the pre-treated feedstocks gave increased yields of organics at the expense of gas. This suggests that more depolymerisation reactions occurred and less fragmentation.

Table 9.4: Pre-wash and dilute acid wash poplar mass balance results

Run No.	SFB28	SFB68	SFB69	SFB70	SFB71
Pre-treatment [PreDi]	none	$4H_2SO_4$	$5H_2SO_4$	$6H_2SO_4$	$7H_2SO_4$
Temp. [°C]	508	502	493	500	502
Res. Time [s]	0.51	0.53	0.51	0.49	0.49
Feedrate [g/h]	88.8	75.4	62.2	60.2	68.1
Moisture [mf wt.%]	7.25	7.00	3.00	7.45	7.99
Ash [mf wt.%]	0.46	0.08	0.05	0.07	0.03
Yields [mf wt.%]					
Char	8.23	6.70	7.32	5.22	7.00
Organics	69.69	79.38	67.97	74.82	73.17
Gas	15.62	7.84	8.92	11.10	8.77
Water	1.47	0.39	4.43	0.87	0.21
Total Liquids	71.16	79.77	72.40	75.69	73.38
Closure	95.01	94.31	88.63	92.00	89.15
Gas [mf wt.%]					
Carbon Monoxide	7.31	4.16	5.01	5.87	4.33
Carbon Dioxide	7.32	3.24	3.36	4.65	3.90
Methane	0.55	0.44	0.32	0.36	0.33
C2 s	0.29	0.00	0.23	1.90	0.21
C3 s	0.98	0.00	0.00	0.00	0.00

Table 9.5 and Table 9.6 show the results of HPLC analysis of the pyrolysis liquids obtained from the above runs. The yields of hydroxyacetaldehyde and levoglucosan give the best indication of the effectiveness of the pretreatments. The results of SFB28 will be compared with the other pre-treated runs in turn. SFB28 was obtained from pyrolysis of untreated poplar and it gave yields of 7.62 mf wt.% hydroxyacetaldehyde and 2.45 mf wt.% levoglucosan. SFB26 was pre-washed only [PreDi4H_2O] and has slightly reduced yields of hydroxyacetaldehyde and higher yields of levoglucosan. This is expected since the likelihood of fragmentation over depolymerisation is increased by the presence of ash, especially potassium. In the case of water washing it was found that potassium and sodium were the elements most easily removed from the biomass. From this it follows that there will be virtually no potassium in any of the other pre-washed and dilute acid washed samples.

Table 9.5: Pre-wash and dilute acid wash poplar chemical analysis results

Run No.	SFB28	SFB26	SFB27	SFB66	SFB67
Pre-treatment	none	$4H_2O$	$1H_2SO_4$	$2H_2SO_4$	$3H_2SO_4$
Temp. [°C]	508	506	498	496	503
Acid Conc. [M]	none	none	0.15	0.10	0.10
Acid Wash Temp. [°C]	none	none	30	30	30
Ash [mf wt.%]	0.46	0.26	0.12	0.10	0.08
Chemicals [mf wt.%]					
Hydroxyacetaldehyde	7.26	7.10	2.45	0.15	4.19
Levoglucosan	2.45	3.12	8.63	18.78	11.68
Formaldehyde	4.76	5.39	1.73	3.28	3.81
Acetic acid	6.73	6.05	3.10	3.34	3.53
Fructose	0.92	1.47	1.37	4.21	1.24
Acetol	1.04	0.73	0.26	0.09	0.44
Others	1.81	2.53	0.96	1.07	1.21
Pyrolytic Lignin	17.09	18.91	23.84	19.99	21.81
Total	42.08	45.30	42.34	50.93	47.92

SFB27, SFB66 and SFB67 were all pre-washed followed by dilute sulphuric acid treatment. They all exhibit reduced yields of hydroxyacetaldehyde, 2.45, 0.15 and 4.19mf wt.% in comparison to 7.26mf wt.% of untreated poplar. The yield of levoglucosan has increased in all cases, from 2.45mf wt.% to 3.12mf wt.% for pre-washed only, up to 18.78mf wt.% for pre-wash followed by 0.1M sulphuric acid at 30°C. It is unclear why this particular concentration should produce such high yields. The other pre-treatments all produced a significant reduction in ash content and were all pyrolysed at similar temperatures.

Runs SFB68, 69, 70 and 71 were pre-washed and then acid washed at 40°C; pyrolysis was carried out at 500°C. HPLC results from the analysis of the pyrolysis liquids produced from these runs are shown in Table 9.6. Again, all runs showed significant decreases in the yield of hydroxyacetaldehyde and increases in the yield of levoglucosan. However, none of the runs produced levoglucosan in as high yield as SFB66.

For all pre-treatments using acid the yields of formaldehyde are significantly reduced compared to untreated poplar [and water washed only]. Formaldehyde is a chemical often associated with the hemicellulose component of biomass; thus its reduction indicates that the hemicellulose component has been modified in some way. The maximum loss of feedstock in the pre-wash and pre-treatment experiments was approximately 8%, which does not account for the complete removal of hemicellulose. This may be the reason for reduced yields of formaldehyde rather than no formaldehyde whatsoever.

Table 9.6: Pre-wash and dilute acid wash poplar chemical analysis results

Run No.	SFB28	SFB68	SFB69	SFB70	SFB71
Pre-treatment	none	$4H_2SO_4$	$5H_2SO_4$	$6H_2SO_4$	$7H_2SO_4$
Temp. [°C]	508	502	493	500	502
Acid Conc. [M]	none	0.10	0.20	0.50	0.50
Wash Temp. [°C]	none	40	40	40	40
Ash [mf wt.%]	0.46	0.08	0.05	0.07	0.03
Chemicals [mf wt.%]					
Hydroxyacetaldehyde	7.26	2.99	5.81	1.93	1.42
Levoglucosan	2.45	3.77	7.20	10.97	12.37
Formaldehyde	4.76	0.65	n/a	1.91	1.80
Acetic acid	6.73	1.31	n/a	3.15	1.75
Fructose	0.92	0.00	n/a	0.00	1.99
Acetol	1.04	0.44	n/a	0.41	0.49
Others	1.81	0.55	n/a	0.48	0.73
Pyrolytic Lignin	17.09	19.81	30.66	23.50	31.86
Total	42.08	29.53	n/a	42.34	52.40

Table 9.7 shows the results from three fast pyrolysis experiments. Untreated IEA poplar was carried out at Aston as part of this work. Demineralised is the highest yield of levoglucosan reported in the literature from a demineralisation experiment. SFB66 was obtained by pre-washing prior to demineralisation. The conditions used for the literature demineralisation and SFB66 were the same [i.e. 0.1M sulphuric acid at 30°C]. It is evident that SFB66 has produced significantly higher yields of levoglucosan than previously reported in the literature. Thus pre-washing prior to demineralisation appears to result in significantly improved yields of levoglucosan. It is clear that the pre-washing does not necessarily result in improved ash removal. Hence it is believed that the pre-washing swells the biomass allowing subsequent treatments better access to permeate into the heart of the particle. The perceived increase in levoglucosan yield may also be due to small amounts of acid [in this case sulphuric] remaining in the biomass and having a catalytic effect.

Table 9.7: Product yields from fast pyrolysis of demineralised IEA poplar

	Untreated	Demineralised	Pre-washed and pre-treated
	SFB28	(89)	SFB66
Temperature [°C]	508	530	496
Moisture content [%]	7.00	0	7.52
Ash [%]	0.46		0.10
Yields [mf wt.%]			
Organics	79.38	60.50	71.43
Water	0.39	18.25	1.78
Char	6.70	2.50	10.40
Gas	7.84	14.13	8.12
Hydroxyacetaldehyde	7.26	3.35	0.15
Levoglucosan	2.45	9.33	18.78
Lignin [aromatics]	17.09	17.8	19.99

9.3 PYROLYSIS OF MINERAL ACID PRE-TREATED IEA POPLAR

IEA Poplar wood with small [300-600μm] and large [600-1000μm] particle sizes was pre-treated as described in Section 8.3.4. A range of mineral acids were used under different conditions of acid strength and temperature. Although 50g samples were used in each of the batch reactors, losses due to handling, filtering and ASTM analysis meant that only approximately 40g of each treatment remained. Also, since little difference appeared to exist between the results from small and large particle sizes the poplar samples from identical pre-treatments were combined to provide more feedstock for the pyrolysis experiments.

Pyrolysis experiments have been carried out using a 150g/h reactor and the mass balance results are shown in Table 9.8 for hydrochloric acid, Table 9.9 for phosphoric and sulphuric acids and Table 9.10 for nitric acid.

Table 9.8 shows mass balance results in order of increasing severity of pretreatment. The yields of char, organics, gas and water are similar to those obtained from pyrolysis of pre-washed and demineralised biomass [Section 9.2]. Char yields range from 4.58-6.15 mf wt.%, organics yields are all in excess of 72 mf wt.%, gas yields range from 10.40-11.27 mf wt.% and water yields range from 0.03-0.93 mf wt.%.

The closures appear to be low, in some cases in excess of 10mf wt.% of the original starting material has not been accounted for. This is believed to be due to a combination of poor gas analysis [as discussed in Chapter 7] and also increased yields of more volatile chemicals, which are much harder to condense and collect.

Table 9.8: Hydrochloric acid IEA treated poplar

Run No.	SFB53	SFB52	SFB55	SFB54	SFB50	SFB51
Temp. [°C]	500	502	498	500	500	502
Res. Time [s]	0.55	0.55	0.54	0.56	0.55	0.54
Feedrate [g/h]	52.2	59.5	56.9	46.3	81.3	66.3
Moisture [mf wt.%]	6.73	7.14	6.90	7.09	7.47	7.04
Ash [mf wt.%]	0.05	0.05	0.02	0.04	0.02	0.04
Pretreatment						
Acid	HCl	HCl	HCl	HCl	HCl	HCl
Conc. [M]	0.1	0.1	1.0	1.0	3.0	3.0
Temp. [°C]	20	50	20	50	20	50
Yields [mf wt.%]						
Char	4.58	6.15	4.67	5.95	5.03	4.78
Organics	72.57	73.74	74.38	75.68	76.86	75.63
Gas	10.40	11.27	10.61	10.32	10.83	11.14
Water	0.92	0.93	0.17	0.06	0.28	0.26
Total Oil	73.49	74.67	74.55	75.74	77.16	75.89
Closure	88.46	92.10	89.82	92.00	93.00	91.81
Chemicals [mf wt.%]						
Hydroxyacetaldehyde	5.20	6.30	5.37	4.62	3.63	8.04
Levoglucosan	6.86	9.77	9.27	8.01	7.15	11.87
Formic acid	2.00	2.29	2.84	1.35	2.85	3.14
Acetic Acid	2.35	2.87	3.19	2.25	2.91	2.58
Fructose	1.26	1.94	1.50	1.63	0.93	2.56
Methanol	1.02	2.05	0.17	1.23	1.02	0.26
Others	0.88	1.21	1.45	0.95	1.71	1.46
Pyrolytic Lignin	25.13	22.61	22.30	22.19	23.88	22.35
Chem. Total	61.59	66.50	61.33	55.80	43.18	69.09

Table 9.9 shows mass balance results for phosphoric and sulphuric acid treated poplar. Both phosphoric acid and sulphuric acid gave high yields of organics. These were found to contain reduced yields of hydroxyacetaldehyde and increased yields of levoglucosan in comparison to untreated poplar wood.

Table 9.9: Phosphoric acid and sulphuric acid treated IEA poplar

Run No.	SFB49	SFB56	SFB57	SFB58
Temp. [°C]	503.6	507.4	501.1	501.7
Res. Time [s]	0.55	0.54	0.55	0.45
Feedrate [g/h]	56.1	38.0	55.3	47.6
Moisture [mf wt.%]	7.92	9.32	7.00	4.00
Ash [mf wt.%]	0.16	0.02	0.01	0.02
Pretreatment				
Acid	H_3PO_4	H_2SO_4	H_2SO_4	H_2SO_4
Conc. [M]	1.37[#]	1.0	1.0	1.0
Temp. [°C]	50	20	50	70
Yields [mf wt.%]				
Char	8.96	8.63	5.73	7.07
Organics	65.19	71.02	77.98	75.32
Gas	13.63	10.74	9.62	8.96
Water	2.66	0.19	1.40	0.72
Total Oil	67.85	70.80	79.38	76.04
Closure	90.44	90.44	94.72	92.08
Chemicals [mf wt.%]				
Hydroxyacetaldehyde	2.55	3.43	3.00	1.16
Levoglucosan	8.29	11.63	11.80	15.90
Formaldehyde	4.00	1.66	1.06	0.91
Acetic Acid	3.50	2.33	1.10	0.43
Methanol	0.21	0.18	0.00	0.12
Fructose	1.28	2.10	3.45	2.44
Others	0.24	1.27	1.23	1.23
Pyrolytic Lignin	23.27	31.44	31.65	29.22
Chem. Total	43.36	75.46	66.95	66.38

[#] Samples of 3 pretreatments combined to give enough feedstock for run

The phosphoric treated poplar was a combination of three different treatments [i.e. 0.1M, 1.0M and 3.0M poplar treated at 50°C] combined to give enough feedstock to carry out a single pyrolysis experiment. It is possible that had the individual pre-treated feedstocks been pyrolysed separately slightly different chemical yields may have been obtained. The combined phosphoric acid treated poplar liquid contains higher yields of formaldehyde and acetic acid than liquids produced by any other pre-treatment. It was also expected to contain high yields of levoglucosenone [an isomer of levoglucosan], but this was not detected using the Aston HPLC system. However, it may be contained in the liquid but undetected, which may account for the comparatively low levoglucosan yield.

Sulphuric acid treated poplar produced liquids containing similar yields of chemicals to those found in hydrochloric acid treated poplar. However, the yield of levoglucosan is much higher for all three pre-treatments than any phosphoric acid or hydrochloric acid treatments.

Table 9.10: Nitric acid treated IEA poplar

Feedstock	Poplar	Poplar	Poplar
Run No.	SFB60	SFB61	SFB62
Temp. [°C]	500	501	508
Res. Time [s]	0.55	0.54	0.55
Feedrate [g/h]	49.3	54.8	44.9
Moisture [mf wt.%]	7.15	5.00	9.38
Ash [mf wt.%]	0.02	0.03	0.01
Pretreatment			
Acid	HNO_3	HNO_3	HNO_3
Conc. [M]	0.1	1.0	3.0
Temp. [°C]	50	50	50
Yields [mf wt.%]			
Char	5.00	6.21	8.28
Organics	76.80	77.51	75.70
Gas	11.08	9.63	12.06
Water	0.53	1.06	0.10
Total Oil	77.33	78.57	75.80
Closure	93.40	94.40	96.13
Chemicals [mf wt.%]			
Hydroxyacetaldehyde	6.72	2.96	3.25
Levoglucosan	5.80	3.88	13.47
Formaldehyde	1.01	0.63	2.91
Acetic Acid	1.92	0.79	1.92
Methanol	0.08	0.00	0.11
Fructose	0.91	0.00	7.25
Others	0.90	0.71	1.01
Pyrolytic Lignin	24.27	21.92	23.19
Chem. Total	42.45	31.22	53.11

The results from nitric acid treated poplar pyrolysis experiments are shown in Table 9.10. Similar to the other acid washing experiments the yield of hydroxyacetaldehyde is lower and the levoglucosan yield is higher for all experiments, compared to untreated poplar. The yield of levoglucosan appears to be marginally lower from nitric acid treated poplar than sulphuric acid treated. 3.0M nitric acid treated poplar did produce the highest yield of fructose for a pre-treated feedstock [in this work].

Figure 9.1 shows levoglucosan yields from poplar treated with hydrochloric or nitric acid at 0.1, 1.0 or 3.0M concentrations. It can be seen that hydrochloric acid treatment at 20°C gave the highest levoglucosan yield at 1.0M. Whereas, at 50°C both hydrochloric and nitric acids produced the highest yield of levoglucosan at 3.0M concentrations. It is also interesting to note that the 20°C curve has a peak, whereas the 50°C curves both have troughs.

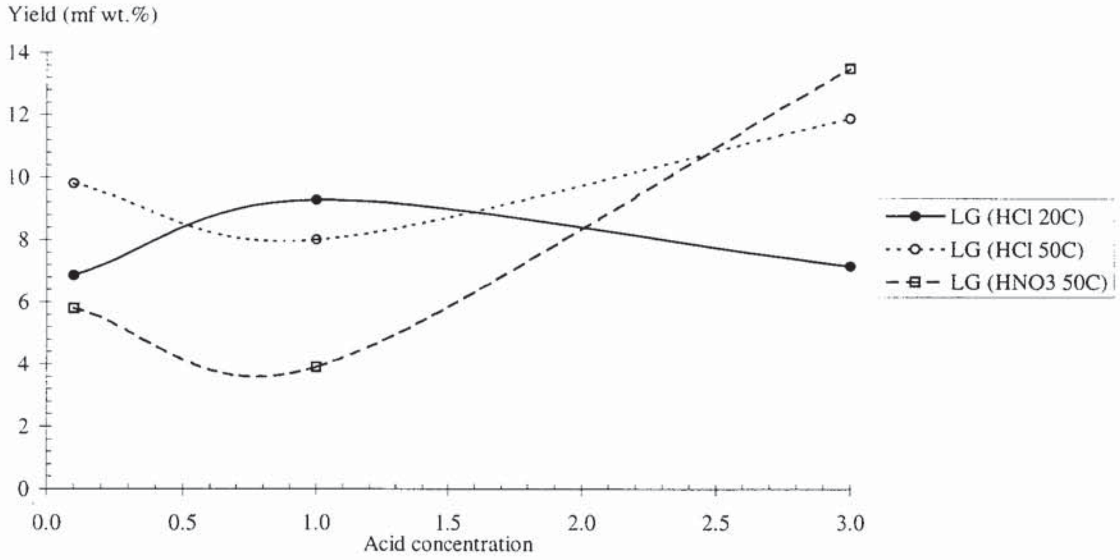


Figure 9.1: Levoglucosan yield versus pre-treatment conditions

Figure 9.2 shows hydroxyacetaldehyde yields from poplar treated with hydrochloric or nitric acid at 0.1, 1.0 or 3.0M concentrations. Similar trends to those in Figure 9.1 can be observed, that is to say, an hydroxyacetaldehyde peak for 1.0M hydrochloric acid poplar treated at 20°C and troughs for 1.0M hydrochloric and nitric acid poplar treated at 50°C.

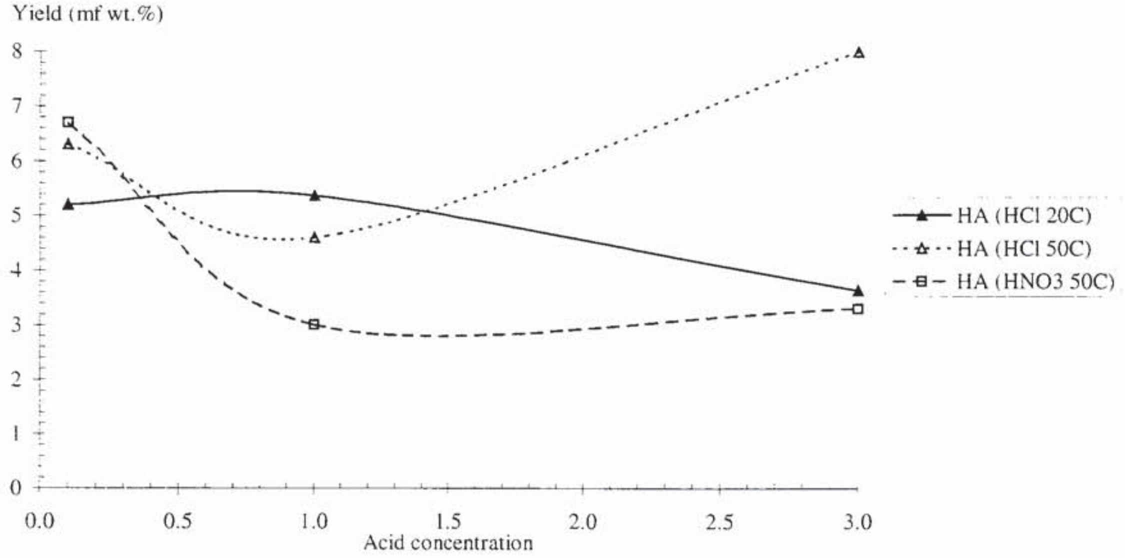


Figure 9.2: Hydroxyacetaldehyde yield versus pre-treatment conditions

Figure 9.3 shows the effect of pre-treatment temperature on levoglucosan and hydroxyacetaldehyde yield. It is evident that higher sulphuric acid pre-treatment temperatures were more effective in producing increased yields of levoglucosan and hydroxyacetaldehyde. This was predicted, since the more severe the pre-treatment conditions the closer to cellulose the feedstock becomes. This trend is not evident with hydrochloric acid. For 1.0M hydrochloric acid, both levoglucosan and hydroxyacetaldehyde yields decreased with increase in pre-treatment temperature. For 0.1M Hydrochloric acid pre-treatment both levoglucosan and hydroxyacetaldehyde yields increased with increasing pre-treatment temperature. It is acknowledged that more experiments should be carried out to confirm these trends.

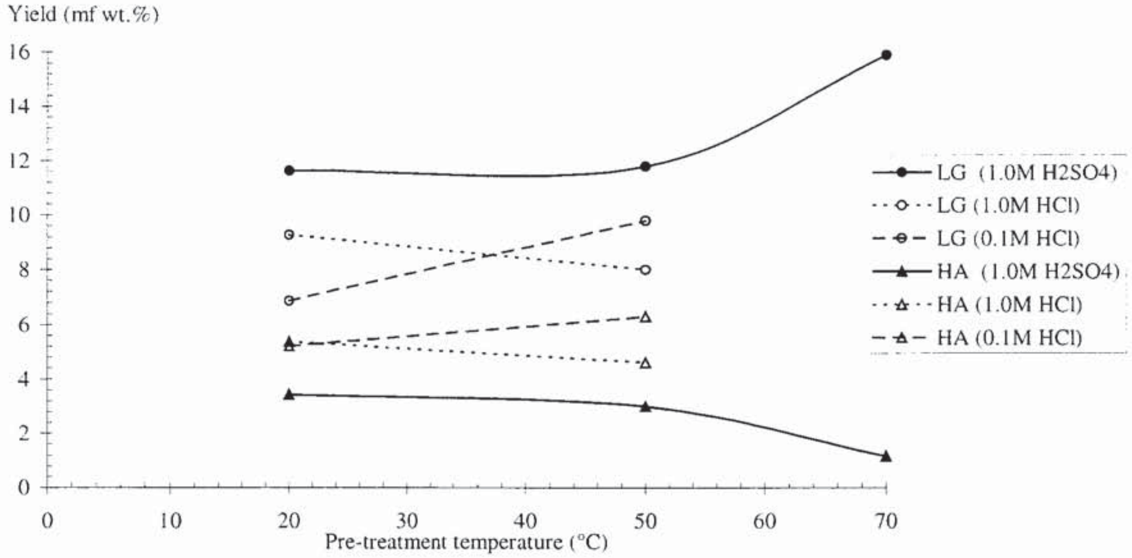


Figure 9.3: Levoglucosan and hydroxyacetaldehyde yield versus pre-treatment temperature

These results do not agree with the findings of Julien et al. (124) as shown in Figure 9.4. They found that treatment with nitric acid gave the highest yield of levoglucosan and that the concentration had little effect on the overall yield. However, their experiments were carried out using cellulose with slow heating rates in a vacuum. It is most likely that the nitric acid remaining in the cellulose was vaporised before the cellulose and hence took no part in the "pyrolysis" reaction. From Figure 9.1 and Figure 9.2 it is evident that nitric acid had a significant effect on the atmospheric fast pyrolysis of biomass and this effect was a function of acid concentration. Although the residual nitric acid in the biomass may have been vaporised, it would remain in the reactor vapour space and hence influence the pyrolysis reactions.

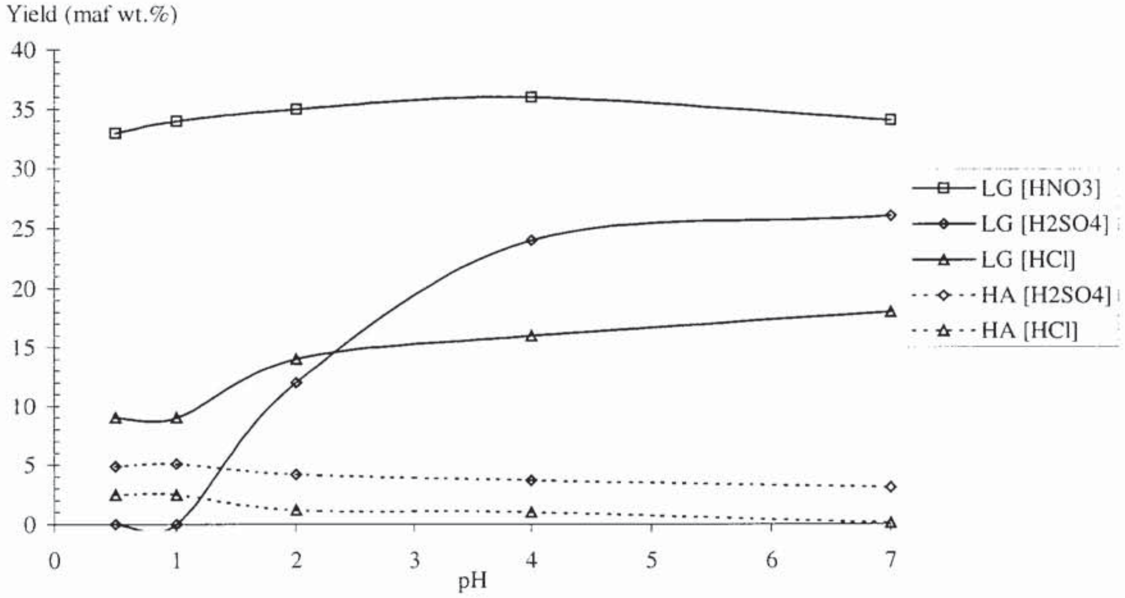


Figure 9.4: Yield of levoglucosan and hydroxyacetaldehyde as a function of pH (124)

Julien et al. (124) found that sulphuric acid performed slightly better than hydrochloric acid in increasing levoglucosan yields. They found that both acids remain in the biomass and hence modify the pyrolysis reactions [slow vacuum]. This effect was also observed in atmospheric flash pyrolysis of pre-treated biomass. Thus from Figure 9.3 it can be seen that the higher concentrations of acid expected to remain in the biomass after treatment at higher temperature [or higher concentration see Figure 9.1 and Figure 9.2 for hydrochloric acid] do improve the yield of levoglucosan.

9.4 PYROLYSIS OF IEA POPLAR CONTAINING ADDITIVES

Poplar containing iron, potassium and ammonium chloride additives has been pyrolysed at approximately 500°C and the product and chemical yields are reported in Table 9.11. Each additive was soaked into the biomass in concentrations of 2% active component; in each case the cation is deemed to be the active component. It may be that the chloride anion has an effect on the products, but since all three additives used the same anion this effect is believed to be negated.

Table 9.11: IEA poplar containing additives

Run No.	SFB28	SFB73	SFB74	SFB75
Temp. [°C]	508	508	508	526
Res. Time [s]	0.51	0.54	0.64	0.77
Feedrate [g/h]	88.8	74.5	84.4	84.6
Moisture [mf wt.%]	7.25	9.34	5.62	6.23
Ash [mf wt.%]	0.46	3.12	2.13	0.33
Pretreatment				
Additive	none	$FeCl_3$	KCl	NH_4Cl
"Active" comp. conc. [%]	0	2.01	1.96	2.02
Char	8.23	33.05	10.22	24.90
Organics	69.69	25.76	53.80	40.51
Gas	15.62	25.73	19.79	15.59
Water	1.47	13.30	12.56	16.62
Total Oil	71.16	39.06	66.36	57.13
Closure	95.01	97.85	96.37	97.61
Chemicals [mf wt.%]				
Hydroxyacetaldehyde	7.26	0.59	11.73	4.65
Levoglucosan	2.45	0.71	1.80	4.09
Formaldehyde	4.76	0.72	6.00	3.05
Acetic Acid	6.73	0.70	6.49	5.07
Methanol	0.92	0.18	0.00	0.00
Fructose	1.04	0.00	0.00	1.19
Xylitol	0.00	0.00	1.17	0.94
Others	1.81	0.67	0.50	0.32
Pyrolytic Lignin	17.09	2.11	18.28	10.48
Chem. Total	42.08	5.67	51.90	31.63

The aim of iron addition was to reduce the effect of lignin on the pyrolysis reactions. The feedstock containing iron was extremely difficult to feed, which is believed to be due to its high char forming properties causing the end of the feed tube to become blocked. The yield of char is the highest ever produced at Aston. The yield of chemicals is very low; it is unclear why this should be.

The addition of potassium was in an effort to increase the yield of hydroxyacetaldehyde, since it is known that feedstocks containing ash tend to produce hydroxyacetaldehyde and also that potassium is one of the more active elements contained in ash. The potassium had the effect of increasing the yields of oxygenates and acids and decreasing the yield of sugars in comparison to untreated poplar. This is believed to be a function of ash in promoting fragmentation reactions [hydroxyacetaldehyde and acid forming] and suppressing depolymerisation reactions [sugar forming].

It was hoped that the addition of ammonium might decrease the yields of aldehydes and ketones by providing extra hydrogen in the reactor. From the above results it is unclear whether this aim was achieved. It is likely that some oxidation did take place due to the lower yield of pyrolytic lignin.

It is widely believed that the chloride ion also has a significant effect on the pyrolysis pathway; results reported in Section 9.3 [hydrochloric acid pre-treated poplar] confirm this. However, from these additives it is evident that they all behaved differently, thus the action of the chloride ion must be modified by [or modify] the action of the cation [i.e. iron, potassium or ammonium].

Overall poplar containing additives was very difficult to feed, since it constantly blocked the feed tube of the reactor. All additives produced char yields higher than untreated poplar. The results are far from conclusive and it is recommended that further work be carried out on the effects of additives and catalysts on the products and chemicals from the fast pyrolysis of biomass.

9.5 PRE-TREATED FEEDSTOCKS COMPARISON

A number of pre-treated feedstocks have been pyrolysed and the mass balances and liquid chemical analyses reported. Table 9.12 shows all of the feedstocks tested along with pre-treatment methods and conditions. The pyrolysis temperature is also shown along with the yield of levoglucosan and hydroxyacetaldehyde, which are known to be the major chemicals from two competing pyrolysis pathways.

Table 9.12: Comparison of pre-treatment conditions and yields of chemicals

Run number	Acid type	Conc. [mf wt.%]	Pre-treat Temp.[°C]	Ash [mf wt.%]	Pyrolysis Temp.[°C]	LG	HA
Pine							
313	none			0.23	501	1.67	6.86
312	HCl	0.1	amb.	0.05	479	4.19	2.39
314	HCl	5	100	0.05	512	22.94	3.86
Poplar							
SFB28	none			0.46	508	2.45	7.26
SFB26	water		amb.	0.26	506	3.12	7.10
Poplar, pre-washed as SFB26							
SFB27	H_2SO_4	0.15	30	0.12	498	8.63	2.45
SFB66	H_2SO_4	0.10	30	0.10	496	18.78	0.15
SFB67	H_2SO_4	0.10	30	0.08	503	11.68	4.19
SFB68	H_2SO_4	0.10	40	0.08	502	3.77	2.99
SFB69	H_2SO_4	0.20	40	0.05	493	7.20	5.81
SFB70	H_2SO_4	0.50	40	0.07	500	10.97	1.93
SFB71	H_2SO_4	0.50	40	0.03	502	12.37	1.42
Poplar, acid washed only							
SFB53	HCl	0.1	20	0.05	500	6.86	5.20
SFB52	HCl	0.1	50	0.05	502	9.77	6.30
SFB55	HCl	1.0	20	0.02	498	9.27	5.37
SFB54	HCl	1.0	50	0.04	500	8.01	4.62
SFB50	HCl	3.0	20	0.02	500	7.15	3.63
SFB51	HCl	3.0	50	0.04	502	11.87	8.04
SFB56	H_2SO_4	1.0	20	0.02	507	11.63	3.43
SFB57	H_2SO_4	1.0	50	0.01	501	11.80	3.00
SFB58	H_2SO_4	1.0	70	0.02	502	15.90	1.16
SFB49	H_3PO_4	1.37	50	0.16	504	8.29	2.55
SFB60	HNO_3	0.1	50	0.02	500	5.80	6.72
SFB61	HNO_3	1.0	50	0.03	501	3.88	2.96
SFB62	HNO_3	3.0	50	0.01	508	13.47	3.25
Poplar, additives							
SFB73	$FeCl_3$	2.01	amb.	3.12	508	0.71	0.59
SFB74	KCl	1.96	amb.	2.13	508	1.80	11.73
SFB75	NH_4Cl	2.02	amb.	0.33	526	4.09	4.65

The highest yield of levoglucosan was 22.94mf wt.% from nitric acid hydrolysed pine. Hydrolysis removed approximately 50% of the biomass, which effectively means that half of the biomass was wasted [i.e. not pyrolysed and had to be disposed of]. Less severe techniques may prove to be more economic, since less biomass is lost and the yields of levoglucosan are also significantly increased [compared to untreated biomass]. The highest yield of levoglucosan from a none hydrolysis pre-treatment was 18.78 mf wt.% obtained from poplar, which was pre-washed and then washed in 0.1M sulphuric acid at 30°C.

Pre-treatment using sulphuric acid appears to consistently produce the highest yields of levoglucosan. Other acids [e.g. hydrochloric, phosphoric and nitric] do produce an increase in the yield of levoglucosan but not as much as sulphuric acid.

Although all component removal pre-treatment methods resulted in a significant reduction in ash, the yield of levoglucosan and hydroxyacetaldehyde also appears to be dependant on other factors. Figure 9.5 shows the relationship between ash content and levoglucosan and hydroxyacetaldehyde yields for untreated and pre-treated samples of IEA poplar pyrolysed at around 500°C.

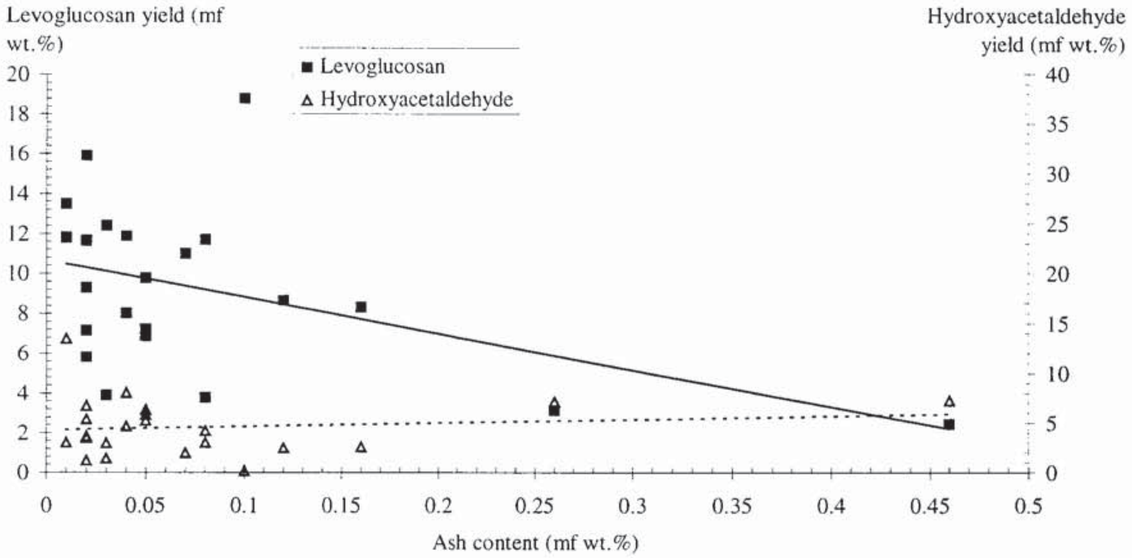


Figure 9.5: Relationship between ash content and chemical yield

From Figure 9.5 it is evident that as ash content increases the yield of levoglucosan decreases. Conversely, as ash content increases the yield of hydroxyacetaldehyde increases. However, for both trends there is an amount of scatter, which suggests that the ash content may not be the most significant factor in influencing chemical yields.

9.6 CONCLUSIONS

Pyrolysis has been carried out on a number of pre-treated feedstocks. Pyrolysis has been used to a limited extent to assess the effectiveness of pre-treatment experiments carried out in Chapter 8. It would appear that chemical analysis of the liquids produced by fast pyrolysis of pre-treated feedstocks can give an indication as to how effective a particular pre-treatment was. It therefore follows that the yield of selected chemicals in fast pyrolysis liquids can be selectively enhanced by pre-treatment of the biomass feedstock.

The yield of levoglucosan has been increased up to 18.58 mf wt.% by a relatively mild treatment [pre-washed IEA poplar washed with 0.1M sulphuric acid at 30°C]. The best previously reported by a demineralisation process was 9.33mf wt.% for 0.1M sulphuric acid demineralised poplar (89). Therefore pre-washing appears to make a considerable difference. Hydrolysis of pine using boiling nitric acid increased the yield of levoglucosan up to 22.94mf wt.% compared to reported literature yields of 30.42mf wt.% for acid hydrolysed poplar (82).

Demineralisation tends to result in the loss of 1-5mf wt.% of the biomass. Hydrolysis can result in losses up to 60mf wt.%. Whether it is better to produce levoglucosan from untreated biomass, demineralised, pre-washed and demineralised, hydrolysed or commercial cellulose will be assessed in the next Chapter.

The yield of hydroxyacetaldehyde has been increased from 7.26 [untreated IEA poplar] to 11.63 mf wt.% [IEA poplar with 2% KCl]. Hydroxyacetaldehyde yields of 17mf wt.% have been reported from 0.01% K_2CO_3 (128). Also it was found that feedstocks containing additives were much more difficult to feed and resulted in higher yields of char.

Although the yields of levoglucosan and hydroxyacetaldehyde can be selectively improved by pre-treatment these yields have not been optimised. It is recommended that further work is carried out to determine the optimum pre-treatment conditions for levoglucosan production and also the best additive for hydroxyacetaldehyde production.

10. TECHNO-ECONOMIC ASSESSMENT

This Chapter investigates and compares the total plant and operating costs for a number of integrated levoglucosan production systems. It compares the costs of five possible scenarios utilising biomass: no chemical pre-treatment, water washing, water pre-wash followed by acid washing, acid hydrolysis and purchasing commercially available cellulose.

The results and procedures from the experimental work reported earlier have been used to provide process schemes and operating data for all but the commercial cellulose scheme. The most economic method for producing levoglucosan from fast pyrolysis of biomass is determined along with levoglucosan production costs and return on investment. Sensitivity studies have been carried out to find out which factors have the largest influence.

10.1 INTRODUCTION

This Chapter is a case study to analyse and compare the economics of a number of integrated processes for the production of levoglucosan from fast pyrolysis of biomass. Levoglucosan is the most attractive chemical for a case study since it is present in low concentrations in pyrolysis liquids from untreated biomass but pyrolysis of pre-treated biomass produces pyrolysis liquid containing significantly higher concentrations. It is the only chemical which can be increased in such a significant manner. Although it has no true market at the present time a number of potential applications have been investigated. These include use as a biodegradable polymer or plastic, high value speciality chemicals precursor or low calorie food filler (2).

10.2 SCENARIOS

Figure 10.1 shows a simplified outline of the five potential scenarios, which are assessed. Waste streams have not been shown in order to keep the diagram simple. All processes have reception areas to receive the raw materials. Starting with 1000 kg of wet biomass [45% water] the following scenarios have been assessed:

1. No chemical pre-treatment [i.e. the biomass is simply prepared for pyrolysis by drying and grinding],
2. Mild chemical pretreatment [i.e. water washing] resulting in the removal of half of the ash,
3. Water pre-washing followed by acid washing to remove half of the hemicellulose and all of the ash,
4. More severe chemical treatment [i.e. boiling acid] resulting in the removal of all of the hemicellulose and ash,
5. Commercially pulped cellulose purchased in a similar amount to that available from 1000kg of wet biomass.

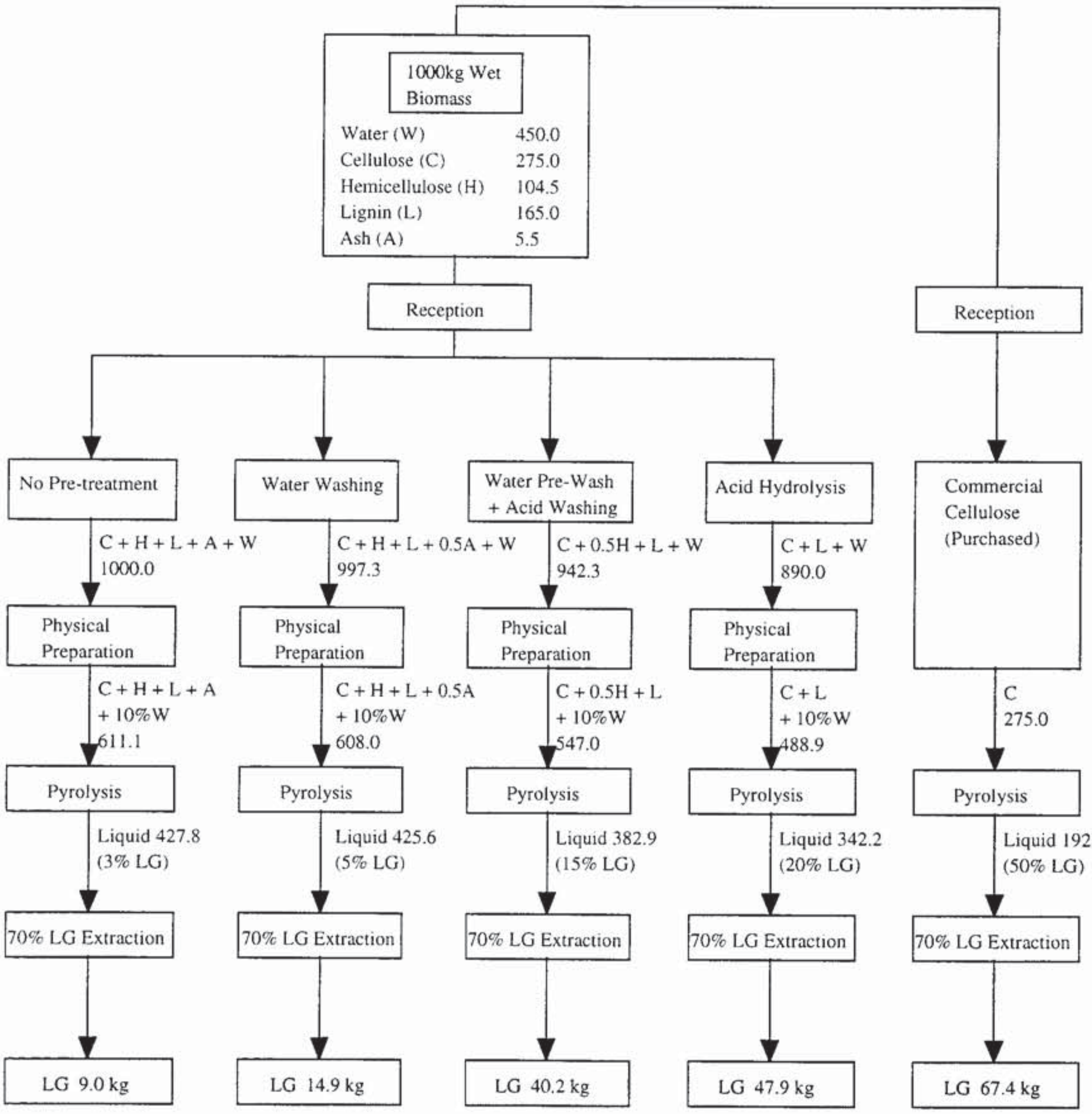


Figure 10.1: Possible process routes for levoglucosan production

The process equipment, which has been used for each of these scenarios is discussed in Section 10.3. All scenarios require physical preparation to reduce the biomass to the correct particle size and moisture content for pyrolysis. Following physical preparation [which may include chemical pre-treatment] the biomass is pyrolysed in a fluidised bed reactor. If there has been no chemical pre-treatment then all of the biomass remains. Hence, there is 611.1kg of material to be pyrolysed; thus the cost of pyrolysing untreated biomass will be higher than that of pre-treated biomass simply because there is more of it.

The pyrolysis process converts the biomass into 70% pyrolysis liquid, the remainder is converted to char and gas [streams not shown]. The pre-treatment used influences the concentration of levoglucosan in the pyrolysis liquid [shown as LG]; generally, the more severe the pre-treatment the higher the concentration of levoglucosan.

Levoglucosan is extracted from the pyrolysis liquid by a series of chemical processes, which are outlined in Section 10.3.4. The extraction will be more expensive for large volumes of liquid containing low concentrations of levoglucosan than for smaller volumes of liquid containing higher concentrations of levoglucosan. Longley et al. quote extraction efficiencies of 71-95% from the base treated pyrolysis liquid (163). However, this efficiency was determined for higher concentrations of levoglucosan. It is expected that at lower concentrations it is harder to purify and extract levoglucosan. To allow for levoglucosan losses in the initial base treatment an assumed 70% efficiency has been used for all scenarios.

The extraction process produces 99% pure levoglucosan, which can be sold. The economics of the process will be based solely on the selling price of levoglucosan. However a sensitivity study is carried out in Section 10.6.

The above scenarios have been developed from experimental work carried out in this project. Each scenario uses experimental data to determine losses, component removal and production yields. The experiments used are as follows:

1. No pre-treatment	poplar wood with no pre-treatment. Pyrolysis results from SFB28 are used to provide pyrolysis liquid levoglucosan yields [3 mf wt.% dry untreated wood basis].

2. Water washing	water washing poplar wood removed 50% of the ash. Pyrolysis liquid levoglucosan yields from SFB26 are used [5 mf wt.% dry pre-treated wood basis].
3. Pre-wash with acid washing	water pre-washing followed by 0.1 wt.% sulphuric acid was found to remove all ash and 50% of the hemicellulose. Pyrolysis liquid levoglucosan yields from SFB66 are used [15 mf wt.% dry pre-treated wood basis].
4. Acid hydrolysis	boiling 5 wt.% sulphuric acid removes all ash and hemicellulose. Pyrolysis liquid levoglucosan yields from work by Scott are used (94) [20 mf wt.% dry pre-treated wood basis].
5. Pulping	Commercial cellulose will be purchased, therefore no pre-treatment, drying or grinding will be required. The cellulose will require reception, storage and feeding into the pyrolysis reactor. Pyrolysis liquid levoglucosan yields from work by Piskorz have been used (158) [50 mf wt.% dry cellulose basis].

10.3 Process Technology

For the production of levoglucosan from the fast pyrolysis of biomass an integrated single site process is envisaged, apart from the commercial cellulose option. All scenarios have been designed to operate at a throughput of 1000kg/h of wet biomass [i.e. 24t/d]. The process is divided into five distinct stages:

Biomass preparation	comprising stages: reception, drying, size reduction and further drying prior to pyrolysis.
Chemical pre-treatment	with four pre-treatment options [no pre-treatment, water washing, pre-wash and acid washing or acid hydrolysis].
Pyrolysis	prepared biomass is pyrolysed in a reactor; products are pyrolysis liquid, gas and char.

Chemical extraction	levoglucosan is extracted from the pyrolysis liquid and purified.
Waste treatment	all waste streams are collected together to be treated to allow commercial aqueous, solid and gas disposal.

These five stages are discussed in the following Sections.

10.3.1 Biomass Preparation

The preparation stage deals with the reception of the biomass feedstock and all the physical steps prior to pyrolysis. It is assumed for the purposes of this work that the biomass will be supplied to the plant as whole tree chips. Reception and preparation of biomass has been thoroughly studied by Toft (70). Therefore systems and costs have been developed from his work.

The preparation flowsheet including pre-treatment options is shown in Figure 10.2. Initial screening is only appropriate for large scale processes [in excess of 720 t/d of biomass] (70). The process under investigation by this project is relatively small scale [24 t/d of wet biomass] and therefore this screening stage prior to storage in the pretreatment section [often seen in larger scale processes] has been omitted from the cost and process calculations.

The equipment typically used to carry out the process described in Figure 10.2 is shown in Figure 10.3 [preparation] and Figure 10.4 [pre-treatment]. It is acknowledged that some of the equipment described here may well be unsuitable for such a small process. However, by using equipment designed for larger plants it should make subsequent scaling up of this economic assessment simpler.

It may be more feasible to produce prepared and pre-treated biomass in a larger separate plant. The desired quantities of pre-treated biomass could then be transported to the pyrolysis and levoglucosan recovery plant on a regular basis. However, unlike commercial cellulose plants, biomass pre-treatment plants do not currently exist; therefore it is not possible to purchase pre-treated biomass. Thus designing and costing the pre-treatment stage is an essential part of this assessment. It is recommended that the separation of the preparation and pre-treatment stages from the pyrolysis and extraction stages be carried out at in the future to allow economies of scale to be exploited.

The chemical pre-treatment [if any] takes place part way through physical preparation. It is dependant on the washing process used whether grinding of the feedstock is required. Therefore it may be possible to avoid the drying and grinding stages prior to pre-treatment. The pre-treatment process and options are discussed in Section 10.3.2. The following is a brief description of the workings of the preparation stages.

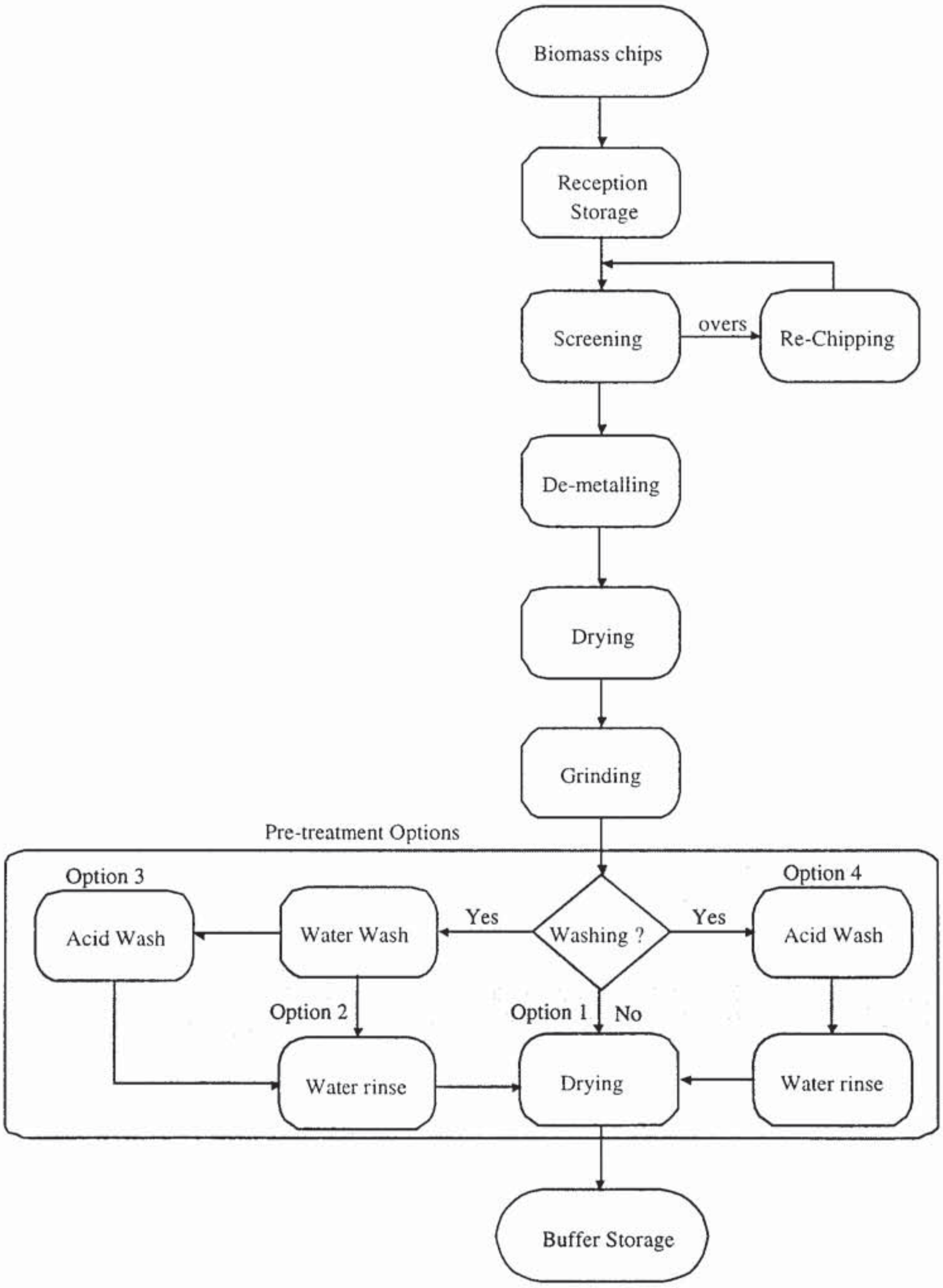


Figure 10.2: Feedstock preparation process flowsheet

Reception

The biomass will be delivered by tipper trucks to a designated reception area. The biomass is weighed on roadside truck scales and sampled to ensure it is suitable. From here the biomass is transferred to storage using a front end loader. It is not economically practical at this scale for specialist unloading equipment [e.g. truck dumpers and conveyors] to be used. Ideally the biomass would be screened before entering storage; however, as the biomass is to be screened later, just prior to the pyrolysis stage, it is not economically viable at this scale to include a screening step here.

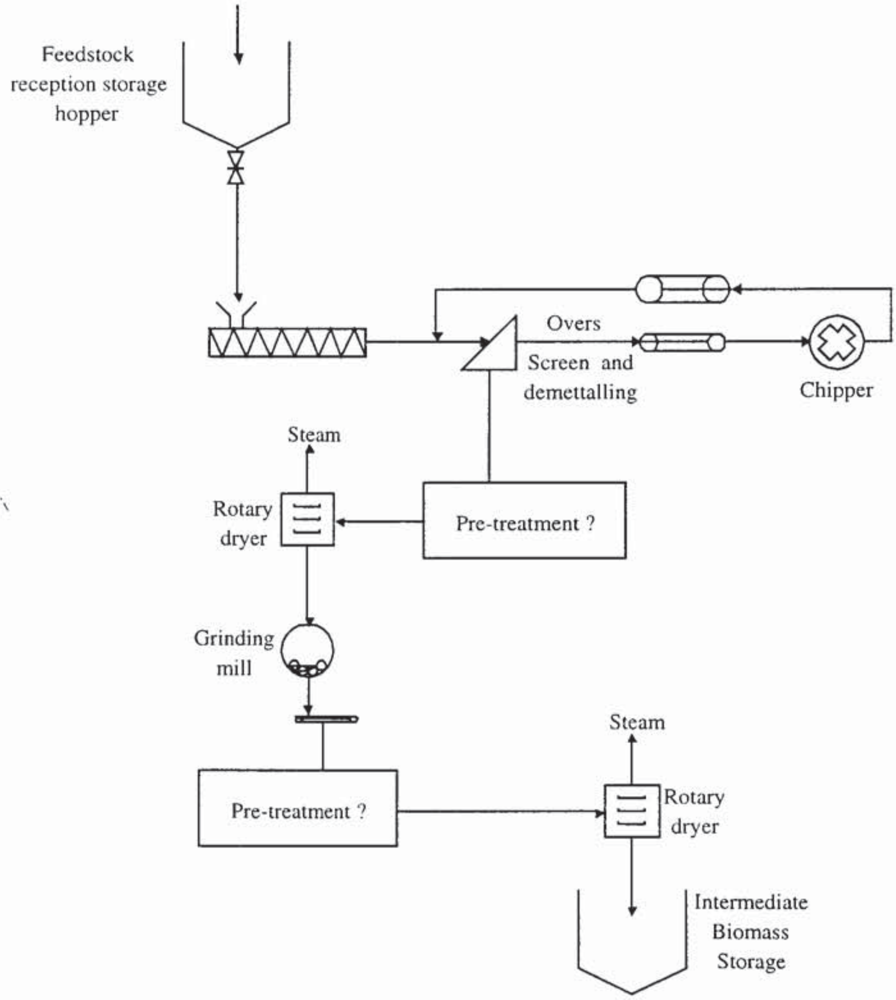


Figure 10.3: Feedstock physical preparation including pre-treatment options

Size reduction

The biomass is stored as a flat-topped pile, set on a drained concrete base to avoid contamination of the soil with leachate from the biomass. From this pile the biomass is reclaimed by the same front end loader from reception, and transferred to a day bin, so that it contains enough biomass for 24 hours, [based on 24 hours per day operation]. A drag chain conveyor recovers the biomass from the day bin and deposits it onto a conveyor, which transports the biomass to a single disc screen. Oversize biomass [which is not suitable for the process equipment/technology] is removed and a conveyor transfers it to size reduction equipment, [e.g. knife hog-chipper]. A magnet is located above the conveyor prior to the screen to remove ferrous objects that could damage equipment. Undersize biomass is not removed at the screen, as it is expected that the process technology will have no problem with a small proportion of fines. The oversize material is conveyed to a knife hog, following which it is conveyed back to the screen.

Following screening the biomass enters a grinding mill, which reduces the particle size to a suitable size for pyrolysis. Following the grinding mill the biomass [or pre-treated biomass if a pre-treatment option has been used] is dried in a rotary mill. From the dryer a closed belt conveyor and bucket elevator take the biomass to an intermediate storage hopper. The biomass is dried to approximately 10 mf wt.% water [dry biomass basis] for the pyrolysis process.

10.3.2 Pre-treatment

There are four on site pre-treatment options, the first of which consists of no pre-treatment [i.e. only physical preparation]. Options 2, 3 and 4 are shown in Figure 10.4 and are discussed in more detail in the following Section. Figure 10.4 contains all possible options; the vessels shown shaded are only required in some of the options. In all cases stainless steel equipment has been used to cope with the acidic conditions [wood is mildly acidic in solution] of water washing and acid washing.

For all options the biomass comes from a biomass buffer storage hopper, which is fed from one of two places in the physical preparation stage [Figure 10.3]. This depends on whether each pre-treatment requires ground particles or just chipped and screened particles. To avoid the extra process cost of drying the particles prior to grinding and pre-treatment it has been assumed that all pre-treatment processes operate normally on biomass, which has only been chipped and screened.

All pre-treatment options are batch processes. This is because the experiments they were developed from were all carried out batchwise. Also, the experiments were conducted using long holding times [usually 24 hours] at atmospheric pressure and ambient temperatures [or slightly above]. The 24 hour reaction time has been assumed to be reduced in most cases to two hours since it is believed that the use of stirred tanks and heating will promote the reactions. It may be that the reactions are completed in a shorter time period, in which case it may be feasible to use a continuous process to remove the desired components followed by filtration and washing. The use of increased pressure would also promote the reactions. However for the scope of this assessment all pre-treatments will be carried out batchwise at atmospheric pressure and at the temperatures stated in each Section.

Option 2 - Water washing

The purpose of water washing is to remove the ash from the biomass, which will improve the concentration of levoglucosan in the pyrolysis liquid when the washed biomass is pyrolysed. From experiments reported in Chapter 8 water washing for 24 hours at atmospheric pressure and room temperature removed approximately 50% of the total ash in poplar. For the purpose of this study the temperature will be increased to 40°C [by using the jacket on the vessel] to increase reaction kinetics and speed up the process. It has been assumed that 50% of the ash will be solubilised from the biomass in 2 hours.

Biomass is metered into the vessel, slurried with water, heated to 40°C and stirred continuously for a holding time of 2 hours. Following this the biomass slurry is pumped out using a centrifugal pump to a screw filter. It may be necessary to introduce extra water to keep the biomass in slurry form to prevent it from blocking pumps and pipes. The screw filter removes approximately 50% of the water from the biomass. From the screw filter the biomass is either fed directly into the second water washing vessel or has extra water added to it so it can be pumped into the vessel. The water rinse is used to make sure that all dissolved salts [from the ash] are removed from the biomass [working on a dilution principal]. From the rinse vessel the slurry is screw filtered then passes back to physical preparation and is dried prior to pyrolysis.

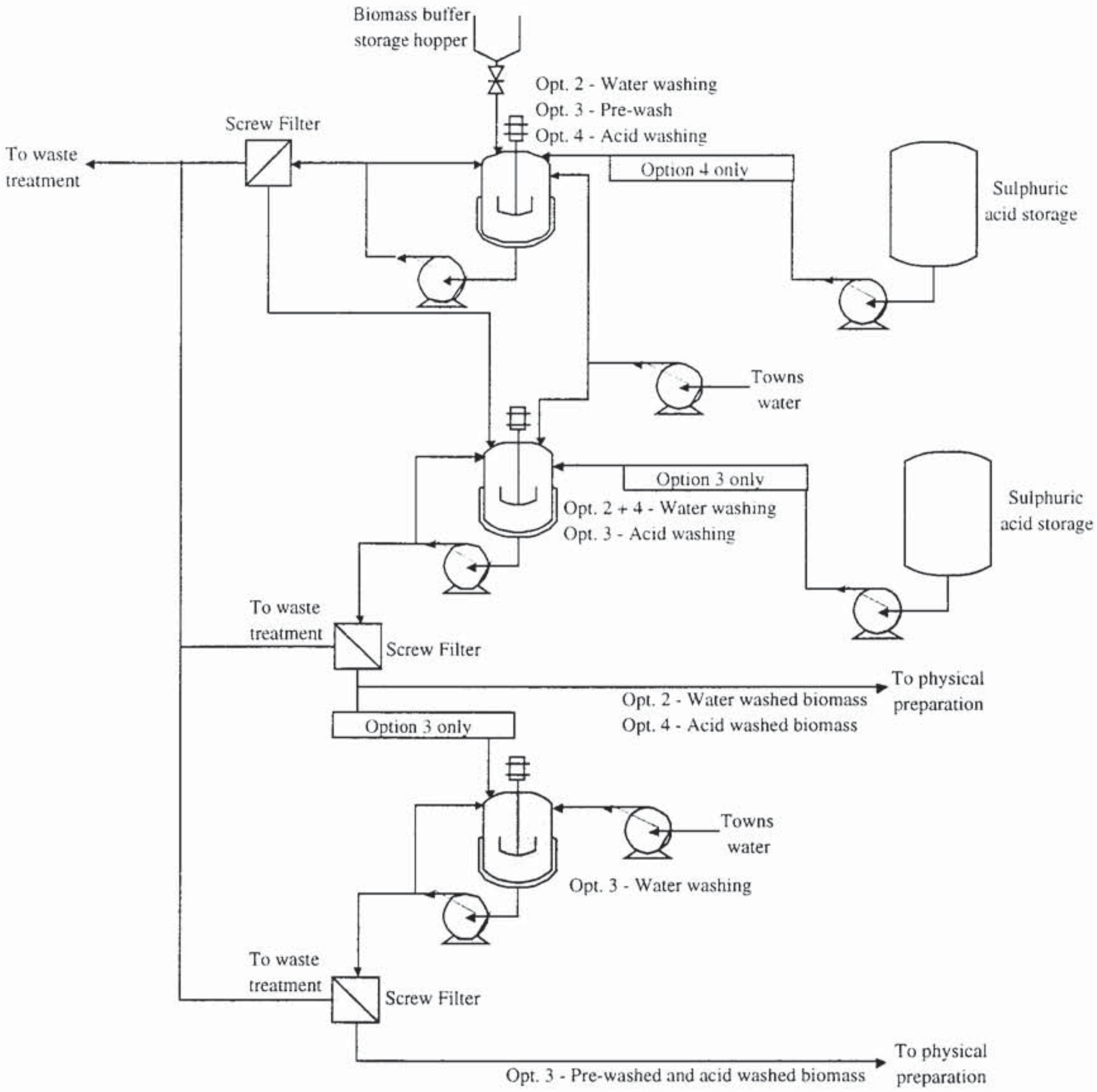


Figure 10.4: Feedstock pre-treatment options process flow diagram

Water pre-wash followed by acid washing

This is an identical process to water washing except an additional stage is introduced between water washing and water rinsing. This additional stage uses 0.1wt.% sulphuric acid to remove all of the ash and 50% of the hemicellulose component [results from Chapter 8 indicate that approximately 4m^3 of acid is required per metric ton wet biomass]. These conditions were determined from experiments reported in Chapter 8. Subsequent pyrolysis of the feedstock pre-treated by this method produced a pyrolysis liquid containing 18 mf wt.% levoglucosan [dry feedstock basis]. However, for this assessment a figure of 15 mf wt.% has been used to allow for any possible experimental error.

As well as the large volumes of aqueous waste, which are produced by water washing the biomass, there is also a significant amount of residual acid from the acid washing stage and subsequent rinsing stage. It is expected that there will be a significant biological oxygen demand caused by the solubilised hemicellulose components. The waste treatment of these liquids is discussed in Section 10.3.5.

Acid hydrolysis

To carry out acid hydrolysis an appropriate amount of acid is metered into the washing vessel [a stainless steel, jacketed, agitated tank]. Laboratory tests [Chapter 8] indicate that 4m^3 of 5wt.% sulphuric acid is required per metric ton of wet biomass. Then the acid is agitated and the correct amount of biomass is measured into the vessel using a screw feeder. The tank jacket heats the contents to boiling point. It has been assumed that the ash and hemicellulose component are dissolved at these conditions in two hours. It is again assumed that the improved mixing and increased temperature reduce reaction times. Work by other workers also confirms this (159, 160).

After two hours hydrolysis the contents of the vessel are pumped out and filtered to remove the biomass from the acid. It is possible for the sulphuric acid to be recycled and the ash extracted and sold for use as fertiliser (161). However, in this process the acid is only used once; it is then neutralised [waste treatment, Section 10.3.5] before disposing to the trade effluent system. The cost of neutralisation and disposal of waste water has been included in the economic evaluation.

10.3.3 Pyrolysis

The pyrolysis stage deals with the thermal processing of the untreated/pre-treated biomass. Considerable work has been carried out by a number of workers to investigate the cost and performance of various pyrolysis processes. Therefore it was deemed unnecessary to repeat previous work and a suitable system for pyrolysis has been chosen (160). A fluidised bed fast pyrolysis system has been chosen, which has known cost [shown in Section 10.4.5] and performance. This produces an assumed pyrolysis liquid yield of 70 mf wt.% [dry feed basis] and 15 mf wt.% gas and char as by-products. The by-product char and gas are both used to provide process heat.

10.3.4 Chemical Extraction

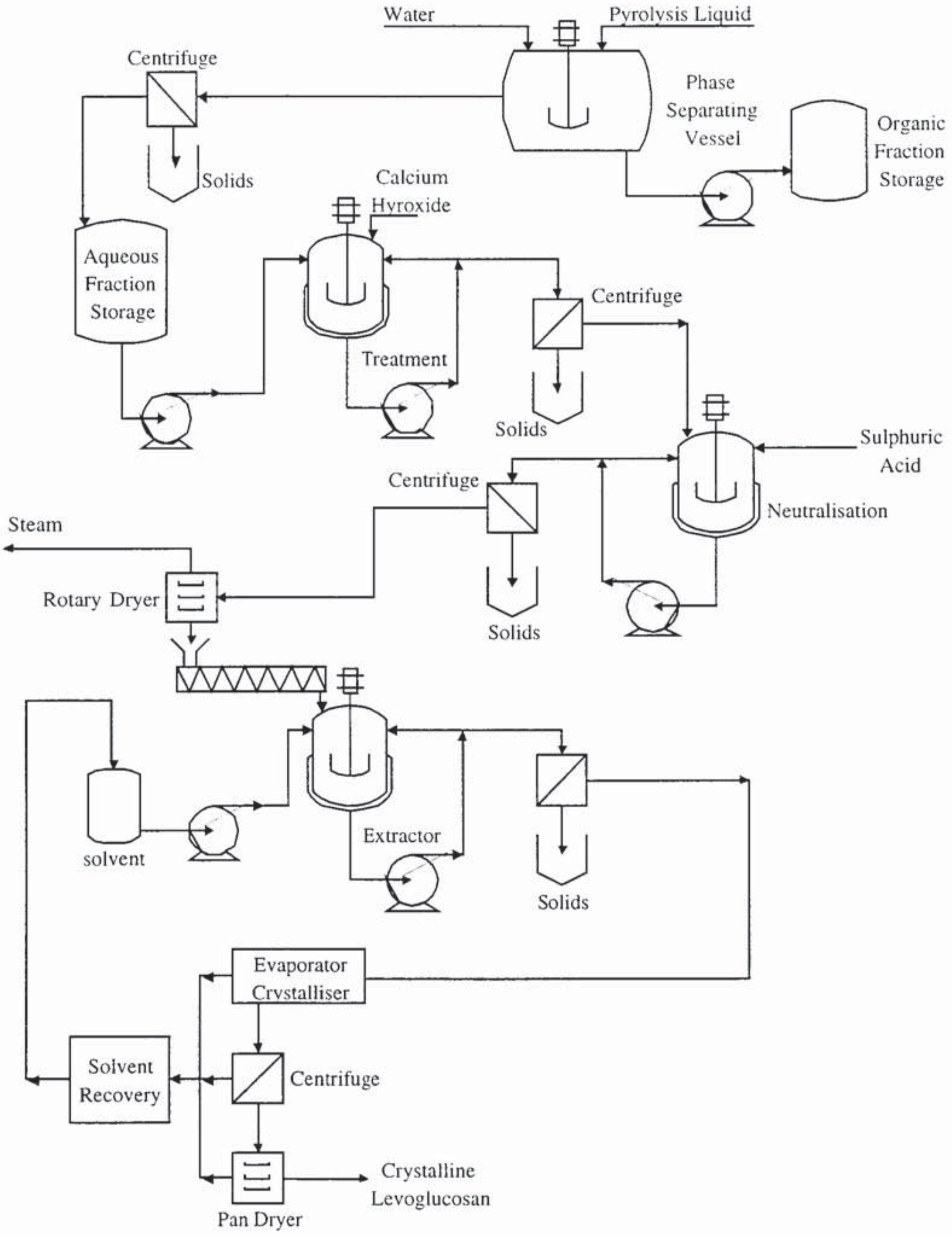


Figure 10.5: Levoglucosan recovery process flowsheet

This stage of the process covers all the steps required in recovering levoglucosan from the pyrolysis liquid. Research into levoglucosan recovery has been carried out and several processes have been patented for this purpose (169, 162). Figure 10.5 shows a typical process flow diagram for the extraction of levoglucosan from pyrolysis liquids (163).

Pyrolysis liquid comprises polar [aqueous] and non-polar [organic] compounds. The addition of water to pyrolysis liquid produces a phase separation [at approximately 35-40 mf wt.% water]. In the phase separation vessel water is added to the pyrolysis liquid until phase separation occurs. The two phases are then separated under gravity.

Levoglucosan is soluble in water and is found in the aqueous phase of the pyrolysis liquid. Once the two phases have separated the organic phase is transferred to storage for use as fuel. The aqueous phase is centrifuged to remove any remaining aqueous insoluble components and then transferred to an intermediate storage facility to await further processing.

Calcium hydroxide is added to the aqueous phase of the pyrolysis liquid. This causes the non-levoglucosan containing components of the liquid [believed to be water soluble lignin-derived phenolic material] to be precipitated out of the liquid. The liquid is then centrifuged to separate the levoglucosan containing liquid from the precipitate. The phenolic precipitate can be burned to provide process heat. However, as with pyrolysis char and gas it is assumed that this has zero value [i.e. energy derived from using it as a fuel cancels out disposal costs]. The phenolic precipitate contains useful chemicals such as resins or adhesives, which may in the future be recovered to improve the process economics. However, for the purposes of this model it is assumed that the waste material is burned.

Following the centrifuge the levoglucosan containing liquid is neutralised with sulphuric acid and the insoluble calcium sulphate is centrifuged from the liquid and disposed of to landfill. The remaining neutralised liquid is dried [drum dryer] to remove water, leaving an anhydrous residue. The residue is then screw fed from the drum dryer to the solvent extraction vessel. The levoglucosan is extracted from this residue using acetone. Acetone is the preferred solvent described by Longley (163) and has also been used in extraction tests by Dick (164). Once extracted, levoglucosan readily crystallises out of the solvent upon cooling and is centrifuged and dried to remove the last traces of the solvent, yielding pure levoglucosan. For the extraction process detailed above, Longley quotes levoglucosan purities of 99% (163).

10.3.5 Waste Treatment

The waste treatment stage deals with all waste streams from the process. Very little waste is generated in the pyrolysis and chemical extraction stages; the majority of the waste requiring treatment is produced from pre-treatment of the biomass. This waste generally contains hydrolysed hemicellulose, dissolved ash and excess acid [if acid has been used]. Even the worst case scenario of a biomass pre-treatment plant using acid pre-treatment to remove 50% of the 1000kg/h biomass input [since the biomass is green it contains 50mf wt.% water] would produce in excess of 6000kg/h of waste water; this water would contain approximately 33mg/l dissolved wood components with an estimated chemical oxygen demand [COD] of 45mg/l. This equates to a biological oxygen demand [BOD_5] of 27mg/l. A typical municipal wastewater would be in the range of 150-1000mg/l (165); thus, the amount of waste produced and the low concentration of contaminants would not warrant the cost of building and operating a waste water treatment plant (171). However, some pre-treatment is required before the waste can be sent to a commercial drain.

To allow the waste to be sent to a commercial drain it must first be neutralised [where necessary] using sodium hydroxide. Where there is a suspected biological/chemical oxygen demand [i.e. following removal of biomass by acid treatment] this will be treated using aerobic digestion. The costs of carrying out these treatments are included in the model and are discussed in Sections 10.4.7 and 10.5.

10.4 COST ESTIMATION MODEL

A spreadsheet model has been produced, which estimates plant and operating costs for the complete levoglucosan production schemes described above. All process equipment has been costed according to the following equations and estimating factors.

10.4.1 Overall installation costs

The direct plant cost [DPC] have been estimated by using the equipment costs in conjunction with the appropriate factors [shown in Table 10.1]. The method is based on factors published by the IChemE (166) and has been adapted by Bridgwater (167) to obtain the factors shown in Table 10.1. The direct plant cost is equal to the equipment cost plus a proportion of the equipment cost that corresponds to each factor in Table 10.1, calculated using Equation 10.1.

$$DPC = a * (\text{Equipment cost})^{b}$$

Equation 10.1Direct plant cost estimation

This procedure is carried out for all relevant parts [i.e. erection, piping, instruments etc.]. The combined factor [i.e. the sum of all parts plus one] can then be multiplied by the original cost of a single unit and the total number of units to get a direct plant cost.

Table 10.1: Equipment cost conversion factors for estimating total equipment costs

Equipment Cost Factors	constant a	exponent b
Average values for equipment in mild steel, US$$_{1991}$ basis		
Erection	1.924	-0.261
Piping - liquids	34.347	-0.38
Piping - gases	31.953	-0.358
Instruments	13.942	-0.33
Electrical	4.2112	-0.231
Civil	1.997	-0.231
Structures & Buildings	4.99	-0.244
Lagging	10.338	-0.419

The factors shown in Table 10.2 are used to estimate the cost of installing equipment. From the direct plant cost the installed plant cost is estimated by multiplying by one plus the sum of column a [i.e. by 125%] (167). These factors take into account the cost of engineering, design, supervision and management overheads. The total plant cost is estimated by taking the installed plant cost and multiplying by one plus column b [i.e. 135%]. This takes into account all other factors [i.e. commissioning, contingency, contractors fee and interest during construction].

Table 10.2: Conversion factors used for estimating plant costs

Conversion Factors For Total Plant Costs	a	b
Engineering, design & supervision	15%	
Management overheads	10%	
Commissioning		5%
Contingency		10%
Contractors' fee		10%
Average interest on working capital		10%

10.4.2 Overall Production Costs

The production costs have been estimated using factors to account for the costs listed below. This method was chosen because there is no historical data relating to the operation of a levoglucosan production process.

- raw materials,
- labour,
- utilities,
- plant overheads,
- plant maintenance,
- capital amortisation.

All production costs are expressed in real terms in $US, 1995 basis. In reality inflation will cause the production costs to rise each year. However this should be balanced by the increase in revenue each year. Therefore it is assumed that the costs are constant.

Raw Materials

The cost of wood chips was taken from the literature (70) as $40/odt [oven dry ton]. The cost of the other materials used is shown below in table 6.3. The chemical and utility prices were taken from the literature (70, 168, 169).

Labour

The labour requirements were established using a model developed from the literature (170). A graphical representation of labour costs against plant output was found to be modelled by Equation 10.2. The labour cost is then determined according to how many man hours of labour are required for a particular plant.

$$L_{pc} = w * n * (q / 1000)^{0.81}$$

Equation 10.2: Labour cost

Where:-

L_{pc} = labour cost for a particular plant (US$/year),
w = average wage of plant operator (US$/h),
n = operating period (h/year),
q = average throughput of the plant (kg/h).

Utilities

The costs of utilities as used in the model are displayed below in Table 10.3 (70, 170). The model estimates the amount of utilities required and uses these values to find the total utilities cost for each stage of the process.

Table 10.3: Costs of raw materials, utilities and labour

	Cost
Raw Materials	
Biomass	40 \$/t
Sulphuric acid	75 \$/t
Calcium hydroxide	1640 \$/t
Acetone	700 \$/t
Utilities	
Nitrogen	82 \$/m3 * 10^3
Diesel	0.51 \$/l
Electricity	0.1 \$/kWh
Cooling water	0.017 \$/t
Process (towns) water	1 \$/t
Steam (100 psig)	5 \$/t
Labour	
Operator wage	12 \$/h

Plant Overheads & Maintenance

The plant overhead and maintenance values are taken from the literature as 4 % of the total plant cost (171).

Capital Amortisation

The yearly cost due to capital amortisation is calculated in real terms (171). The following arbitrary values have been used in the model:-

• Annual rate of inflation,	4 %
• Annual nominal interest rate,	10 %
• Length of project,	15 years.

10.4.3 Feedstock Reception and Preparation

All scenarios [except commercial cellulose] are based on the feedstock reception and preparation equipment and operating characteristics shown in Table 10.4. The operating characteristics are the same for all scenarios. All scenarios work on 1t/h wet biomass, which in order to reduce operator man hours can only be delivered during a fixed number of hours during the week [i.e. normal day shift hours]. Therefore an average of 81t/d must be delivered to operate the plant on a continuous basis [i.e. 24 hours per day, 7 days per week]. However, all operating characteristics can be varied in the model, but this will have a knock-on effect on the other stages in the process.

Table 10.4: Levoglucosan production plant general operating characteristics

Operating Characteristics	
Feedstock delivered	81 t/d
Delivery period	10 h/d for 5 d/week
Feedstock processed, average	1 t/h
Feedstock processed, design	2 t/h
Unloading time	30 min for 22 t load
Option limiting capacity	440 t/d theoretical
Option limiting capacity	293 t/d design
Front end loader operating hours	10 h/d for 5 d/week
Front end loader fuel economy	30 l/h
Oversize feedstock delivered	5 wt % wet basis

The equipment used to physically prepare the wet biomass is shown in Table 10.5 along with capacities [or values for non-process equipment]. Table 10.6 shows the equations used to calculate the power consumption and the total equipment capital cost.

Table 10.5: Reception and feedstock physical preparation equipment

Item	Description	Reference	Capacity
All items in mild steel unless specified			
Paved unloading area	Fixed 25m *25m	(70)	625 m^2
Front end loader	$4m^3$ bucket, 25 t/h	(70)	2 wet t/h
Storage step	Storage bin, loading & unloading included	(70)	2 wet t/h
Screening step	Single screen & conveyors	(70)	2 wet t/h
Re-chipping step	Knife hog & conveyors	(70)	0.1 wet t/h
Grinding step	Pulveriser & conveyors	(70)	0.65 wet t/h
Buffer storage	Storage silo & conveyors	(70)	2 wet m^3/h

Table 10.6: Equations used for calculating power and total plant cost for reception and physical preparation equipment

Equipment	Power kW/unit	Equipment cost $US/unit
Paved unloading area	none	23854
Front end loader	fuel price	172800
Storage step	$2.103*(\text{capacity})^{0.703}$	$137.68*(\text{capacity})^{0.5988}*1000$
Screening step	$1.718*(\text{capacity})^{0.427}$	$112.45*(\text{capacity})^{0.3435}*1000$
Re-chipping step	$23*(\text{capacity})^{0.456}$	$194.18*(\text{capacity})^{0.3398}*1000$
Grinding step	$111.4*(\text{capacity})^{0.9917}$	$226.5*(\text{capacity})^{0.7053}*1000$
Buffer storage	$0.717*(\text{capacity})^{0.7}$	$98.82*(\text{capacity})^{0.3531}*1000$

10.4.4 Feedstock Pre-treatment

Feedstock pre-treatment is the only part of the model, which changes with different scenarios. Thus the number of vessels and pumps will change depending on whether water washing is used or water pre-washing followed by acid washing. The operating characteristics are shown in Table 10.7. The pre-treatment process operates 24 hours per day on a 1t/h basis. The operating period of 8000h/y is standard engineering practice to allow for approximately one month down time per year.

Table 10.7: Feedstock pre-treatment operating characteristics

Operating Characteristics	
Feedstock washed	24 t/d
Maximum operating period	24 h/d for 7 d/week
Feedstock washed, average	1.0 t/h
Feedstock washed, design	1.5 t/h
Actual Operating Period	8000 h/y

The feedstock is pre-treated using combinations of the equipment listed in Table 10.8. The capital cost and operating costs of each of these pieces of equipment have been calculated by using the equations in Table 10.9. The number of units used in each of the pre-treatment scenarios are listed in Table 10.10.

Table 10.8: Feedstock pre-treatment equipment capacities

Item	Description	Reference	Capacity
All items in mild steel unless specified			
Steel acid washing tanks	S. S. jacketed vessel	(171)	25 m^3
Agitators (for above vessel)	S. S. turbine	(171)	55 HP
Water rinsing tanks	M. S. vessel	(171)	25 m^3
Pumps	S.S. centrifugal	(171)	30 m^3/h
Screw conveyor	M. S. 9 inch diameter	(171)	6.1 m
Storage tank	S. S. H_2SO_4 storage	(171)	6 m^3
Filter	S. S. screw press	(172)	6.1 m
Dryer	S. S. rotary	(171, 172)	20 m^2

Table 10.9: Feedstock pre-treatment unit cost and unit power equations

Item	Unit cost equation	Unit power equation
All items in mild steel unless specified		
Steel acid washing tanks	50*(capacity*220)$^{0.77}$	0
Agitators (for above vessel)	5613*(capacity$^{0.56}$)	0.7355*capacity
Water rinsing tanks	500*(220*capacity)$^{0.53}$	0
Pumps	5000	0.7355*8
Screw conveyor	(329*capacity)+1000	3.7*hours
Storage tank	16*(capacity*220)$^{0.71}$	0
Filter	106000	37*hours
Dryer	5214*(capacity*10.76)$^{0.45}$	15+(wet feed*1000*0.0084)

Table 10.10: Number of units required for each pre-treatment scenario

Item	Untreated	Water Washed	Pre-washed and acid washed	Acid hydrolysed
Steel acid washing tanks	0	0	1	1
Agitators (for above vessel)	0	2	3	2
Water rinsing tanks	0	2	2	1
Pumps	0	3	4	3
Screw conveyor	0	1	1	1
Storage tank	0	0	1	1
Filter	0	2	3	2
Dryer	0	1	1	1

10.4.5 Pyrolysis

A fluidised bed pyrolysis plant operating at 1000 kg/h dry biomass has been estimated to cost 1920kUS_{1995}$ basis (173). This can be scaled up or down by using Equation 10.3.

$$FFB_{pc} = 1920 * (DB_{tp} / 1000)^{0.7}$$

Equation 10.3: Fast fluidised bed pyrolysis plant capital cost estimating equation

Where:-

FFB_{pc} = new fast fluidised bed pyrolyser cost (k$US).
DB_{tp} = dry biomass throughput of the plant (kg/h).

10.4.6 Levoglucosan Extraction

The equipment previously described in Section 10.3.4 is listed in Table 10.11. A description of all items used, the reference source, number of units and capacities of each unit is included. A cost has been estimated for each piece of equipment. The equation used to calculate the cost is shown in Table 10.12 along with equations used to estimate the power consumed [for those items which require electricity].

Table 10.11: Levoglucosan extraction equipment capacities

Item	Description	Source	No. units	Capacity
All items in mild steel unless specified				
Separating vessel	S. S. horizontal tank	(171)	1	10 m^3
Crude bio-oil intermediate storage	S. S. storage tank	(171)	1	15 m^3
Storage tank	S. S. small storage tank	(171)	4	10 m^3
Transfer/supply pump	S.S. centrifugal	(172)	9	30 m^3/h
Treatment vessel	S. S. agitated & jacketed	(171)	3	2 m^3
Filter	S. S. centrifugal discharge	(171)	4	1 m^2
Waste skip	S. S. skip	(171)	3	3 m^3
Dryer	S. S. drum dryer	(172)	1	2 m^2
Crystalliser	S. S. cooling evaporative	(171)	1	100 kg/h
Dryer	S. S. pan dryer	(172)	1	1 m^2
Screw conveyor	M. S. 9 inch diameter	(171, 172)		2 6.1 m
Bucket conveyor elevator	S. S. fully enclosed	(171, 172)		1 8 m
Solid storage hopper	S. S. bulk solids container	(172)	1	4 m^3

Table 10.12: Levoglucosan extraction unit cost and unit power equations

Item	Unit cost equation	Unit power equation
All items in mild steel unless specified		
Separating vessel	$16*(\text{capacity}*220)^{0.71}$	0
Crude bio-oil intermediate storage	$16*(\text{capacity}*220)^{0.71}$	0
Storage tank	$16*(\text{capacity}*220)^{0.71}$	0
Transfer/supply pump	5000	0.7355*8
Treatment vessel	$50*(\text{capacity}*220)^{0.53}$	10*capacity*220/1000*0.7355
Filter	$2*715*(\text{capacity}*10.76)^{0.61}$	0.7355*8
Waste skip	1000	0
Dryer	$9100*(\text{capacity}*10.76)^{0.43}$	15+(capacity*1000*0.0084)
Crystalliser	$935*(\text{capacity})^{0.68}$	10*hours
Dryer	$8750*(\text{capacity}*10.76)^{0.45}$	15+(capacity*1000*0.0084)
Screw conveyor	(329*capacity)+1000	3.7*hours
Bucket conveyor elevator	$2376*(\text{capacity}*3.281)^{0.5}$	0.75*hours
Solid storage hopper	1204/2*capacity	0

10.4.7 Waste Treatment

The pre-treatment process produces large quantities of aqueous waste, which may contain dissolved salts, hydrolysed hemicellulose and excess acid. Before the aqueous waste can be sent to a commercial drain it must first be pre-treated. The cost of this pre-treatment is included in the model. For wastes containing acid the amount of alkali required for neutralisation is calculated and costs estimated.

Where there is a suspected biological oxygen demand [i.e. where biomass has been removed] the cost of anaerobic digestion has been estimated by multiplying overall waste disposal costs by a factor [shown in Table 10.13] equal to the amount of biomass removed in the pre-treatment step.

Table 10.13 Waste treatment factors used in model

Scenario	1	2	3	4	5
Dry biomass removed [mf wt.%]	0	0.5	10.5	20	0
Factor used in model	1.00	1.05	2.05	3.00	1.00

Following aqueous waste pre-treatment [i.e. neutralisation and digestion] the treated water can be disposed of to drain. This is estimated to cost 0.001$/kg (171).

10.5 RESULTS

Using the five scenarios described in Section 10.2 and process equipment described in Section 10.3 plant costs and production costs have been estimated. The pre-treatment, pyrolysis and extraction conditions can all be modified so the model is extremely versatile. Where there is no pre-treatment the model sets the capital and running costs of pre-treatment equipment to zero. From the model the capital cost and plant operating costs shown in Table 10.14 were obtained. All costs were calculated in $US at 1995 rates.

Plant capital costs

All scenarios operate on 1000kg/h wet biomass basis or the equivalent for commercial cellulose. Therefore physical preparation plant is of a similar size [and cost] for all scenarios. The size of the preparation plant decreases slightly with increasing severity of pre-treatment since as more biomass is removed by pre-treatment less has to be physically prepared for pyrolysis. Although commercial cellulose [scenario 5] is delivered as a dry powder it still passes through the same preparation process to ensure it is of the correct particle size and moisture content.

Pre-treatment capital costs are zero for scenarios 1 [no pre-treatment] and 5 [commercial cellulose] since no pre-treatment is required for these options. Scenario 4 [acid hydrolysis] has the lowest pre-treatment plant cost since more of the biomass is removed by the initial acid treatment allowing downstream equipment to be smaller than for other scenarios. Scenario 3 [water pre-wash followed by acid washing] has the highest capital cost since an extra stage has been introduced [i.e. pre-washing]. The extra stage effectively increases the capital cost by 50%.

Table 10.14: Results obtained from the model

Scenario	1	2	3	4	5
	[UT]	[WW]	[WW+AW]	[AH]	[Cell.]
[k$US, 1995]					
Plant capital costs					
Physical preparation	924	924	919	914	632
Pre-treatment	0	3276	4571	3219	0
Pyrolysis	1260	1256	1167	1080	776
Extraction	1223	1217	1096	981	550
Total plant costs	3407	6672	7753	6193	1958
Plant operating costs					
Utilities	369	469	502	472	328
Feedstock	176	176	176	176	1320
Raw materials	4001	4049	2916	3993	3394
Labour	748	942	924	906	302
Maintenance	136	267	310	248	78
Overheads	136	267	310	248	78
Capital amortisation	375	734	852	681	215
Waste treatment	0.1	34.4	97.2	465.3	0.1
Total production costs	5942	6938	6088	7189	5716
Production cost/ton LG	82.5	58.2	18.9	18.8	10.6
Tons levoglucosan/year	72	119	322	383	539

The size of the pyrolysis plant reduces with increasing severity of pre-treatment [i.e. as more biomass is removed less remains to be pyrolysed]. Thus scenario 1 has the largest pyrolysis plant and scenario 5 the smallest.

The size of extraction plant also decreases with increase in pre-treatment severity. This effectively follows on from pyrolysis, since if less biomass is pyrolysed less pyrolysis liquid is produced.

The total plant cost is the sum of the costs of each of the above stages. Scenario 5 has the smallest physical preparation, pyrolysis and extraction stages, which means it has the lowest capital cost. Scenario 1 has no pre-treatment stage and therefore has the next lowest capital cost. Scenario 4 has slightly lower capital cost than scenario 2 since all stages are smaller due to the more severe pre-treatment. Scenario 3 has the highest capital cost due to the extra equipment required for the additional pre-treatment [pre-washing] stage.

Plant operating costs

The utility costs are typically a function of total capital cost, since as equipment size or number of units increases the power required for their operation will increase. The amount [and therefore cost] of the biomass feedstock is the same [1000kg/h wet biomass] for all scenarios except scenario 5. Scenario 5 is based on purchasing commercial cellulose in a similar amount as is present in biomass. However, commercial cellulose is more expensive than biomass [i.e. US$600/t rather than US$40/t].

Raw materials covers all chemicals used in the complete process. However the bulk of the raw materials are used in the extraction stage hence scenarios, which require the extraction of a low concentration of levoglucosan from a large quantity of pyrolysis liquid generally require more raw materials. However, scenarios using acid pre-treatment also use more raw materials.

Labour costs are a function of throughput and number of stages. Thus scenarios 3 and 5 have no pre-treatment stage, but scenario 5 processes much less feed material than scenario 3. Scenarios 2, 3 and 4 all have pre-treatment stages but as the pre-treatment severity increases the amount of processed material is reduced hence labour cost reduces.

Maintenance, overheads and capital amortisation are all a function of total plant cost. They are set arbitrarily at 4%, nominal annual interest rate is set at 10% and the project life is set for 10 years.

Very little waste is produced from the pyrolysis and extraction stages of the process; hence waste treatment costs are highest for those scenarios with pre-treatment. Scenario 4 utilises the strongest acid pre-treatment and therefore requires the most waste treatment.

10.6 SENSITIVITY STUDY

The total plant and operating costs have been determined for a fixed set of conditions. However, it is likely that some of these conditions may change. Therefore a sensitivity study has been carried out to allow the factors, which most influence the profitability of levoglucosan production to be determined. The return on investment [i.e. the profit as a percentage of the initial capital invested] has been assessed for the following sensitivity options. In all cases the plant cost was spread over a 10 year period and it was assumed that production would not start until the third year. The production of levoglucosan was assumed to be fixed at the levels shown in Table 10.14 and the levoglucosan price has been arbitrarily fixed at US$100/kg. The factors examined are:

- Levoglucosan selling price,
- Levoglucosan production,
- Capital cost,
- Total production cost,
- Utilities,
- Feedstock,
- Raw materials,
- Waste treatment.

10.6.1 Levoglucosan Selling Price

From Table 10.14 it is evident that the production cost of a ton of levoglucosan is highest from untreated biomass and lowest from commercial cellulose. However, as a measure of profitability the total plant costs and operation costs were used to determine the required levoglucosan selling price to give 0, 10 and 20% return on the invested capital cost of the plant. The results of this assessment are shown in Table 10.15.

It is evident that despite increased capital and operating costs the pre-treatment of biomass prior to pyrolysis results in much lower levoglucosan costs. This is mostly because very little product is produced in no pre-treatment and water washing scenarios; therefore there is little potential to make profit. It may be possible to improve the economics of these processes by selling the residual liquids [after chemical extraction] as fuels. However, an investigation in to the potential markets of secondary products from this process is a suggested topic for future work.

Table 10.15: Return on capital invested

Scenario	1 [UT]	2 [WW]	3 [WW+AW]	4 [AH]	5 [Cell.]
[k$US, 1995]					
Total plant capital cost	3407	6672	7753	6193	1958
Total production cost	5942	6938	6088	7189	5716
Tons levoglucosan/year	72	119	322	383	539
Production cost/ton LG	82.5	58.2	18.9	18.8	10.6
Levoglucosan selling price [US$/kg] for return on plant capital cost					
ROI 0%	89.02	66.02	22.22	20.99	11.10
ROI 10%	89.61	66.72	22.52	21.20	11.15
ROI 20%	90.20	67.41	22.82	21.40	11.19

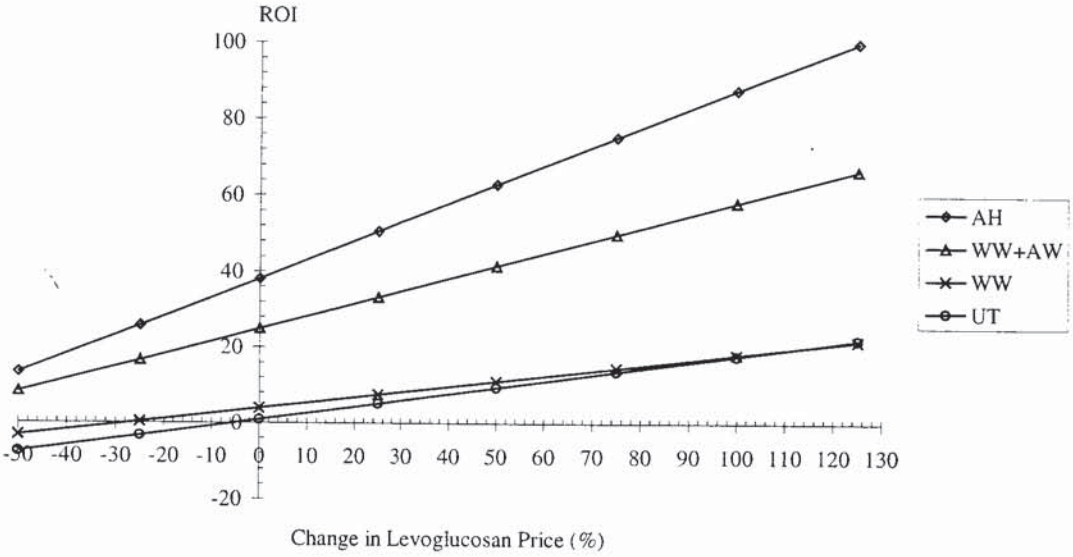


Figure 10.6: Change in levoglucosan price vs. plant profitability

The current selling price of levoglucosan as a specialist chemical is approximately $30/g (97). However, this price would be severely reduced if/when a large scale plant began production in significant quantities. A commercial price of US$100/kg would make all of the above scenarios profitable. Figure 10.6 shows the effect of change in levoglucosan selling price from an arbitrarily assumed US$100/kg. It is evident that a reduction in levoglucosan selling price significantly affects the profitability of the scenarios.

10.6.2 Levoglucosan Production

From Figure 10.7 it is evident that plant profitability is sensitive to the amount of levoglucosan produced. Thus, if estimates of pyrolysis liquid levoglucosan concentrations or extraction efficiencies were too high the plant profitability would be reduced. Since levoglucosan is the only product from this process the effect of lower levoglucosan production is more noticeable for scenarios, which produce less levoglucosan. Therefore, no pre-treatment and water washed scenarios are more sensitive to changes in levoglucosan production than scenarios involving pre-treatment [i.e. pre-wash with acid washing and acid hydrolysis].

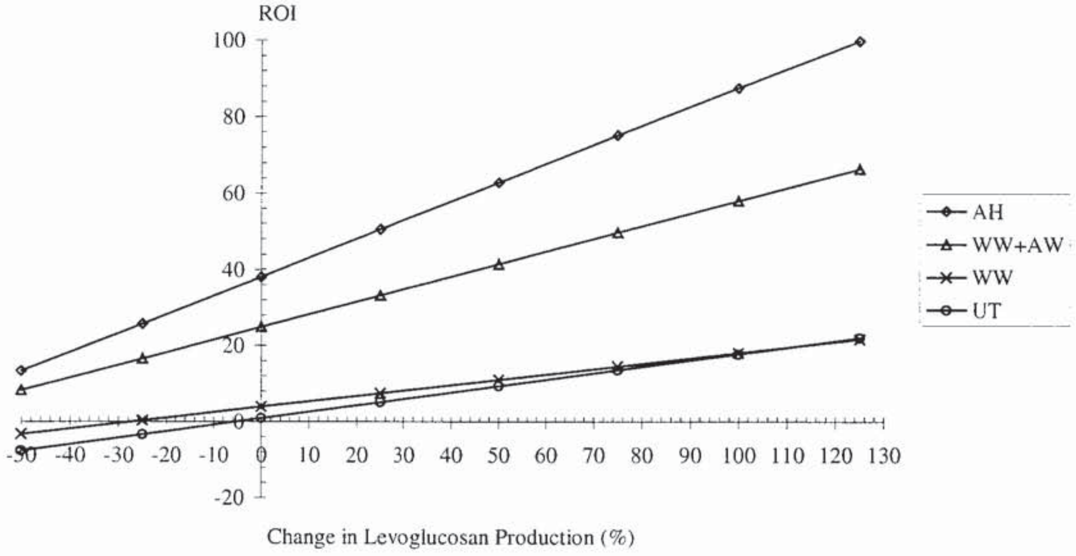


Figure 10.7: Change in levoglucosan production vs. plant profitability

10.6.3 Capital Cost

Capital costs have been varied by ±125% and the effect on ROI is shown in Figure 10.8. The commercial cellulose scenario has been left out [in this case and all subsequent cases] since with a levoglucosan price of US$100/kg it is twice as profitable as the acid hydrolysed scenario [AH]. From Figure 10.8 it is evident that all scenarios remain profitable until the total plant cost increases to +50% of the original cost. Scenarios 3 and 4 show return on investment in excess of 10% even after the capital cost has doubled. Therefore, capital cost has very little effect on plant profitability, especially for scenarios using pre-treatment.

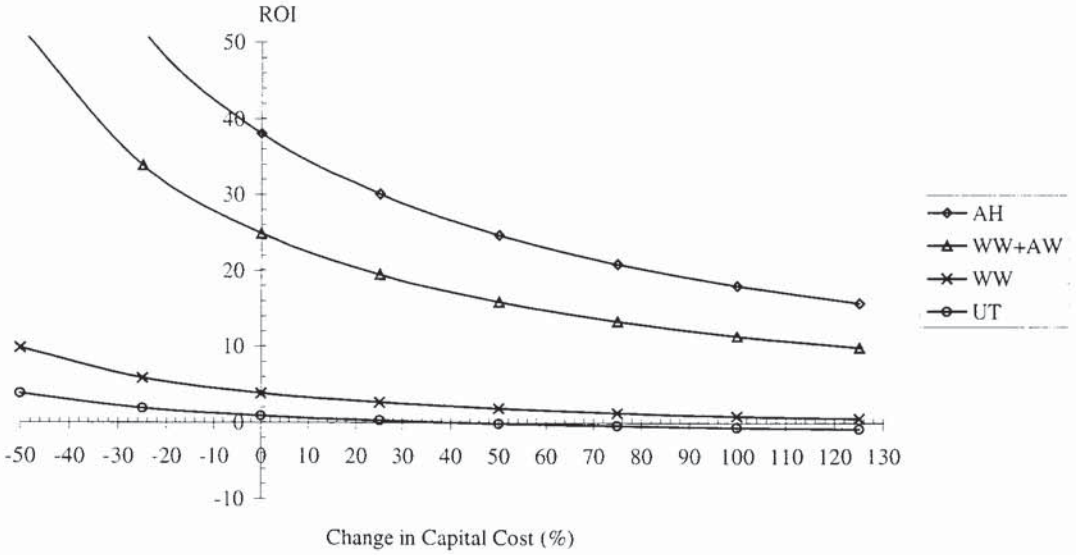


Figure 10.8: Change in capital cost vs. plant profitability

10.6.4 Total Production Costs

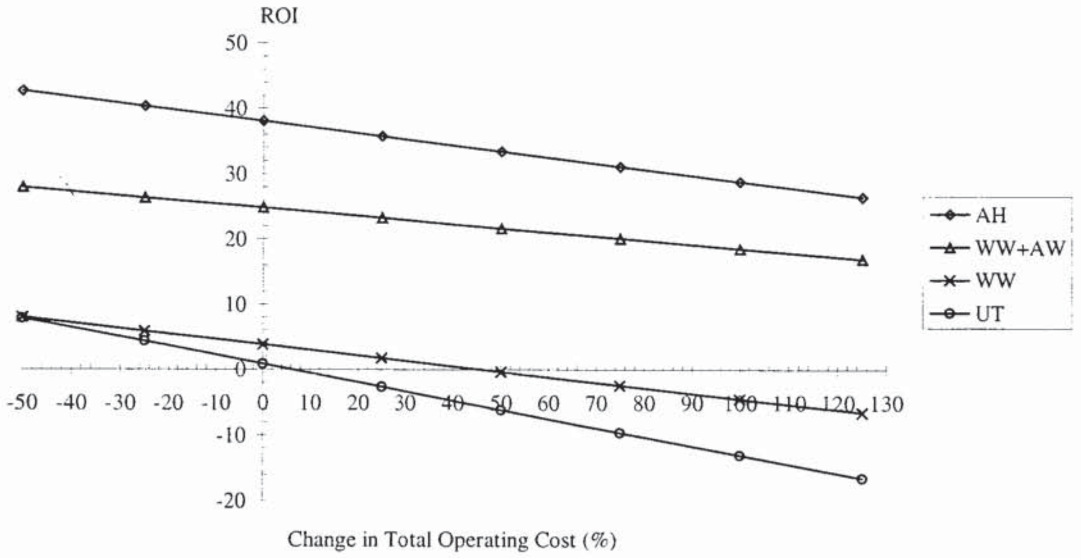


Figure 10.9: Change in operating cost vs. plant profitability

From Figure 10.9 it is evident that increase in operating cost has a significant effect on levoglucosan production profitability. An increase of less than 10% makes the no pre-treatment [UT] scenario unfeasible and an increase of 50% makes the water washed [WW] scenario unfeasible. It is also noticeable that if operating costs should decrease by 50% or more the no pre-treatment scenario becomes more profitable than the water washed scenario.

10.6.5 Utilities

From Figure 10.10 it is evident that utility costs have little effect on the profitability of the levoglucosan production process. All scenarios show only a gradual decrease in profits with increase in utility costs.

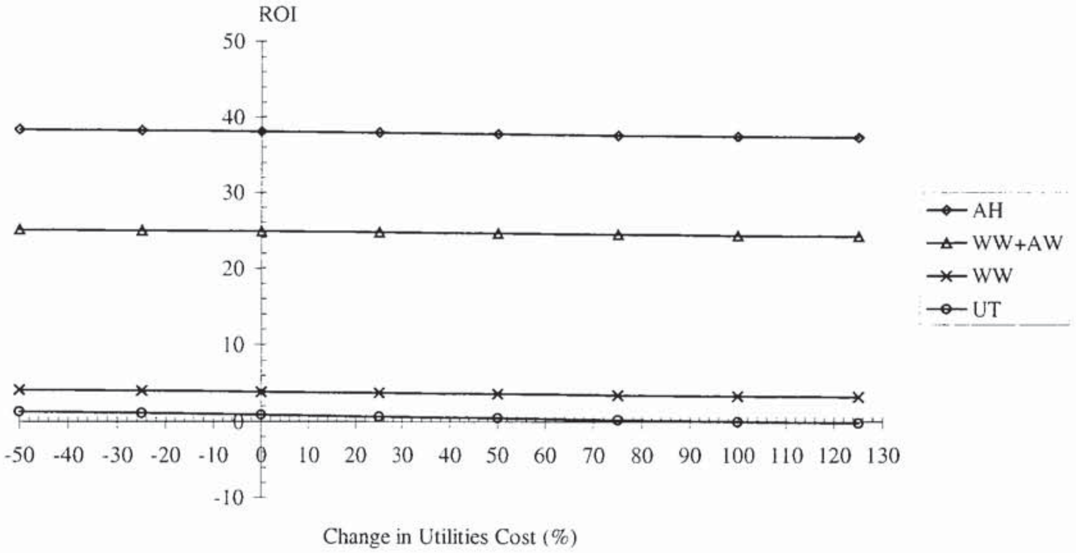


Figure 10.10: Change in the cost of utilities vs. plant profitability

10.6.6 Feedstock

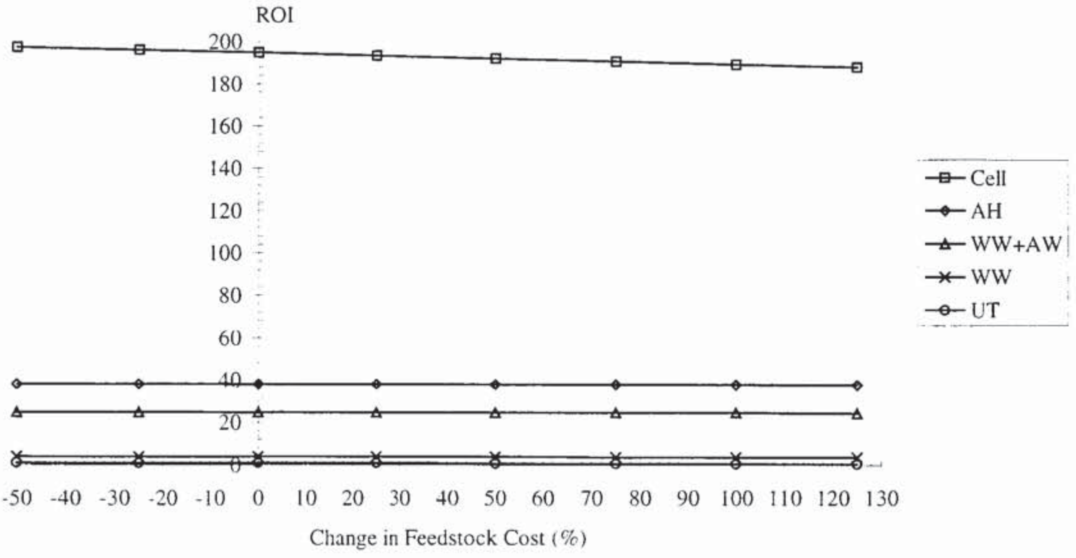


Figure 10.11: Change in feedstock cost vs. plant profitability

An increase in feedstock costs has little effect on profitability [Figure 10.11, above]. Even the cellulose scenario, which has feedstock costs 10 times higher than biomass, continues to make profit when the cost of the feedstock is more than doubled.

10.6.7 Raw Materials

From Table 10.14 it can be seen that the cost of raw materials make up the majority of the plant operating costs. Since total operating costs have a significant effect on profitability a change in raw material costs will also have this effect. From Figure 10.12 it is evident that the no-pre-treatment scenario is most susceptible to changes in raw material costs. This susceptibility is due to the fact that the majority of raw materials are utilised in the extraction stage, which is much larger for the no pre-treatment scenario than for other scenarios.

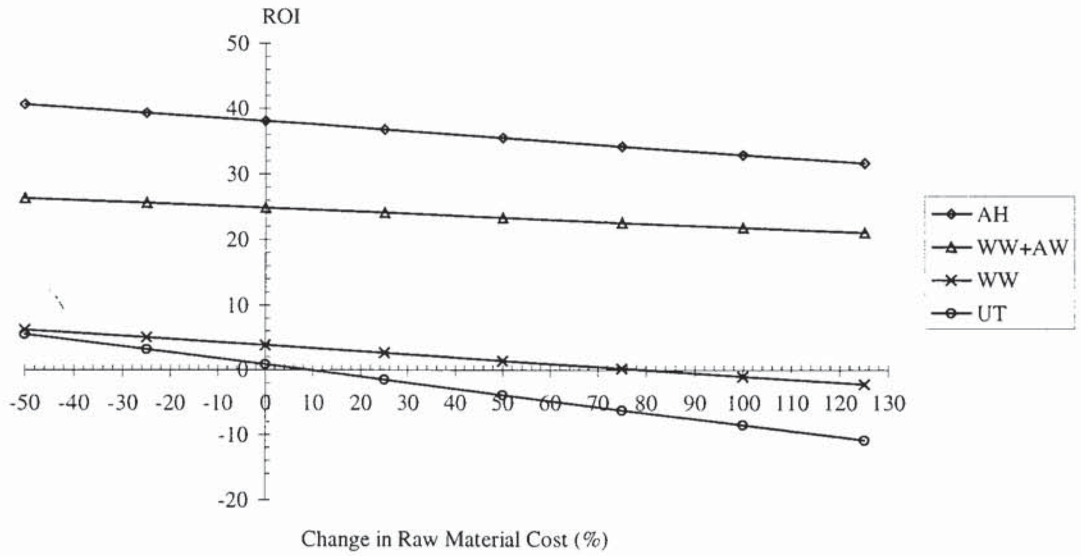


Figure 10.12: Change in raw material cost vs. plant profitability

10.6.8 Waste Treatment

The waste treatment costs make up only a small part of the total operating costs. Even for the acid hydrolysed [AH] scenario, which has the highest waste treatment costs, the effect on profitability is not significant. This is evident from Figure 10.13.

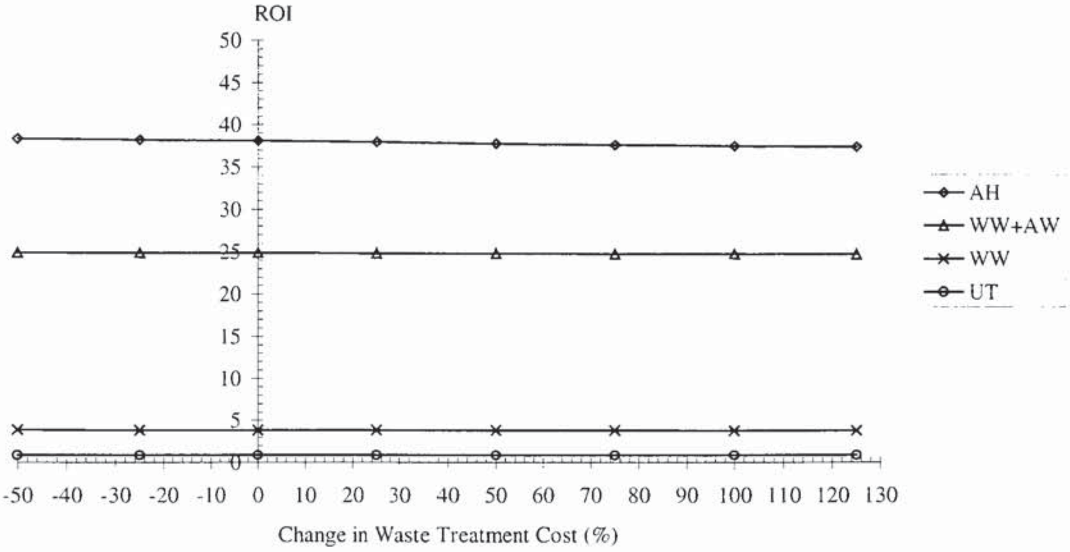


Figure 10.13: Change in waste treatment cost vs. plant profitability

10.6.9 Summary

The profitability of levoglucosan production from a range of untreated [i.e. no pre-treatment] and pre-treated biomass feedstocks is most sensitive to the plant operating costs. The majority of the plant operating costs are from raw materials, of which most are used in the levoglucosan extraction stage. The scenarios which have a small concentration of levoglucosan in the pyrolysis liquid are therefore more susceptible to profit fluctuations caused by changes in raw material prices.

The capital cost of the plant does not have a significant impact on profitability. Thus despite increased capital costs for scenarios with pre-treatment stages the plants remain profitable even when the capital cost is doubled. Thus it is better to pre-treat biomass for levoglucosan production to increase levoglucosan production and reduce extraction costs or better still to utilise commercially available cellulose.

10.7 CONCLUSIONS

An integrated process for the production of levoglucosan has been modelled. The model assesses pre-treatment, pyrolysis and levoglucosan extraction stages. Using this model, capital costs and operating costs have been estimated for untreated biomass, a range of pre-treatments and commercial cellulose.

It has been found that the introduction of pre-treatment into the levoglucosan production process almost doubled the total capital cost. However, the profitability of the process is more sensitive to the operating costs rather than the capital cost. The majority of the operating cost is made up of raw materials required for the extraction of levoglucosan. Thus by pre-treating biomass the raw material costs can be reduced.

Biomass pre-treatment can remove a substantial amount of the biomass hence reducing pyrolysis costs. Thus even though pre-treatment requires extra raw materials and waste disposal introduces extra cost into the process, this is far outweighed by the revenue gained from the sale of levoglucosan. Thus it is more cost effective to pre-treat biomass to increase the concentration of levoglucosan in the pyrolysis liquid than it is to extract low concentrations of levoglucosan from untreated biomass pyrolysis liquids.

The market price of levoglucosan has the largest effect on whether a process is viable or not. For the most successful pre-treatment method obtained in the course of this work [i.e. acid hydrolysis] the market price of levoglucosan must be higher than $US 21/kg for the process to profitable after an expected 10 year life span. However, it would appear to be more economic to purchase commercial cellulose since this gives a minimum market price of US$ 11/kg.

11. CONCLUSIONS

The two primary objectives of this project were:

1. to compare different feedstocks under fast pyrolysis conditions,
2. to develop feedstock pre-treatment processes which result in a selective increase in the concentration of certain chemicals in the fast pyrolysis liquid.

11.1 PRODUCTION OF LIQUIDS

In total seventy five fast pyrolysis experiments have been carried out on a 150g/h reactor with a product collection system comprising an ice cooled condenser, dry ice cooled condenser, electrostatic precipitator and cotton wool filter. Good mass balance closures have been obtained [i.e. between 90 and 100%] for 80% of the experiments. For the other experiments losses have been clearly identified. This proves that small scale reactors produce consistently good results.

Pyrolysis products have been analysed by a number of techniques. Although the equipment to carry out these analyses was already in the laboratory, experimental techniques and procedures have been investigated and improved throughout the course of this work. Water content measurement is now reproducible to ±0.01mf wt.% using a Karl Fischer Coulometer. HPLC analysis can determine the chemical content of the pyrolysis liquid to ±0.5mf wt.%. Gas chromatography was the weakest part of the mass balance procedure with accuracys of ±0.5mf wt.% per gas component [i.e. carbon monoxide, carbon dioxide, methane, etc.].

Mass spectroscopy was tested as an alternative to gas chromatography to determine gas yields. It was found to be less accurate and less reliable than GC analysis.

The gas analysis system has subsequently been redesigned and now generates much more reproducible and accurate results, typically 0.05mf wt.% per component. The new system has been used as part of this work and has resulted in much better mass balance closures, in excess of 96% for runs SFB73, 74 and 75.

Experimental reproducibility has been found to be good. All pyrolysis product yields [i.e. organics, char, gas and water] can be described by quadratic equations. In most cases R^2 values of 0.9 or more have been achieved. For all fast pyrolysis experiments the gas/vapour residence time has been kept within 0.50-0.75 seconds. The effect of residence time variation within these limits has been found to only affect the pyrolysis liquid yields as much as normal experimental variation.

Six feedstocks have been pyrolysed ranging from rape meal to wood. Poplar and pine have been previously tested by other institutes and comparable results obtained. Pine bark, rape straw, rape meal and miscanthus have not been previously tested. For each feedstock tested the reactor temperature has been varied between 400 and 600°C to find the maximum organic liquid yield and the temperature at which it occurs [shown in Table 11.1].

Table 11.1: Organic liquid yields from different feedstocks

	Maximum organics [mf wt.%]	Maximum organics [maf wt.%]	Temperature [°C]	Cellulose [mf wt.%]	Ash [mf wt.%]
IEA Poplar	72	72.4	485	59.4	0.50
Pine	68	68.2	477	37.4	0.23
Miscanthus	55	56.8	458	41.4	3.16
Rape straw	48	50.6	457	32.4	5.18
Rape meal	47	50.9	429	5.00	7.68
Pine bark	38	38.8	505	34.3	1.94

Although the liquid yield has been maximised for a range of feedstocks it is likely that the liquid quality will be more important for the production of a fuel. The maximisation of the pyrolysis liquid yield is believed to be the first stage in producing pyrolysis liquids for fuel applications. The next series of experiments should investigate the quality of the pyrolysis liquid in terms of its stability [chemical/thermal], viscosity and energy value. This is a suggested topic for further work and will be discussed in the next Chapter.

Fast pyrolysis of poplar and pine produced very little water of pyrolysis. It may be that for the production of pyrolysis liquids for fuel the presence of water may improve the liquid quality. Therefore it may be better to pyrolyse wetter feedstocks although this will result in slower pyrolysis and possibly lower yields of lower energy value liquids.

Thus there may be a compromise between liquid stability and energy value. An investigation into the properties of pyrolysis liquids, their stability and the effects of parameters such as feedstock moisture content should be investigated in the future.

Pyrolysis liquid yield is generally a function of feedstock composition. In general the higher the cellulose content and the lower the ash the higher the pyrolysis liquid yield. Therefore woody biomass such as IEA poplar and pine produced the highest organic liquid yields and forest residues such as pine bark with low cellulose and high ash content produced the lowest organic liquid yields.

Similarities were found between pyrolysis results from feedstocks used in this work and those available in the literature. Pine bark maximum organics yield was obtained at 505°C which was the same as poplar bark [literature]. Rape straw was found to behave similarly to other straws [i.e. wheat in literature] and miscanthus. Pine used in this work produced maximum organics yields at a lower temperature than pine work published in the literature.

Miscanthus is a relatively new energy crop. It produced "average" liquid yields, which were not as good as wood, but better than forestry or agricultural residues. Once mature [i.e. after three years growth], miscanthus can be harvested every year and produces 40ton/hectare. In comparison coppiced willow can only be harvested every 3-4 years and produces 10ton/hectare/year. Thus 3-4 times less land would be required to grow miscanthus which may make it better to pyrolyse miscanthus despite the lower pyrolysis liquid yields. Further work should be carried out on the economics of miscanthus growing over short rotation coppice or other forms of biomass.

Rape meal is the waste residue after oil seed extraction; it is traditionally fed to farm animals but alternative uses are always being sought. Rape meal had a much higher bulk density than other biomass types which initially caused feeding problems. Consequently the feeding system had to be modified to reduce the gas flowrate and hence reduce the rape meal feedrate. Once these problems had been overcome pyrolysis produced low liquid yields. Although rape meal had the highest ash content and lowest cellulose content it did not produce the lowest yields of pyrolysis liquid. It is believed that the processing which is carried out on this feedstock may result in much of the "active" ash being removed. The processed nature of rape meal and the suspected high protein content may be why the maximum organic yield was obtained at the lowest temperature of all feedstocks tested.

If the organics yield is calculated on a moisture and ash free basis [maf wt.%] the yields are not changed significantly, nor is the rank order affected [apart from rape straw and rape meal]. A plot of maximum organic liquid yields versus ash content for a number of feedstocks [Figure 11.1] proves that ash has a significant influence on the pyrolysis reactions.

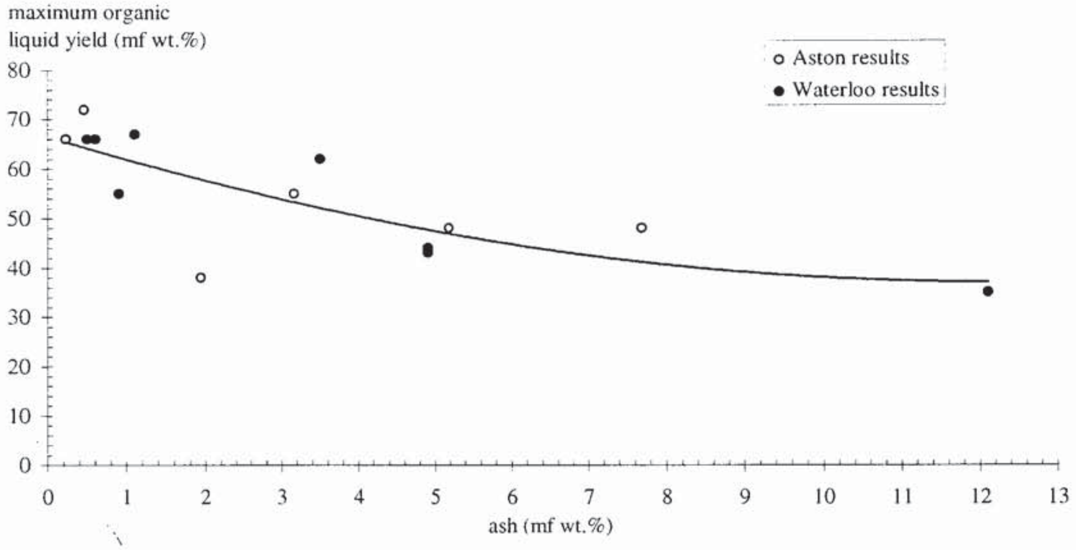


Figure 11.1: Maximum yield of organics versus ash content

11.2 PRODUCTION OF CHEMICALS

Chemical analysis of the liquid products produced from IEA poplar over a range of temperatures did not show the same trends as observed from the pyrolysis of pure cellulose. Even scaling the chemical yields from IEA poplar to compensate for the lower cellulose content does not bring the concentrations close to those obtained from pure cellulose. It is therefore concluded that the production of chemicals from biomass is not merely a summation of the chemicals obtained from the individual products.

Analysis of biomass composition is time consuming, costly and only accurate to a limited extent [i.e. 1-10% depending on the method used]. The results can be used, to a limited extent, to estimate the chemicals contained in the pyrolysis liquid from a particular feedstock. Certain components of the biomass form particular chemicals when pyrolysed, for example cellulose forms hydroxyacetaldehyde and levoglucosan

[Table 11.2]. However, the yield of these chemicals is often lower than expected due to the interaction of the components during fast pyrolysis.

Table 11.2: Chemicals contained in pyrolysis liquids produced at 500°C from different feedstocks

Feedstock	Pine Bark	Rape Meal	Rape Straw	Miscanthus	Pine	IEA Poplar
Run No.	SFB05	SFB38	SFB44	SFB31	SFB13	SFB28
Cellulose [mf wt.%]	34.3	5	32.4	41.4	37.4	59.4
H.cell. [mf wt.%]	18.0	28	41.8	24.9	32.2	19.0
Lignin [mf wt.%]	13.7	59*	16.7	23.7	27.2	18.4
Ash [mf wt.%]	1.94	7.68	5.18	3.16	0.23	0.50
Moisture	14.94	1.00	8.51	8.46	0.04	7.25
Hydroxyacetaldehyde	1.21	0.00	3.03	6.78	7.94	7.26
Levoglucosan	0.90	0.50	0.94	1.93	2.84	2.45
Formic acid	0.81	0.26	1.21	3.07	2.44	4.76
Acetic acid	0.75	0.66	4.57	7.48	1.70	6.73
Fructose	0.25	0.00	0.13	0.42	1.03	0.92
Glyoxal	0.14	0.00	0.23	0.00	0.48	0.42
Acetol	0.75	0.02	2.07	2.56	0.71	1.04
Others	0.51	1.08	0.24	0.80	0.73	1.39
Pyrolytic Lignin	0.93	29.50	15.54	19.60	24.93	20.6
Total Chemicals	**5.62**	**32.02**	**27.74**	**42.63**	**42.32**	**42.08**

* rape meal lignin calculated by difference, will contain protein

Of the feedstocks tested IEA poplar produced the highest yield of organic liquids and also the highest yield of aqueous soluble chemicals. Therefore poplar was used as the feedstock in the pre-treatment experiments. Pine also produced similar yields of liquids and chemicals due to the high cellulose content and was used in the pre-treatment experiments conducted at the University of Waterloo.

When pyrolysed over a range of temperatures [450-550°C] poplar did not exhibit clearly defined regimes of depolymerisation [levoglucosan production] and fragmentation [hydroxyacetaldehyde production]. It was found that the highest yield of total chemical products was obtained at the maximum organic liquid yield which was 485°C. It is likely that this is also true for other feedstocks. Thus it may be best to produce chemicals at the temperature which produces the optimum yield of pyrolysis liquid. Unfortunately, pyrolysis liquids for feedstocks other than poplar were only analysed from the 500°C runs. If chemicals are produced from untreated feedstocks it is recommended that the process be optimised for a particular chemical from a particular feedstock. Optimisation of yields of a particular chemical will require a similar investigation to the maximum pyrolysis liquid yield.

Rape straw and miscanthus have a high hemicellulose content and both produced liquids containing high yields of formic and acetic acids. Rape straw and miscanthus also produced high yields of hydroxyacetaldehyde in comparison to levoglucosan which may have been due to the high ash content or the fast pyrolysis reaction being carried out at 500°C rather than 458°C which was found to be the optimum temperature for liquids production for these feedstocks.

Experiments using the same pine feedstock were conducted at Waterloo and Aston. Similar results were obtained from the pyrolysis experiments. However, results from HPLC analysis of the chemicals in the pyrolysis liquid were significantly different, which could be due to differences in the HPLC system. Thus, when reporting chemical composition of pyrolysis liquids it is important that the type of analysis used is quoted. Analysis of pyrolysis liquid requires experience as well as skill; therefore, it is essential that round robin analysis studies continue to ensure that the best analysis methods are used and that they produce consistent results.

11.2.1 Ash Removal Pre-treatment

All pre-treatment experiments were conducted in such a way that the effectiveness could be measured. In some cases the methods used to assess the pre-treatment experiments have not been accurate enough to detect the small changes in the biomass. Since mild pre-treatment techniques such as water washing and dilute acid washing remove only a small fraction of the biomass it is difficult to quantify. Overall it has been found that the best way to assess how effective a pre-treatment will be is to pyrolyse the pre-treated feedstock.

A single soxhlet experiment removed approximately 3mf wt.% of material from the biomass. It is believed that this material is mostly ash and hemicellulose, although this was not confirmed. Soxhlet experiments were found to be too small to produce enough pre-treated biomass for pyrolysis experiments. Also, much of the treated biomass was wasted during removal from the thimble. This technique is similar, in principal, to co/counter current extraction which could be employed as a demineralisation process at larger scale.

Percolation experiments using dilute nitric acid removed approximately 5mf wt.% of the pine. This removed material was not analysed but subsequent ash analysis of the pine showed a reduction from 0.23 to 0.05mf wt.%. Therefore some hemicellulose must also have been removed in the process.

Percolation experiments were also carried out using sulphuric acid over a range of conditions [acid concentration from 1-5wt.% and temperatures from 25-60°C]. Even the mildest conditions [i.e. 1wt.% acid at 25°C] removed almost all of the potassium and sodium ions from IEA poplar. Unfortunately these experiments did not produce enough pre-treated poplar for pyrolysis experiments to be carried out. Also the slow percolation rate [5-15ml/cm^3 biomass] meant that the process would be time consuming for the production of large amounts of biomass. However, in the future it may be possible to scale this process up and improve the kinetics by increasing the temperature and/or the pressure.

ICP-AES [Inductively Coupled Plasma Atomic Emission Spectrography] was used to determine the ions in IEA poplar [both untreated and sulphuric acid percolated]. Although this analysis is quite expensive the results proved reliable. It is recommended that future demineralisation experiments use this type of analysis to assess how effective the pre-treatment has been.

ICP-AES was also used to measure the sulphur levels in untreated and sulphuric acid percolated IEA poplar. The sulphur levels remained relatively constant over all sulphuric acid concentration and temperatures. This indicates that virtually no sulphuric acid was retained in the biomass either as acid or sulphate. Thus, the percolation process is successful at removing potassium and sodium ions using mild sulphuric acid. The sulphuric acid was removed from the biomass by percolating de-ionised water [twice the volume of sulphuric acid used] at a similar rate.

A series of experiments were conducted to treat larger samples [500g] of biomass. In order to improve the effectiveness of the acid soak the biomass samples were first soaked in de-ionised water for 24 hours before being rinsed with more de-ionised water and then soaked in a dilute sulphuric acid solution for a further 24 hours. This initial pre-soaking appears to open up the pores in the biomass allowing the acid better access to the cells. Experiments using pre-soaks were all effective in reducing ash levels to similar levels as acid washing experiments, but at milder conditions [i.e. more dilute acid and lower temperature].

For the pre-soak and acid wash experiments an elemental balance on the potassium and sodium ions was attempted. The results previously obtained from ICP-AES were used as the reference level in the untreated biomass and the dissolved ions from the pre-soak and the acid wash were measured by flame photometry. It was found that flame photometry was not accurate enough to measure the dissolved ions and is not recommended for future use. The best way to measure the ions would be to carry out ICP-AES on the wood before pre-soaking, after pre-soaking and after acid soaking.

HPLC analysis carried out on the pre-soak liquor found traces of sugars. But these sugars were not identified or quantified. However, the presence of sugars does indicate that even water soaking at ambient temperatures will remove some of the hemicellulose as well as ash. Subsequent acid soaking results in the removal of even more hemicellulose. The presence of sugars and dissolved biomass components in the aqueous waste from a pre-treatment process will require extra waste treatment on a commercial scale.

Pre-soaking biomass followed by rinsing, reduced ash levels from 0.42 to 0.26 mf wt.%. A subsequent soak in sulphuric acid followed by rinsing, reduced ash levels to between 0.16 and 0.03 mf wt.% depending on acid concentration and temperature. The optimum pre-wash and acid wash conditions were 24 hours soaking in de-ionised water at 30°C, rinsing, soaking in 0.1M H_2SO_4 at 30°C and rinsing. This pre-treatment resulted in the lowest biomass losses [0.91%] but reduced ash levels to 0.08%.

Sulphuric, hydrochloric, phosphoric and nitric acids were also used in a series of tests on 50g samples of IEA poplar. Based on the results of ASTM ash analysis over the conditions tested the following gave the most significant reduction in ash content:

- 1.0M H_2SO_4 at 20°C on 300-600μm poplar,
- 1.0M HCl at 20°C on 600-1000μm poplar,
- 0.1M H_3PO_4 at 50°C on 600-1000μm poplar,
- 0.1M HNO_3 at 50°C on 600-1000μm poplar.

In an effort to measure how fast the demineralisation reaction progresses the concentration of sodium and potassium ions in each batch reactor were measured periodically using flame photometry. The concentration of potassium ions was found to have a general downward trend for all experiments conducted at 20°C, which is due to the dilution effect [each time a sample was taken for analysis it was replaced with fresh acid]. At higher temperatures this downward trend is less pronounced which may be due to increased rate of ion removal from the biomass. Thus at higher temperatures it would appear that the potassium was removed more quickly from the biomass.

The quality of these results was limited by the inaccuracy of flame photometry. These experiments should be repeated with continuous potassium and sodium ion measurements in order to allow reaction rates to be determined. This type of work is essential for scaling up pre-treatment processes, especially if equipment is to be changed from batch stirred tank reactors with long holding times to continuous reactors with much shorter residence times.

Boiling nitric acid [2 litres of 5 wt.%] was used to hydrolyse pine wood [100g] for 4 hours. This treatment removed 50% of the biomass.

In order to limit the number of pyrolysis experiments to an acceptable level pre-treated biomass feedstocks were pyrolysed at 500°C. However, it is recommended that further work be carried out to optimise the yield of chemicals [i.e. levoglucosan or hydroxyacetaldehyde] by changing the pyrolysis process conditions for the more successful pre-treated feedstocks.

Pre-treated feedstocks tend to produce slightly higher yields of organics on a dry pre-treated feedstock basis [compared to untreated feedstocks]. The increase in organics tends to be at the expense of gas. Char and water yields tend to be similar to those of untreated feedstocks. The pyrolysis results from pre-treated [ash removed] feedstocks are assessed by comparison of levoglucosan and hydroxyacetaldehyde yields to those of untreated poplar. All pre-treated feedstock work is summarised in Table 11.3.

Compared to untreated poplar, poplar which was soaked in water for 24 hours and then rinsed produced a pyrolysis liquid with an increased yield of levoglucosan and decreased yield of hydroxyacetaldehyde. Poplar which was pre-soaked and then acid washed gave further increased yields of levoglucosan and reduced yields of hydroxyacetaldehyde. However, ICP-AES analysis suggests that most of the potassium and sodium ions are removed by mild treatments such as water washing. Thus it is likely that the "active" ash component will have been removed just by water washing alone. The subsequent increase in levoglucosan following acid washing is more attributable to either changes in the biomass structure caused by the acid or small amounts of acid remaining in the biomass causing depolymerisation reactions. The effect of the acid is certainly more than just demineralisation of the poplar.

Table 11.3: Comparison of pre-treatment conditions and yields of chemicals

Run number	Acid type	Conc. [wt.%]	Pre-treat Temp.[°C]	Ash [mf wt.%]	Pyrolysis Temp.[°C]	LG	HA
Pine							
313	none			0.23	501	1.67	6.86
312	HCl	0.1	amb.	0.05	479	4.19	2.39
314	HCl	5	100	0.05	512	22.94	3.86
Poplar							
SFB28	none			0.46	508	2.45	7.26
SFB26	water		amb.	0.26	506	3.12	7.10
Poplar, pre-soaked as SFB26							
SFB27	H_2SO_4	0.15	30	0.12	498	8.63	2.45
SFB66	H_2SO_4	0.10	30	0.10	496	18.78	0.15
SFB67	H_2SO_4	0.10	30	0.08	503	11.68	4.19
SFB68	H_2SO_4	0.10	40	0.08	502	3.77	2.99
SFB69	H_2SO_4	0.20	40	0.05	493	7.20	5.81
SFB70	H_2SO_4	0.50	40	0.07	500	10.97	1.93
SFB71	H_2SO_4	0.50	40	0.03	502	12.37	1.42
Poplar, acid washed only							
SFB53	HCl	0.1	20	0.05	500	6.86	5.20
SFB52	HCl	0.1	50	0.05	502	9.77	6.30
SFB55	HCl	1.0	20	0.02	498	9.27	5.37
SFB54	HCl	1.0	50	0.04	500	8.01	4.62
SFB50	HCl	3.0	20	0.02	500	7.15	3.63
SFB51	HCl	3.0	50	0.04	502	11.87	8.04
SFB56	H_2SO_4	1.0	20	0.02	507	11.63	3.43
SFB57	H_2SO_4	1.0	50	0.01	501	11.80	3.00
SFB58	H_2SO_4	1.0	70	0.02	502	15.90	1.16
SFB49	H_3PO_4	1.37	50	0.16	504	8.29	2.55
SFB60	HNO_3	0.1	50	0.02	500	5.80	6.72
SFB61	HNO_3	1.0	50	0.03	501	3.88	2.96
SFB62	HNO_3	3.0	50	0.01	508	13.47	3.25
Poplar, additives							
SFB73	$FeCl_3$	2.01	amb.	3.12	508	0.71	0.59
SFB74	KCl	1.96	amb.	2.13	508	1.80	11.73
SFB75	NH_4Cl	2.02	amb.	0.33	526	4.09	4.65

The highest yield of levoglucosan obtained in this work was 22.94mf wt.% from nitric acid hydrolysed pine. Hydrolysis removed approximately 50% of the biomass, which effectively means that half of the biomass was wasted [i.e. not pyrolysed and had to be disposed of].

Less severe techniques may prove to be more economic, since less biomass is lost and the yields of levoglucosan are also significantly increased [compared to untreated biomass]. The highest yield of levoglucosan from a none hydrolysis pre-treatment was 18.78 mf wt.% obtained from poplar, which was pre-soaked and then washed in 0.1M sulphuric acid at 30°C. The best literature value for such mild conditions is 9.33 mf wt.% levoglucosan from poplar treated with 0.1M sulphuric acid at 30°C. Variations in sulphuric acid concentration [from 0.10-0.50wt.%] and temperature [from 30-40°C] seem to have little influence on the levoglucosan yield.

All pre-treated feedstocks, especially those which have been acid treated have lower yields of formaldehyde. Since formaldehyde predominantly originates from the hemicellulose component this suggests that it has been modified or removed.

Pre-treatment using sulphuric acid appears to consistently produce the highest yields of levoglucosan. Other acids [e.g. hydrochloric, phosphoric and nitric] do produce an increase in the yield of levoglucosan but not as much as sulphuric acid. However, 3wt.% nitric acid treated poplar gave the highest yield of fructose in this work [7.25 mf wt.%].

Figure 11.2 shows the relationship between ash content and levoglucosan and hydroxyacetaldehyde yields for untreated and pre-treated samples of IEA poplar pyrolysed at around 500°C. All component removal pre-treatment methods resulted in a significant reduction in ash. The yield of levoglucosan and hydroxyacetaldehyde although clearly influenced by the amount of ash in the feedstock also appears to be dependant on other factors. Of the factors investigated, it seems most likely that the presence of residual amounts of acid in the biomass feedstock is responsible for the spread of results in Figure 11.2. Alternatively, it may be that "active" ash would give a better correlation for levoglucosan and hydroxyacetaldehyde yields. However, the exact composition of "active" ash must first be determined.

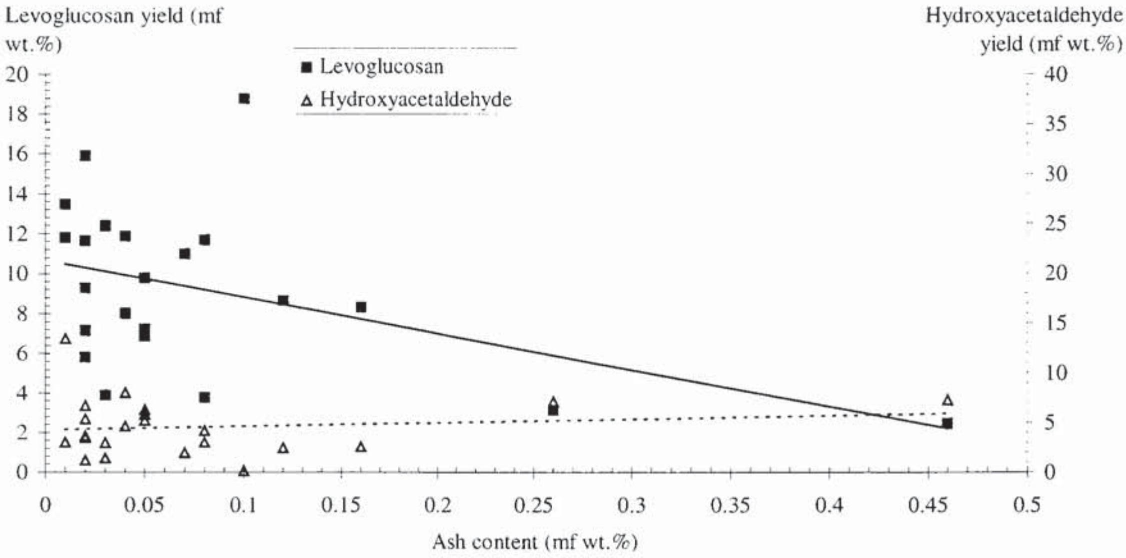


Figure 11.2: Relationship between ash content and chemical yield

This preliminary investigation has shown that the yield of levoglucosan can be significantly increased by pre-treatment. The yield of levoglucosan from mild treatments involving dilute acids at ambient conditions has approached the maximum yields of levoglucosan obtained from hydrolysed poplar. The use of pre-soaking appears to significantly improve the effectiveness of the acid washing allowing much less severe conditions to be used. Optimisation of the pre-treatment process by further investigation into the effects of acid type, concentration and treatment temperature should be carried out, along with a thorough investigation into the effect of small amounts of acid in the biomass feedstock. The yield of levoglucosan could also be optimised by changing the pyrolysis process conditions, probably by reducing reactor temperature and gas/vapour residence time.

11.2.2 Additives

Additives were dissolved in water and introduced into samples of IEA poplar by soaking and slowly drying. This may not be the best commercial method since it requires that the biomass is dried to less than 10% moisture after treatment. On a commercial scale it is likely that the additive would be metered directly into the reactor. However, for small scale, soaking ensures that the additive is thoroughly mixed with the biomass and that it has probably penetrated into the centre of the cell.

Poplar which contained 2% iron chloride was difficult to feed since it formed char which tended to block up the area around the feed tube. It produced the highest yields of char for any pyrolysis run at Aston. The yields of chemicals from this feedstock were low which is probably due to the increased formation of char and gas. There is no evidence to suggest that iron played any role in reducing the lignin reactions in the pyrolysis reactor.

2% potassium chloride did significantly increase the yield of hydroxyacetaldehyde from 7.26 to 11.73 mf wt.%. This is the highest yield of hydroxyacetaldehyde produced in this work, although not as high as literature yields [17mf wt.% from poplar containing 0.01%K_2CO_3]. The yields of oxygenates and acids were increased and the yields of sugars were decreased which is a consequence of fragmentation reactions being promoted over depolymerisation.

The introduction of ammonium chloride into the fast pyrolysis reaction appears to have brought about oxidation reactions since the yield of pyrolytic lignin was much lower than usual. However the low yield of pyrolytic lignin could also be a consequence of the reduced organics and increased char and gas yields.

Both the anion and the cation clearly have an effect on the pyrolysis reaction. Iron, potassium and ammonium chlorides all gave significantly different pyrolysis product and chemical yields. Further work on the effects of additives is required. Additives may be useful not only to increase the yield of certain chemicals but also to improve pyrolysis liquid stability and physical properties.

11.3 TECHNOECONOMIC ASSESSMENT

Technoeconomic assessment has been carried out on five scenarios for the production of levoglucosan from fast pyrolysis. All scenarios contain the following stages; biomass physical preparation, biomass chemical pre-treatment [optional], fast pyrolysis and levoglucosan extraction. There is already a considerable amount of information on biomass physical preparation and fast pyrolysis. However, chemical pre-treatment has been designed and costed from experimental results in this work and levoglucosan extraction has been designed from the literature. This is the first time an integrated process like this has been technoeconomically assessed.

The five chemical pre-treatment scenarios are; no chemical pre-treatment, water washing, water pre-washing followed by dilute acid washing, acid hydrolysis and purchase of commercial cellulose. For all washing/hydrolysis scenarios batchwise processing has been used since this was found to be the most effective in the practical work and is also more cost effective for the long reaction times required for demineralisation.

Pre-treatment of biomass produces large quantities of aqueous waste. This waste generally contains hydrolysed hemicellulose, dissolved ash and excess acid [if acid has been used]. Even the worst case scenario of a biomass pre-treatment plant using acid pre-treatment to remove 50% of the 1000kg/h biomass input [the biomass contains 50mf wt.% water] would produce in excess of 6000kg/h of waste water; this water would contain approximately 33mg/l dissolved wood components with an estimated chemical oxygen demand [COD] of 45mg/l. This equates to a biological oxygen demand [BOD_5] of 27mg/l. A typical municipal wastewater would be in the range of 150-1000mg/l; thus, the amount of waste produced and the low concentration of contaminants would not warrant the cost building and operating a waste water treatment plant. However, some pre-treatment is required before the waste can be sent to a commercial drain. Waste water pre-treatment consists of neutralisation of acids and removal of biological/chemical oxygen demand [i.e. hydrolysed biomass components] probably by aerobic digestion if necessary.

Biomass pre-treatment can remove a substantial amount of the biomass [hemicellulose] hence reducing pyrolysis costs. Thus even though pre-treatment requires extra raw materials and waste disposal introduces extra cost into the process, this is far outweighed by the extra revenue gained from the sale of more levoglucosan. Thus it is more cost effective to pre-treat biomass to increase the concentration of levoglucosan in the pyrolysis liquid than it is to extract low concentrations of levoglucosan from untreated biomass pyrolysis liquids.

It has been found that the introduction of pre-treatment into the levoglucosan production process almost doubles the total capital cost. The introduction of a pre-washing stage increases the capital cost by a further 50% due to the introduction of an extra stage.

The factors which most affect plant profitability are levoglucosan selling price, levoglucosan production, plant capital cost, plant operating cost and raw materials.

Because levoglucosan is the only product from this plant the plant profitability is sensitive to the retail price of levoglucosan and also how much levoglucosan is produced. The profitability of the process is more sensitive to the operating costs than the capital cost. The majority of the operating cost is made up of raw materials required for the extraction of levoglucosan. Thus by pre-treating biomass the raw material costs can be reduced.

Based on 1000kg/h wet biomass the five scenarios produced the capital and operating costs shown in Table 11.4. The amount of levoglucosan produced by each plant, the cost per ton of levoglucosan and the minimum levoglucosan price to obtain zero return on investment after ten years are also shown.

Table 11.4: Results obtained from the model

Scenario	1 [UT]	2 [WW]	3 [WW+AW]	4 [AH]	5 [Cell.]
[k$US, 1995]					
Total capital costs	3407	6672	7753	6193	1958
Total production costs	5942	6938	6088	7189	5716
Production cost/ton LG	82.5	58.2	18.9	18.8	10.6
Tons levoglucosan/year	72	119	322	383	539
Levoglucosan selling price [US$/kg] for return on plant capital cost					
ROI 0%	89.02	66.02	22.22	20.99	11.10

UT - no chemical pre-treatment, WW - water washing, WW+AW - water washing followed by acid washing, AH - acid hydrolysis, Cell. - purchase of commercial cellulose.

Despite the cost of cellulose being 15 times more expensive than wood, it is more profitable to produce levoglucosan from commercial cellulose than to pre-treat wood. It may be that the sale of residues such as the aqueous insoluble fraction of the pyrolysis liquid may be used to improve the economics of the process.

12. RECOMMENDATIONS

The following recommendations are made:

12.1 PRODUCTION OF LIQUIDS

The production of liquid fuels from fast pyrolysis of biomass requires optimisation before commercial production can begin. The first stage of this optimisation is the maximisation of the pyrolysis liquid yield under fast pyrolysis conditions for a number of biomass feedstocks, which has been carried out as part of this work. The next stage is to investigate the properties which are required of pyrolysis liquid for it to be used as a fuel. It is likely that the required fuel properties will be low viscosity, high heating value and physical stability with time and temperature.

It may be that pyrolysis process conditions have to be changed in order to improve the fuel properties. In this case there will be a direct play-off between product quality and quantity. The presence of microfine char in the pyrolysis liquid is believed to have a detrimental effect on liquid quality. The presence of pyrolytic lignin in the pyrolysis liquid has also been linked to chemical instability. However, all of these factors require further investigation.

The pyrolytic char is known to contain alkali metal cations. Since microfine char is present in the pyrolysis liquid it could result in corrosion problems if pyrolysis liquids are used in fuel applications. Pyrolysis liquids produced from low ash feedstocks have been reported to have less odour. It may be that pyrolysis liquid derived from biomass containing high ash levels [hence alkali metals] result in worse odours. However, it is suggested that further work is carried out to confirm these theories.

The moisture content of the feedstock can be increased to produce pyrolysis liquids containing more water. Although this will result in slower pyrolysis and lower pyrolysis liquid yields the reduced viscosity of the pyrolysis liquid [due to the higher water content] may be beneficial. The increased water content will also result in the pyrolysis liquid having a lower heating value. Further work should be carried out to determine whether heating value is more important than low viscosity for fuel applications.

It has been established that feedstock composition plays a significant role in determining pyrolysis liquid yields. It may be possible to select biomass of a particular composition either by choosing a new species of plant, early harvesting [i.e. seasonal selection] or genetic modification of a plant to give the desired composition. By ensuring that the feedstock is of the correct composition, costly pre-treatment and waste disposal can be avoided. Therefore it is recommended that work continues on pyrolysis of novel feedstocks and that the effects of seasonal variation and genetic engineering are investigated.

12.2 PRODUCTION OF CHEMICALS

Further work should be carried out on optimising the yield of chemicals from a range of biomass feedstocks. It may be that novel feedstocks will result in higher yields of the current fast pyrolysis chemicals or may result in the production of new chemicals. In either case for chemicals production optimisation will be required.

Continued assessment/development of pyrolysis liquid analysis techniques should be carried out. Despite new analytical methods it is still only possible to analyse approximately 70% of the chemicals contained in fast pyrolysis liquids. Work should also continue to ensure that these techniques are reproducible and produce reliable results across the whole of the biomass pyrolysis community.

12.2.1 Ash Removal Pre-treatment

The elements which form "active" ash require further investigation. Once these elements have been established it will be necessary to optimise conditions for their removal. The demineralisation rate of biomass is relatively slow but may be increased by using pressure and elevated temperatures. The provision of optimum conditions and kinetic data will allow pre-treatments to be efficiently scaled up for commercial applications.

Although preliminary investigations have shown that water pre-washing improves pre-treatment effectiveness and that sulphuric acid appears to be significantly better than any other acid, the conditions for pre-treatment have not been optimised. Optimisation can be carried out at two levels. Optimisation may require maximum ash removal with minimum biomass wastage in which case it can de assessed directly. Alternatively, it may be related more to the production of levoglucosan [or other chemicals] in which case pyrolysis will have to be used as the method of measuring pre-treatment effectiveness. Once the pre-treatment process has been optimised it may also be necessary to optimise fast pyrolysis conditions to produce the maximum amount of the desired product.

12.2.2 Additives

Further work on the effects of additives on the fast pyrolysis reaction is required. The role of the anion and the cation is still not clearly understood. In order to investigate a greater number of additives it may be necessary to use smaller scale pyrolysis apparatus. For example, a micro-pyrolysis reactor linked directly to a GC-MS or other analytical instrument may only require small samples of feedstock [i.e. less than 1g] to carry out mass balance and chemical product studies. In this way hundreds of additives could be compared. As part of the investigations into additives the role of "active" ash and small amounts of acid [i.e. residual acid from pre-treatment processes] should be investigated.

As well as influencing the pyrolysis reaction for the production of chemicals, additives may also be able to improve pyrolysis liquid quality and stability. The chemical instability of the pyrolysis liquid is mostly attributed to the presence of carbonyl groups. It may be that the introduction of certain additives into the pyrolysis reactor can significantly reduce the number of oxygenated chemicals in the fast pyrolysis liquid and hence improve its chemical and possibly thermal stability.

12.3 TECHNOECONOMIC ASSESSMENT

Although some feedstocks produce lower quantities of pyrolysis liquids than others they may grow in a shorter time period and hence require less land. An integrated growing and harvesting model should be included in the technoeconomic assessment of levoglucosan production.

It may be possible to separate the pre-treatment, pyrolysis and extraction stages to allow economies of scale to be exploited. This would allow larger plants to be built but would require an investigation of transport costs. However, the world-wide demand for levoglucosan should be examined closely to ensure that plants which are too large are not assessed.

It may be possible to improve the economics of levoglucosan production by making secondary products [i.e. selling residues/wastes]. Possible markets should be investigated for the pyrolysis char, pyrolysis gas and aqueous insoluble residue.

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APPENDIX A - PUBLICATIONS

The following is a list of publications which were carried out during the course of this work. Most of the work contained in these publications is included in the thesis.

RA Hague and AV Bridgwater, "The Production of Selected Chemicals from Fast Pyrolysis of Modified Biomass Feedstocks", Proc. Biomass for Energy, Environment, Agriculture and Industry, Eds. P. Chartier, AACM Beenackers amd G Grassi, Pergamon 1995 , p. 1734-1741.

GVC Peacocke, RA Hague and AV Bridgwater, "Selective Production of Chemicals by Biomass Fast Pyrolysis using Two Different Reactors", Paper 89, Institution of Chemical Engineers Research Event, Edinburgh, January 1995.

RA Hague and AV Bridgwater, "Effects of Pretreatment on the Fast Pyrolysis of Biomass", Proc 9th EC Conference on Biomass for Energy, Copenhagen, June 1996,

GVC Peacocke, RA Hague and AV Bridgwater, "Pyrolysis of Pretreated and Normal Feedstocks for the Production of Fuels and Chemicals", IChem E Research Event, Leeds, April 1996.

RA Hague and AV Bridgwater, "The Production of Selected Chemicals from Fast Pyrolysis of Modified Biomass Feedstocks", IChem E Research Event, Leeds, April 1996

GVC Peacocke, CM Dick, RA Hague, LA Cooke and AV Bridgwater, "Comparison of Ablative and Fluid Bed Fast Pyrolysis Products: Yields and Analyses", Biomass for Energy and the Environment, Proceedings of the 9th European Bioenergy Conference, Chartier, P., Ferrero, G.L., Henius, U.M, Hultberg, S., Sachau, J. And Wiinblad, W. (Eds.), 1996, Pergamon Press, Volume 3, p. 1632-1637.

AV Bridgwater, CM Dick and RA Hague, "The Fast Pyrolysis of Oilseed Rape", Report to ETSU, ETSU B/M5/00533/16/REP (ETSU 1996).

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HH Sheena, RA Hague, NM Robinson, EH Salter, GVC Peacocke and AV Bridgwater, "Effect of Fast Pyrolysis Parameters on Liquid Product Composition", I.Chem.E. Research Event, 1998, Newcastle, April 1998, available on CD-ROM, Institute of Chemical Engineers, Rugby, UK.

APPENDIX B - GAS ANALYSIS

Molecular sieve system

Gases detected: H_2, O_2, N_2, CO
Instrument: Pye Unicam Series 204 Gas chromatograph fitted with a Valco electrically actuated sampling valve which is heated by a Valco instrumentation temperature controller.
Detector: Thermal conductivity detector
Column: 5' stainless steel, 1/4" OD [3/16" ID] Molecular sieve 5A, mesh range 80/100.
Manufacturer: Phase Separations
Carrier gas: Helium
Carrier flowrate: 30ml/min
Detector temperature: 150°C
Injector temperature: 150°C
Column temperature: 70°C
Sampling valve temperature: 70°C
Sample volume: 1ml

Poropak Q system

Gases detected: CO_2
Instrument: Pye Unicam Series 204 Gas chromatograph fitted with a Valco electrically actuated sampling valve which is heated by a Valco instrumentation temperature controller.
Detector: Thermal conductivity detector
Column: 5' stainless steel, 1/4" OD [3/16" ID] Poropak Q, mesh range 80/100.
Manufacturer: Phase Separations
Carrier gas: Helium
Carrier flowrate: 30ml/min
Detector temperature: 150°C
Injector temperature: 150°C
Column temperature: 70°C
Sampling valve temperature: 70°C
Sample volume: 1ml

Picric acid system

Gases detected: C_1-C_5 gases
Instrument: Perkin-Elmer Sigma 2B Gas Chromatograph fitted with a gas sampling valve
Detector: Flame Ionisation Detector [FID]
Column: 6' stainless steel, 1/8" OD [0.085" ID] 0.19% Picric acid on Graphpac-GC, mesh range 80/100,.

Manufacturer: Alltech
Carrier gas: Helium
Carrier flowrate: 15ml/min
Detector temperature: 150°C
Injector temperature: 150°C
Column temperature: 30°C
Sampling valve temperature: 30°C
Sample volume: 1ml
Detector range & attenuation: 32*10
Integrator: Spectra-Physics SP4100 computing integrator.

APPENDIX C - PYROLYSIS LIQUID ANALYSIS

Analysis methods followed here are based on those developed at the University of Waterloo, Canada. This method was adopted initially for a comparative assessment of methods and procedures used for the analysis of oils and to develop a robust and reproducible chromatographic methodologies for future qualitative and quantitative analyses of pyrolysis oils.

Preliminary analyses of oil samples produced by Aston's ablative pyrolysis unit were carried out on a commercial HPLC system for evaluation. The chromatographic system comprised a thermostatic oven [60°C] housing a 300 x 4.6mm column [Spherisorb-NH_2] and a refractive index detector. Analysis was performed isocratically with an aqueous mobile phase [flow rate 1 ml/min] containing 0.007N phosphoric acid.

Subsequently, a heated multi-column dual detection HPLC system was commissioned to analyse pyrolysis oil liquids using different analytical methodologies. The chromatographic system is configured around a quaternary gradient Crystal 200 HPLC pump [ATI/Unicam], coupled to a Crystal 250 Diode Array Detector, DAD [ATI/Unicam] in series with a Refractive Index Detector [Gilson, model 132] and a Fraction Collector [Gilson, model 203]. Solvents are vacuum degassed using a four-channel Degassex unit [Phenomenox, model DG-401]. In this system the DAD is working in tandem with the RI detector [i.e. in a hyphenated RI-DAD technique], thereby enhancing the sensitivity of detection and the identification of chemicals based on UV visible light absorbing chromophores.

The multi-column assembly employs two six-port column switching valves [Rheodyne, model 7060]. Three different HPLC columns, with corresponding guard columns, are placed in a heated column oven [Biorad]. The columns are used to effect separation of aqueous soluble and insoluble fractions of pyrolysis oil. Samples are injected through an injector valve [Rheodyne, model 7125] fitted with 20µl sample loop. An autostart switch triggers simultaneously data acquisition from DAD directly and the RI detector via a data capture unit [DCU]. Chromascan 3 software [windows 3.1] handles data from DAD, and 4880 software collects and processes data from RI detector. The system may be run under computer control and results printed on a colour printer [Hewlett Packard DeskJet 870Cxi].

Sample preparation and treatment for HPLC analysis

Sample preparation including treatment and cleanup is a crucial step in any analytical procedure Aqueous extracts of raw pyrolysis liquids were prepared for HPLC analysis by the following procedure. A known amount of water was added to a known mass of oil [approx. ratio 2:1], the mixture was thoroughly shaken, centrifuged [5 min, 4000rpm] and filtered through a syringe filter [Gelman, acrodisc CR13]. The clear aqueous filtrate was stored in the dark at room temperature and was analysed within three hours. The amount of aqueous-insolubles [lignin-fraction] was determined gravimetrically. Sampling errors are to be expected, especially for samples containing particulates which adhere to the storage bottle or sludge-like material which would not normally be homogeneously mixed with the bulk of the oil especially upon storage.

Normally, HPLC analysis of 10 μl of an aqueous extract was completed in one hour using Biorad HPX-87H [cation exchange] column [30 x 0.78 cm] at 65°C with water [0.500 ml/min] as the mobile phase [pH 1.7].

Separation of the major components of the aqueous extract of raw liquids appears sufficient when RI detector is in place. This separation does not appear adequate, however, when the UV detector [DAD] is used to follow the elution of solutes [chemicals] as they emerge from the Biorad column under the RI-optimised separation conditions above. This anomalous behaviour is explained in terms of the insensitivity of RI [by orders of magnitude] compared to UV detection.

Calibration and Sample Analysis by HPLC

An external 'standards' mixture [Table Appendix C .1] was used for the quantitative determination of chemicals in the aqueous filtrate. The external standard comprises a mixture of fifteen chemicals; the mixture was prepared to closely resemble the low concentration levels of chemicals which are typically representative of cellulose pyrolysis products. The reproducibility of injections [10μl], as determined by area measurements of the individual peaks, using the external standard mixture over a period of one month is shown in Table Appendix C .2.

Table Appendix C .1: External “standards” constituents and residence times for Biorad HPX-87H column

Chemicals Identified	Code	Retention Time [min] 0.005M, H2SO4, 0.5ml/min, 65°C
Cellobiose	CB	9.22
Glucose	G	11.32
Fructose + Xylitol	F	12.23
Levoglucosan	LG	14.35
Hydroxyacetaldehyde	HA	15.15
Formic acid	FC	16.58
Acetic acid	HOAc	17.78
Acetol	A	20.08
Methanol	MeOH	22.43
γ-Butyrolactone	BL	26.83
2-Furoic acid	FUA	32.1
3-Methyl-1,2-cyclopentanedione	MCPD	35.4

Table Appendix C .2: Stability of peak areas of solutes measured over 1 month

HPX-87H, 0.005M H_2SO_4, 0.5ml/m, 65 C									
Chemical Identified	no.	RT	Code	2/12	3/12	26/11	22/11	18/11	6/11
Cellobiose	1	9.22	CB	2.084	1.929	1.967	2.022	2.158	1.914
Glucose	2	11.32	G	1.442	1.061	1.435	1.384	1.466	1.156
Fructose + Xylitol	3	12.23	F+X	2.507	2.794	2.389	2.427	2.617	2.183
Levoglucosan	4	14.35	LG	2.022	3.984	2.042	1.801	2.011	1.66
Hydroxyacetaldehyde	5	15.15	HA	3.309	3.11	3.09	3.026	3.248	2.762
Formic acid	6	16.58	FC	1.693	1.793	1.979	1.936	2.133	1.794
Acetic acid	7	17.78	HOAc	6.292	6.351	6.142	6.424	6.758	5.925
Acetol	8	20.08	A	7.828	7.453	7.261	7.522	7.799	6.909
Methanol	9	22.43	MeOH	1.297	1.068	1.343	1.401	1.984	0.997
γ-Butyrolactone	10	26.83	BL	3.082	2.464	2.706	2.793	1.127	1.843
2-Furoic acid	11	32.1	FUA				1.066	1.081	1.159
3-Methyl-1,2- -Cyclopentanedione	12	35.4	MCPD	2.045	1.981		0.525	0.881	0.853
Furfuraldehyde	13	50.3	FFD				7.515		6.037

Typical HPLC analysis of aqueous filtrates of pyrolysis oils show in excess of 30 components some of which are shown in Table Appendix C .3; many of these components occur in small amounts [less than 0.05%]. Less than half of these components occur in significant amounts and these were detected and quantified [to obtain absolute concentrations] based on comparisons with retention times of standards in the external 'standard' mixture. The other components were not quantified although a guesstimate of their amount can be determined from area measurements of their corresponding chromatographic peaks compared to that of a nearby identifiable peak [with the assumption that similar separation mechanisms and detector responses are applicable]. A spreadsheet was used to calculate the concentration of each component in the raw pyrolysis oil.

Table Appendix C .3: Chemicals generally proposed to be present in aqueous extracts of bio-oil

Chemical	Code	RT [old]	Mass [g]	Mass [%]	Comments	RT [new]
		8.08		0.000		
Cellobiose	CB	8.47	0.0079	0.052		8.95
		9.02		0.000		
Guaiacol	GUL	9.51	0	0.000		
d-Glyceraldehyde	DGL	10.04	0	0.000		
		10.45		0.000		
Glucose	G	10.55	0.0120	0.080		11.07
Mannose	M	11.27		0.000		
Fructose	F	11.35	0.0062	0.041		11.92
Xylose	XYL	11.4		0.000		
Galactose	GA			0.000		
Glyoxal	GX	12.05	0.0001	0.001	v. insol.	
		12.58		0.000		
Xylitol	X	13.03	0	0.000		
		13.21		0.000		
Levoglucosan	LG	13.83	0.0077	0.051		14.53
Methylglyoxal	MGX	14.21		0.000		
Anhydromannose	AHM	14.25		0.000		
Hydroxy- -acetaldehyde	HA	14.75	0.0034	0.023		15.47
		15.51		0.000		
Formic acid	FC	15.97	0.0940	0.624	Aldrich	16.85
Furfural alcohol	FFA	14.7		0.000		
Formaldehyde	FD	16.02		0.000		
Paraldehyde	PAR			0.000		
		17.03		0.000		
Acetic acid	HOAc	17.33	0.0650	0.432	Janssen, 99.8%	18.23
Laevulic acid	LAEV	17.48		0.000		
Ethylene glycol	EG			0.000		
		18.43		0.000		
		19.07		0.000		
2,2-Oxy diethanol	ODE	19.23	0	0.000		
Acetol	A	19.6	0.0660	0.438	Merck, 97%	20.53
Propane-1,3-diol	POD			0.000		

Acetaldehyde	AC			0.000		
		20.7		0.000		
Methanol	MeOH	22.75	0.9000	5.976	Fisher, HPLC	23.95
		23.2		0.000		
3-Hydroxy-2-methyl-1,6-pyrone	PYR	0	0	0.000		
		24.3		0.000		
Ethanol	EtOH	25.82	0.399	2.649	Fisher, HPLC	27.43
Propanol *	PrOH			0.000		
Isopropanol *	IPA			0.000		
γ-Butyrolactone	BL	26.83	0	0.000		
		28.2		0.000		
		29.2		0.000		
		30.4		0.000		
2-Furoic acid	FUA	32.1	0.0030	0.020	Aldrich	35.63
		34.4		0.000		
3-Methyl-1,2-cyclopentanedione	MCPD	35.4	0.0080	0.053		38.48
		37.05		0.000		
		40.1		0.000		
		44.2		0.000		
		48.3		0.000		
		51.6		0.000		
Furfuraldehyde	FFD	52	0.0230	0.153	Aldrich, 99%	53.50
Water			13.4650	89.41		
Total Mass			**15.06**	**100.00**		

- - not normally present in pyrolysis liquid

APPENDIX D - FLAME PHOTOMETRY

Flame photometry is an analytical technique which measures the change in intensity of light. The introduction of various elements into the flame changes its intensity which can be measured using special filters for each particular element. It can analyse the concentrations of potassium, sodium and calcium. It is a comparative method which must first be calibrated with solutions of known concentrations [ppm levels] of the elements.

Using a range of concentrations of each element a calibration curve can be set up for each element [shown in Figure Appendix D .1]. Hence the concentration of the elements K and Na can be measured in an unknown sample. Unfortunately due to equipment problems [broken calcium filter] no results could be determined for calcium.

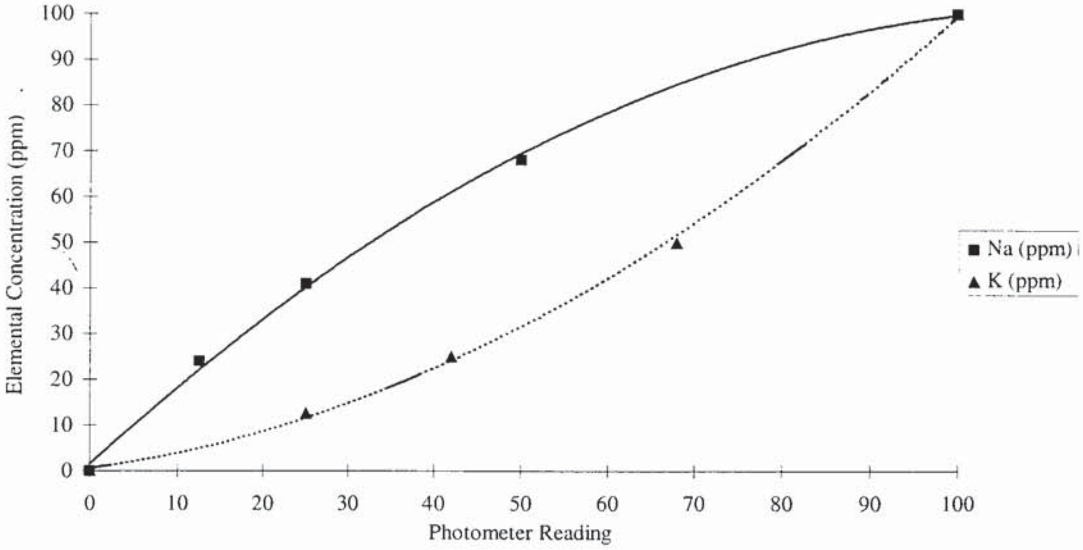

Figure Appendix D .1: Calibration curves for flame photometer

APPENDIX E - RESULTS FROM EXPERIMENTS INVESTIGATING MINERAL ACID TYPE

The following figures show the relationship over time of dissolved potassium and sodium ions from a range of biomass sizes, mineral acid types, mineral acid concentrations and batch reactor temperatures. The ppm concentrations are calculated from the measured levels of ions in solution [flame photometry].

Sulphuric acid washing

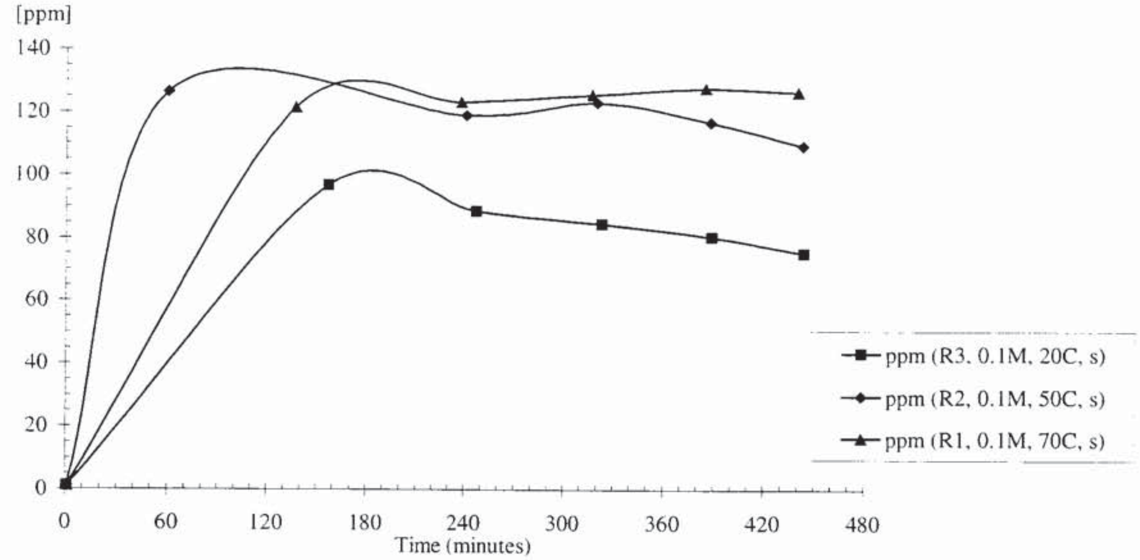

Figure Appendix E .1: **Small biomass 0.1M sulphuric acid wash - potassium concentration in solution versus time**

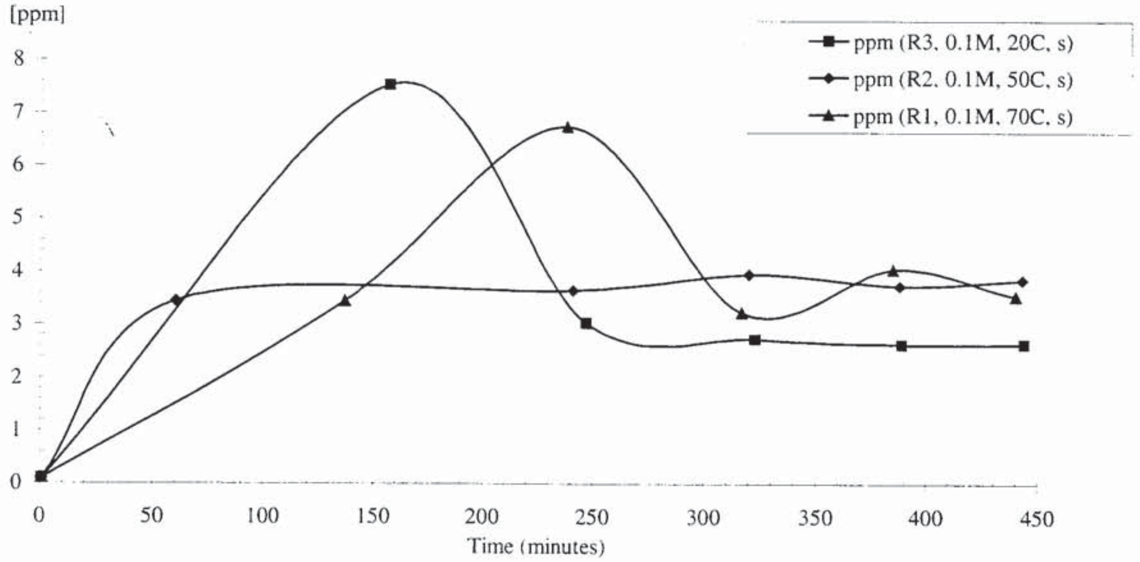

Figure Appendix E .2: **Small biomass 0.1M sulphuric acid wash - sodium concentration in solution versus time**

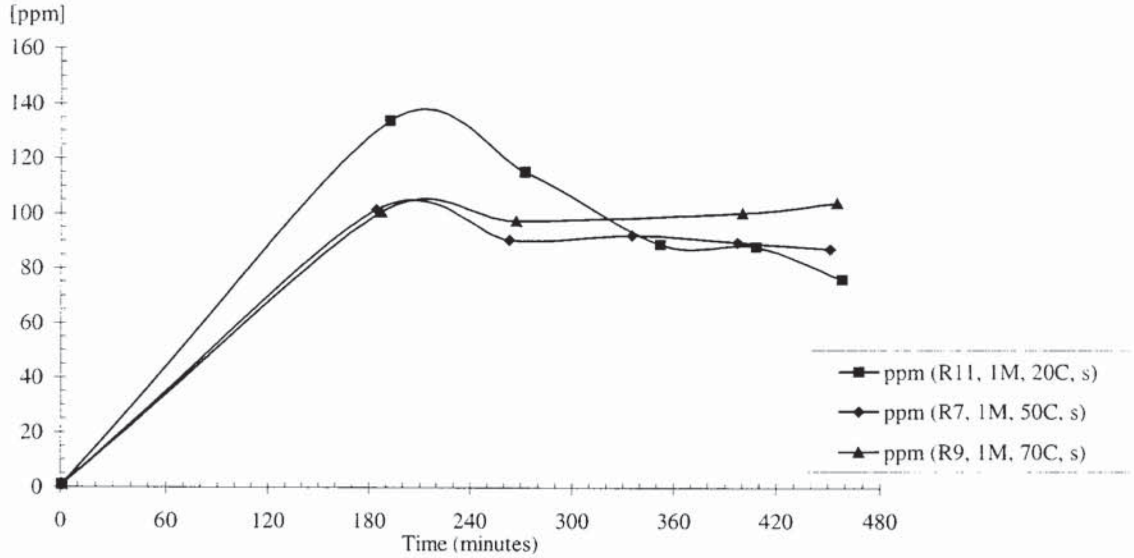

Figure Appendix E .3: **Small biomass 1.0M sulphuric acid wash - potassium concentration in solution versus time**

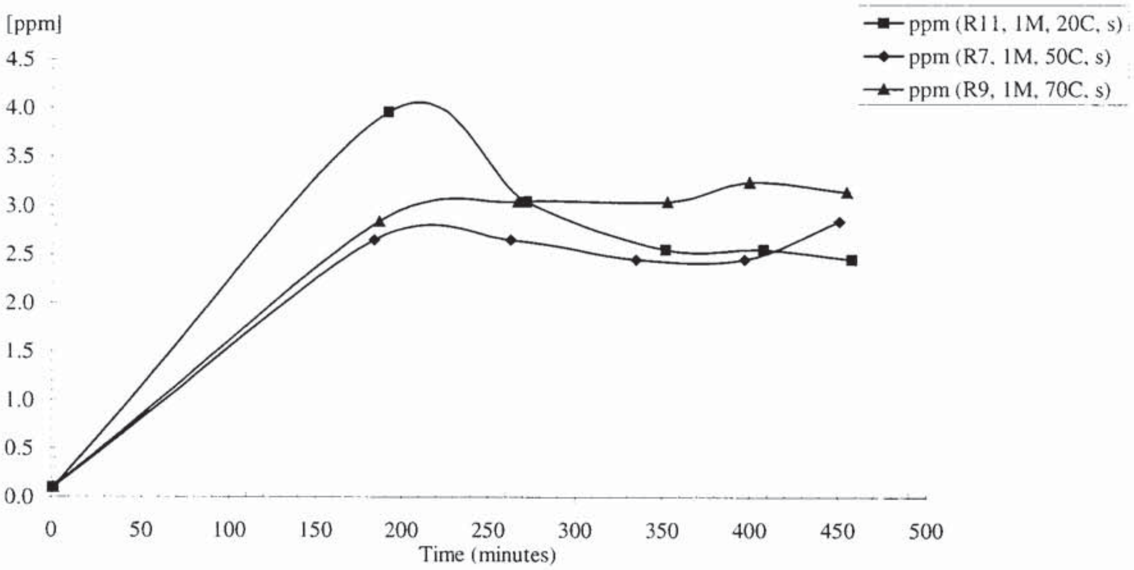

Figure Appendix E .4: **Small biomass 1.0M sulphuric acid wash - sodium concentration in solution versus time**

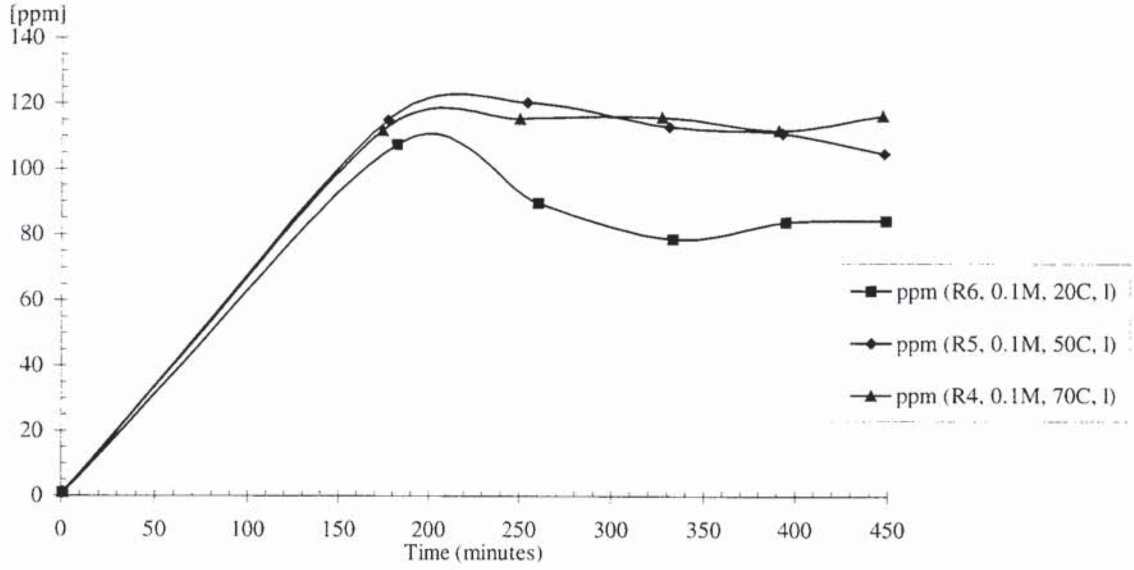

Figure Appendix E .5: **Large biomass 0.1M sulphuric acid wash - potassium concentration in solution versus time**

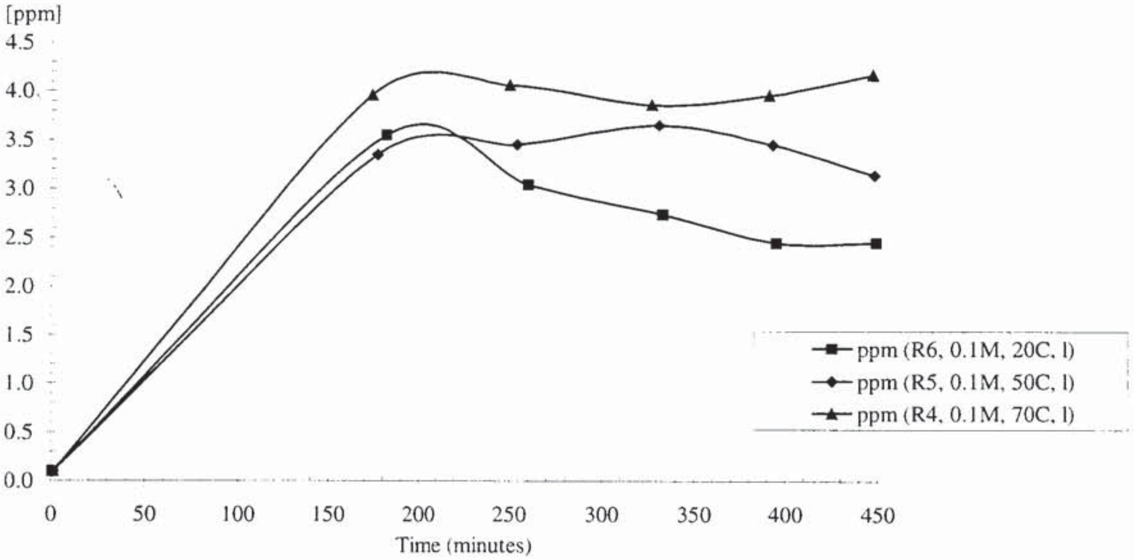

Figure Appendix E .6: **Large biomass 0.1M sulphuric acid wash - sodium concentration in solution versus time**

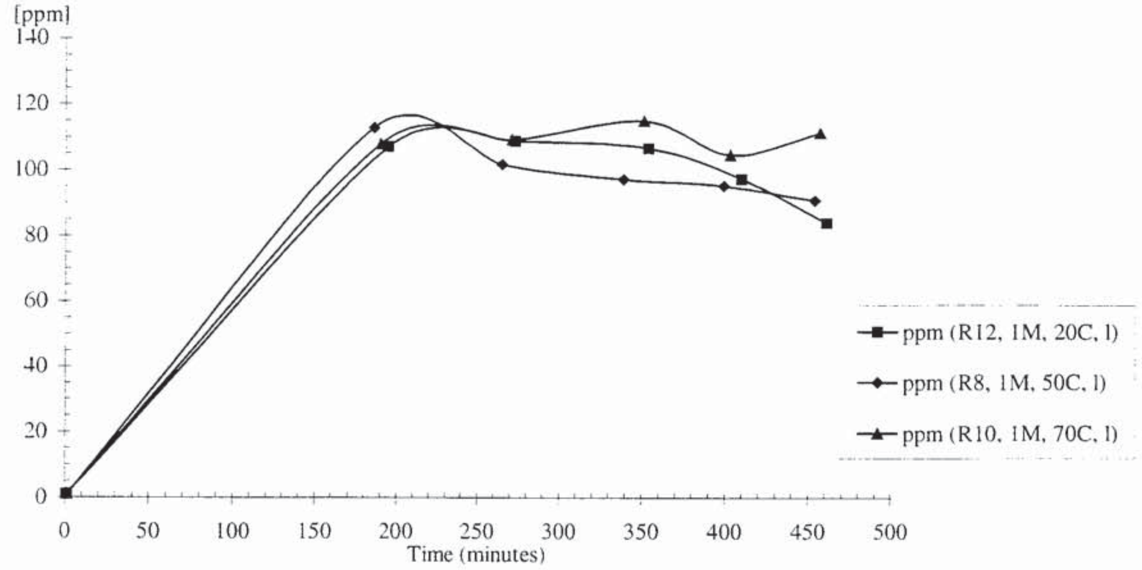

Figure Appendix E .7: **Large biomass 1.0M sulphuric acid wash - potassium concentration in solution versus time**

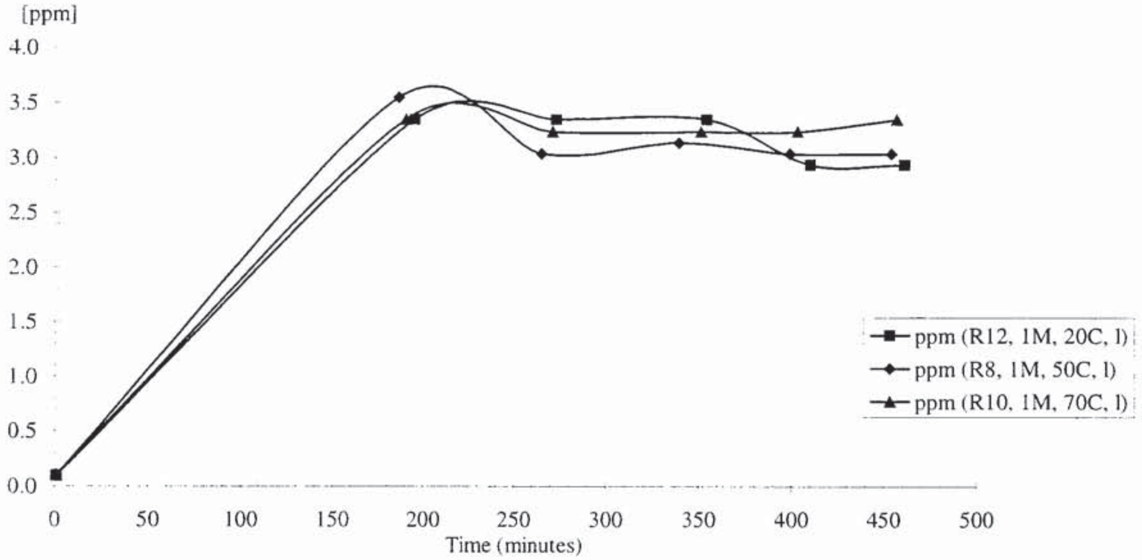

Figure Appendix E .8: **Large biomass 1.0M sulphuric acid wash - sodium concentration in solution versus time**

Hydrochloric acid washing

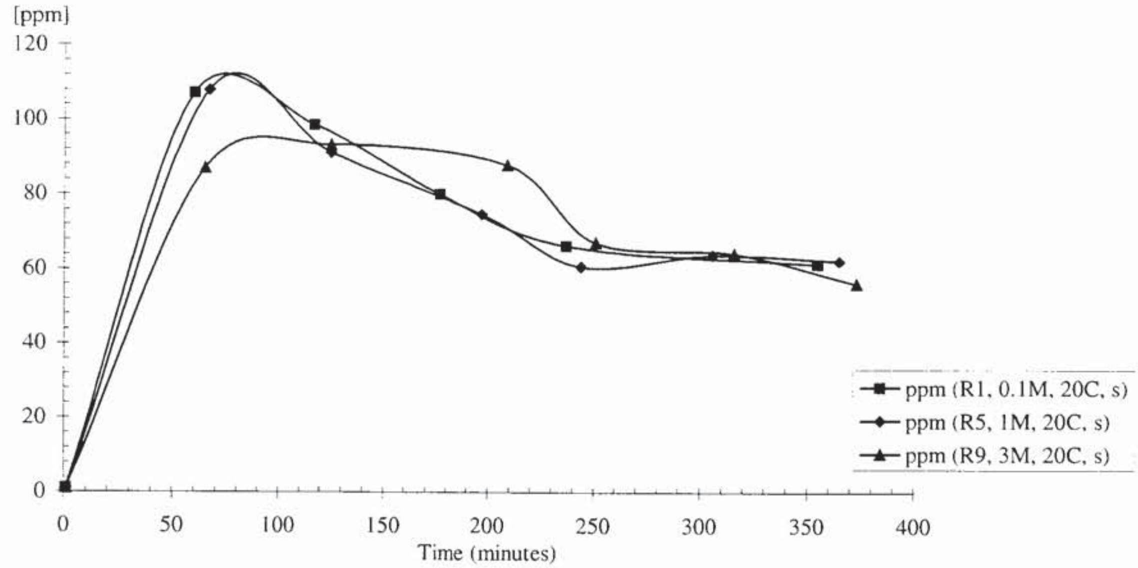

Figure Appendix E .9: Small biomass 20°C hydrochloric acid wash - potassium concentration in solution versus time

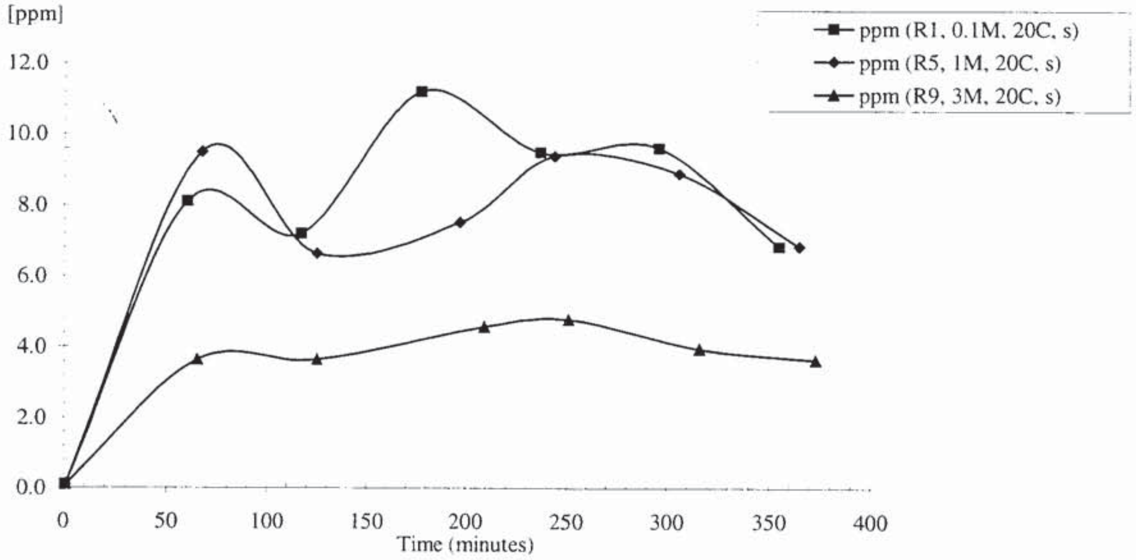

Figure Appendix E .10: Small biomass 20°C hydrochloric acid wash - sodium concentration in solution versus time

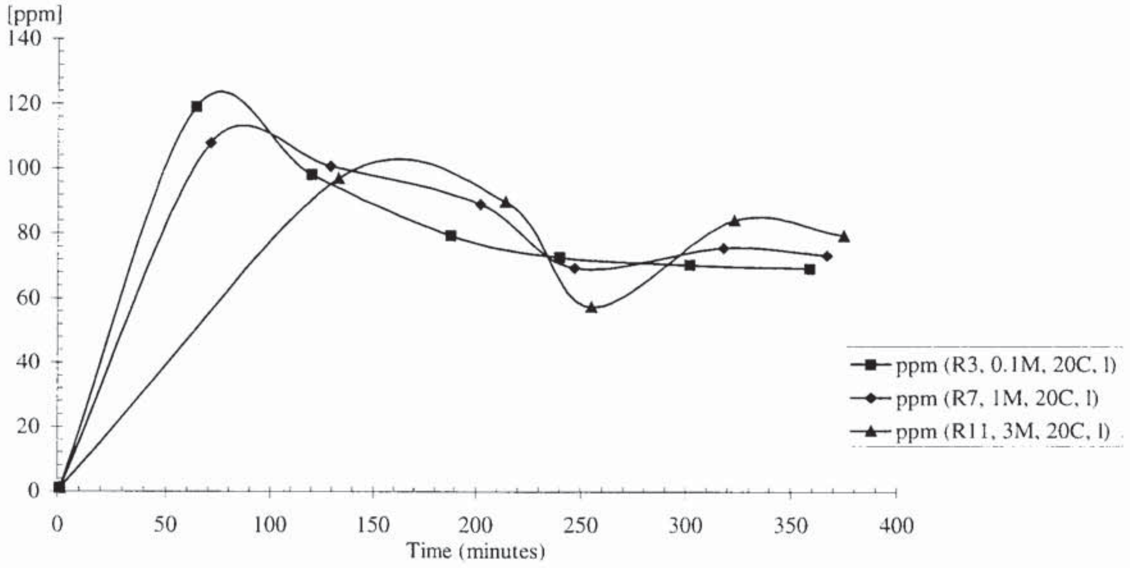

Figure Appendix E .11: Large biomass 20°C hydrochloric acid wash - potassium concentration in solution versus time

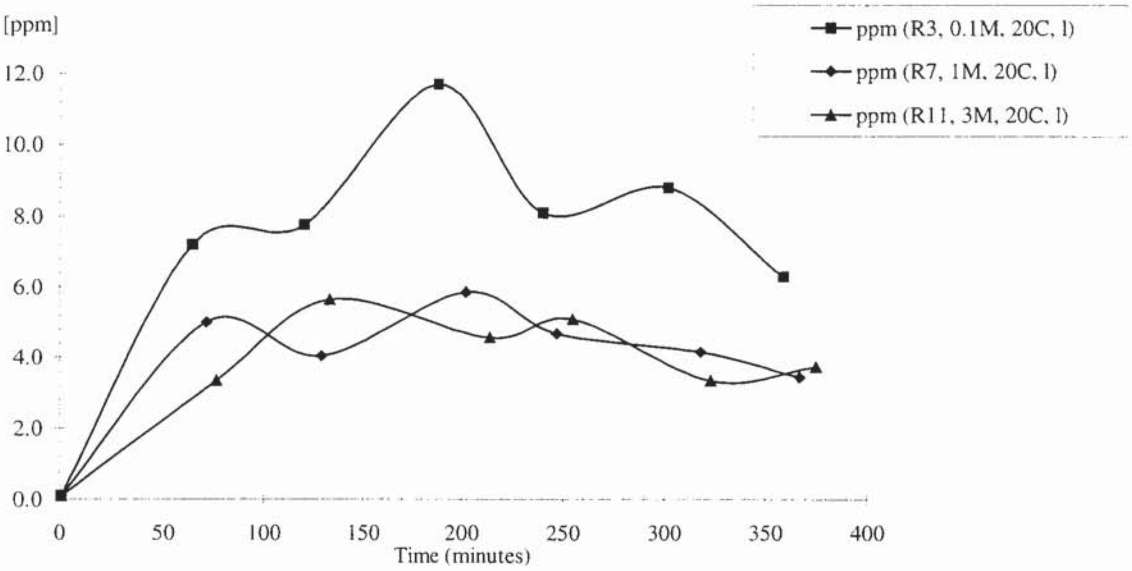

Figure Appendix E .12: Large biomass 20°C hydrochloric acid wash - sodium concentration in solution versus time

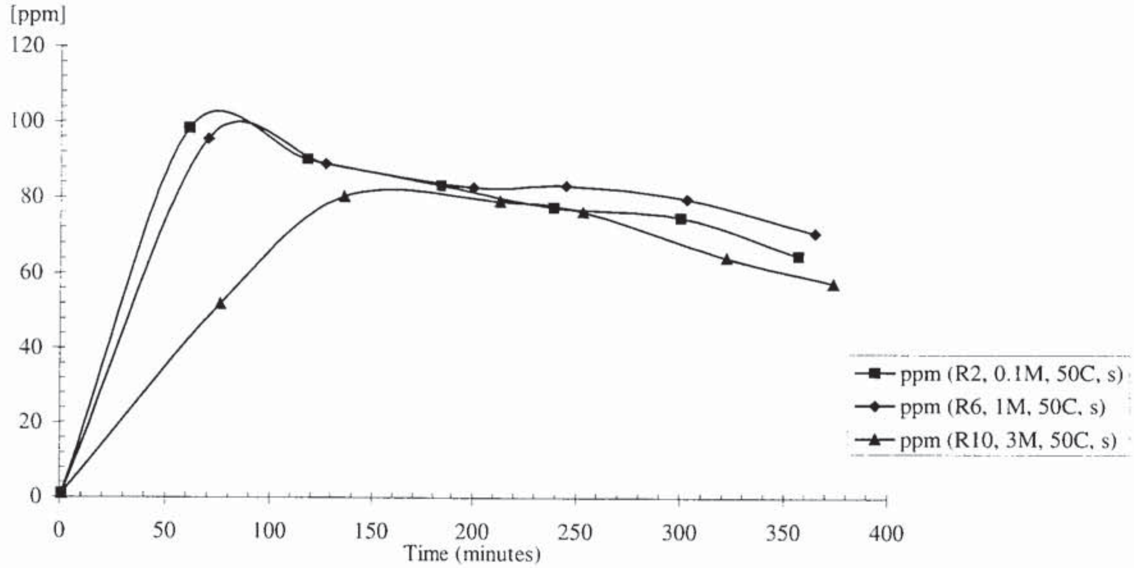

Figure Appendix E .13: **Small biomass 50°C hydrochloric acid wash - potassium concentration in solution versus time**

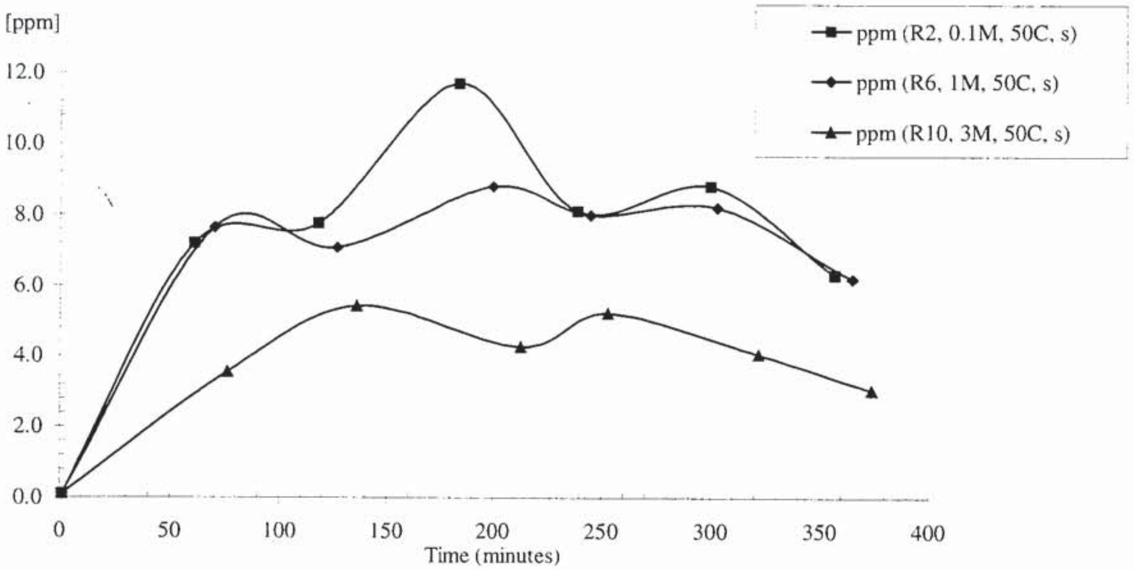

Figure Appendix E .14: **Small biomass 50°C hydrochloric acid wash - sodium concentration in solution versus time**

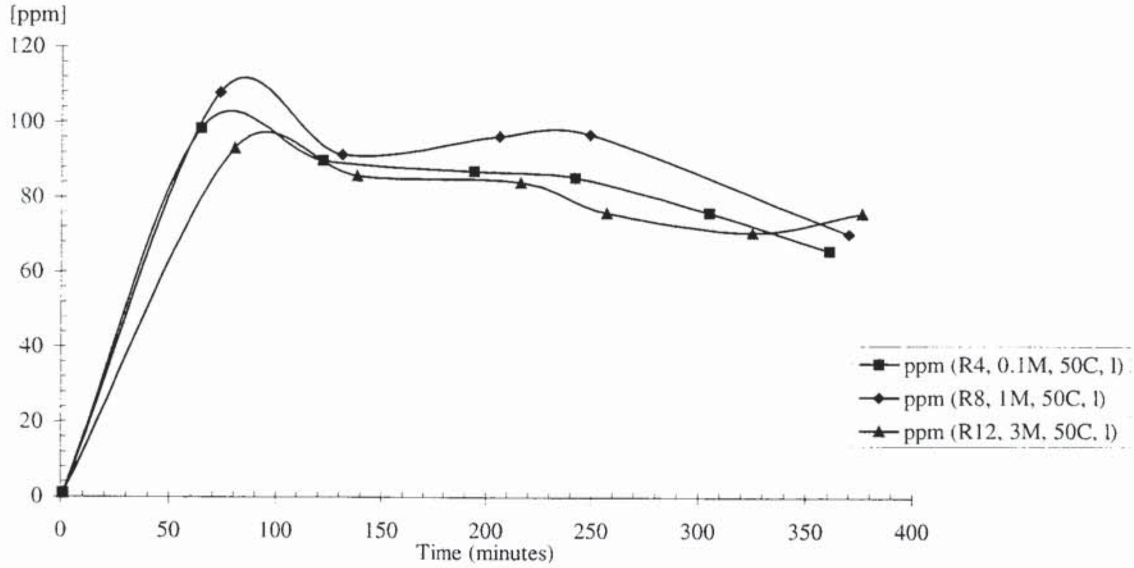

Figure Appendix E .15: **Large biomass 50°C hydrochloric acid wash - potassium concentration in solution versus time**

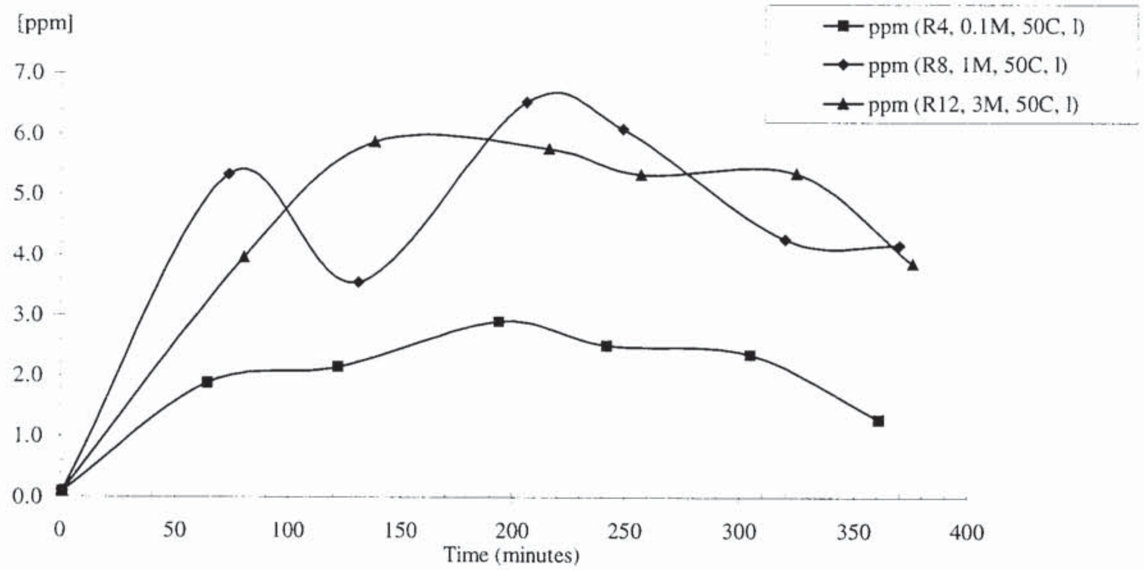

Figure Appendix E .16: **Large biomass 50°C hydrochloric acid wash - sodium concentration in solution versus time**

Phosphoric acid washing

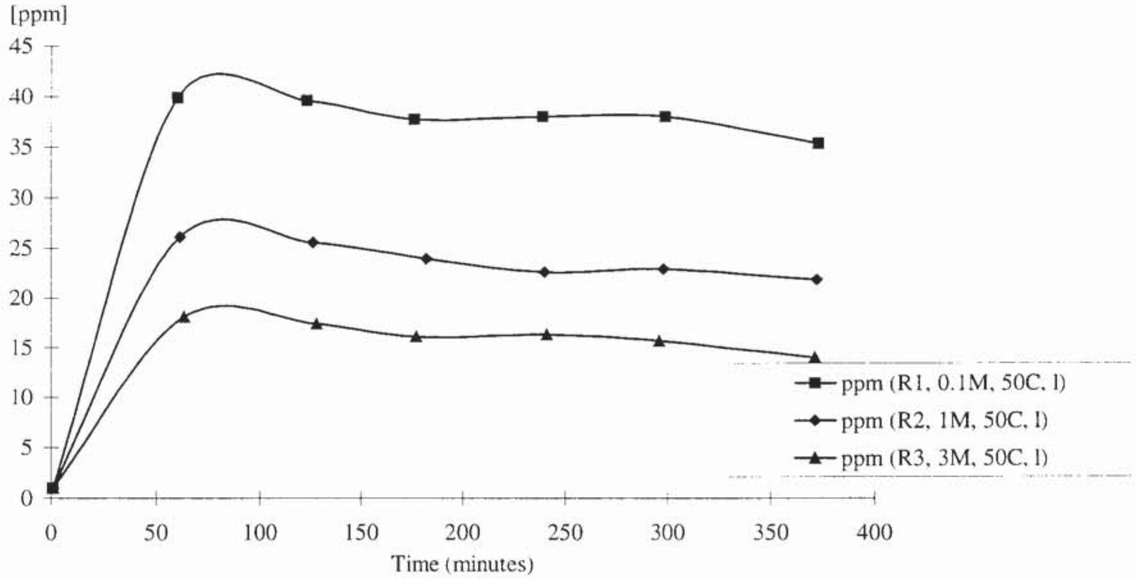

Figure Appendix E .17: **Large biomass 50°C phosphoric acid wash - potassium concentration in solution versus time**

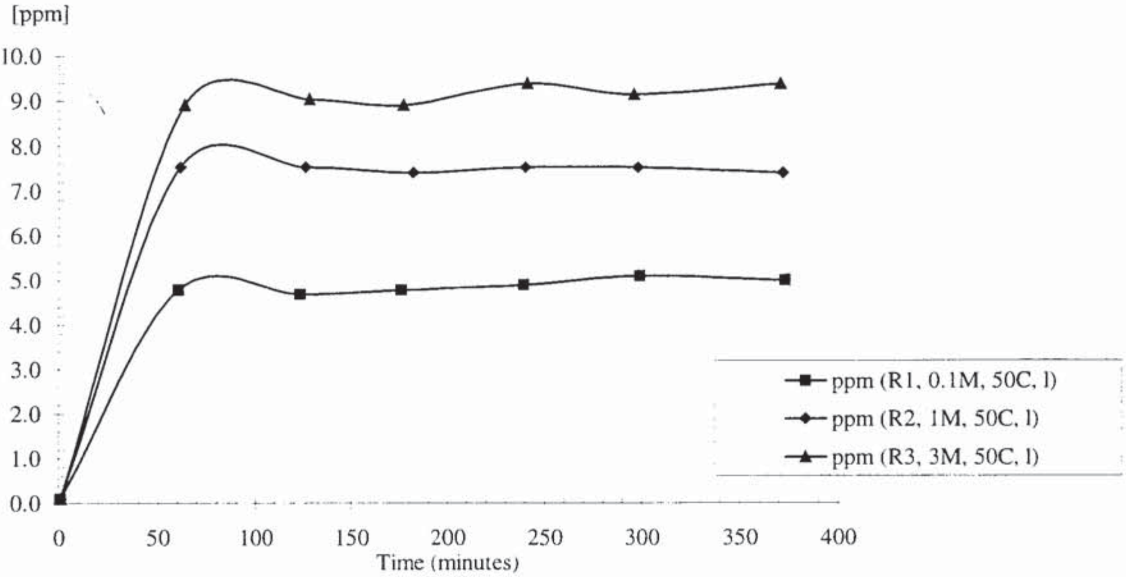

Figure Appendix E .18: **Large biomass 50°C phosphoric acid wash - sodium concentration in solution versus time**

Nitric acid washing

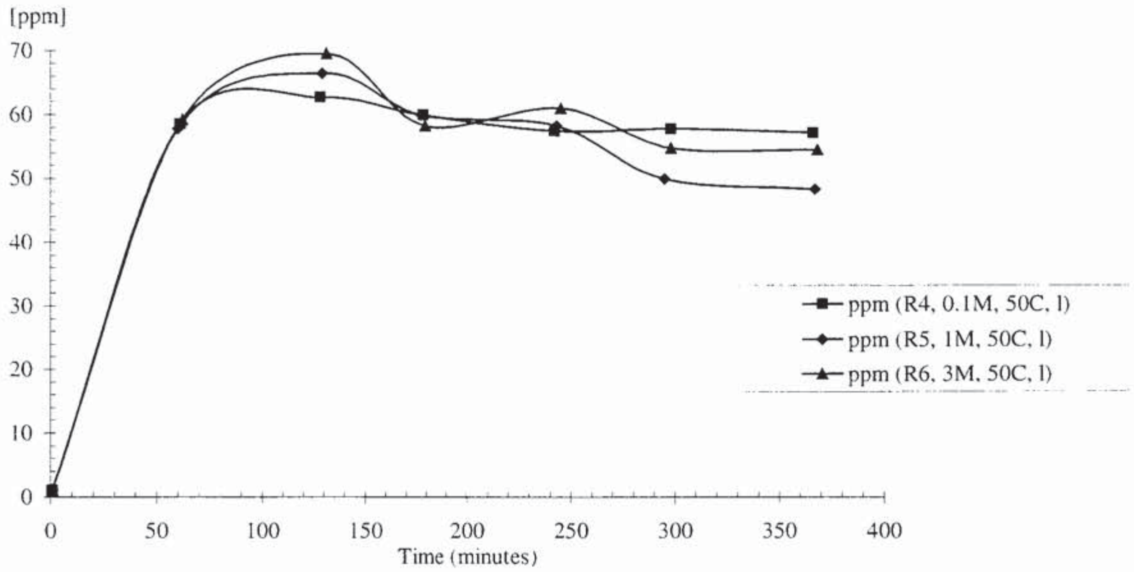

Figure Appendix E .19: **Large biomass 50°C nitric acid wash - potassium concentration in solution versus time**

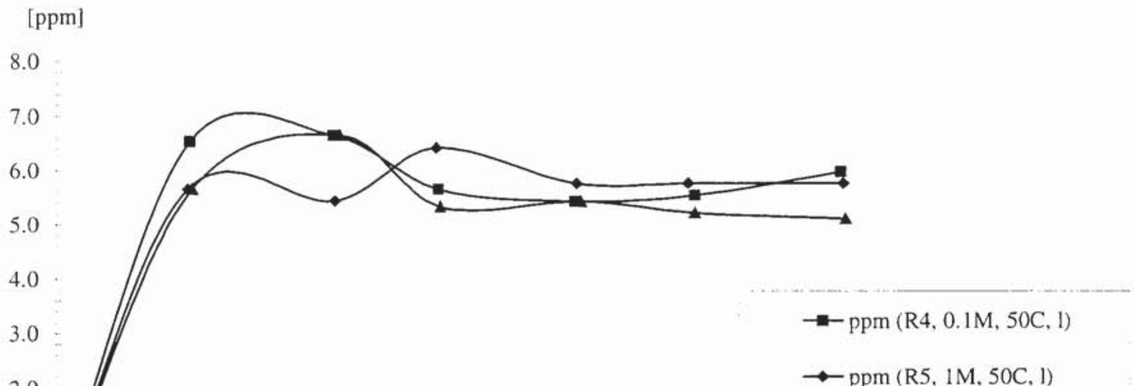

Figure Appendix E .20: **Large biomass 50°C nitric acid wash - sodium concentration in solution versus time**