AN ASSESSMENT OF PYROLYSIS FOR PROCESSING EMPTY FRUIT BUNCHES

A THESIS SUBMITTED
BY
NURHAYATI ABDULLAH, B.Sc., M.Sc.

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Aston University

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ASTON UNIVERSITY

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Nurhayati Abdullah
A candidate for the degree of Doctor of Philosophy
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THESIS SUMMARY

Pyrolysis is formally defined as chemical decomposition induced in organic materials by heat in the absence of oxygen. The pyrolysis process is an advanced conversion technology that has the ability to produce more useful and valuable pyrolysis liquids [bio-oil] in 65-75% yield on dry feed from a wide variety of waste and biomass streams. The oil palm industry in Malaysia produces wastes in large quantities of empty fruit bunch after shell and fibre, thus the presence of these oil palm wastes has created a major disposal problem.

There are two primary objectives of this work. The first objective is to determine the fast pyrolysis conditions required in order to maximise the pyrolysis liquid yield from the empty fruit bunches [EFB] waste. The second objective is to improve the quality and quantity of pyrolysis liquid by water washing pre-treatment of the EFB prior to pyrolysis.

The pyrolysis liquid yield is affected by the reactor process parameters for a particular biomass feedstock. The maximum pyrolysis liquid yield has been determined along with the temperature and vapour residence time at which this maximum occurs by a series of pyrolysis experiments over the temperature range of 400-600°C and the vapour residence time range of 0.79-1.32s.

Pre-treatment technique by water washing have been devised with particular emphasis on the removal of ash, which is required to modify the pyrolysis reaction sufficiently to produce homogenous bio-oil. The water washing experiments were designed and carried out at temperatures between ambient and boiling for a range of feestock sizes using soaking or stirring method, with the objective to gain a better understanding of the basic factors impacting water washing of EFB that will provide a basis for subsequent techno-economic optimisation.

The reduction of ash content to less than about 3 mf wt% required in order to produce homogenous liquids or to avoid phase separation of liquids. The organics yield achieved up to 61.34 mf wt% that brings the total liquids up to 72.36 mf wt% for the washed feedstock of ash content 1.03 mf wt%.

Future development of this work would be to employ a system that is capable to collect the liquid in one single collecting point for the purpose of analysing the liquid quality. As water washing had been investigated in sufficient detail, therefore, the techno-economic analysis on water washing pre-treatment would be done in the future.

Key words: EFB, pyrolysis, ash, water washing pre-treatment.

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CONTENTS

LIST OF TABLES

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

APPENDIX TABLES

LIST OF FIGURES

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

CHAPTER 9

APPENDIX FIGURES

1. INTRODUCTION

Fast pyrolysis of biomass at moderate temperatures [400-600°C] produces three products; pyrolysis liquid [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.

The main industry in Malaysia is production of palm oil, which results in substantial quantities of waste. This waste is currently left on the ground or burned, resulting in significant environmental problems as well as loss of a valuable renewable energy resource.

This research has two objectives. Firstly, to evaluate the suitability of one of the major waste products - empty fruit bunches [EFB] for pyrolysis and to determine the pyrolysis process conditions, for production of pyrolysis liquid. Secondly, to explore feedstock pre-treatment processes in order to optimise the pyrolysis liquids.

1.1 BACKGROUND TO THERMAL CONVERSION PROCESSES

Energy is essential for life as we know it today, and the provision of reliable energy sources, without adverse environmental effects, is one of the major problems facing the world. Most governments accept the need to change their energy consumption patterns in order to avoid the chances of global warming and provide a sustainable future. Uncertainty about the future of fusion research has increased the importance of "renewable" energy sources. Of the various possible renewable energy options, wood and other forms of are widely considered to be major potential fuels and renewable sources of energy for the future. Environmental concerns over fossil fuel usage and the greenhouse effect were expressed and stricter emission regulations were issued when petroleum supplies were limited until in the 1980's (1).

The term 'biomass' refers to organic matter which can be converted into energy and is a versatile energy source. Biomass is one of the oldest and most well-established energy sources in the world which has a higher contribution to the overall energy supply (2). Biomass does not add carbon dioxide to the atmosphere as it absorbs the same amount of carbon in growing as it releases when consumed as a fuel. Furthermore, liquid fuels from biomass contain low quantities of sulphur and therefore give less impact upon conversion of the fuels in terms of sulphur dioxide emissions.

There is a wide range of processes available for converting biomass and wastes into more valuable fuels such as fuel oil, fuel gas or higher value products for the chemical industry (3). Converting biomass and wastes into a solid, liquid or gaseous fuel can be achieved by physical, biological [anaerobic digestion and fermentation], chemical or thermal methods. Thermochemical processing is one of technologies available which has received considerable attention for converting biomass into a more valuable and usable products.

There are four main thermochemical methods of converting biomass to provide energy (4):

a. *Direct Combustion* technology is commercially available and presents minimum risk to investors. The product is heat for steam production and hence electricity generation, which must be used immediately (5, 6). During this process, biomass is first pyrolysed to gases and vapours, and char, both of which are partially oxidised with oxygen in flaming combustion (7).

b. *Gasification* is a process to provide a fuel gas for combustion for heat, or in an engine or turbine for electricity generation (5, 6). This process is designed to produce non-condensable gases. Gasification is the addition of a small amount of oxygen or air directly to the reactor to provide the process heat by exothermic reaction of biomass with oxidant. The gas is very costly to store or transport so it has to be used immediately.

c. Pyrolysis is a process that occur when biomass is heated in the absence of an oxidising atmosphere to produce a mixture of solid char, condensable liquids and gases (7). The liquid product is referred to by many names including pyrolysis liquid, pyrolysis oil, bio-crude-oil, bio-oil, bio-fuel-oil, pyroligneous tar, pyroligneous acid, wood liquids, wood oil, wood distillates and liquid wood. The traditional pyrolysis processes make charcoal, while fast pyrolysis is an advanced process that can produce high yields of liquid with minimum of gas and char (8). This liquid fuel can substitute for fuel oil in any static heating or electricity generation application (5, 6). The liquid can also be used to produce a range of speciality and commodity chemicals (9).

d. *Liquefaction* process does not require preliminary drying of the feedstock. It operates at a relatively low temperature and it converts all of the biomass but leaving only a small unusable residue [about 5% of feedstock]. In general, this process converts the biomass into the mixture of gas [2–10 wt. %], char [5–40 wt. %] and oil [up to 40 wt. %] (10). The crude liquid product separates spontaneously from aqueous phase after the reactions. In liquefaction process, biomass is heated with alkali under pressure at temperatures up to 400°C.

Compared to other thermochemical methods as mentioned above, fast pyrolysis is at a relatively early stage of development (11). However, the process of fast pyrolysis is one of the most recent renewable energy processes and has received increasing attention since this process produces the liquid product, bio-oil, that is clean compared to charcoal and can be readily stored and/or transported, also the liquid's density is very high at around 1.2 kg/litre (8).

1.2 OIL PALM INDUSTRY IN MALAYSIA

Oil palm is the most important product from Malaysia that has helped to change the scenario of it's agriculture and economy. In 1994, Malaysia accounts for 51% of the world's palm oil needs, thus making Malaysia the largest palm oil producer in the world. Lignocellulosic biomass which is produced from the oil palm industries include oil palm trunks [OPT], leaves generated from re-plantation, leaves dropped from time to time, empty fruit bunches [EFB] and palm pressed fibres [PPF], shell and palm oil mill effluent palm [POME]. However, the presence of these oil palm wastes has created a major disposal problem. One of the unique aspects of Malaysian renewable energy sources is that the palm oil mill is self-sufficient in energy, using PPF, EFB and shell as fuel to generate steam in waste-fuel boilers for processing, and power-generation with steam turbines as described in Chapter 3.

1.3 OBJECTIVE

There are two main objectives to this research. The first objective of this research is to evaluate the suitability of the empty fruit bunches waste to the fast pyrolysis system. Fast pyrolysis is one of the most recent renewable energy processes that is described in detail in Section 2.1. This study is to determine the optimum pyrolysis process parameter [reactor temperature and vapour residence time], which capable to produce maximum pyrolysis liquids yield.

The second objective of this research is to explore feedstock pre-treatment water washing in order to eliminate the ash content in the feedstocks since the high ash content promotes the second reaction of thermochemical biomass process as mentioned in detail in Chapter 4.

1.4 STRUCTURE OF THE THESIS

The thesis is arranged into the following chapters:

Chapter 2, Fast Pyrolysis

This chapter describes the fast pyrolysis process and factors affecting pyrolysis products. The factors, which have the greatest influence, are reviewed in detail. This chapter forms the basis for the experimental work described in Chapter 5.

Chapter 3, Oil Palm Wastes

This chapter provides details of the biomass waste that are produce in Malaysia and demonstrates why safe, environmentally acceptable and efficient disposal is essential to the wellbeing and future Malaysia.

This chapter also describes generally about oil palm wastes as a lignocellulosic biomass, which can be categorised as woody biomass and non–woody biomass. These categories serve a guide to determine the type of biomass that will be investigated. This chapter also illustrates the biological structure and chemical structure of biomass, as this is important in its pre-treatment.

The oil palm plantation and the mass balance of the oil palm industry are reviewed in more detail. The oil palm industry produces wastes in large quantities of empty fruit bunch after shell and fibre. As the palm oil mill is self-sufficient in energy, empty fruit bunches could be important to process by using the pyrolysis technology.

Chapter 4, Pre-treatment of Feedstock by Water Washing

This chapter critically reviews past and current pre-treatment work of biomass water washing. Pre-treatment of feedstock by water washing is defined as a chemical process carried out by using the cold and hot water to eliminate the ash in biomass and modify the biomass lignocellulose polymers.

This chapter also reviews the pyrolysis experiment on de-ashed biomass. The study of pyrolysis on de-ashed biomass upon water washing pre-treatment has received very limited attention by researchers.

Chapter 5, Water Washing Experiments

This chapter describes experimental programme with the removal of ash content in the feedstock material. This is because high ash content in biomass promotes the second reaction of thermochemical biomass process and produces non-homogeneous liquids [two phase of liquids].

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

Chapter 6, Experimental Set-up

The characteristics of Empty Fruit Bunches [EFB] used in the experiments are described in this chapter. Samples received were in dry condition, and in the form of whole bunches. Thus, these samples were chopped and ground to get the feedstocks in correct sizes.

Pyrolysis experiments were carried out in a fluidised bed reactor with a nominal capacity of 150g/h. The equipment and procedures for operating the pyrolysis system, analytical equipment and method obtaining mass balances are described. A critical assessment of the mass balance and its analytical procedures are included.

Chapter 7, Experimental Programme and Results

A number of unwashed feedstock were fast pyrolysed over a range of temperatures from 400-600°C. In all cases the maximum yield of organics has been determined along with the temperature at which this maximum occurs. The results from a variety of feedstocks from published sources are included and critically compared with results from this work.

Chapter 8, Conclusions

This chapter draws conclusions based on the work presented in previous chapters.

Chapter 9, Recommendations

This chapter gives recommendations for the continuing assessment of pyrolysis for processing empty fruit bunches by employing a system which had a single collection point. The development of water washing pre-treatment and a suggestion for another application is also discussed in this chapter.

2. FAST PYROLYSIS

This chapter describes the fast pyrolysis process by means of a literature review. The fast pyrolysis parameters, which have the greatest influence on product yield and liquid quality, are discussed in detail.

2.1 PRINCIPLES OF FAST PYROLYSIS

Fast pyrolysis is a thermal decomposition process that occurs at moderate temperatures in which the biomass is rapidly heated in the absence of oxygen or air to produce a mixture of condensable liquids, gases and char (12). It is an advanced process that is carefully controlled to give high yields of liquid with minimum of gas and char (8). This liquid can be used as a substitute for liquid fossil fuels in some applications (13).

The component of wood which has received the most attention is cellulose due to its high abundance in most biomass types, and is described in Section 3.7.2. The proposed pathways of cellulose to illustrate the fundamental steps in pyrolysis are reviewed (14,15,16,17). Kilzer and Broido (14) reviewed cellulose pyrolysis and proposed the reaction mechanism as shown in Figure 2.1.

Figure 2.1: Pure cellulose pyrolysis pathway of Kilzer and Broido (14)

This model suggested that the lower temperature pathway was evident at temperatures less than 280°C, while depolymerisation of the cellulose occurred with the formation of levoglucosan as the main volatile product at temperature above 280°C. As noted by Kilzer and Broido (14), anhydro-derived sugars were identified in products formed at temperature 350-500°C. They carried out the experiments at 420°C and they found the product yields and compositions were not representative of the lower temperature route [i.e. less than 300°].

Shafizadeh (15) proposed a more detailed reaction pathway than that proposed by Kilzer and Broido (14) cellulose pyrolysis as shown in Figure 2.2. His model described that due to dehydration reactions, the main products being water, char, CO and CO_2, as shown in pathway 1 that occurs at temperature below 280°C. Pathway 2 is preferred at temperature of 300-500°C with depolymerisation giving levoglucosan as the main product. Pathway 3 is preferred at temperature above 500°C resulting in the formation of low molecular gases and volatile products.

Figure 2.2: First cellulose pyrolysis pathway by Shafizadeh (15)

Shafizadeh then carried out the pyrolysis experiment on de-ashed biomass upon water and acid washing pre-treatment in order to enhance yields of levoglucosan. He found that acid washing rather than water washing increased the yields of levoglucosan and liquids more significantly. However, he confused whether the increased yields were because of the ash removal, a modification of the cellulose structure, or the addition of small quantities of acid to the cellulose structure, or a combination of all three. Therefore, he tried to explain by introducing the second pathway as shown in Figure 2.3.

Figure 2.3: Second cellulose pyrolysis pathway by Shafizadeh (adapted from 11)

Shafizadeh type kinetic model or so called Broido-Shafizadeh model as shown in Figure 2.3 are perhaps the most widely used for cellulose pyrolysis and also in the belief that cellulose is representative of whole wood. Therefore this model can be applied for the whole biomass (11).

Several studies have been published describing results from the fast pyrolysis of biomass with different ash content, for example, Scott et al. (18,19), Nurul et al.(20). Scott and Piskorz (18) carried out fast pyrolysis experiment on aspen-poplar wood of ash content 0.39 mf wt%. In this research, they pyrolysed the feedstock at temperature from 450-650°C with very short residence time from 1.07-0.38s. Scott et al (19) investigated the pyrolysis experiment on corn stover and wheat straw as a non-woody biomass which have high ash content compared to woody biomass. The ash content of corn stover and wheat straw is 11.0 mf wt% and 4.6 mf wt% respectively. Nurul et al. (20) studied the characteristics of liquid and char produced from pyrolysis experiment on oil palm shell. Oil palm shell can be categorised as non-woody biomass and it has ash content of 2.3 mf wt%. The results from a variety of feedstocks as mentioned above will be discussed and critically compared with results from this work, as report in Section 7.4. A number of researches had been done by the bio-energy research group at the University of Waterloo over the last several years (21,22,23,24). In these researches, they were successful in determining the optimum conditions for maximum liquid yields from various biomass materials, i.e. IEA poplar, St. Lawrence poplar, wayman poplar, biohol pine and stake poplar. These pyrolysis experiments were operated at temperatures from 450–550°C with a very short volatiles residence time [0.5s].

Normally, the maximum liquid yields produced from woods is up to 80 wt% on dry feed basis at 500–520°C with vapour residence times not more than 1s (6). If residence times are very short, depolymerisation of lignin will be incomplete due to random cleavage and inter-reaction of the lignin macromolecule resulting in a less homogenous liquid product. Longer residence time can cause secondary cracking of the primary products, reducing yield and adversely affecting bio-oil properties. After cooling and condensation, a dark brown mobile liquid is formed which has a heating value of about half that of conventional fuel oil.

The essential features of a fast pyrolysis process for producing liquids are (6):

- very high heating and heat transfer rates at the reaction interface, which usually requires a finely ground biomass feed, > 10 000°C/s.
- carefully controlled pyrolysis reaction temperature of around 500°C and vapour phase temperature of 400 – 450°C.
- short vapour residence times of typically less than 2 seconds.
- rapid cooling of pyrolysis vapours to give the bio-oil product.

A conceptual schematic of fast pyrolysis is shown in Figure 2.4. The reactor is constructed of stainless steel with full gas flow and temperature control [see Section 6.3]. The preparatory stages included oven-drying, grinding and sieving of the feedstock [see Section 6.2].

Figure 2.4: Conceptual Fast Pyrolysis Process (adapted from 11)

2.2 FAST PYROLYSIS TECHNOLOGY REQUIREMENTS

Fluidised bed reactor had been used for all tests in this work, therefore the following discussion focuses on the requirements of the fluidised bed reactor technology for fast pyrolysis.

2.2.1 Reactor Configuration

Pyrolysis has received considerable creativity and innovation in devising reactor system that provide the essential ingredients of high heating rates, moderate temperatures and short vapour product residence times for liquids. Three main methods of achieving fast pyrolysis are ablative pyrolysis, fluid bed and circulating fluid bed pyrolysis and vacuum pyrolysis (6). Fluid beds and circulating fluid beds are the most popular configurations due to their ease of operation and ready to scale-up. The 'best' method is yet to be established with most processes giving 65–75 wt% liquids based on dry wood input (6). A more detailed review of a typical bubbling fluidised bed reactor system has been included in Section 6.3 since this was the technology used during experimentation.

2.2.2 Heating Rate and Heat Transfer

The high heating rate is necessary to heat the particles sufficiently. Many researchers recognised that high biomass heating rate as a key feature for minimisation of char formation (25, 26, 27, 28). According to Maniatis and Buekens (29), heating rate had little effect on the yield of products above 100K/s.

The two dominant modes of heat transfer in fast pyrolysis technologies are conductive and convective. Two important requirements for heat transfer in a pyrolysis reactor (13):

1. Transfer to the reactor heat transfer medium [gas and solid in fluid and transport bed reactor].
2. Transfer from the heat transfer medium to the pyrolysing biomass.

A high transfer rate can be achieved by adopting these following methods in fluidised bed reactor:

a. Hot fluidising gas

Fluidising nitrogen was heated before entering the reactor with a probable small contribution from gas-solid convection heat transfer of up to 10%.

b. Fluidising medium

Fluid bed pyrolysis utilises sand as the fluidising medium and the inherently good solids mixing to transfer approximately 90% of the heat to the biomass by solid-solid heat transfer.

c. Ground biomass feed

The thermal conductivity of biomass is very poor [0.1 W/mK along the grain], and hence the time taken for the centre of the particle to reach the reaction temperature increases with particle size. The biomass particles have to be very small to fulfil the requirement of rapid heating.

2.2.3 Feedstock Preparation

Biomass behaviour in the reactor will be influenced by the presence of water in the biomass. Wetter biomass takes longer to reach reaction temperature. Therefore, drying is usually required to less than 10% moisture content on a wet basis for most laboratory experiments and commercial processes. Pyrolysis liquids always contains at least about 15% water at an assumed product yield of around 60 wt% organics and 11 wt% reaction water (13). The presence of water in pyrolysis liquid is complex as it affects stability, viscosity, pH, corrosiveness, and other liquid properties. Furthermore, this water cannot be removed by conventional methods such as distillation.

2.2.4 Reaction Temperature

Reaction temperature is the temperature at which biomass is pyrolysed. This temperature is difficult to measure. Reactor temperture is much higher due to the need for a temperature gradient to affect heat transfer. Therefore, the best approximation to the true temperature of pyrolysis will be the average reactor temperature. In general, a total product yield with a maximum at typically 500-520°C for most forms of woody biomass, but other crops may have maxima at different temperatures (13).

2.2.5 Rapid Quenching of the Vapours

In fast pyrolysis process, the most accepted theory is that primary vapours are first produced. These primary vapours then further degrade to secondary tars and gases if held at a high temperature for long enough for secondary reactions to occur. Fast pyrolysis process involves very high heating rates combined with moderate temperatures of less than 650°C, short residence times and rapid quenching of liquid pyrolysis products in order to produce liquids yields of up to 70% wt on a dry feed basis. These high heating rates, of up to a claimed 1000°C/s or even 10 000°C/s, at temperatures below about 650°C and with rapid quenching, cause the liquid intermediate products of pyrolysis to condense before further reaction breakdown higher-molecular-weight species into gaseous products (4). Most workers have used some system of rapid cooling of the vapours in order to collect the highest yield of pyrolysis liquids and avoid secondary reaction.

2.2.6 Short Vapour Residence Time

The vapour residence time is a measure of how long the pyrolysis vapours remain in the hot reactor environment. The longer the vapours remain in the hot reactor the more opportunity they have to react or continue reacting, thus cause secondary cracking of primary product. Therefore, yields of specific products and organics liquids will be reduced (7). Boroson et al. (30) have demonstrated that the average molecular weight decreases with the degree of secondary reaction, i.e. increasing residence time and temperature. Secondary reactions lead to the production of low molecular weight products and gas and should be avoided for the production of liquid.

2.2.7 Char Removal

Char is usually present in the pyrolysis liquids, due to inefficiencies in char removal equipment such as cyclones leading to carryover of char into the liquid collection system (31). The particle size of the char formed is highly dependent upon the particle size of feed used, the relative attrition of the char by the pyrolysis reactor system and the mechanism of char formation. Many of the pyrolysis reactors act as particle classifiers, retaining the char in the recycle loop until it is ground down fine enough to not be collected with the recycled sand, larger char, and/or partially pyrolysed materials (7).

2.3 FACTOR AFFECTING PYROLYSIS PRODUCTS

The factors which affect pyrolysis products have been discussed by many researchers (32,33,34). This chapter will review those factors that have a significant effect on yields and properties of pyrolysis products.

2.3.1 Type of Feedstock

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. In considering the overall chemical composition of biomass, it must be emphasized that biomass is not a homogenous material. Just as cell dimensions vary in wood taken from various parts of the tree, so does its chemical composition (35). For example, poplar heartwood will be different to poplar bark. Each component will also differ from species to species, for example lignin from poplar will be different from that from pine. Therefore, every biomass type when fast pyrolysed produces different yields of liquid, char and also different chemicals in the liquid. The analysis results of typical biomass feedstocks, as a rough guide it was assumed that about one half of wood is cellulose, one-fourth hemicellulose and one-fourth lignin is shows in Table 3.4.

Hague (34) has successfully pyrolysed a range of feedstocks such as pine bark, rape straw, rape meal, miscanthus, pine and poplar using a 150g/h fluidised bed reactor. He found that the pyrolysis of agricultural residues tends to result in the lowest yield of organics, whereas wood tends to give the highest yield of organics. Meier et. al. (36) had studied physical properties [i.e. water content, viscosity and stability] of pyrolysis liquids produced from different wood components. They found that both the viscosity and the water content increase with the time and temperature of storage.

2.3.2 Feedstock Particle Size

The particle size of biomass has an important bearing on the ability to be heated quickly in a given heat flux environment. Biomass particles are rarely spherical or even cubicle, but tend to have a length that is several times larger than the thickness or the width like a pin chip (37). Heat is transferred from the hot gas to the biomass particle and from the hot solid to the biomass particle by convection and conduction respectively. A heated volumetric element within the biomass particle subsequently decomposes into char and vapour fragments. Due to the volumetric vapour production, a pressure is built up inside the porous particle, which is at a maximum in the particle centre and decreases towards the particle surface. Vapours formed inside the biomass pores are subject to further cracking, which leads to the formation of char, gases and thermally stable tars as shows in Figure 2.5 (38).

Figure 2.5: Decomposing wood particle including reactions involved (38)

Nurul et al. (20) studied the pyrolysis behaviour of palm shell and found that the highest liquid yields were obtained with the middle size of particle size 212–425 µm. Scott et al. (18) had pyrolysed aspen poplar of particle sizes 44-105µm, 105-250µm and 250-500µm, and they found that the highest organic yields are obtained with aspen poplar particles of intermediate size [105-250µm]. Organics yields of 51.0, 58.9 and 53.0 mf wt% were obtained for each size fraction respectively. This may be due to the fact that the smaller size particles were either overheated, or too quickly blown from the reactor before pyrolysis take place producing more char; and the larger size particles were not adequately heated up so causing incomplete pyrolysis. The secondary reactions within the particle become significant with increasing particle size.

2.3.3 Feedstock Pre-treatment

Pre-treatment covers both the physical preparation of the biomass including drying, comminuting, and screening, and chemical modification. Comminution and screening are methods used to reduce the particle size and change the particle shape. In chemical modification, pre-treatment is defined as a chemical process carried out prior to pyrolysis, which either modifies the biomass lignocellulose polymers or adds substances into the lignocellulose complex (34).

The removal of biomass components prior to fast pyrolysis has several potential applications and benefits.

1. The ash component is known to catalyse certain fast pyrolysis pathways. Its removal will influence the pyrolysis reaction pathway (19,39). The ash tends to be incorporated into the char during fast pyrolysis. There is a small amount of char in the pyrolysis liquid, therefore the alkali metals contained in the liquid could cause fouling and corrosion problems if the pyrolysis liquid is used in a fuel application.

2. The number and diversity of biomass chemical pre-cursor entering the pyrolysis reactor will be reduced if the number of biomass components are reduced. However, the particular biomass components tend to form specific chemical when pyrolysed (40). If hemicellulose component of a biomass was removed, it will produce lower product yield because less material being fed into the pyrolysis reactor. However, by removing the hemicellulose components the levoglucosan yield may increase.

3. Certain chemicals from the hemicellulose component such as acetic acid and furfural derived products cause much of the odour problems associated with pyrolysis, thus this problem will be reduced by removing the hemicellulose component (34).

The loosely bound ash is easily removed, typically using demineralised water to wash it from the cells. However, the ash, which bound to the cell walls and the hemicellulose are 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 and water washing pre-treatment will only be able to remove approximately 50% of the ash. The ash content of wood is usually low between 0.2-2.0% [e.g. pine 0.23%, poplar 0.46% and pine bark 1.94%]. Empty Fruit Bunches [EFB] is the feedstock used in this work, had high ash content of 5.4 mf wt% as shown in Table 3.4.

The effects of demineralisation have been investigated by a number of researchers. Most researcher has been working out with acid washing while very little water washing experimentation has been carried out. A review of pre-treatment with particular emphasis on the removal of ash will be presented in Chapter 4. Investigation on the pyrolysis reaction that would increase the yield of some specific chemicals is beyond the scope of this thesis. The removal of ash, typically by a water washing process, is the focus of this work reported in Chapter 5.

2.3.4 Feedstock Moisture Content

The effect of water in biomass is complex since it will influence the biomass behaviour in the reactor, the physical properties and the heating value of the recovered pyrolysis liquid. The feed is normally dried to less than 10 mf wt% in most laboratory experiments and commercial processes [29,41,42,43,44]. This is because higher pyrolysis liquid yields are obtained from dryer feedstock, and will be illustrated below.

Gray et al. (42) studied the effect of moisture on ash free Woodex. 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. Kelbon (43) had performed pyrolysis of large moist particles. She investigated the effect of moisture content by pyrolysing feedstock of

10 mf wt%, 60 mf wt% and 110 mf wt%. She found that by increasing the water content of feedstock, the onset of pyrolysis will be delayed due to moisture vaporisation by as much as 150 seconds. Maniatis and Buekens (29) had performed pyrolysis on a bone dry sample and a sample containing 10% moisture. They found that pyrolysis of the moist sample resulted in about 10% more water in the product. This result is in agreement with Piskorz (44) which reported by Peacocke (32), 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.

According Hague (34), 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.

The presence of water in the biomass delays the onset of pyrolysis, therefore, 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 and maybe also for the production of pyrolysis liquids. Therefore it would seem likely that feedstock moisture contents in excess of 10 mf wt% should be avoided.

2.3.5 Reactor Temperature

Reactor temperature is the measurable variable which indicates the temperature of pyrolysis is being carried out. Most researchers (18,24,45,46) had proved that the reactor temperature is the main controlling factor on product yields and also the yield of chemicals in the pyrolysis liquid.

Many researches had proved that the maximum organic liquids can be obtained at reactor temperature of 500°C, whereas the char yield decreases and gas yield increases with temperature (18,19). According to Peacocke (32), at 500°C, the energy supplied to the biomass is sufficient to reach the decomposition temperature, provide the energy required for the endothermal heat of pyrolysis and vaporize the organic liquids without any additional energy available for significant secondary reactions. Secondary reactions happen once the primary volatile product is broken down into smaller molecule hydrocarbons.

Hague (34) had done a thoroughly review in his PhD thesis. A brief summary was that the maximum organic liquid yield is obtained at 400-600°C, depending on feedstock type (24, 45, 46, 47). Fast pyrolysis product yields are illustrated in Figure 2.6 (48).

Figure 2.6: Flash Pyrolysis Product Yields versus Temperature (48)

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 (24), to 85 mf wt% for sweet gum hardwood at 627°C (49). 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 (19,23,50). Gas and water yields remain relatively stable up to around 500°C. Above 500°C, 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 (51,52).

2.3.6 Vapour Residence Time

Vapour residence time is a measure of how long the pyrolysis vapours remain in the hot reactor environment. It is can define as the ratio of net empty reactor volume to total vapour volumetric throughput [i.e. the sum of the carrier gas and product gas/vapour].

The significant of gas/vapour residence time is that long residence times [>2s] at temperatures above 500°C lead to reduced yields of organic liquids due to secondary gas vapour phase reactions. 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] (19,39). Therefore, it is necessary to minimize the rate of secondary reactions if a high liquid product yield is desired. It is shows that the residence time having a significant effect on product yields.

Scott and Piskorz (53) had studied the effect of vapour residence time on 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, and the results are shown in Figure 2.7. The results showed that as vapour residence time increases the yield of organic liquids decreases.

Figure 2.7: Organic liquid yield with gas/vapour residence time (53)

2.3.7 Secondary Vapour Cracking

Biomass is a complex substance and its thermal decomposition is multistage complicated process. Broido-Shafizadeh model was expected to be the most general chemical pathway of cellulose pyrolysis but they can be also applied to the whole biomass, which are shown as Figure 2.3.

The model has two competing pathways namely fragmentation and depolymerisation as shown in Figure 2.8 (34). 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 2.8: Depolymerisation and fragmentation of cellulose (34)

Longer residence time can cause secondary cracking of the primary products at temperature above 500°C, reducing yield and adversely affecting pyrolysis liquid properties. Secondary reactions lead to the production of low molecular weight products and gas and should be avoided for the production of liquids and speciality chemicals. After rapid cooling and condensation reactions at vapour product temperatures below 400°C, a dark brown mobile liquid is formed. However, these low molecular weight volatiles could be chemically re-condensed to give higher weight compounds in the pyrolysis during cooling process. If the volatiles or vapours remain in the hot reactor the more opportunity they have to react or continue reacting. It means that they will further crack to small molecular or permanent gases, those are so-called secondary reaction in pyrolysis process. According to Browne (54), the secondary reactions increases the quantities of water and carbon dioxide in the gaseous products without increasing the quantity of carbon monoxide.

Many researchers had proved that maximum liquid yields are obtained with high heating rates at reaction temperatures around 500°C and with short vapour residence times to minimise secondary reactions (55).

2.4 SUMMARY

Fast pyrolysis technologies and factors which control fast pyrolysis products have been reviewed and discussed. The factors which have the largest effect on modifying the product will form the basis for the experimental work described in Chapter 6.

Reactor temperature has given the largest influence on product and chemical yields. Many researchers had found 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.

Secondary reactions lead to the production of low molecular weight products and gas and should be avoided for the production of liquids and speciality chemicals. The presence of ash in the biomass has a profound effect on the pyrolysis product and liquid yields as high ash in biomass generally promotes secondary reactions of primary pyrolysis products (19,39). The effect of ash will be reviewed and discussed in Chapter 4.

3. OIL PALM WASTES

This chapter reviews the renewable energy industry in Malaysia. Malaysia introduced renewable energy as the country's fifth fuel source after oil, gas, coal and hydro-power. Malaysia is the world's largest producer and exporter of palm oil, however, the presence of oil palm wastes has created a major disposal problem, therefore, oil palm waste such as Empty Fruit Bunches could be important to process by using the fast pyrolysis technology.

This chapter also describes three keys area which influence the fast pyrolysis and pre-treatment of biomass. The first area is characteristics of biomass which can be categorised as woody biomass and non-woody biomass. The second area is the biological structures of biomass which make up biomass. The third area is chemical structure of biomass. The biological structure of biomass has a profound effect on how difficulty to break it chemically and physically.

3.1 INTRODUCTION

Malaysia has been using energy at about 340 million boe every year. The total contribution of biomass to the primary energy supply of Malaysia has been estimated to be at least 2.5 MTOE in 1995 (56,57). In other words, the total contribution of biomass in agricultural sector is about 14% of the primary energy supply, but this is only 26.8% of the total biological waste in Malaysia, and the balance of the waste [73.2%] would be left to decompose naturally or by burning. If this waste had been used to produce energy, it is expected that the biomass contribution for the energy utilisation in the country would have increased to 53% (58).

Among the renewable energy sources, biomass is a primary source because Malaysia is an agriculture-based country which is rich in agricultural and forest waste for producing bio energy (59).

3.2 ENERGY STRATEGY IN MALAYSIA

The Malaysian government introduced the National Energy Policy in 1979 which constitutes the framework for present and future energy programmes in the energy sector (60):

- A supply objective, which is to provide adequate, secure and cost-effective energy supply through developing and utilising competing energy resources, both renewable and non-renewable.
- A utilisation objective, which is to promote efficient utilisation of energy and to discourage wasteful and non-productive patterns of energy consumption.
- An environmental objective, which is to minimise the negative environmental impacts of the energy supply chain [i.e. energy production, transportation, conversion and utilisation].

In 2001, the Ministry of Energy, Communications and Multimedia launched the Small Renewable Energy Power [SREP] Programme to encourage and intensify the utilisation of renewable energy [oil palm wastes, wood residues and rice husks] for grid-connected electricity (61,62). Under this programme, simplification of the renewable energy purchase agreement [REPA] and connection to the grid between renewable energy developers and the incumbent utility will be encouraged. This is in line with the fifth fuel resource under the country's Fuel Diversification Policy, as stipulated in the objectives of the Third Outline Perspective Plan for 2001 – 2010 [OPP3] and the Eighth Malaysia Plan for the period from 2001 to 2005 (63).

The total power generation in Malaysia in 2000 was 65,162 GWh with the mean power demand at 7,440 MW based on Statistics of the Electricity Supply Industry in Malaysia (63). Tenaga National Berhad is expected to install an additional 4530 MW to its existing generating capacity resulting in a total generation capacity of 11,970 MW by year 2005. Based conservatively on the year 2005, the projected generation capacity is 11,970 MW for Malaysia, a target of 5% of the country's total power generation by renewable energy of about 600 MW. Therefore, a total of 60 units or 120 units of renewable energy biomass-based power plants of 10 MW or 5 MW each respectively will be set up by the year 2005. A 5.2 MW power plant is going to be set up at Pantai Remis Palm Oil Mill in Perak state using, for the first time, EFB from the mill. It will be connected to the grid to supply power to a small town located a few kilometres from the station and export to TNB [Tenaga National Berhad] at the rate of US$0.043 kWh^{-1} (62,63,64).

As part of the Government's effort to reduce the national stock of crude palm oil [CPO], the combustion of medium fuel oil blended with CPO commenced at Prai power station in March 2001 marking a new epoch in the history of power generation in Malaysia. In addition, a more ambitious plan to develop a 500,000 tonne per year palm oil diesel plant to provide alternative fuel for diesel engines, will certainly make inroads in the oil-intensive transport sector. A detailed feasibility study is already under way and palm diesel is expected to enter the market by 2006 (65).

Thus, new and renewable energy is indeed in line with the national energy policies and should be pursued equally with other sources stipulated in the plan.

3.3 RENEWABLE ENERGY SCENARIO IN MALAYSIA

Malaysia is made up of Peninsular Malaysia and the states of Sabah and Sarawak on the island of Borneo. The Malaysian population is increasing at the rate of 2.3% per annum with the present population at 21.7 million, and it is estimated that by the year 2100 the demand for energy will have increased to about five times what it is now (66). Due to a rapid industrialisation policy, Malaysia had until the middle of the year 1997 experienced rapid economic growth. The country recorded GDP [Gross Domestic Product] of more than 8.6% between 1991 and 1996. Energy demand has continued to grow at a slightly higher rate than the GDP. During the same period, the demand for electricity has increased by 14% per annum (59).

The utilisation of renewable energy will contribute to the improvement in the security of the energy supply in the medium and long-term. Several 'green energy' sources such as biomass, biogas, solar and mini-hydro are known as renewable energy in Malaysia. The use of renewable energy is important in helping to prolong the fossil fuel reserves although Malaysia is fortunate to be endowed with indigenous oil and natural gas resources.

The total input of biomass to the primary energy supply of Malaysia has been estimated to be at least 2.5 MTOE [Million Tonne Oil Equivalent] which capable to generate electricity with capacity of about 2,000 MW (56,57). Table 3.1 shows the potential biomass energy in the agricultural sector. The main contribution is from palm oil mills and the second contribution is from rubber wood and wood waste.

Table 3.1: Potential Biomass Energy in Agricultural Sector (56,57)

One of the unique aspects of Malaysian renewable energy sources is the biomass produce from palm oil mill industries in which the energy for the processing of the palm oil comes from the waste itself. The consumption of renewable energy was estimated to be about 13% of the country's total energy consumption in 1995 (66), two thirds of which is from biomass [wastes from the palm oil, timber and rubber industries] and one third is from hydro-power.

Besides the solid residues, palm oil mills also generate liquid effluent using the anaerobic process to produce biogas. The biogas which contains methane, carbon dioxide and hydrogen sulphide is used as fuel in steam boilers and thermal heaters in the palm oil refineries (66).

About 39 units of mini-hydro plants with a total capacity of 16 MW have been installed in Malaysia (66). These plants were used to cater for household needs and cottage industries in remote areas.

As Malaysia is located in the Tropics, and receives a fair amount of sunshine, coupled with large forest and agricultural activities, the interest in renewable energy sources via solar energy use, biomass and hydro-electricity is high (67). Various studies conducted in Malaysia have indicated that the used of biomass as a source of energy is one of the most promising ways of effectively using the residues. Some of the commercial projects and research activities are include treatment of palm oil mill effluent (68,69), pyrolysis of oil palm shell (20), chars from oil palm waste (70), solid biofuels from biowastes (71), briquetting of palm fibre and shell (72), palm oil effluent as a source of bioenergy (73) ethanol fermentation from oil palm trunk (74) and converting oil palm trunks and cocoa wood to liquid fuels (75).

3.4 OIL PALM PLANTATION IN MALAYSIA

Traditionally the oil palm [Elaeis guineensis] was grown in semi-wild groves in tropical Africa. It was first introduced to Malaysia for planting in the Botanical Gardens in Singapore in 1870 (76).

Germination takes around 3 months, after which the seedlings are planted in small plastic bags where they are left in a so-called pre-nursery for several months. They are transplanted into bigger plastic bags and grow in a nursery for several more months to a size of about 1 meter, before they are transplanted into a field at an age of around 1 year.

The new improved crosses begin to flower after less than one year of transplantation and produce their first bunches of fruit after less than 2 years. At this age, their leaves have a size of over 2 meters in height and diameter. During its young age, the trunk grows at a rate of about 35 to 75 cm per year and produces alternate rows of leaves, depending on its gene (77). The base of the old leaves surround the stem and begin falling off at the age of 12 to 15 years (78). By this time, growth and production have slowed down.

In the oil palm plantation the number of leaves that are generated in a year increase from 30 to 40 at the age of 5 to 6 years. After that, the generation of leaves decreases to about 20 to 25 per year (78). The average economic life-span of the oil palm is 25 years to 30 years (58). A marked increase in the cultivation of oil palm began in 1960 (79), so that the year 1990 onwards will see a peak in replanting. This will be a good opportunity to harness the by-products of the oil palm. During the re-plantation, the heights of the oil palm tree are in the range of 7 m to 13 m, with a width of between 45 cm to 65 cm, measuring 1.5 m from the surface of the soil. There are about 41 leaves in each frond of the mature oil palm tree. It is estimated that in the year 2000, the process of re-plantation would generate about 8.36 million tonnes dried biomass, consisting of 7.02 million tonnes of trunk and 1.34 million tonnes of leaves (80).

Due to the high moisture of about 70% fresh weight, the newly chopped tree trunk cannot be burnt in the plantation. To leave the old trunk for natural decomposition not only obstructs the re-plantation process but harbours insects that would harm the new trees as well. The tree trunk usually takes between five to six years to decompose (81).

3.5 OPTIONS FOR THE DISPOSAL OF OIL PALM WASTES

The total land area in Malaysia amounts to 32.90 million hectares. According to Hoi Why Kong et al (82), the major agricultural crops grown in Malaysia are rubber [39.67 %], oil palm [34.56 %], rice [12.68 %], cocoa [6.75 %] and coconut [6.34 %]. In 1994, Malaysia produced 51% of the world's palm oil needs, thus making Malaysia the largest palm oil producer in the world (83).

Lignocellulosic biomass which is produced from the oil palm industries include oil palm trunks [OPT], leaves generated from re-plantation, leaves dropped from time to time, empty fruit bunches [EFB] and palm pressed fibres [PPF]. Table 3.2 shows the breakdown of waste from palm oil production.

Table 3.2: Wastes from palm oil production (84)

One of the major characteristics of the forestry and agricultural sector is the production of large quantities of processing residues that have no economic value other than energy generation. Their presence in recent years has created a major disposal problem due to the fact that open burning is being discouraged by the Department of Environment in Malaysia.

Other than biomass from the plantations, the palm oil industry also produces other types of waste in large quantities mainly EFB, PPF, shell and palm oil mill effluent [POME]. Table 3.3 shows the breakdown of product or waste from each bunch of fresh fruit [FFB].

Table 3.3: Products/wastes from each bunch of FFB (72)

The EFB are usually air dried until the moisture content reaches about 40% when it is ready to be used as fuel in the palm oil processing plant (83). The burnt waste is then used as the fertiliser in plantations (85). Other than that, EFB were also used in the plantations as a mulch (86). Some plantation owners claim that the benefits of EFB as a fertiliser and as a soil conditioning agent are significant, whilst other mill owners welcome alternative methods of disposal. This is due to the inconvenience of handling and transporting, as well as the costs and problems concerning disposal of the waste on the plantation. However, open burning is no longer allowed by the authority because this process causes air pollution and by this means of disposal no energy is recovered (87).

Oil-palm fronds have been successfully used as a substitute for tropical grasses by ruminant producers in Malaysia (88). Nowadays, the PPF is usually burnt in the palm oil processing plant as fuel and the excess is disposed of in the plantations (89). The PPF are burnt in a boiler with some palm shells to produce the power for running the mill [self-sufficient]. The boilers used are normally of grate-type beds which are manufactured locally (66). Most of the crude palm oil mills harness the energy from the shell and fibre in their own low-pressure boilers and normally the oil palm trunk would be left to decompose naturally at the plantation (83). This practice not only disturbs the process of plantation due to the low decomposition rate, it also encourages the spread of diseases and insects like *rhinoces beetles* and *ganoderma* that are harmful to the plant plantation (83). Moreover, most of the plantations have to adopt the push-felling technique and trunk-shredding which leads to burning (90).

3.6 OIL PALM WASTES AS A LIGNOCELLULOSIC BIOMASS

Lignocellulosic biomass produced from the oil palm industries consists of oil palm trunks [OPT], leaves generated from re-plantation, leaves dropped from time to time, empty fruit bunches [EFB] and palm pressed fibres [PPF]. The breakdown of waste from palm oil production is shown in Table 3.2.

Lignocellulosic biomass or biomass in general is a renewable energy resource derived from the carbonaceous waste of various human and natural activities. Biomass does not add carbon dioxide to the atmosphere as it absorbs the same amount of carbon in growing as it releases when consumed as a fuel (91). Its advantage is that it can be used to generate electricity with the same equipment or power plants that are now burning fossil fuels. Biomass is an important source of energy and the most important fuel worldwide after coal, oil and natural gas. Biomass composition also affects the yields of various speciality chemicals in the oil. One of the main reasons that thermochemical conversion of biomass is attractive because it has a high volatiles content which is 87% for wood compared to 5.4% for anthracite (92).

Biomass is derived from numerous sources, including the by-products from the timber industry, agricultural crops, raw material from the forest, major parts of household waste and wood. Wood is the most of biomass type had been studied. The general chemistry and structure of wood is similar to that of other biomass types; therefore this chapter will deal mostly with wood characteristics.

Biomass falls into two main groups which known as woody biomass and non-woody biomass.

3.6.1 Woody Biomass

Woody biomass resources include waste materials derived from forest products, untreated wood products, waste wood and energy crops such as willow and poplar. Woody biomass consists of wood, bark, branches, twigs, stumps and roots. The following criteria will serve to distinguish woody biomass (93).

a. They must be vascular plants. Plants devoid of vascular tissue cannot produce wood.

b. They must be perennial plants which must live for a number of years.

c. They must posses a stem that persists from year to year. In the case of the tree, this is also called the "bole" or "trunk".

d. Typical woody biomass exhibit secondary thickening. They have a means of thickening their stems by subsequent growth in diameter which is not traceable to terminal growing points.

Woody biomass is classified into two groups: hardwoods and softwoods (93). The softwoods, otherwise known as coniferous woods, are produced by coniferous and usually evergreen trees such as the pines, spruces and hemlocks. The leaves are needlelike, linear, awl-shaped or scalelike, and the seeds are borne either in cones in the axil of a scale or naked. Softwood is belonging to the Order Coniferales of the Gymnosperms. The hardwoods, on the other hand, are obtained from broad-leaved trees such as elm, oak, ash and poplar which scattered through various plant orders and families. The leaves are broad except in rare instances and are usually deciduous in the temperate zones. Hardwood trees are Angiosperms of the subgroup known as Dicotyledons.

Woody biomass can be burnt directly as a raw product, or processed into solid fuel such as pellets or briquettes which are combusted to create heat or steam to generate electricity.

3.6.2 Non-woody Biomass

Non-woody biomass resources include waste materials derived from human and animal wastes such as slurry, chicken litter, industrial and municipal biodegradable wastes including food processing wastes. The crop such as rape, wheat, barley, sugar beet, sugar cane and maize can be categorised as non-woody biomass as well, and they can be process to produce the biofuels.

Non-woody biomass has a number of applications depending on the source. Biogas, landfill gas and fermentation harness the natural process of anaerobic digestion. This is the decomposition of an organic substance by bacterial action in the absence of air and in warm and wet conditions. In fermentation, anaerobic digestion converts sugars into ethanol with the use of micro organisms, usually yeast. Bio-ethanol can be used as a fuel by mixing it with gasoline or using it directly in a modified combustion engine.

Non-woody biomass has more loosely bound fibres and this indicating a lower proportion of lignin (94) [see Table 3.4]. It was also found that non-woody biomass have high level of ash. Therefore EFB can be categorised as non-woody biomass.

3.7 STRUCTURE OF BIOMASS

Part of the purpose of this work is to influence the quality of pyrolysis liquid from fast pyrolysis of biomass. This can be done by water washing pre-treatment of feedstock, which is described in Chapter 4. Water washing on feedstock was carried out in order to eliminate the ash content in biomass. Therefore, it is important to know the location of ash within the biomass structure. However, there is no information on the structure of EFB provided, furthermore, information on the structure of non-woody biomass is very limited. Therefore, the author discussed the structure of woody biomass as it represents for all lignocellulosic biomass structure.

Structure of biomass can be classified into biological structure and chemical structure of biomass, as mentioned in the following sections.

3.7.1 Biological Structure of Biomass

Biomass [wood] is composed of millions of individual woody cells (35). These cells differ in size and shape, depending upon their physiological role in the tree, most of them being many times longer than broad. They are arranged in recognisable species patterns of distribution within the wood, the organization varying with the species. The long cells, which are arranged longitudinally, make up the bulk of the wood and provide "grain" to the material. When thin sections of wood are examine with a light microscope, cellular composition can be readily be observed which is shown in Figure 3.1 below.

Figure 3.1: Simplified cross-section of a single wood cell (95)

From Figure 3.1, the layer of intercellular substance between cells is called the middle lamella. It appears to consist chiefly of lignin. Each cell possesses a limiting wall enclosing a lumen [cell cavity]. Fibre cell wall consists of two main layers, the primary [P] and the secondary [S] wall layers. The primary wall is a very thin layer [0.05-0.1μm] and it is formed during the surface growth of the cell wall. The secondary wall comprises actually three sublayers termed S1 [outer layer], S2 [middle layer] and S3 [inner layer]. The S layer forms the largest part of the cell wall: S1 [0.1-0.3μm, contains 3-6 microfibrillar layers], S2 [1-8μm, 30-150 microfibrillar layers], S3 [<0.1μm, contains less than 6 microfibrillar layers].

The amount of hemicellulose is about the same in each layer because the layers need to swell and contract together without stress between them when moisture content changes (96). The cellulose content of each layer increases steadily from the outer 'primary' layer to the innermost 'secondary' layer. The lignin content consequently decreases in that sequence. The cellulose microfibrils lie parallel to each other within each layer, and spiral around the cell's long direction. Different layers have different angles of spiralling.

The hemicellulose combined with the lignin acts as glue that holds together the layers and the cellulose microfibrils within each layer. Cellulose, as the skeletal substance, contributes its high tensile strength to the complex of wood structure. The role of lignin is to provide rigidity to the tree, making upright growth possible. It also adds toxicity, thus making wood durable. Its concentration in the middle lamella serves the purpose of cementing individual cells together.

Most cells have their long directions parallel in the direction of tree growth [some bundles of cells lie perpendicular to this majority, forming the 'rays' seen in a radial section]. The wall of each cell has a cross-sectional shape that is rectangular with slightly rounded corners. Adjacent cells have their walls glued to one-another by a mixture of about three-quarters lignin and a quarter hemicellulose. The glue layer is about as thick as an individual cell-wall layer except at the rounded corners, where it fills the space. Pairs of glued-together adjacent cell walls act as structural units. There are evenly-spaced holes in the cell walls called 'pits' which are usually lined up with similar holes in adjacent cell walls. These holes allow the passage of water or air between cells, and ultimately between the inside and outside of a piece of wood.

The primary wall [high cellulose] is on the outside of the cell and therefore plays an important part in determining the surface properties, which are important in producing a good quality paper. The pulp and paper making industry uses Sulphite or Kraft processes (97, 98, 99) to dissolve the lignin to leave long cellulose fibres.

The water washing pre-treatment, which will be described in Chapter 4, are concerned with the removal of the ash component. Ash exists in three places of the cell. First, it comes from the oxidation of the cell wall [primary wall, S1-S3] as shown in Figure 3.1, which produce acid groups holding inorganic ions. Second, it exists as low levels of salts from the cytoplasm remaining in the lumen. Third, it contained with hemicelulose, which present in biomass to fix inorganic counterions. The ash, which incorporated into the hollow lumen originates from the sap is easily removed because it is loosely bound to the cell. However, the ash, which incorporated into the cell walls, is not easy to remove. Therefore, reagents is requires to remove the inorganic material. The cell wall [primary wall, S1-S3] contains high level of lignin, which is resistant to a number of chemical reagents. This means that more concentrated reagents or more severe conditions [temperature and pressure] are required to penetrate through this lignin barrier.

3.7.2 Chemical Structure of Biomass

Biomass is a complex aggregate of compounds which can be divided into two major groups: cell-wall components and extraneous materials [extractives] as shown in Figure 3.2. The cell-wall components consist primarily of cellulose and lignin. Cellulose is the most abundant constituent, comprising about 70 – 80% of the wood structure. Lignin which comprises from 20 – 30% of the wood structure is the cementing agent which binds the individual wood fibres together to form a substance of strength and rigidity.

The extraneous materials are not part of the wood structure, but they contribute properties such as colour, odour, taste and resistance to decay. They include tannins, starches, oils, resins, acids, fats and waxes. They are found within the hollow portions of the wood cells, and can be removed from the wood by neutral solvents such as water, alcohol, benzol, acetone and ether.

Figure 3.2: Composition of biomass (100)

In nature, biomass has three major constituents: about half cellulose: a quarter hemicelluloses and extractives: and a quarter lignin for a typical woody biomass (37). These three major components decompose in different temperature ranges resulting in a large number of parallel and consecutive reactions during particle conversion and give rise to many reaction products (101). Different biomass constitutions have consequences to the pyrolysis products which can be observed through the pyrolysis product yields and the quality of the oil. For example high ash content will reduce the pyrolysis liquid product (19). Biomass composition also affects the yields of various speciality chemicals in the oil. One of the main reasons that thermochemical conversion of biomass is attractive because it has a high volatiles content which is 87% for wood compared to 5.4% for anthracite (92). Table 3.4 shows typical component analysis for various biomass types. The cellulose, hemicellulose and lignin components will be described more fully in the following sections.

Table 3.4: Analysis of typical biomass feedstock (91)

3.7.2.1 Cellulose

Cellulose is the principle constituent of wood. The elemental formula for cellulose is $[C_6H_{10}O_5]_n$. Depending on the species of wood, cellulose comprises about 50% of its mass. Celulose has a linear structure and this linear structure is what gives the wood's cells their strength and rigidity. Figure 3.3 shows the cellulose structure which consists of long chain molecules (91). Cellulose decomposes at 200-260°C (102). Cellulose is also a biopolymer of glucose. In this case, the glucose moieties are strung together by ß-glycosidic linkages. The ß-linkages in cellulose form linear chains that are highly stable and much more resistant to chemical attack because of the high degree of hydrogen bonding that can occur between chains of cellulose. Hydrogen bonding between cellulose chains makes the polymers more rigid, inhibiting the flexing of the molecules that must occur in the hydrolytic breaking of the glycosidic linkages. 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 3.3]. It is necessary to hydrolyse the glucosidic bonds for analysis or prior to fermentation to alcohol. Further hydrolysis will yield the monomer D-glucose; however with concentrated acids some reversion will take place resulting in the production of oligosaccharides.

Figure 3.3: Cellulose structure (91)

3.7.2.2 Hemicellulose

Hemicellulose is a fourth form of sugar polymers found in biomass. They are relatively low-molecular-weight, non-cellulosic polysaccharides which occur in plant cell walls together with lignin and cellulose. Hemicellulose are isolated by extraction of untreated or of delignified wood with water or, more frequently, with aqueous alkali. It has a similar structure as cellulose does, and decomposes at 240-350°C (102). Hemicellulose consists of short, highly branched, chains of sugars. It contains five-carbon sugars [usually D-xylose and L-arabinose] and six-carbon sugars [D-galactose, D-glucose and D-mannose] and uronic acid. The sugars are highly substituted with acetic acid. Its branched nature renders hemicellulose amorphous and relatively easy to hydrolyze to its constituent sugars. Mannan is a polymer of d-mannose which is most prominent in softwoods, and xylan which is a polymer of d-xylose found in hardwoods as shown in Figure 3.4 (103). When hydrolyzed, the hemicellulose from hardwoods releases products high in xylose [a five-carbon sugar] while the hemicellulose contained in softwoods yields more six-carbon sugars (104). Hemicellulose is source of furan derivatives and gives higher yields of char, water and acetic acids during pyrolysis reactions due to its higher reactivity compared to that of cellulose.

Figure 3.4: Hemicellulose structure (103)

3.7.2.3 Lignin

Lignin, the encrusting substance in wood, is a polymer of three closely-related phenylpropane units, which can be hydroxyl, guaiacyl or syringyl. Coniferous or soft wood lignins are comprised exclusively of guaiacyl-propyl units, whereas deciduous or hard wood lignins contain both guaiacyl- and syringyl-propyl units. Grasses and some hard wood have the p-hydroxyphenyl unit as a major constituent (100). Examples are illustrated in Figure 3.5. Unlike cellulose and hemicellulose, lignin cannot be depolymerized by hydrolysis. Cleavage of the principal bonds in lignin requires oxidation. Lignin has a significantly greater complexity than cellulose or hemicellulose. It decomposes at temperatures between 280 and 500°C. When lignin is heated to about 450°C, only about 50% volatilizes. What remains of the mass of lignin is char (104), and, as it is deposited in wood, is a colourless, completely amorphous substance. Characteristic decomposition products are phenolic ethers, guaiacol and pyrogallol 1,3-dimethyl ether and their derivatives.

Figure 3.5: Lignin Monomers (100)

3.7.2.4 Extractives

Extractives include tannins and other polyphenolics, colouring matter, essential oils, fats, resins, waxes, gum starch, and simple metabolic intermediates. The organic component takes the form of extractives, which contribute to such wood properties as colour, odour, taste, decay resistance, density, hygroscopicity and flammability (105). This component is termed extractives because it can be removed from wood by extraction with solvents, such as water, alcohol, acetone, benzene, or ether. Most of the extractives are located in the heartwood, the presence of some of them being the source of general darkening of this portion of the tree. Extractives may constitute roughly 5% to 30% of the wood substance, depending on such factors as species, growth conditions, and time of year when the tree cut. When the extractive materials are particularly toxic, the heartwood portion of the tree is relatively resistant to attack by biological deteriorating agencies.

3.7.2.5 Ash

The minerals taken up and retained by plants when growing are classified as ash. The term ash refer to all inorganic components of plant fibres (106). The ash content of wood is usually 0.2-0.5% (35). Ash is comprised of salts of alkali metals of which some are held loosely in the biomass structure and some are bound more tightly as discussed in Section 3.7.1. The most common elements in ash are potassium, magnesium, sodium and calcium (107).

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. Table 3.5 shows that the ash content of woody biomass is lower compared to the ash content of non-woody biomass.

Table 3.5: Ash content of non-woody biomass and woody biomass (108)

3.8 THE OIL PALM INDUSTRY IN MALAYSIA

As the world's largest producer and exporter of palm oil, Malaysia accounts for more than 50% of the world's palm oil output and more than 60% of the world's palm oil exports (109). In order to provide a better understanding of the palm oil industry in Malaysia, the following sections give an overview of oil palm industry in Malaysia including oil palm plantation and the mass balance of the oil palm industry as it is self-sufficient in energy.

3.8.1 Malaysian Palm Oil Scenario

The first commercial oil palm estate in Malaysia was set up in 1917 at Tennamaran estate, Selangor. Palm oil is one of the seventeen major oils and fats in the world market. The government encouraged crop diversification from rubber to oil palm in the late 1950s.

Malaysia became the world's largest producer and exporter of palm oil, replacing Nigeria as the chief producer in 1971. The total area under oil palm in Malaysia in 1971 was 329,000 hectares while there were 220,000 hectares in Nigeria (109). Malaysia accounts for 52% of world palm oil production and 64% of world exports in 1997. The area utilised for oil palm plantations in Malaysia had increased to 3.216 million hectares in the year 1999.

The oil palm fruit produces two distinct oils which are palm oil and palm kernel oil. Palm oil is obtained from the mesocarp while palm kernel oil is obtained from the seed or kernel. Palm oil is used mainly for the production of margarine and compounds in cooking fats and oils and also for the production of candles, detergents, soap and cosmetic products. Production of palm kernel oil is about 12% of the production of its palm oil.

The success of the Malaysian palm oil industry is the result of the ideal climatic conditions, efficient milling and refining technologies and facilities, research and development, and efficient and adequate management skills. Practically all palm oil mills generate their own heat and power through the co-generation system (66). There were 325 palm oil mills with a capacity of 59,067,520 tonnes of FFB in operation in 1998, and this increased to 334 mills with a capacity of 61,793,720 tonnes FFB in 1999 (109). The Malaysian government is fully committed to the expansion of the industry and encourages global expansion of palm oil production. Palm oil is now readily accepted globally and Malaysia has exported palm oil to more than 140 countries in the world.

3.8.2 The Mass Balance of The Oil Palm Industry

The palm oil mill is self-sufficient in energy, using waste fibre and shell as fuel to generate steam in waste-fuel boilers for processing, and power-generation with steam turbines. The energy demand and the mass balance of 1 tonne FFB of palm oil mill process are shown in Figure 3.6 (66). The breakdowns of product or waste from each bunch of fresh fruit [FFB] are shown in Table 3.3.

The FELDA palm oil mill in Sungai Tengi, Selangor, Malaysia, has been selected for the analysis since it employs the standard oil extracting process (110). In the standard milling process, used in the factories with a milling capacity of over 10 tonnes of raw material per hour, water is added into a digester (111). More than 19.7 million tonnes FFB were processed in 2000 (110). The standard sized mills processing 60 tonnes/hour of fruit bunches normally produce 40 tonnes/hour of steam. Part of the steam is used to generate 800 kW of electricity and the rest is used as process steam. It is estimated that the total generating capacity of the mills is about 200 MW (66). Figure 3.7 shows a proposed plan for the operational process and product of the palm oil industry if used EFB as fuel beside palm shell and fibre.

As the fresh fruit bunches reach the processing plant, the sterilisation process begins with the steam temperature at 140°C, pressure at 2.5 to 3.2 kg/cm^2 for 50 minutes (110). After this process, the stripping process will take over. In the stripping process, a rotating divesting machine is used to separate the sterilized oil palm fruit from the sterilized bunch stalks. The empty fruit bunches (EFB) will fall in the collector and are brought to the burning place as a fuel. After the bunches have been stripped, the sterilised fruits are fed into a digester where water at 80°C is added. This is performed in steam-heated vessels with stirring arms, known as digesters or kettles. The most usual method of extracting oil from the digested palm fruit is by pressing. The type of press used in this palm oil is the screw type press.

The crude oil extracted from the digested palm fruit by pressing contains varying amounts of water, together with impurities consisting of vegetable matter, some of which is dissolved in the water. Centrifugal and vacuum driers are used to further purify the oil before pumping it into a storage tank. When the digested fruit is pressed to extract the oil, a cake made up of nuts and fibre is produced. The composition of this cake varies considerably, being dependent on the type of fruit. The cake is given a preliminary breaking treatment before being fed into the nut/fibre separator called depericarper.

When the fibre has been separated from the nuts, the latter can then be prepared for cracking. Any uncracked nuts must be removed and recycled and the shell separated from the kernels. The waste fibre and shell are also transported to the burning place as a fuel. The kernels are packed and sold to kernel oil mills.

The palm oil mills also generate about 2.5 m^3 of liquid POME for every tonnes of palm oil produced, and 28m^3 of biogas are generated for every m^3 of POME treated (66). The biogas with methane content of 60–70%, 30–40% CO_2 and small traces of hydrogen sulphide is used as fuel in steam boilers and thermal heaters in palm oil refineries. In a gas engine, about 1.8 kWh of electricity could be generated from $1m^3$ of biogas. Usually the gases are distributed from the palm oil mill to other industries which use gases, such as the ceramic industry or palm oil refining industries.

Figure 3.6:Energy demand and potential biomass generated in palm oil industry (66)

Figure 3.7: **Proposed plan for operation of a Palm Oil Mill (adapted from 110)**

3.9 IMPORTANCE OF PYROLYSIS OF OIL PALM WASTE

The process of fast pyrolysis is one of the most recent renewable energy processes which promises high yields of liquid with minimum of gas and char if this process is carefully controlled. This process is perceived to offer logistical and hence economic advantages over other thermal conversion processes (13). This is because the liquid product can be stored until required or readily transported to where it can be most effectively utilised, also the liquid's density is very high around 1.2 kg/litre (8).

Although Malaysia is the world's largest producer and exporter of palm oil, it also generates large quantities of oil palm wastes. Therefore, an investigation on fast pyrolysis technology to convert oil palm waste such as Empty Fruit Bunches to liquids is important.

3.10 SUMMARY

This research study considers the pyrolysis technology for processing empty fruit bunches waste, then develops the pre-treatment water washing process of feedstock for the production of liquids which had a good potential as a fuel. Fast pyrolysis technology for processing empty fruit bunches [EFB] into liquids becomes important since the presence of oil palm waste has created a major disposal problem. This chapter describes the biological structure of biomass and chemical structure of biomass which influence pre-treatment water washing and fast pyrolysis process. The water washing pre-treatment was studied in order to optimise the pyrolysis liquids, and this is discussed in Chapter 4 and 5.

4. PRE-TREATMENT OF FEEDSTOCK BY WATER WASHING

Literature on biomass pre-treatment by water washing is reviewed with particular emphasis on the removal of ash, which is required to modify the pyrolysis reaction sufficiently to produce homogenous bio-oil.

The simple water washing experiments were carried out to remove ash in the feedstock. The equipment for water washing experiments and procedures for operating the water washing system, and obtaining mass balances are described.

4.1 INTRODUCTION

A major objective of the water washing work was to remove the ash from biomass in order to improve the quality of bio-oil and possibly to increase bio-oil yield. Producing high yield bio-oil would have a significant economic advantage (112). For all the pyrolysis experiments utilising unwashed EFB reported in this thesis, the liquid product separated into two phases as reported in Chapter 7.

The process of pyrolysis is complex, but the most accepted theory is that primary vapours are first produced. These primary vapours then further degrade to secondary tars, char and gases, and this degradation can be enhanced by catalysis, high temperature and longer residence time. High ash in biomass generally promotes secondary reactions of primary pyrolysis products since some ash components, primarily potassium and sodium, are known to be catalytically active (19,39). Therefore, secondary reactions should be avoided for the production of liquid as reported in Section 2.3.7. Another aim of the experiments was to gain a better understanding of the basic factors impacting water washing of EFB to provide a basis for subsequent techno-economic optimisation. The water washing experiments that have been performed are discussed in detail in Chapter 5.

4.2 ASH

The basic composition of biomass was discussed in Section 3.7.2. Since ash is of primary concern for its effect on primary and secondary reactions, ash content and composition is reviewed detail below.

Lignocellulosic materials are mostly composed of macromolecular substances, in particular cellulose, hemicellulose and lignin, as discussed in Section 3.7.2. Ash and aqueous and organic-solvent extractives are also found in minor proportions (113). Ash in lignocellulosic materials is considered to be the residue remaining after the sample has been incinerated removing its organic constituents (114). Thus, the ash fraction is an indicator of the inorganic substances present in the native substrate (115,116). The major cations present in ash from lignocellulosic materials are K, P, Mg, Na and Ca. Other elements, such as S and Mn, are present in minor amounts (117). Trace constituents, such as Al, Fe, Zn, Cu, Ti, Pb, Ni, V, Co, Ag and Mo, are also found in most substrates (118,119,120). The anions that are usually present in ash are chloride, carbonate, sulphate, silicate, oxide and hydroxide (115,121).

Table 4.1 shows the proportion of elements contained in the ash from a variety of biomass feedstocks. From this table it can be seen that ash from straws and grasses have high silica content, whereas wood ash [ash from Douglas Fir wood] contains much less silica. Therefore, water washing of woody biomass would be expected to have a more significant impact on the overall reduction of ash content, as it will be dominated by sodium and potassium.

It is well known that the presence of alkaline cations in biomass affect the mechanism of thermal decomposition during fast pyrolysis. Several researchers (122,123,124) have demonstrated that if these inorganics are removed from the biomass before pyrolysis that the mechanism of thermal decomposition is markedly affected and the predominat reaction is one of depolymerization. Pan et al. (125) studied the influence of the removal of inorganic salts and of ion-exchanged cations on volatile products from the pyrolysis of wood. They found that potassium but not calcium and silica acts as a catalyst in pyrolytic reactions. Raveendran et al. (126) studied the influence of alkaline cations on volatile products from synthetic biomass and they found that potassium is more catalytically active than silica.

As discussed in Section 3.7.2.5, 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. These are contained as carbonates, phosphates, silicates and sulphates; and are concentrated in three locations within plant cells. 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 to hemicellulose. A single wood cell was shown in Figure 3.1. The ash, which is loosely bound to the cell, is easily removed, using demineralised water to wash it from the cells (127,128). However, the ash, which is bound to the cell walls and the hemicellulose is not easy to remove. Therefore, it may require more severe agents such as acid, and more aggressive techniques (34) for its removal. The removal of ash utilising a water washing process is the focus of this chapter.

Table 4.1: Ash composition of straws, waste residues and wood (127)

4.3 LITERATURE REVIEW

The area of water washing has received very limited attention by researchers. The most relevant work found in the literature was carried out by Jenkins et al. (127), Piyali Das et al. (129), Di Blasi et al. (128), Davidsson et. al. (130) and Scott et al. (131). A critical review of these references will be presented in the following section.

4.3.1 Jenkins et al.

Jenkins et al. (127) studied ash reduction in rice straw and wheat straw in order to reduce slagging and fouling in furnaces and other thermal conversion systems. Alkali in the ash of crop biomass fuels, mainly potassium and sodium, creates serious slagging and fouling in conventional boilers. The principal causes fouling and slagging have recently investigated for biomass fuels (132,133,134,135,136). However, the fouling can be related also to the presence of chlorine, silicon, sulphur, calcium and magnesium (137,138).

They carried out water washing experiments on six different methods as follow:

1. The straw was not subjected to washing, and whole straw was analysed as harvested.
2. A total of 100g whole straw samples were hand sprayed with tap water for a period of 1 minute.
3. A total of 100g milled straw was flushed with 20 litres tap water.
4. A total of 100g milled straw was flushed with 20 litres distilled water.
5. A total of 50g milled straw was flushed with 7 litres distilled water.
6. A total of 100g whole straw was submerged for 24 hours in 7 litres distilled water.

The straw was hammermilled through a 19mm round hole screen prior to leaching for method 3 and 4 but the straw for method 5 obtained by milling through a 0.85 mm screen. For method 3, 4 and 5, either tap water or distilled water was poured through the sample spread over a fine mesh stainless steel screen. A total of 20 litres of water was poured through each 100 g sample in 1 litre increments for both method 3 and 4. However, a total of 7 litres of distilled water in 0.5 litre increments was used for method 5. Table 4.2 shows that flushing was quite effective for wheat straw, yielding averages of 5.0 mf wt% and 4.2 mf wt% ash for tap water and distilled water respectively.

Table 4.2: Ash content of untreated and treated straws (127)

For rice straw it can be concluded that the greatest ash reduction is achieved by soaking the biomass in distilled water at ambient temperature for 24 hours. The effect of soaking the biomass in tap water rather than distilled water was not tested by the authors; they only considered this variation for flushing.

Table 4.3 shows that the soaking method effectively reduced the ash from the wheat straw. Moreover, 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. The table also shows that the ash content of rice straw can be reduced the most by soaking for 24 hours. Although the overall level of ash reduction is low for rice straw, the levels of chlorine, potassium and sodium were significantly reduced. Analyses of total ash contents in Table 4.3 are somewhat lower in general for both rice straw and wheat straw than for the analyses reported in Table 4.2. The difference is believed to be due to the sampling procedure, in which some fine material was lost from the samples analysed for major elements.

The results from these experiments show 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. All components except silica and calcium were significantly reduced although only a small proportion of the ash for rice straw was removed [i.e. 18.63 to 17.10 mf wt%]. Silica only can be removed by acid washing because hydrofluoric acid has the distinctive property of attacking silica.

Table 4.3: Ash analysis on oxide basis for straw (127)

The authors do not report whether soaking straw in tap water was tested. If the effects were similar to those of distilled water so as were the flushing tests, soaking in tap water would have a significant economic advantage over soaking in distilled water. The soaking method employed by Jenkins et al. (127) had been used as a basis for initial washing work as ash content of feedstock can be reduced the most by soaking for 24 hours in distilled water, and this work will be mentioned later in the Section 5.1.

4.3.2 Piyali Das et al.

Piyali Das et al. (129) investigated vacuum pyrolysis of deashed sugarcane bagasse. The objective of their work was to understand the change in the quantity and quality of the oil fraction obtained from the pyrolysis, after pre-treatment for deashing of original biomass. They believed that the presence of alkali metals in ash catalyses the polymerization reactions in the oils and thereby increase the viscosity (139,140). Moreover, these alkali metals in ash, form deposits in combustion applications, particularly in turbines, where the damage potential is considerably high.

The oven dried bagasse samples were ground to pass through 60-mesh sieve for the washing experiments. They carried out washing experiments on nine different methods as follows:

1. The bagasse samples were not subjected to washing.
2. A total of 100g bagasse samples were soaked for 1 hour in 1.2 litres distilled water.
3. A total of 100g bagasse samples were soaked for 24 hours in 1.2 litres distilled water.
4. A total of 100g bagasse samples were soaked for 24 hours in 0.6 litre distilled water.
5. A total of 100g bagasse samples were soaked for 1 hour in 1.2 litres 5[M] HC*l*.
6. A total of 100g bagasse samples were soaked for 1 hour in 1.2 litres of 0.5% HF.
7. A total of 100g bagasse samples were soaked for 1 hour in 1.2 litres of 1% HF.
8. A total of 100g bagasse samples were soaked for 1 hour in 1.2 litres of 2% HF.
9. A total of 100g bagasse samples were soaked for 1 hour in 1.2 litres of 3% HF.

For all treatments, mixtures were leached and occasionally stirred for predetermined time at 25°C. For treatment 5-9, in which the samples were soaked with acid, the samples were then washed with distilled water after filtered off. The washing process continued until the wash water remained neutral.

The pre-treatment processes are aimed at maximum extraction of ash. In case of HF treatment, leaching with 3% HF solution was finally selected based on minimum concentration of HF solution required for the reduction of ash to a fairly negligible limit. The percentage ash in untreated and treated bagasse are presented in Table 4.4. It shows that treatment with HC*l* leads to an apparent increase of ash percentage, which is attributed to the relatively higher removal of other components in bagasse. Water leaching has a moderate effect on ash removal. The best results is achieved with HF treatment, in which case the ash percentage was reduced to as low as 0.03 mf wt% when treated with 3% HF solution. Each of deashing treatments is associated with the mass reduction [loss feedstock] in the original biomass feedstock. The degree of deashing as well as the mass reduction of the original biomass associated with each process was found to be different. The mass reduction for treatment 1 is 18-20 mf wt% but it was same for treatment 2 and 3 which is 26-27 mf wt%. The acid leaching caused higher mass reduction with as high as 50 mf wt% with 5M HC*l* treatment.

Table 4.4: Pre-treatment processes and percentage of ash in untreated and treated sugarcane bagasse (129)

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Table 4.5 shows the elemental composition of ash obtained by ICP-AES [Inductively Coupled Plasma Atomic Emission Spectra] analysis. The authors only reported the results for treatment 1, 2, 5 and 9. It shows that treatment with HC*l* leads to an apparent increase of ash percentage [i.e. 1.83 to 2.12 mf wt%]. This may be attributed to relatively higher removal of other components in bagasse. It was found that simple water leaching washed out the alkalis like Na and K wherein, 5[M] HC*l* leaching further removes other alkali metals like Mg, and Ca, but 3% HF leaching removes almost all the ash elements including silica. It is well known that hydrofluoric acid [HF] has the distinctive property of attacking silica.

Table 4.5: Elemental composition of untreated and treated sugarcane bagasse (129)

The chemical composition [extractives, hemicellulose, cellulose and lignin] of untreated and treated sugarcane bagasse was also carried out by Technical Association of Pulp and Paper Industries [TAPPI] methods, and the results are shown in Table 4.6. The authors only carried out the composition analysis on treatment 1, 2, 5 and 9 only.

In case of water leaching, it was found that the extractives were washed out which reduced from 25.8 mf wt% to 13.1 mf wt%. While leaching with 5[M] HC*l*, it was found that this solution hydrolysed the hemicellulose fraction to a drastic reduction but there was a resultant increased in the apparent cellulose percentage in the deashed sugarcane bagasse. This aspect is confirmed by leaching with HF solution in which leaching with HF not only increased the relative percentage of cellulose in the deashed sugarcane bagasse by removing extractives and hemicellulose, but also completely removed ash elements as shown in Table 4.4.

The soaking method employed by Piyali Das et al. (129) was similar to the work reported in this thesis in which the biomass was soaked for 24 hours in distilled water. They also studied the impact of ratio of biomass to water on percentage of ash reduction and effect of deashing treatments on pyrolysis product which is part of this work. Investigation and understand the nature of change in the chemical composition in the biomass due to different pre-treatment is very interesting. Although this is beyond the scope of this work, it is recommended that this type of study can be performed in the future.

Piyali Das et al. also conducted vacuum pyrolysis experiments on deashed sugarcane bagasse and this will be reviewed in detail in Section 4.4.

Table 4.6: Chemical composition of untreated and treated sugarcane bagasse (129)

4.3.3 Di Blasi et al.

Di Blasi et al. (128) studied the influence of water washing treatments on the degradation characteristics of wheat straw. They also investigated the pyrolysis of unwashed and washed straw. They carried out washing experiments by soaking 1g of wheat straw of size 2-3cm for 2 hours in 100m*l* hot distilled water at temperature of 90°C. Table 4.7 shows the ash analysis on oxide basis for unwashed and washed straw. The contents of K, Mg, Na and Ca which expressed on an oxide basis are determined by atomic absorption spectrophotometry.

Table 4.7: Ash analysis on oxide basis for unwashed straw and washed straw (128)

It was found that the ash content of this biomass had been reduced from 5.25 mf wt% to 2.20 mf wt% and removes almost completely potassium by this washing method.

Degradation of unwashed and washed wheat straw were investigated by thermogravimetric analysis utilising a heating rate of 20Kmin^{-1} with a final temperature of 1100K. They found that the temperature at which the hemicellulose and cellulose degradation in air for washed wheat straw is about 240°C which is higher compared to 200°C for unwashed wheat straw.

A bench scale system was used to investigate the pyrolysis of unwashed and washed wheat straw samples. They found that the liquid yields increased with the decrease in char yields for washed straw. For example, at temperature of 500°C, the liquid yield is 43 mf wt% for unwashed feedstock compared to 58 mf wt% for washed feedstock, while the char yield is 28 mf wt% for unwashed feedstock compared to 23 mf wt% for washed feedstock.

Washing method by soaking in hot water at temperature 90°C employed by Di Blasi et al. (128) was similar to work report in this thesis. The results of their work are particularly relevant to the work reported in Section 5.2.5 [TGA Analysis] and Section 7.3 [Pyrolysis of Washed Feedstock].

4.3.4 Davidsson et al.

Davidsson et al. (130) studied the influence of different washing techniques on alkali release during pyrolysis of wheat straw, wood waste [mainly pine and birch] and cellulose. However, the authors do not stated the exact species make up the wood waste. The usefulness of crops fuels in energy production is limited by maintenance problem such as sintering, fouling and hot corrosion (132). These processes are largely due to the presence of potassium and chlorine, which reduce the capacity, efficiency and availability of thermal conversion plants using biomass.

They carried out washing experiments on three different methods as follows:

1. Biomass sample of 1g was placed on filter paper and rinsed with 5ml de-ionised water at 20-25°C.
2. Biomass sample of 1g was placed on filter paper and rinsed with 20m*l* de-ionised water at 20-25°C.
3. Biomass sample of 1g was immersed for 4 hours in 5m*l* of 1 M acetic acid at 20-25°C. After filtration, the sample was rinsed with 10m*l* of de-ionised water and allowed to dry.

The washed sample was then allowed to dry in a desiccator at room temperature for at least 24 hours, and these samples were subjected to a constant heating of 20°C in N_2 atmosphere to measure the release rate of alkali compounds. The alkali metals were release form the untreated biomass in two temperature intervals: first, in connection with the pyrolysis process taking place at 200-500°C, and second, from the material remaining after pyrolysis at temperature above 600°C. Table 4.8 shows the reduction in alkali release compared to untreated samples in percentage. WS1 and WS2 are referred to wheat straw of size 0.5-2mm and 0.05-0.5mm respectively.

It was found that water washing reduces the released amount by up to 32% below 600°C, being more effective for the wood waste than for the wheat waste samples. The washing efficiency may be connected with the grain sizes, since the efficiency is higher for the finely milled WS2 than for the more coarsely ground WS1 sample. The acid treatment reduces the released amount below 600°C by around 70%. For the alkali release at temperature of 600-1000°C, the effects of the washing treatments are similar for these three biomass samples. It was also found that water washing of wood waste with 20m*l* de-ionised water gives a reduction in total alkali emission by about 35%, and acid leaching leaching gives a reduction of about 70%. For the wheat straws, the corresponding values are 50-80% for water washing and about 90% for acid leaching.

Table 4.8: Reduction in alkali release compared to untreated samples in percentage (130)

Davidsson et al. (130) studied the impact of grain size on washing efficiency by observing the reduction of alkali release during pyrolysis process, but the author of this thesis studied the impact of grain size by washing the feedstock at ambient temperature to 90°C by observing the ash reduction in biomass, and this work will be mentioned later in the Section 5.1.

4.3.5 Scott et al.

Scott et al. (131) published a preliminary study of the removal rates of alkaline cations present in poplar wood [potassium and calcium mainly] by washing with hot water and mild acid. The feedstock used was a clean sawdust of size less than 0.5mm, 0.8 mf wt% ash and dried to less than 10 mf wt% moisture content. Prior to a run, the glass column of about 3cm ID and 30cm length was filled with 25g of sawdust by adding a slurry in stages. The column was submerged in a water bath, and allowed to come to the desired operating temperature before a run was commenced. Three runs to determine the effect of temperature [30-60°C] and flow rate of slurry [4.9-15.0 m*l* min^{-1}] were carried out with 0.1 wt% nitric acid as the washing solution, and one run with distilled water at a temperature of 60°C.

Analysis of cation concentrations [H^+, Ca^{2+} and K^+] in the effluent was performed with three electrodes. They found that hot water washing alone is able to remove a major amount of the alkaline cations from wood as the results indicated that over 90% of the potassium and over 65% of the calcium were readily washed out by hot water. A mild acid can readily remove most of alkaline cations from biomass and it is more significant at temperature of 60°C. The results showed that the higher flow rate of slurry does not appear to cause any significant reduction in cation removal as the residence time of the wash solution in the bed was very short.

Scott et al. (131) performed the washing experiment by soaking the biomass in hot water at temperature 60°C, and the author of this thesis was washed the feedstock at 55°C as a basis for initial washing work, and this work will be mentioned later in the Section 5.1.

4.4 IMPACT OF ASH CONTENT ON BIO-OIL YIELD AND QUALITY

The study of pyrolysis on deashed biomass upon water washing pre-treatment has received very limited attention by researchers. Most of the researchers studied the pyrolysis product of deashed biomass that had been treated with acid washing. However, in general, deashing can enhance the organic liquid yield, initial decomposition temperature and rate of pyrolysis. The most relevant work found in the literature was carried out by Piyali Das et al. (129). Raveendran et al (126) studied the effect of ash on the pyrolysis products of feedstocks that were treated with mild acid washing. Their work will be reviewed in this section in order to study how the existences of ash in the biomass influences the organic yield.

Piyali Das et al. (129) investigated vacuum pyrolysis of deashed sugarcane bagasse focussing on the effect of deashing treatments on sugarcane bagasse pyrolysis product distribution [liquid, char and gas] and to understand the influence of this ash on the stability of liquid product. Sugarcane bagasse had been subjected to three different types of pre-treatments in their study. The pre-treatments were water washing, washing with 5[M] HC*l* solution and washing with HF solution ranging between a concentration 0.5 and 3%, and their work on washing pre-treatment had been reviewed critically in Section 4.3.2. These untreated and deashed sugarcane bagasses samples were then pyrolysed, and this will be reviewed below.

They conducted vacuum pyrolysis experiments on untreated and treated sugarcane bagasse. The reactor was electrically heated at a maximum temperature of 500°C under an initial reactor vacuum of 5kPa. At the end of each pyrolysis run, the reactor was cooled to room temperature under nitrogen flow and the char was collected from the biomass basket hung inside the reactor. The volatiles were gradually condensed in a pre-weighed condensing train. The condensates of dew point 60-65°C were collected and the balance was condensed in ice bath at temperature 5-7°C. The total condensable collected in the condensing train is termed as total liquid.

Table 4.9 shows the effect of deashing treatments on sugarcane bagasse pyrolysis product distribution [char, gas and total liquid including oil fraction]. It was found that the oil yield increased and the char yield decreased when ash content decreased. As well reported that upon deashing, both amount of volatiles and the rate of their evolution increases (42,141,142,143). In the presence of ash elements, the volatiles escaping undergo secondary cracking and form a soot deposit on the residual char. The liquid yield is highest [72.9 mf wt%] for treatment 9 [3% HF treatment] as the ash content of bagasse is 0.03 mf wt%.

Table 4.9: Pyrolysis product distribution of untreated and treated sugarcane bagasse (129)

It was found that the pyrolysis product distribution relates well to the chemical composition of sugarcane bagasse [see Table 4.4 and Table 4.6]. Referring to treatment 5 [leaching with 5M HCl], it was found that the percentage mass reduction was so high [50 mf wt%]. This acid solution had hydrolysed the hemicellulose fraction to a large extent leading to a drastic reduction of hemicellulose and extractives with a resultant increase in the apparent cellulose percentage in the deashed sugarcane bagasse, but the reduction in ash is not manifested; rather it actually seems to be increased. Therefore, the percentage increase in the oil yield is marginal and is not as high as it should have been.

Investigation on the stability characteristics of sugarcane bagasse pyrolysis oil was carried out. The variation of viscosity was monitored for untreated and treated bagasse pyrolysis oils, both stored at room temperature [25°C]. The viscosity was measured at 60°C. It was seen that compared to untreated bagasse oil initial viscosity as well as rate of change of viscosity of treated bagasse oil is higher. This is may be attributed to the more polar fractions present in treated oils. Pre-treatment hydrolysed cellulose and hemicellulose which results in the increase of more acidic as well as polar fraction in the oil leading to higher rate of increase of viscosity in the treated oil compared to untreated oil. The effect is more severe in case of acid pre-treatment, which leads to accelerate polymerisation giving more acidic oil having less water content.

The above experiments produced some interesting results, which are relevant to this work. Pre-treatment of sugarcane bagasse with water, dilute HC*l* solution and dilute HF solution showed a remarkable change in the pyrolysis product distribution. Simple water washing [with least possible water] for longer period is effective enough to reduce the extractives along with some selected ash components in bagasse. Although HF treatment removed the ash elements almost completely, but it didn't help in improving the stability. Similarly to treatment with HCl which leads to a marginal increase in oil yield but results in an increase in viscosity of oil. The stability of pyrolysis oil produced from EFB in this work was not carried out because the oil produced from 150 g/h rig is not enough to determine the viscosity index of the oil [see Sections 7.3.3.5 and 7.3.3.6], except for EBW09 as the oil produced used the 1kg/h rig. Even though this work only concentrated on water washing, however in order to study the existence of ash that influence the organic yield, the author felt that the above experiment is important to review as comparison purpose.

Raveendran et al. (126) investigated the effect of ash on the products of pyrolysis from 13 Bombay feedstocks. Table 4.10 lists the feedstocks which were used for their work along with component analysis. The objective of their work was to understand the influence of mineral matter on products yield. They studied two types of sample, the first was demineralised biomass and the second was synthetic biomass. Both demineralised and synthetic biomass were then assessed by thermogravimetric analysis [TGA].

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

Table 4.10: Component analysis of biomass, mf wt% (126)

Synthetic biomass was prepared by mixing individual biomass constituents [cellulose, lignin, xylan, extractives and ash] in proper proportions shown in Table 4.10. 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. The authors did not mentioned whether the other individual components were isolated from the specific biomass type or were supplied from a stock of cellulose, hemicellulose, lignin and xylan.

Thermal analysis of feedstocks, which were untreated, demineralised, synthetic and synthetic without ash, was carried out using thermogravimetric analysis at a heating rate of 50K/min in nitrogen flow. 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. However, these effects did not occur for rice husk, groundnut shell and coir pith. It was found that these biomass types had a high lignin content and high mineral matter notably potassium before demineralisation. The effect was less significant for wheat straw because of the lower lignin content and even had high potassium content. Thermal analysis of original biomass compared to synthetic biomass gave good matches, which the TGA and DTG curves matching closely. Therefore, it is a good correlation between deashed and synthetic biomass.

Pyrolysis experiments were carried out on untreated and demineralised samples of coir pith, corn cob, groundnut shell, rice husk and wood in a packed bed pyrolyser at 773 K. The volatiles were collected and quenched in a train of ice water cooled flasks, and nitrogen gas was used as carrier gas. 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 4.11 shows the results of the pyrolysis experiments. It was found that coir pith, groundnut shell and rice husk have an increased char yields after demineralisation, and the increase in char yield is much greater for rice husk than for coir pith and groundnut shell. The char yields decreased after demineralisation for other feedstock. There is a substantial increase in liquid yields for all feedstocks.

The results from above experiments are relevant to this work which is aimed at increased liquids production. It showed that the deashed feedstocks had produced higher yields of volatile products than untreated feedstocks, thus, the volatile products increased by removing the ash from biomass. However, exceptions to this are feedstocks containing high levels of potassium in conjunction with high lignin content such as coir pith, groundnut shell and rice husk.

A comparison of fast pyrolysis products from natural biomass against those from synthetic would be interesting to study. However, this is beyond the scope of this thesis. Therefore, it is recommended that pyrolysis experiment on natural biomass and synthetic biomass should be performed in the future to assess the effectiveness of deashed and synthetic biomass.

Table 4.11: Influence of ash on pyrolysis products (126)

4.5 KEY POINTS AND RELEVANCE FOR EXPERIMENTAL PLAN

Literature review in Section 4.3 suggested two key areas for investigation:

1. The effect of water alone on reducing ash content and it's effect on pyrolysis products yields.

2. The investigation of deashing process considering the variable of residence time, the ratio of biomass to water, temperature, amount of agitation utilised and particle size.

In order to make a comparison with the experiments done by Jenkins et al (127), the experimental conditions employed for this work have been chosen based on the work of Jenkins et al (127) who had soaked 100g of whole straw for 24 hours in 7*l* of distilled water at ambient temperature. Several important variables, however, were not investigated by Jenkins et al (127), such as residence time, the ratio of biomass to water, temperature, amount of agitation utilised and particle size. The author of this thesis investigated the impact of these variables as mentioned above. The work done by Davidsson et al. (130) and Scott et al. (131) allows some comparison with published experience for these variables, as well. Instead of using distilled water, the tap water was use for another series of experiment with same variables in order to study the impact of tap water on washing efficiency.

Subsequent to these experiments, the washing experiments at ambient temperature and utilised distilled water with aim to explore the impact of varying residence time, varying particle size and amount of wash water employed per 100g of biomass were carried out. Comparison to the experiments carried out by Piyali Das et al. (129) can be done as they studied the impact of the ratio of biomass to water on washing efficiency and the impact of ash in producing pyrolysis liquid. The results from water washing experiments are presented, analysed and discussed in Chapter 5.

The water washing experiment were designed and carried out at temperatures between ambient and boiling for a range of feedstock sizes and using soaking or stirring method. This equipment for washing experiments is discussed in more detail in Section 4.7.

4.6 FEEDSTOCK PREPARATION

The Empty Fruit Bunches [EFB] used in this work were supplied by the Malaysian Palm Oil Board [MPOB] and received in November 2002. Samples received were in the form of whole bunches. The bunches had to be chopped into smaller size pieces using a hand saw before they would fit into a shredder. This machine cut the pieces down into stringy strands of different lengths and sizes [2-3cm]. A Fritsch grinder with a screen size of 500μm was then used in order to achieve a feedstock size of less than 500μm. Feedstock moisture content was also measured to ensure that it was less than 10 wt% on a dry feed basis. NREL Standard Analytical Method LAP005 for ash analysis was carried out 5 times for each bag and the range of variation is relatively narrow [5.27-5.72 mf wt%]. Table 4.12 shows that with sieved feedstock the ash content is highest for the smallest particle size fraction. The mass average ash content from Table 4.12 is 5.39 mf wt%, which is within the range of feedstock ash content found in the EFB used for the water washing experiments [4.87-5.72 mf wt%].

Water washing experiments have been performed employing feedstock of three size ranges: 250-355μm, 1cm and 2-3cm. Size range of 250-355μm was chosen as it is used for a 150 g/h fluidised bed bench scale unit by the author and particle of size 2-3cm was chosen as it is a first particle size that was produced from grass cutter. In order to better understand the trend of diffusion processes within the feedstock, particle of size 1cm was chosen as it is about half of the difference between two ranges size as mentioned above. Three temperatures were looked at ambient temperature [26-28°C; ambient for Malaysia], 55°C and 90°C. Feedstock was sieved using standard test sieves of mesh 250μm and 355μm to obtain the feedstock of size 250-355μm. The feedstocks that emanated from the shredder had a size range of 2-3cm. The pieces were then cut down to approximately 1 cm using scissors. This procedure was followed for all experiments requiring such a size reduction step.

Table 4.12: Ash content of untreated EFB by size fraction

Feed particle size [μm]	Mass fraction	Average ash [mf wt%]
less than 250	22	7.44
250-355	30	5.29
355-500	42	4.82
more than 500	6	4.72
mass average	-	5.39

MPOB provided EFB which was 18 months old and was collected from an oil palm mill. This feedstock is referred to as "unwashed feedstock". The method of harvesting employed for the unwashed feedstock allowed contact of EFB with soil. Furthermore, it should be mentioned that the unwashed feedstock was taken from the oil palm mill after a sterilisation step, as the fruits are only separated from the sterilised bunch stalks in the stripping process. It is also possible that the unwashed feedstock would again have been in contact with soil during subsequent storage on the site of the oil palm mill. However, the physical shape and size of fruit bunches makes it much less likely that soil contamination is a significant factor than may be the case for some other biomass feedsstocks, such as straw, where harvesting equipment may scoop up a lot of soil together with the straw being cut in the field.

As described in Section 3.8.2, the first stage of extraction process of palm oil is sterilisation in which fresh fruit bunches [FFB] were subjected to live steam at temperature 140°C under a pressure of 2.5 to 3.2 kg/cm^2 for 50 minutes. The purpose of sterilisation is to deactivate the enzymes that responsible for the breakdown of oil into free fatty acid [FFA] and to loosen fruit from bunches. Therefore, it was expected that the structural of EFB would become weakening after gone through the sterilisation process. According to Gil Garrote et al. (144) due to the severe sterilisation, some solubilisation of hemicellulose may be expected but this condition are not harsh enough for the formation of large quantity of monomeric sugar. The hydrolysis of cellulose may be negligible as the condition need to hydrolyse the cellulose is more aggressive [i.e hydrolysed with enzymes and acid at high temperature more than 200°C] than hemicellulose (145).

There will be chemical and structural changes in the EFB caused by sterilisation process, but investigating in detail such as how much hemicellulose has hydrolysed and what oligosaccharides has produced through the sterilisation is beyond the scope of this thesis. However, it is possible that the composition analysis to be carried out in the future to determine hemicellulose hydrolysis products.

MPOB sourced EFB that was subsequently subjected to a quick water wash of about 60 seconds is referred to as "quick washed feedstock".

"Fresh feedstock" is EFB, which was sent by a relative to the author from Malaysia. During harvesting of this EFB, it was not allowed to come into contact with the soil in order to ensure that this EFB is free from any contamination. Furthermore, it's a more recently harvested feedstock and has not been subjected to sterilisation.

4.7 WATER WASHING SYSTEM AND A MASS BALANCE

Water washing tests were carried out in a glass reactor of size 2L, which was placed in a temperature adjustable water bath capable of operation between ambient temperature and close to boiling at atmospheric pressure that is about 20 to just under 100 degrees Celsius. A diagram of the water washing system employed in this work for simple soaking is shown in Figure 4.1. Feedstock of size 250-355 μm, 1 cm and 2-3 cm is referred to as respectively "small", "medium" and "large".

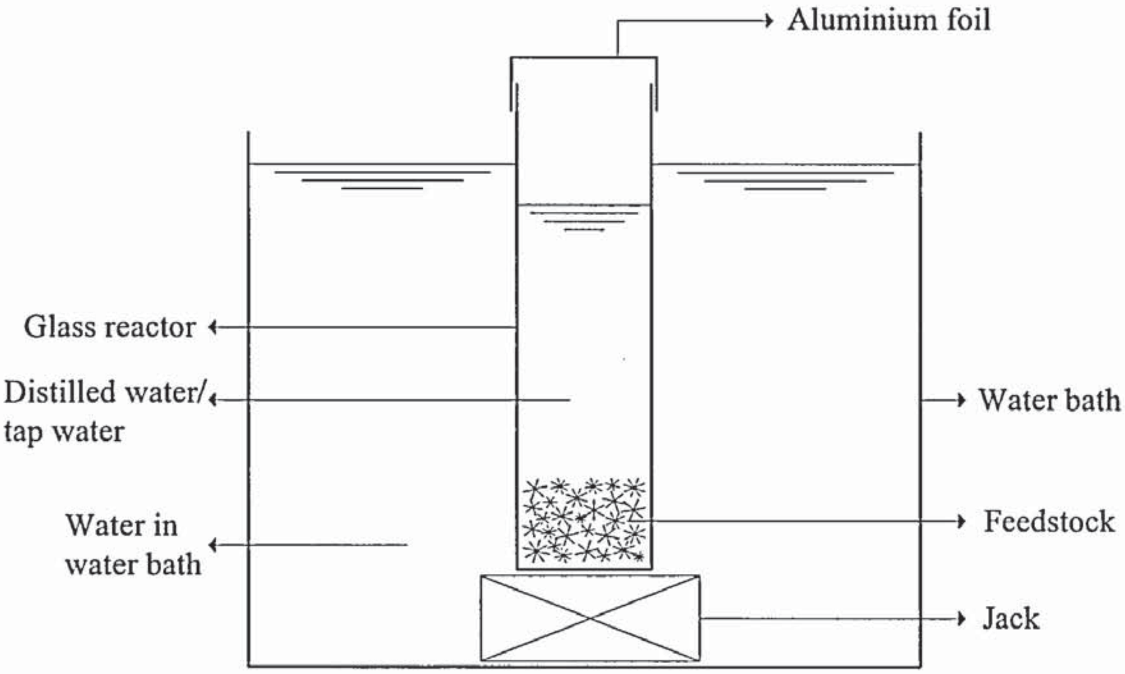


Figure 4.1: Diagram of water washing system for simple soaking

Figure 4.2 represents a flow chart of the water washing process of feedstock in chip form [medium size and large size]. The feedstock was soaked or stirred with a stainless stirrer [100-600 rpm], in distilled water or tap water, and at a fixed temperature. During this step, the glass reactor was covered with aluminium foil to maintain a constant temperature. The next step is sieving, for which a 60 mesh stainless steel sieve was used to separate the wet washed feedstock from the waste liquor. To remove any feedstock sticking to the glass reactor, it was washed out with a small amount of distilled water, and the feedstock was then allowed to drain for about 5 minutes to make sure that as much waste liquor as reasonably achievable was separated from the washed feedstock. The waste liquor was then filtered again with a 100 mesh stainless steel sieve. The filtrate obtained in this operation will be referred to as "leachate" and the filter cake as "sediment".

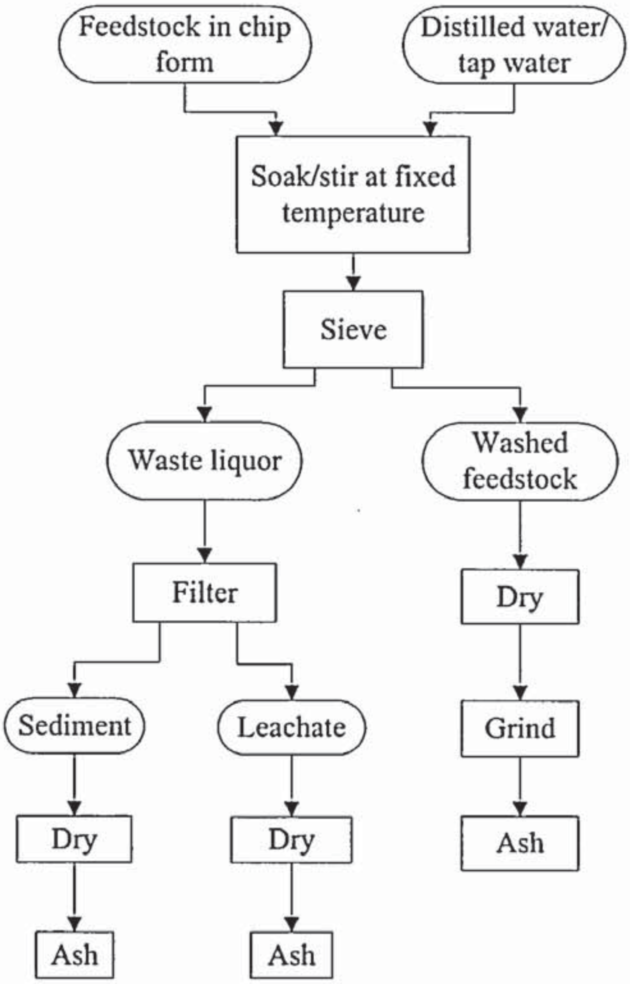


Figure 4.2: Water washing process of EFB in chip form

The filter cake was allowed to drain for 5 minutes in order to reduce the amount of leachate retained in the sediment to a minimum. The wet washed feedstock, wet sediment and leachate were then weighed for mass balance purposes and after that dried in a fan oven at 105°C for 24 hours. ASTM moisture and ash analysis was carried out and these analyses are described in detail in Section 6.2.3 [Moisture content] and Section 6.2.4 [Ash content]. The procedure for feedstock of small size, which is in the form of sawdust, only differs from the one shown in Figure 4.2 for chipped feedstock in that no grinding step is required before ashing.

In the mass balance as shown in Table 4.13, the input biomass is subdivided into ash and organic biomass constituents. The output is in the form of washed biomass, sediment and leachate, as can be gathered from the procedure already explained through Figure 4.2. Three balances are made, one for ash, one for organic biomass components and one for dry feedstock. In each case, the amount in the input biomass is compared with the total found in the three output categories of washed biomass, sediment and leachate. In turn this results in the calculation of three closures, overall, for ash and for organic biomass constituents. Furthermore, the amount of material washed out, that is the difference between washed and unwashed biomass, is calculated and compared with the amounts that can be found in the leachate and sediment, in order to obtain a measure of how great a fraction of the washed out material can be accounted for in those two output categories.

Each experiment is given a number followed by the prefix W [washing] followed by an alphanumerical code summarising the conditions of the water washing test; this code is explained in detail in Section 5.2.1. The temperature of the water in the glass reactor is controlled to a fixed value set for each experiment. The residence time of the feedstock indicates how long the feedstock is left in the glass reactor for each water washing test. The moisture and ash content of the feedstock before and after the run are calculated by the methods described in Sections 6.2.3 and 6.2.4 respectively. The total mass of ash contained in the feedstock before and after a run is needed in order to calculate a mass balance of ash. The weight of feedstock on a dry basis before and after a run was measured in order to calculate feedstock weight loss on a percentage basis during washing, and also the feedstock mass balance for each water washing test.

Table 4.13: Example of mass balance reporting for water washing analysis

Run no.	W1######
Temperature [°C]	Operating temperature of water bath.
Type of water	Either tap water or distilled water.
Residence time [hour]	Duration of washing.
Method of washing	Either soaking or stirring.
Amount of water [*l*]	Volume of water utilised per 100g feedstock.
Average ash content before wash [mf wt%]	Average ash content of the feedstock before water washing.
Average ash content after wash [mf wt%]	Average ash content of the feedstock after water washing.
Total ash before wash [g, dry basis]	Mass of ash contained in the unwashed feedstock before water washing.
Total ash after wash [g, dry basis]	Mass of ash contained in the washed feedstock.
Closure of ash balance	Percentage of ash input contained in the unwashed feedstock and, if utilised for washing, also in the tap water, recovered in the three output categories [leachate, sediment and washed feedstock].
Feed before wash [g, dry basis]	The weight of feedstock on a dry basis before water washing.
Feed remaining after wash [g, dry basis]	The weight of washed feedstock on a dry basis.
Total feed and residue [g, dry basis]	The total weight of all three output categories [leachate, sediment and washed feedstock] after washing on a dry basis.
Difference [g, dry basis]	The weight loss of the washed feedstock compared to the unwashed feedstock on a dry basis.
Percentage loss [mf wt%]	The above weight loss expressed as a percentage of the unwashed feedstock on a dry basis.
Closure of feed balance	Percentage of feed input recovered as products.

4.8 ANALYTICAL EQUIPMENT AND PROCEDURES UTILISED FOR WASHING EXPERIMENTS

The following is a description of analyses performed on unwashed feedstock and washed feedstock in order to find the properties of these feedstocks biomass.

4.8.1 Calorimetry

High heating value [HHV] is an important biomass property, as it indicates how much energy the biomass contains. Biomass represents a form of stored solar energy which has been converted through the photosynthetic activity of plants. To determine the HHV of the feedstock, bomb calorimetric technique has been employed in this work. Typical analysis errors for biomass samples are the range ±0.3% (146). Calorimetry is the quantitative measurement of the heat required or evolved during a chemical process. The bomb calorimeter provides the most suitable and accurate apparatus for the determination of the calorific values of solid and liquid fuels. A diagram of the bomb calorimeter is shown in Figure 4.3.

It is very useful for measuring the total amount of heat that a material can give off when burned completely. Much emphasis is placed on insulating the reaction to prevent heat loss. The reaction is carried out in a closed vessel, called a "bomb", which can withstand high pressures.

In this work, the bomb body consists of a hollow cylindrical vessel (147), 5 in. internal depth, 2¼ in. internal diameter and ½ in. thick, fitted with four plane facets which are a loose fit for a stout square sectioned socket in which the bomb may be placed while being assembled. On the top of the cylinder sits the bomb head which carries two electrodes, AA, one of which is connected to a ignition lead, while the other, bent into the form of a ring, serves as a holder for the crucible, B. Centrally placed in the bomb head, C is the valve for the introduction of oxygen. The stirrer is used for allowing free circulation of water on all sides. The experimental procedure employed is attached in Appendix F. This procedure is based on British Standard methods for the analysis and testing of petroleum products (147).

Figure 4.3: Typical bomb calorimeter assembly (adapted from 147)

Bomb calorimetry was performed on unwashed feedstock and washed feedstock for a range of ash contents and for two moisture contents in order to study the impact of ash and measured moisture content. The results of these experiments will be discussed in detail in Section 5.2.4.

4.8.2 Thermogravimetric Analysis

Thermogravimetric Analysis [TGA] is a thermal analysis technique used to measure changes in the weight [mass] of a sample as a function of temperature or time as it is subjected to a controlled temperature program in a controlled atmosphere (148). However, not all thermal events cause a change in the sample mass [e.g. melting, crystallisation, glass transition], but there are some important exceptions such as absorption, oxidation and decomposition. Thermogravimetry characterises the decomposition and thermal stability of materials under a variety of conditions and examines the kinetics of the physico-chemical processes accruing in the sample.

TGA was carried out on unwashed and washed feedstock for a range of ash content in order to evaluate the qualitative composition of the feedstock, in particular with regards to hemicellulose, cellulose, lignin and their thermal degradation behaviour. Each TGA was performed under 100m*l*/min nitrogen with a heating rate of 10°C/min. These analyses were carried out by a colleague of the author of this thesis, who used the Pyris 1 TGA which is a computer-controlled analyser.

4.8.3 Scanning Electron Microscope

The Scanning Electron Microscope [SEM] is one of the most versatile and widely used tools of modern science as it allows the study of both morphology and composition of biological and physical materials. Scanning electron microscopy combines high magnifications with exceptional depth of field to allow detailed microstructural examination of most materials. Sample preparation is quick and simple and the images obtained can have immense diagnostic value. Fracture surface topography, 3-D particulate morphology and surface finish can be qualitatively assessed by visual inspection (149).

Electron Dispersive X-ray Spectroscopy [EDX] analysis can be done within SEM, points on the sample can be targeted with an x-ray beam and their elemental composition determined quantitatively. By scanning many such points, elemental 'maps' of a surface can be produced to identify where individual elements are concentrated within the sample.

SEM analysis and EDX analysis were carried out on unwashed and washed feedstock for a range of ash content in order to study their surface structure and elemental composition. These analyses were performed at Aston Microscopy of Engineering with the assistance of the expert operator, who used a Cambridge S-90 Scanning Electron Microscope with digital computer imaging.

5. WATER WASHING EXPERIMENTS

The water washing experimental set-up was described in detail in Chapter 4. This chapter deals specifically with the results of water washing experiments.

A detailed investigation into water washing undertaken by the author is described in this chapter.

5.1 OVERVIEW OF WATER WASHING EXPERIMENTS

The main objective of this work is to investigate water washing of EFB in order to improve the quality and quantity of bio-oil by removing the ash from biomass, and this work will be mentioned later in Chapter 7. Therefore, a better understanding of the basic factors impacting water washing of EFB is important. The variables investigated include:

a. Use of agitation.

   The water washing efficiency was studied by comparing between soak and stir method. Stir method is expected to be more aggressive as it will enhance localised concentration gradient compared to soak method.

b. Type of water.

   This variable was studied using distilled water and tap water. Distilled water and tap water have acidic [pH 6.4] and alkaline [pH 8.7] property respectively. Thus, the different property of these water that will give greater effectiveness in removing the ash from biomass were studied.

c. Temperature of water.

   The effect of varying temperature from ambient to nearly boiling water at 90°C were studied for small and large feedstock in soak and stir method. Washing the small feedstock at 90°C using stir method is expected to be most aggressive in this water washing experiments.

d. EFB particle size.

   Two ranges size of EFB were studied. The particle of size 250-355μm and 2-3cm are referring to small and large feedstock respectively. In order to study the impact of feedstock harvesting, processing and by observing the diffusion process within the feedstock, an additional of medium feedstock of size 1cm was studied as well.

e. Residence time of EFB in water.
   The effect of varying residence time from very short washing time [several minutes] to long washing time [several hours] were studied for small and large feedstock with objective to define the minimum residence time needed to achieve equilibrium between feedstock and wash water.

f. Amount of water per 100g of biomass.
   The impact of varying amount of water employed per 100g of biomass for small and large feedstock were studied with objective to define the minimum water amount needed to get the wash water saturated with minerals.

g. Use of fresh i.e clean uncontaminated EFB and old i.e EFB that has been stored on the ground and been contaminated with soil.

   This variable was investigated in order to study the impact of feedstock harvesting, processing and storage, therefore the diffusion process within these feedstock were studied at ambient temperature to nearly boiling water at 90°C. The description of fresh EFB and old EFB is described in detail in Section 4.6.

The following categories of water washing experiments were performed:

1. Basic parameters:
   A series of 24 tests on feedstock of small and large size [see Section 4.6], employing a constant amount of wash water [7*l* per 100g of biomass], but systematically varying the type of water, the operating temperature and the washing method. All possible permutations of these options were investigated, which explains the total number of tests [24=2*2*3*2]. The residence time was largely kept constant, as well. However for soaking at ambient temperature, that is for four of the 24 experiments, a residence

time of 24 hours was chosen rather than the two hours employed for all other tests [twenty experiments].

2. Residence time of small feedstock in water:
   A series of eleven tests solely varying the residence time keeping all other variables constant [soaking at ambient temperature of small feedstock employing 4*l* of distilled water per 100g of biomass].
3. Amount of water per 100g small feedstock:
   A series of four tests solely varying the amount of wash water keeping all other variables constant [soaking in distilled water for 2 hours at ambient temperature of small feedstock].
4. Residence time of large feedstock in water:
   A series of ten tests varying the residence time keeping most other variables constant [washing at ambient temperature of large feedstock employing 5*l* of distilled wash water per 100g of biomass]. In the six tests looking at residence times greater than 2 minutes soaking was employed, while in the four quick washes manual agitation was utilised. The quick wash utilising a residence time of 1 minute was repeated to investigate the effect of employing a Whatman No.1 filter paper to filter the waste liquor instead of a 100 mesh stainless steel mesh.
5. Amount of water per 100g large feedstock:
   A series of three tests solely varying the amount of wash water per 100g of biomass keeping all other variables constant [soaking in distilled water for two hours at ambient temperature of large feedstock].
6. Tests to study diffusion of unwashed feedstock:
   A series of nine tests varying particle size [small, medium and large] and operating temperature with all other variables kept constant [soaking for two hours in 5*l* of distilled water per 100g of biomass]. As for all previous experiments unwashed feedstock sourced from MPOB was employed.
7. Tests to study diffusion of "quick washed" feedstock:
   Nine tests as per series 6 but employing "quick washed" feedstock [see Section 4.6].

8. Tests to study diffusion of "fresh feedstock":

   Nine tests as per series 6 but employing "fresh" feedstock [see Section 4.6].

To give an even clearer picture to the reader these experiments are also listed systematically in Table 5.1. The effectiveness of each washing test was quantified by observing the percentage of ash reduction. The highest percentage of ash reduction indicates the best water washing test parameters. The results from Jenkins et al (127) and Piyali Das et al (129) for their work on water washing show that ash is proxy indicator of potassium and sodium. They indicate that the reduction in ash is clearly not proportional to the reductions in alkali metals. However, there is a correlation, and it can therefore be assumed that a given level of ash reduction will likely roughly correspond to a particular level of alkali metal reduction, at least for water washing, as removal of alkali and earth alkali metals dominates the overall reduction in ash content.

A total of 79 water washing experiments, all with mass balance closures greater than 95% for ash and feedstock, were carried out in this work. The nine experimental categories described above were subdivided into three work areas, namely initial investigation into basic parameters, the effects of varying residence time and amount of wash water and finally the impact of feedstock harvesting, processing and storage. These work areas are explained in Sections 5.1.1 to 5.1.3. The actual results of the water washing tests will be described and discussed in detail in Section 5.2. The variables used for each water washing experiments are given in Appendix E.

Table 5.1: Experimental plan of water washing

Category no.	Type of water	Particle size	Residence time, min.	Washing method	Temp., °C	Amount of water, *l*	No. of exp.
1	distilled water and tap water	small and large	1440	soak	26-28	7	4
	distilled water and tap water	small and large	120	soak	55, 90	7	8
	distilled water and tap water	small and large	120	stir	26-28, 55, 90	7	12
2	distilled water	small	0.2, 10, 20, 30, 60, 120, 180, 240, 360, 420, 480	soak	26-28	4	11
3	distilled water	small	120	soak	26-28	0.75, 1.25, 2.25, 4	4
4	distilled water	large	0.5, 1, 2 [quick washed]	manual agitation	26-28	5	4
			10, 20, 30, 60, 120, 180	soak	26-28	5	6
5	distilled water	large	120	soak	26-28	1.5, 3, 5	3
6	distilled water	small, medium and large	120	soak	26-28, 55, 90	5	9
7	distilled water	small, medium and large [quick washed feedstock]	120	soak	26-28, 55, 90	5	9
8	distilled water	small, medium and large [fresh feedstock]	120	soak	26-28, 55, 90	5	9

5.1.1 Initial Investigation into Basic Parameters

This work area encompasses the 24 experiments listed in category no. 1 in Table 5.1. Four parameters were investigated systematically, namely temperature of water, particle size, type of water and the use of agitation. While the effects of varying temperature and particle size are considered further in the other two work areas, only distilled water and soaking were employed there. As explained in Section 5.2, the impact of using distilled water or of stirring was usually relatively modest. More importantly, the composition of tap water varies across the world, while this is not the case for distilled water. It was therefore felt that the use of distilled water would facilitate comparisons with other work and also ensure greater repeatability and consistency of the results. Agitation may contribute to mass balance errors, as it provides extra opportunities for losses or contamination, be it biomass sticking to the stirrer or through the hole in the aluminium foil necessary to allow the stirrer shaft through, and adds greater complexity to performing experiments at little scientific benefit.

The experimental conditions employed for this work area have been chosen based on the work of Jenkins et al (127) who had soaked 100g of whole straw for 24 hours in 7*l* of distilled water which given the highest ash reduction of almost 50%. This method was chosen because the author expected that by using the longest residence time and large amount of water will give the highest ash reduction as well. A comparison to the experiments done by Jenkins et al (127) was most appropriate, when employing similar conditions, as was the case for the four soaking tests at ambient temperature. Water amount of 7*l* and residence time of 24 hours is the starting figure for this work. This work will be explored in order to study the impact of varying water amount employed per 100g biomass and varying residence time.

5.1.2 Impact of Residence Time and Amount of Water

This area of work encompasses categories no. 2 and 3 [for small feedstock] and no. 4 and 5 [for large feedstock] in Table 5.1. The aim of this work was to explore the impact of varying residence time and amount of wash water employed per 100g of biomass. All runs for this series of experiments were carried out at ambient temperature. As the initial work indicated that ambient temperatures were sufficient to achieve very high ash reductions, it was felt that the use of ambient temperature would probably prove most economical for later industrial washing operations. To reduce the number of experiments in the matrix it was therefore decided that it would be appropriate not to vary the temperature for this area of work.

A total of 28 tests were performed, fifteen for small feedstock and another thirteen for large feedstock. Eleven tests were carried out by soaking small feedstock in distilled water over a range of residence times [0.2 min, 10 min, 20 min, 30 min, 60 min, 120 min, 180 min, 240 min, 360 min, 420 min and 480 min]. Approximately 4*l* of distilled water was used per 100g of feedstock. These experiments indicated that after approximately 120 minutes a plateau was reached in terms of the amount of ash reduction achieved. Soaking for longer would yield virtually no further ash reduction.

This residence time was therefore chosen to explore the effect of varying the amount of wash water employed per 100g of biomass in four tests for small feedstock [0.75*l*, 1.25*l*, 2.25*l* and 4*l*].

A similar set of tests was performed for large feedstock to investigate the effect of varying residence time and amount of wash water employed per 100g of biomass. In ten tests the residence time was varied, while employing a constant amount of wash water [5*l*]. For very short washing times [0.5 min, 1 min and 2 min] manual agitation was employed. The water washing test performed for a residence time of 1 minute was later repeated to investigate the effect of utilising a Whatman No.1 filter paper instead of a 100 mesh stainless steel mesh. For longer residence times [10 min, 20 min, 30 min, 60 min, 120 min and 180 min] simple soaking was employed. The experiments again indicated, though less so than for small feedstock, that after approximately 120 minutes relatively little further ash reduction could be achieved. Consequently, and to be more comparable with other tests utilising the same residence time, three tests varying the amount of wash water employed per 100g of biomass [1.5*l*, 3*l*, and 5*l*] were carried out with a residence time of 120 min.

5.13 Impact of Feedstock Harvesting, Processing and Storage

In this work area the experiments listed in categories no. 6, 7 and 8 in Table 5.1 are considered. The aim of this work was to gain a better understanding of the impact of any contamination during harvesting or storage, and of any degradation due to processing or long periods of storage. Furthermore, the effects of temperature and particle size are considered in more detail.

In all 27 tests 5*l* of wash water were used. Three feedstocks are considered, firstly "unwashed" feedstock, secondly, "quick washed" feedstock, and thirdly, "fresh" feedstock. As explained earlier in Section 4.6, "unwashed" feedstock was supplied by MPOB. "Quick washed" feedstock is MBOB sourced feedstock that was subjected to a quick wash of about 60 seconds at Aston. Fresh feedstock refers to EFB, which was harvested by a relative of the author who took great care to avoid any possible contamination either during the harvesting process or during later storage.

5.2 RESULTS AND DISCUSSION

The results of the water washing experiments are discussed in the following sections.

5.2.1 Initial Water Washing Experiments

The results of all the 79 washing tests are summarised in a number of tables in this chapter. The first table presented is Table 5.2. At this point it is appropriate to introduce the acronyms used to identify each test quickly. W1SSOATT [from Table 5.2] will be taken as an example. The first letter is always W, which stands for washing experiment. All the tests are numbered sequentially, following the first letter. This number is followed by a letter designating the particle size, S standing for small [250-355μm], M for medium [1cm] and L for large [2-3cm]. Then the washing method is pointed out utilising two letters with SO standing for soaking and ST for stirring. This is followed by the designator for the temperature of washing with AT standing for ambient temperature [26-28°C], 55 for 55°C and 90 for 90°C. The last letter indicates the type of water used for washing with T standing for tap water and D for distilled water.

Table 5.2 and Table 5.3 summarise the washing tests performed for small particle by soaking and stirring respectively. The tests performed for large particles can be found in Table 5.4 and Table 5.5. A total of 24 water washing tests are described in these four tables, with each table containing six tests. In all of these water washing tests, 7*l* of water were used per 100g feedstock. Unwashed feedstock in these tests is MPOB sourced EFB not previously subjected to any washing. The results of the mass balance for ash and feedstock and also the percentage loss of feed after washing are shown for each experiment in these tables. However, in order to calculate the mass balance for feedstock, the weight of feedstock before washing must be added with the ash contained in tap water [0.14 mf wt%] for the feedstock washed with tap water. As example, for run number W1SSOATT, the weight of feedstock before washing is 23.70 mf wt% and it will become 23.84 mf wt% if added with 0.14 mf wt%, thus the mass balance for feedstock is 99.9.

Table 5.2: Run conditions and mass balance summary for water washing by soaking for particles of size 250-355 μm

Run no.	Unwashed EFB	W1SSOATT	W2SSOATD	W3SSO55T	W4SSO55D	W5SSO90T	W6SSO90D
Temp. [°C]	-	26-28	26-28	55	55	90	90
Residence time [hour]	-	24	24	2	2	2	2
Type of water	-	tap water	distilled water	tap water	distilled water	tap water	distilled water
Amount of water [*l*]	-	7	7	7	7	7	7
Average ash content [mf wt%]	5.27	1.42	1.06	1.38	1.25	1.26	1.13
Percentage of ash reduction [%]	-	73.1	79.9	73.8	76.3	76.1	78.6
In feed before washing							
Total ash [g, dry basis]	-	1.39	1.25	1.39	1.25	1.39	1.25
Total recovering after washing							
Total ash [g, dry basis]	-	1.36	1.25	1.37	1.20	1.32	1.25
Closure of ash balance	-	97.8	99.9	98.9	95.9	95.1	99.9
Before washing							
Feed [g, dry basis]	-	23.70	23.72	23.73	23.69	23.70	23.69
After washing							
Feed remaining [g, dry basis]	-	22.17	21.86	21.61	21.43	21.19	21.10
Total of feed and residue [g, dry basis]	-	23.80	23.72	23.47	23.35	23.25	23.35
Difference [g, dry basis]	-	1.53	1.85	2.11	2.26	2.51	2.59
Percentage loss [mf wt%]	-	6.45	7.81	8.90	9.53	10.6	10.9
Ash loss, g	-	1.07	1.02	1.08	0.98	1.20	1.0
Non-ash loss, g	-	0.46	0.84	1.03	1.28	1.30	1.59
Non-ash unaccounted, g	-	-0.14	-0.01	0.24	0.29	0.30	0.34
Closure of feed	-	99.9	100	98.3	98.6	97.5	98.6

Table 5.3: Run conditions and mass balance summary for water washing by stirring for particles of size 250-355 μm

Run no.	Unwashed EFB	W7SSTATT	W8SSTATD	W9SST55T	W10SST55D	W11SST90T	W12SST90D
Temp. [°C]	-	26-28	26-28	55	55	90	90
Residence time [hour]	-	2	2	2	2	2	2
Type of water	-	tap water	distilled water	tap water	distilled water	tap water	distilled water
Amount of water [*l*]	-	7	7	7	7	7	7
Average ash content [mf wt%]	5.27	1.26	1.20	1.23	1.16	1.14	1.08
Percentage of ash reduction [%]	-	76.1	77.2	76.7	77.9	78.3	79.5
In feed before washing							
Total ash [g, dry basis]	-	1.39	1.25	1.39	1.25	1.39	1.25
Total recovering after washing							
Total ash [g, dry basis]	-	1.32	1.24	1.35	1.19	1.32	1.24
Closure of ash balance	-	95.0	99.7	97.2	95.6	95.4	99.6
Before washing							
Feed [g, dry basis]	-	23.70	23.70	23.70	23.70	23.69	23.70
After washing							
Feed remaining [g, dry basis]	-	21.87	21.62	20.69	20.50	20.28	20.25
Total of feed and residue [g, dry basis]	-	23.61	23.59	23.39	23.30	23.12	23.29
Difference [g, dry basis]	-	1.82	2.07	3.0	3.19	3.41	3.44
Percentage loss [mf wt%]	-	7.70	8.75	12.68	13.48	14.39	14.53
Ash loss, g	-	1.0	0.98	1.13	1.01	1.15	1.02
Non-ash loss, g	-	0.72	1.09	1.87	2.19	2.25	2.43
Non-ash unaccounted, g	-	0.02	0.10	0.27	0.34	0.50	0.40
Closure of feed	-	99.1	99.6	98.1	98.3	97.0	98.3

Table 5.4: Run conditions and mass balance summary for water washing by soaking for particles of size 2-3 cm

Run no.	Unwashed EFB	W13LSOATT	W14LSOATD	W15LSO55T	W16LSO55D	W17LSO90T	W18LSO90D
Temp. [°C]	-	26-28	26-28	55	55	90	90
Residence time [hour]	-	24	24	2	2	2	2
Type of water	-	tap water	distilled water	tap water	distilled water	tap water	distilled water
Amount of water [*l*]	-	7	7	7	7	7	7
Average ash content [mf wt%]	5.43	1.45	1.29	1.42	1.39	1.37	1.25
Percentage of ash reduction [%]	-	73.3	76.3	73.9	74.5	74.8	77.0
In feed before washing							
Total ash [g, dry basis]	-	1.45	1.31	1.44	1.31	1.44	1.30
Total recovering after washing							
Total ash [g, dry basis]	-	1.41	1.25	1.41	1.30	1.40	1.30
Closure of ash balance	-	97.5	95.7	98.0	99.8	96.8	99.9
Before washing							
Feed [g, dry basis]	-	24.05	24.15	24.0	24.05	24.03	23.97
After washing							
Feed remaining [g, dry basis]	-	23.21	23.06	22.14	22.14	22.02	21.92
Total of feed and residue [g, dry basis]	-	24.23	24.31	23.99	23.94	23.63	23.53
Difference [g, dry basis]	-	0.84	1.09	1.87	1.91	2.01	2.05
Percentage loss [mf wt%]	-	3.51	4.53	7.78	7.94	8.36	8.54
Ash loss, g	-	1.11	1.01	1.13	1.00	1.14	1.03
Non-ash loss, g	-	0.0	0.08	0.74	0.91	0.87	1.02
Non-ash unaccounted, g	-	-0.21	-0.21	-0.01	0.10	0.36	0.44
Closure of feed	-	100	101	99.3	99.6	97.7	98.2

Table 5.5: Run conditions and mass balance summary for water washing by stirring for particles of size 2-3 cm

Run no.	Unwashed EFB	W19LSTATT	W20LSTATD	W21LST55T	W22LST55D	W23LST90T	W24LST90D
Temp. [°C]	-	26-28	26-28	55	55	90	90
Residence time [hour]	-	2	2	2	2	2	2
Type of water	-	tap water	distilled water	tap water	distilled water	tap water	distilled water
Amount of water [*l*]	-	7	7	7	7	7	7
Average ash content [mf wt%]	5.43	1.42	1.28	1.35	1.23	1.24	1.15
Percentage of ash reduction [%]	-	73.9	76.5	75.2	77.3	77.2	78.8
In feed before washing							
Total ash [g, dry basis]	-	1.44	1.30	1.45	1.31	1.44	1.30
Total recovering after washing							
Total ash [g, dry basis]	-	1.37	1.25	1.42	1.28	1.44	1.25
Closure of ash balance	-	95.0	96.0	98.4	97.7	100	95.8
Before washing							
Feed [g, dry basis]	-	23.97	24.0	24.07	24.13	23.98	24.01
After washing							
Feed remaining [g, dry basis]	-	22.79	22.63	22.21	22.08	21.65	21.62
Total of feed and residue [g, dry basis]	-	24.16	25.09	24.21	24.60	23.37	23.50
Difference [g, dry basis]	-	1.18	1.37	1.86	2.06	2.34	2.40
Percentage loss [mf wt%]	-	4.92	5.71	7.71	8.52	9.75	9.98
Ash loss, g	-	1.12	1.01	1.15	1.04	1.17	1.05
Non-ash loss, g	-	0.06	0.36	0.71	1.02	1.16	1.34
Non-ash unaccounted, g	-	-0.27	-1.14	-0.17	-0.50	0.62	0.45
Closure of feed	-	100	104	100	102	96.9	97.9

Some closures in the overall feedstock balances in this work are greater than 100%. This is unlikely to be due to contamination for a number of reasons. Firstly, an aluminium foil has been employed to prevent dust from settling into the washing vessel. Secondly, dust may be expected to contain a large amount of ash and to therefore disproportionately affect the ash rather than the overall balance. Thirdly, the feedstock closure is a function of both particle size and temperature, with no feedstock closure above 100% for a temperature of 90°C or for small particles. Contamination from dust, however, may be expected to be relatively random. Possible sources of error include mismeasurement of the moisture content of feedstock, sediment or leachate, either due to their hygroscopic nature, which may apply particularly in the case of leachate, or due to the loss of light organic volatiles either during drying or during washing. These possibilities will be discussed further in the light of other results obtained in this work, which are presented later on in this chapter.

The results from all the four tables show that ash content was reduced by every treatment employed. The average ash content for unwashed EFB was 5.27 mf wt%. The lowest ash content achieved is 1.06 mf wt%. The treatment employed in this case was soaking small feedstock in distilled water for 24 hours, and the percentage of ash reduction is 79.9%. Using the same treatment on large feedstock reduced the ash level to 1.29 mf wt%, which is equivalent to an ash reduction of 76.3%. Jenkins et al. (127) achieved a much smaller ash reduction for straw with the same treatment, which is likely due to the much higher silicate content of their feedstock, as the reduction in potassium was similarly large as the overall reduction for EFB in this work. This question will be further discussed later on in the chapter. It can be said that the ash reduction is higher for small compared to large feedstock, as was also found by Davidsson et al (130) who argue that the grain size would be expected to impact washing efficiency. Stirring the feedstock in hot distilled water for 2 hours at 90°C was also very effective, yielding averages of 1.08 and 1.15 mf wt% ash for small and large feedstock respectively. However, generally the percentage of ash reduction is more than 70% for all treatments every one of which achieves an ash content at least as low as 1.45 mf wt%.

The results shown in Table 5.2 to Table 5.3 and Table 5.4 to Table 5.5 are also illustrated in Figure 5.1 and Figure 5.2 respectively. Figure 5.1 and Figure 5.2 give the percentage ash reduction for washing over a temperature range of 27-90°C, for small and large particles respectively. In all instances, stirring was found to be more effective than soaking, as would be expected based on the fact that stirring enhances localised concentration gradients by carrying more highly concentrated solution away from the plant matter and replacing it with wash water from the main body of liquid, thereby reducing the need for diffusion to perform this task. Stirring may also enhance washing through weakening of the biomass structure, which may result in some size reduction or the breakage of for example cell walls. The effect of stirring is generally modest, particularly so for small particles using distilled water at high temperature and also for large particles when employing lower temperature wash water. The ash reduction was never enhanced by more than about 3%, and in the two cases just cited by only about 1%.

The impact of using tap water rather than distilled water can be seen in these figures as well. The figures indicate that distilled water is more effective at washing out ash than tap water. Distilled water has a pH value of 6.4, while the pH of tap water is about 8.7. The relative acidity of distilled water may partially explain its greater washing effectiveness. Moreover, tap water already contains a large number of ions in solution, as shown by the measured conductivity of 102 μS/cm whereas the conductivity of distilled water is zero. The conductivity of distilled water and tap water were both measured with a HI 9033 multirange conductivity meter. Greater concentration gradients would be expected to drive faster diffusion and osmotic pressure may even be large enough to destroy some cell components, giving two further reasons for the beneficial effect of using distilled water. At this point it should also be mentioned again that the ash contained in tap water has been measured by drying and was accounted for in the mass balance.

The impact of changing over to tap water is similarly modest as the difference made by stirring rather than soaking.

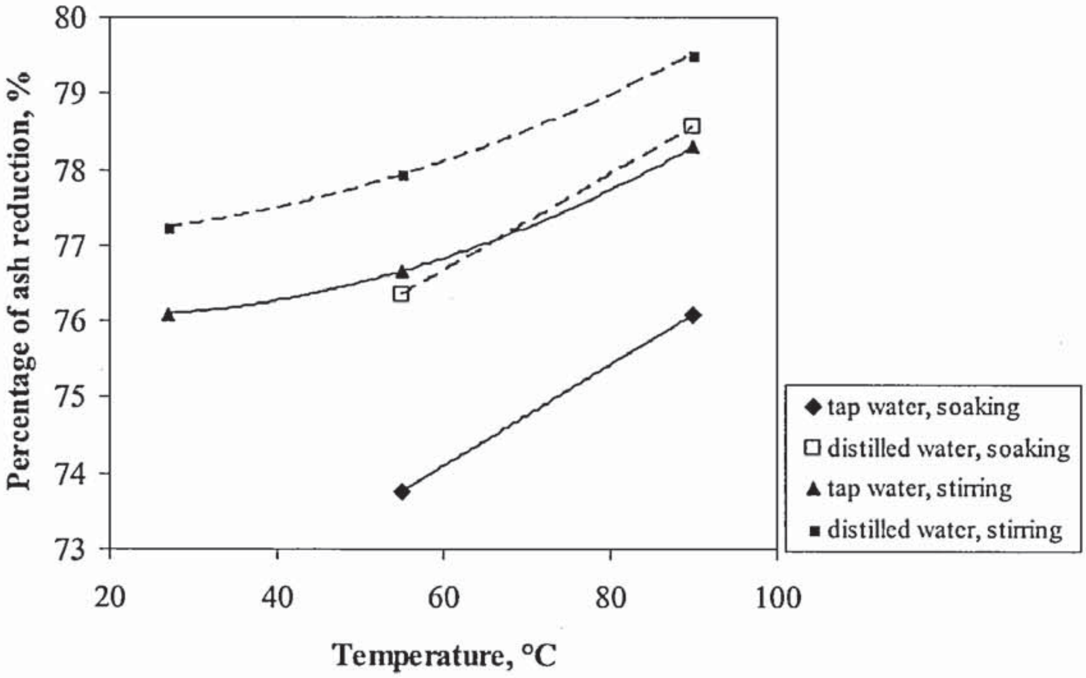


Figure 5.1: **Percentage ash reduction for particle of size 250-355 μm**

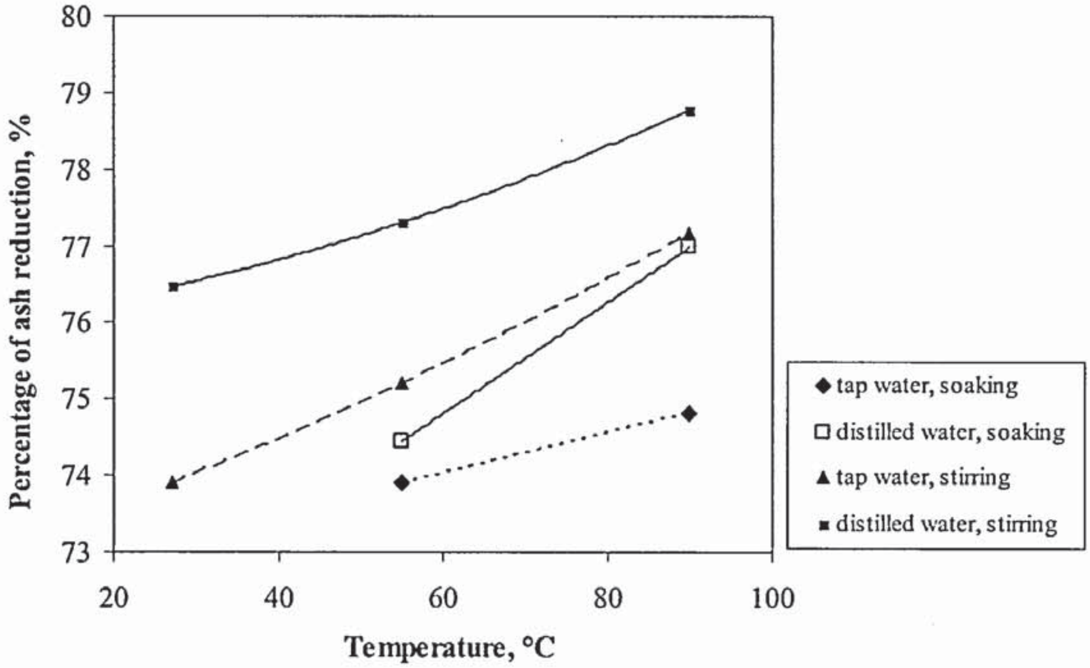


Figure 5.2: **Percentage ash reduction for particle of size 2-3 cm**

Figure 5.1 and Figure 5.2 also show that increased temperature enhances ash removal consistently, though again the differences are relatively modest. This may be due to greater rates of diffusion brought about by the faster movement of molecules at higher temperatures. It is also possible that the biomass becomes structurally weaker, enabling ash to more easily diffuse out. And thirdly, the solubility of the minerals making up the ash may increase at higher temperature, which would also enhance diffusion.

Figure 5.3 illustrates the impact of soaking small or large feedstock for 24 hours in distilled or tap water.

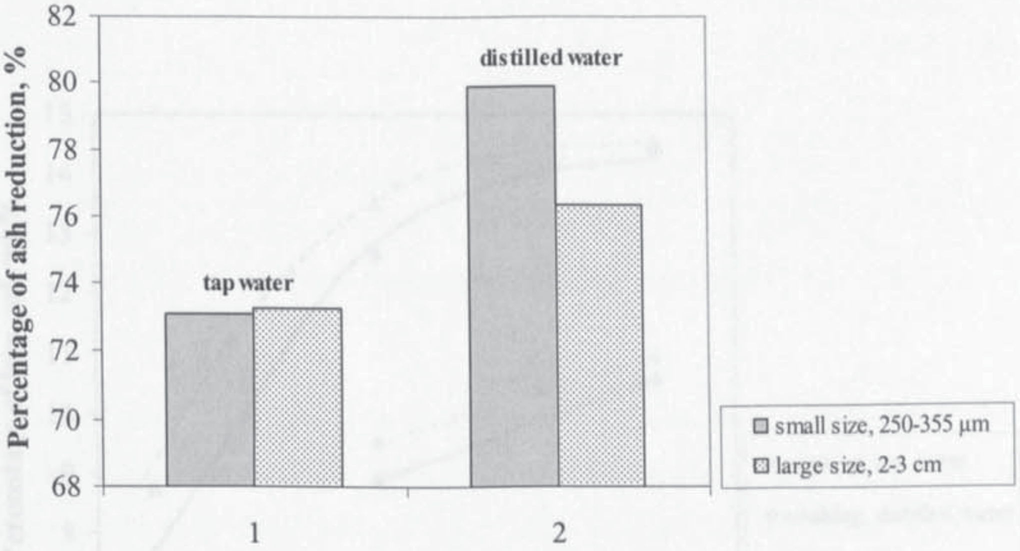


Figure 5.3: **Percentage ash reduction for particles of size 250-355 µm and 2-3 cm when soaking for 24 hours at ambient temperature**

Soaking small feedstock in tap water at ambient temperature gives virtually the same reduction in ash content as soaking large feedstock. On the other hand, when distilled water was employed particle size does have a significant impact. The size of the ash reduction would be expected to level off over time, as the wash water becomes saturated with minerals and an equilibrium was established. The results illustrated in Figure 5.3 may be indicative of the fact that this equilibrium point has been reached after 24 hours for both small and large particles when employing tap water. While on the other hand, there is still some room for further ash loss through diffusion when employing distilled water for washing.

The percentage loss of feedstock from washing for small and large feedstock is represented in Figure 5.4 and Figure 5.5 respectively. From both figures it was noticeable that biomass losses increase significantly as the temperature of the water washing test was raised. This fact may be explained in a similar fashion as for ash. Higher temperatures enhance diffusion directly, may increase solubility and lead to a structural weakening of the biomass. It is, however, remarkable how large the impact of temperature on biomass losses is, particularly when compared with the rather modest improvement for ash removal.

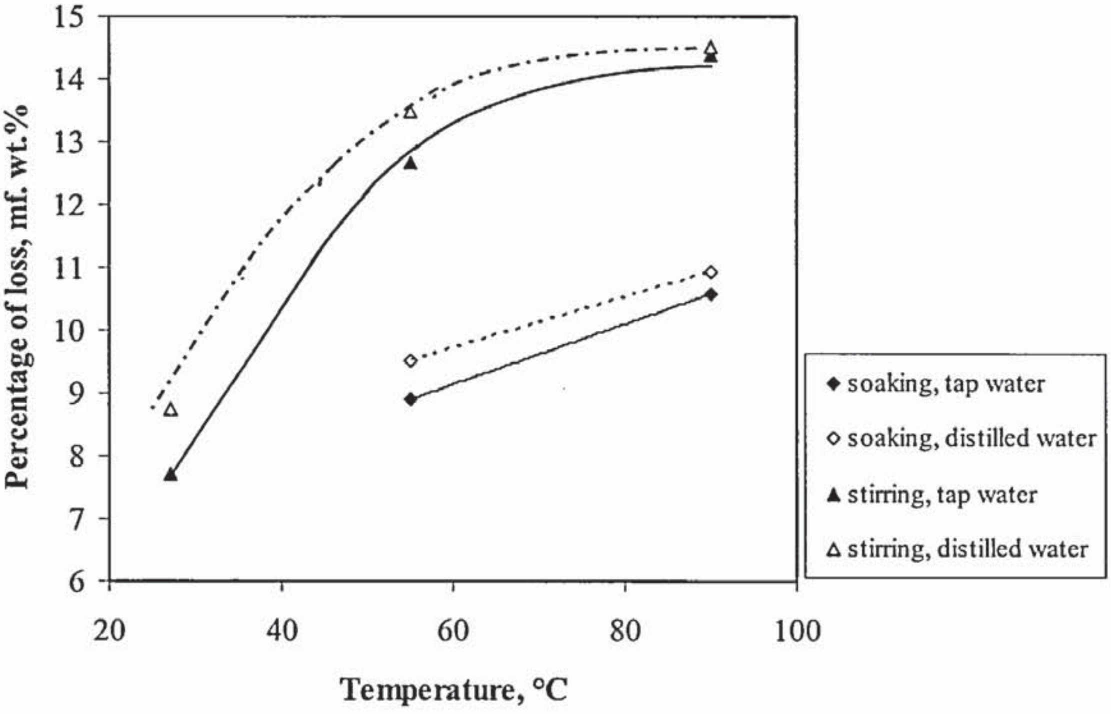


Figure 5.4: Percentage loss of feedstock for particle of size 250-355 μm

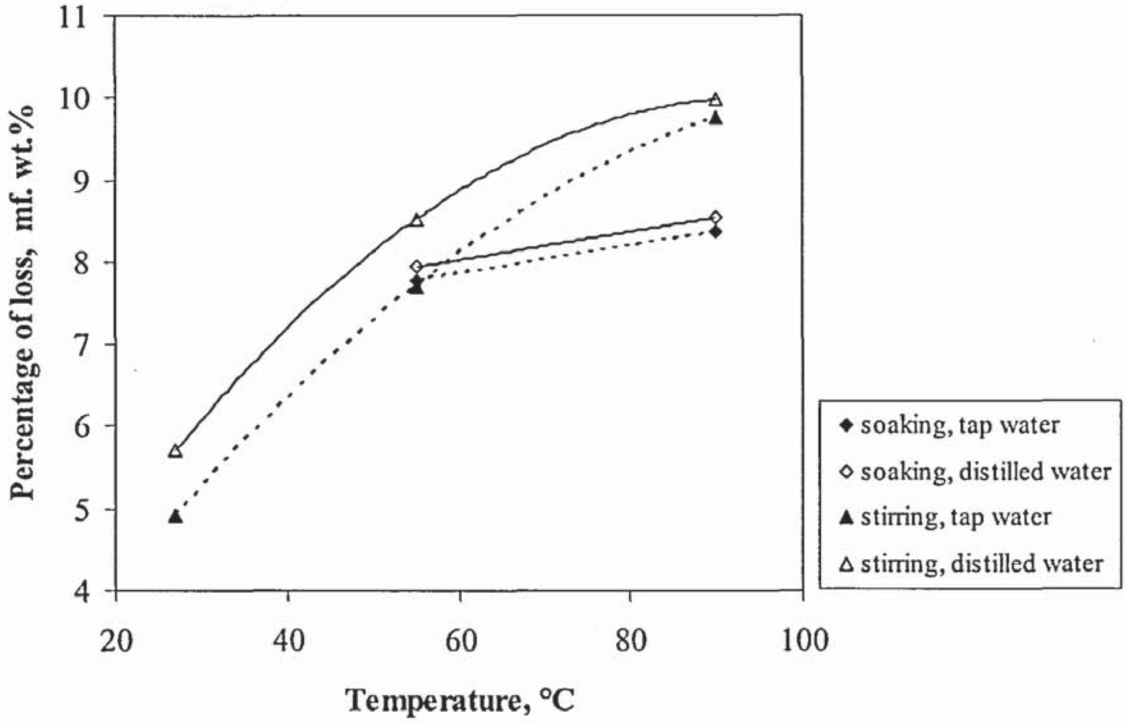


Figure 5.5: Percentage loss of feedstock for particle of size 2-3 cm

Most ionic and molecular solids are more soluble in hot water than in cold water but with an exception of a few (150). If the solution process absorbs energy then the solubility will be increased as the temperature was increased. If the solution process releases energy then the solubility will decrease with increasing temperature. As example, the solubility of sodium chloride is constant, lithium sulphate was decreased but silver nitrate was increased when the temperature was raised from 0°C to 100°C (150).

The trend lines as drawn in Figure 5.1 to Figure 5.2, and Figure 5.4 to Figure 5.5 are not meant to imply that experiment result in between 55°C and 90°C can be linearly interpolated, for example if an experiment was carried at 70°C, the author would not necessarily expect the result to lie on the line as drawn in Figure 5.1. In fact, it is not unreasonable to expect that experimental point to be found below the line as drawn in Figure 5.1.

Figure 5.6 shows that the percentage loss of feedstock for small feedstock is higher than for large feedstock. It is possible that some of these losses could be due to handling such as small amounts of biomass remaining on stainless sieve, stirrer and glass reactor. However, any feedstock sticking to the stirrer and glass reactor were removed by washing out with a small amount of distilled water.

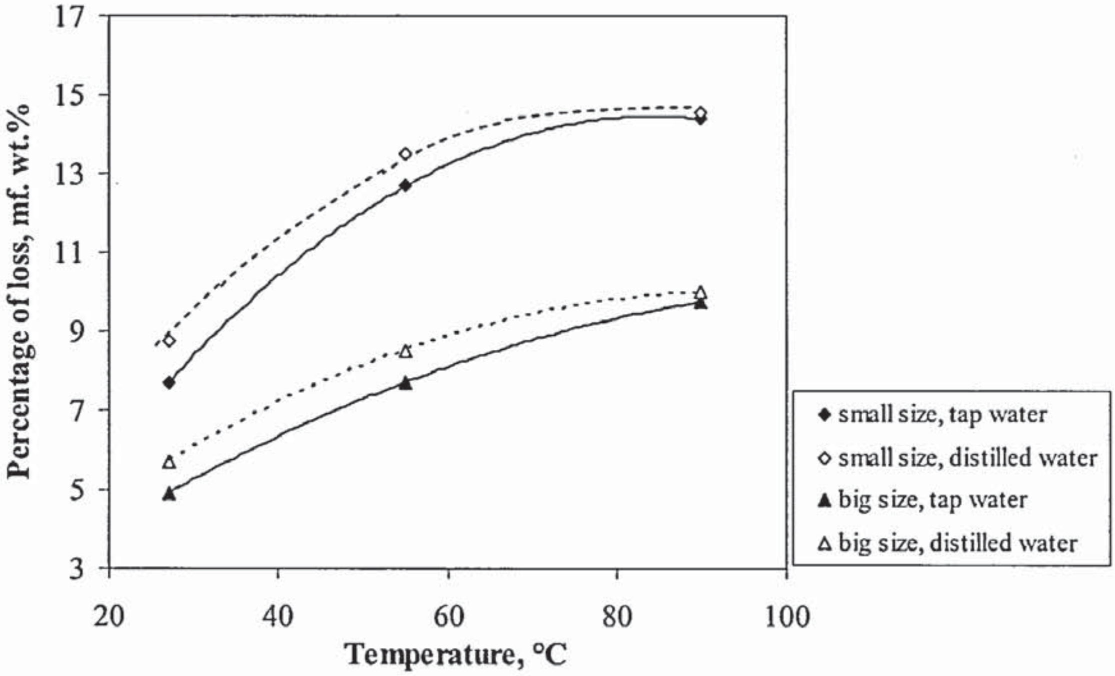


Figure 5.6: Percentage of weight loss between biomass of size 250-355 μm and biomass of size 2-3 cm by stirring method

It is also believed that the feedstock loss during the feedstock transferring process from glass reactor to sieve even though every care was taken to remove all feedstock from the glass reactor to sieve and from the sieve to the beaker. This experimental loss had been minimised by washing large feedstock as shown in Figure 5.6. The percentage loss of feedstock increased significantly by increasing of water temperature for both size of feedstock. It may suggest that stirring and temperature improve microscopic mixing of wash water and feedstock, thus enhance diffusion directly, may increase solubility and lead to a structural weakening of the biomass.

There are several possibilities for the losses of the feedstock composition during water washing such as organic compounds that are soluble in water which consists of low molecular weight organic compounds [e.g acetic acid] that could evaporate during drying and organic compounds that are soluble in water [e.g sugar] but would not evaporate during drying. The organic compound that easily dissolved without structural breakdown of the biomass and bound to biomass or contained behind membranes, however, most of them would not evaporate during drying. The composition of feedstock loss possibly contain of soluble inorganics for example potassium chloride that forms an integral part of the biomass itself. These soluble inorganic compounds were easily dissolved without structural breakdown of the biomass and may be bound to biomass or contained behind membranes. The last possibility for the composition of feedstock loss is insoluble soil particles which could be found in sediment of size larger than 150μm and only can be found in filter cake of size smaller than 150μm. It may contain of soluble inorganics from particle surface such as fertilizer contamination [e.g potassium chloride].

Small biomass particles larger than 150μm may be found in sediment, while particles smaller than 150μm can be found in the filter cake as shown in Table 5.8. This gives the comparison of sediment and leachate ash content for W41LSOATR2 and W79LSOATR1 obtained by using a 100 mesh [150μm] stainless filter and Whatman No.1 filter paper [11μm] respectively to sieve the waste liquor. It can be seen that the ash content of sediment for W41LSOATR2 which was 4.08 mf wt%, increased to 9.49 mf wt% in W79LSOATR1, while the ash content of leachate for W41LSOATR2 which was 44.0 mf wt%, decreased to 34.1 mf wt% in W79LSOATR1. It was also found that the amount of sediment for W41LSOATR2 which was 0.11g increased to 0.28g in W79LSOATR1 that used the filter paper to separate the sediment from leachate. However, the amount of leachate for W41LSOATR2 which was 0.83g, increased to 0.98g in W79LSOATR1 which is contradictory to expectation. This may suggest that the feedstock for W79LSOATR1 has aged as this washing test was performed 10 months after the washing test for W41LSOATR2, thus the biomass is more amenable to breakdown.

The unaccounted losses of non-ash during water washing process for each method are also included in Table 5.2 to Table 5.5 as well. Figure 5.7 and Figure 5.8 illustrate the unaccounted losses of non-ash due to soaking method and stir method respectively.

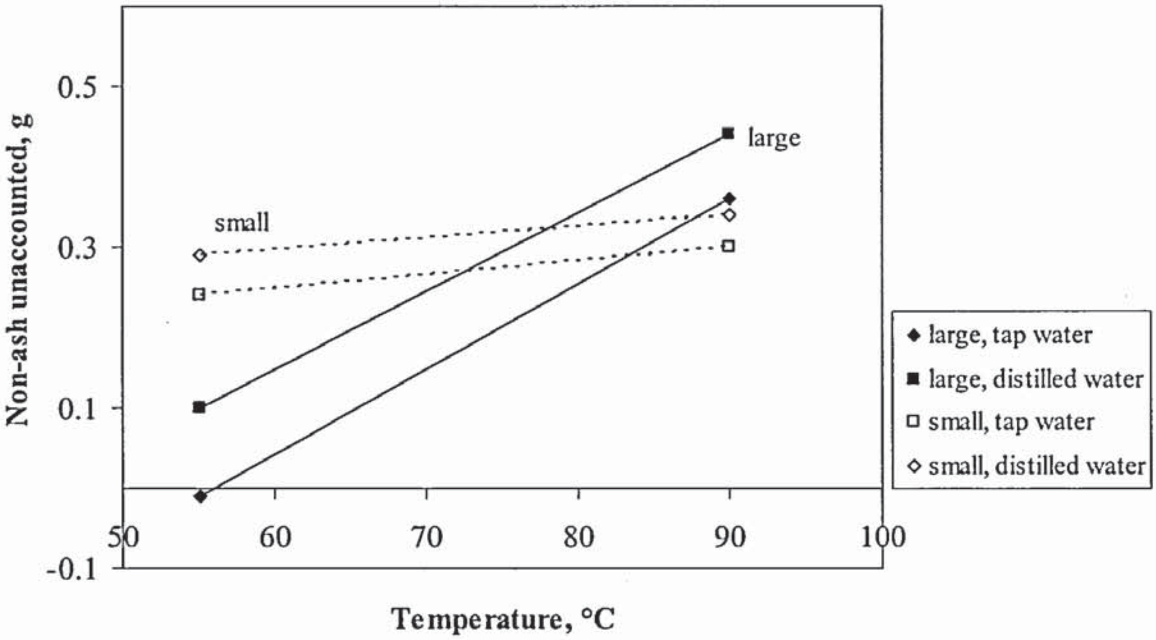


Figure 5.7: **The unaccounted losses of non-ash by soaking method for feedstock of size 250-355μm and 2-3cm**

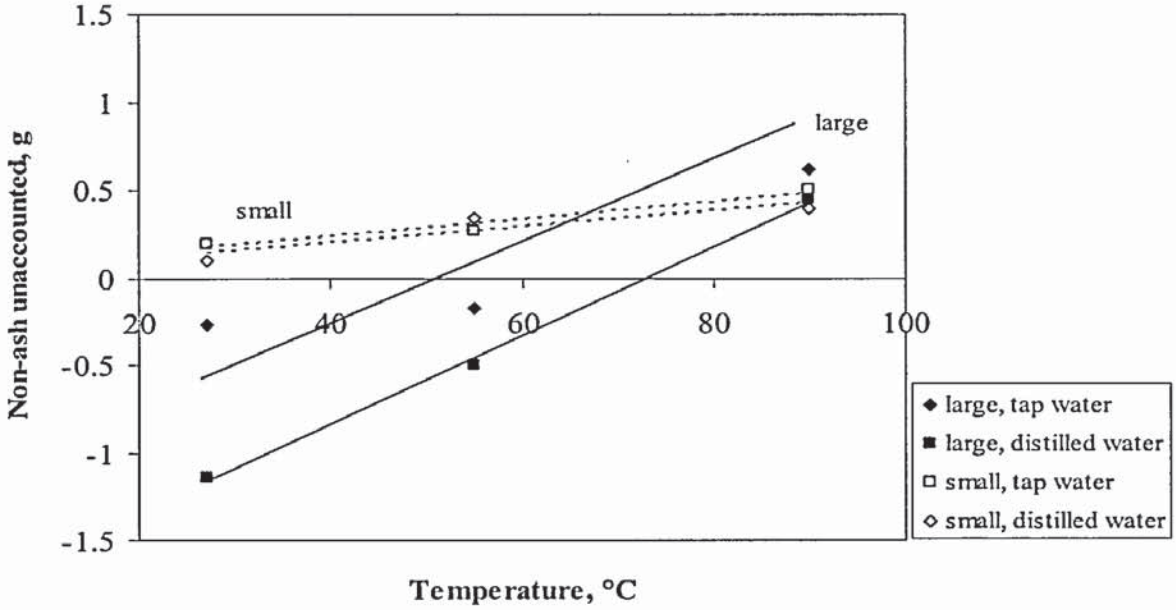


Figure 5.8: **The unaccounted losses of non-ash by stirring method for feedstock of size 250-355μm and 2-3cm**

The unaccounted non-ash losses at ambient temperature were not included in Figure 5.8 since the water washing test at ambient temperature was carried out for 24 hours at ambient temperature whereas the other water washing tests were at 55°C and 90°C which were run for 2 hours; thus, they are not entirely comparable. The loss of feedstock may have been due to loss of unaccounted non-ash such as volatiles that are easy to evaporate at high temperature. From Figure 5.7 and Figure 5.8, it can be deduced that the unaccounted loss of non-ash for large feedstock increases significantly as the temperature of wash water increases, however, the unaccounted loss of non-ash is less temperature dependent for small feedstock. This may suggest that as temperature increases the rate of volatiles evaporating into air increases. Furthermore, the small feedstock can easily be lost during water washing as it is can stick to the glass reactor, glove and stirrer. The amount of non-ash unaccounted for in the stirring method is higher compared to the soak method for both small and large feedstock. This may be due to the fact that stirring leads to a structural weakening of the biomass, allowing the rate of volatiles evaporation to increase.

Future washing tests will be carried out by using distilled water since this facilitates comparison with other work and also ensures greater repeatability and consistency of the results. Furthermore, the impact of changing over to tap water is modest [see Figure 5.4 to Figure 5.6]. As washing at ambient temperature may be more economical and in order to reduce the number of washing test, therefore, the subsequent wash tests will be carried out at ambient temperature.

5.2.2: Impact of Residence Time and Amount of Water

Table 5.6 summarises the run conditions together with the results for water wash tests of feedstock of size 250-355μm by soaking them in distilled water at ambient temperature over a range of residence time from 0.2 min to 480 min. Altogether eleven tests were carried out. Approximately 4*l* of distilled water was used per 100g feedstock and this was same for all runs. Washing with 7*l* of water caused high ash reduction therefore the amount was reduced to 4*l* for small feedstock and 5*l* for large feedstock.

Table 5.6: Run condition and ash reduction percentage by soaking over a range of residence time the feedstock of size 250-355μm

Run no*	Residence time [min]	Amount of water (*l*)	Washing method	Average ash content [mf wt%]	Percentage of ash reduction [%]	Electrical conductivity of leachate [μS/cm]
Unwashed EFB	-	-	-	4.87	-	-
W25SSOATR1	0.2	4	soak	2.71	44.4	750
W26SSOATR2	10	4	soak	1.67	65.7	1470
W27SSOATR3	20	4	soak	1.66	66.9	1490
W28SSOATR4	30	4	soak	1.63	66.5	1500
W29SSOATR5	60	4	soak	1.52	68.8	1510
W30SSOATR6	120	4	soak	1.35	72.3	1520
W31SSOATR7	180	4	soak	1.35	72.3	1525
W32SSOATR8	240	4	soak	1.35	72.3	1527
W33SSOATR9	360	4	soak	1.35	72.3	1530
W34SSOATR10	420	4	soak	1.34	72.5	1530
W35SSOATR11	480	4	soak	1.33	72.7	1530

*The last letter begin with R denoted the residence time of feedstock in distilled water, followed by the experiment sequence carried out at various residence time.

Figure 5.9 shows the percentage of ash reduction as function of residence time for the washing test on small feedstock. It was found that the percentage of ash reduction increased drastically for first 10 minutes and reached a constant value after 120 minutes. This may be due to the fact that the ash can be easily removed as diffusion becomes faster when the concentration gradient is high for first 10 minutes and then diffusion is slower as the wash water becomes saturated with minerals and reaches equilibrium.

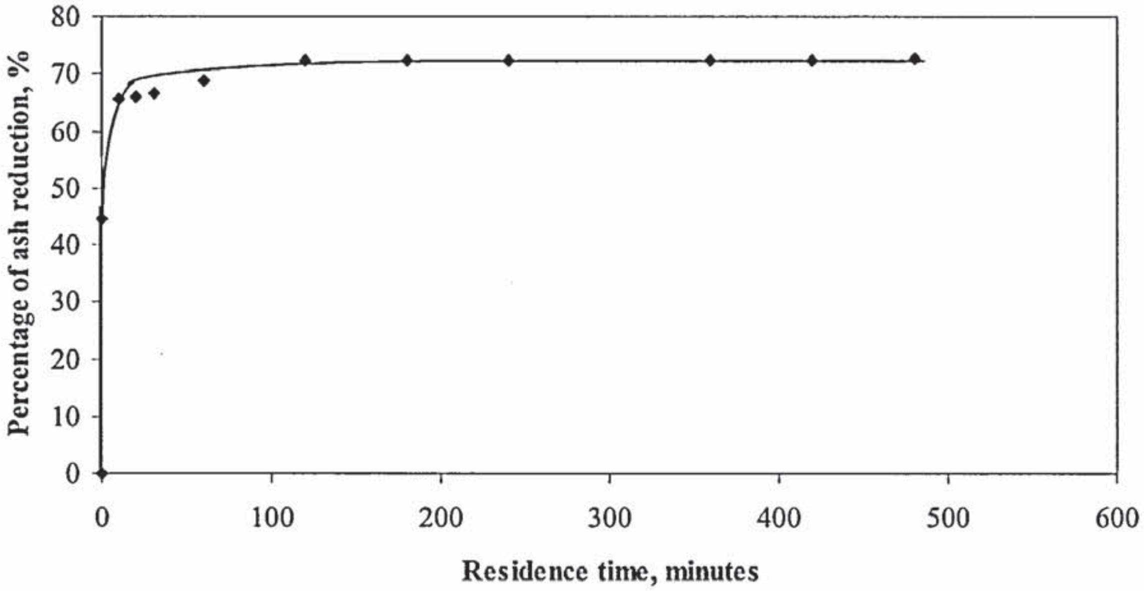


Figure 5.9: **The percentage of ash reduction as the function of residence time by soaking the feedstock of size 250-355μm**

Figure 5.10 illustrates the relation between the percentage reduction of ash in feedstock and incremental electrical conductivity of leachate after soaking the feedstock of size 250-355μm over a range of residence times. Residence times of the washing are plotted on a log scale because of the wide range of values. It shows that the increase of ash reduction is mirrored by the increase in electrical conductivity of the leachate. This may suggest that the increase in ash reduction will affect the increase in alkali metal and organic ions [e.g acetic acid] contain in leachate thus increase the electrical conductivity of the leachate.

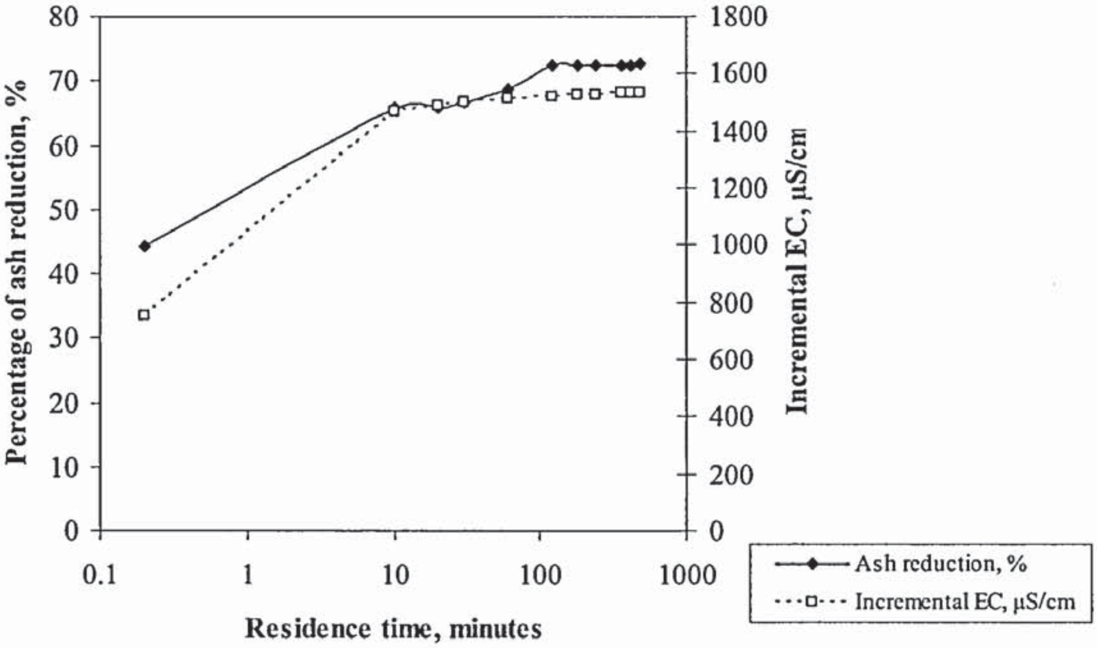


Figure 5.10: The ash reduction percentage of feedstock and incremental electrical conductivity of leachate by soaking the feedstock of size 250-355µm

Table 5.7 summarises the run conditions together with the results of four water washing for feedstock of size 250-355µm by soaking for 120 minutes at ambient temperature over a range of distilled water volume from 0.75*l* to 4*l*.

Figure 5.11 illustrates the results for the washed feedstock of size 250-355µm. This displays the percentage ash reduction as the function water volume. It shows that the amount of water used per 100g feedstock has a significant effect on the ash removal. As the percentage of ash reduction increased, the electrical conductivity of leachate decreased drastically with the increasing water volume. This may be because by increasing the water, the concentration of leachate decreases, thus electrical conductivity of leachate was reduced. It was found that the percentage reduction in ash is lower at low water volume and it increases with increasing water quantity, which reaches almost constant at 4*l* of water. This may suggest that initially the ash is difficult to remove with small amount of water since the water becomes saturated with minerals. However, with increasing water quantities, enhance the diffusion directly, thus the ash removal will continue to increase until the wash water becomes saturated with minerals and reaches equilibrium. It also indicates that by soaking 100g feedstock in 4*l* water, the percentage of ash reduction reached 75.3%.

Table 5.7: Run condition and ash reduction percentage by soaking the feedstock of size 250-355 μm over a range of water amount

Run no*	Residence time [min]	Amount of water [*l*]	Washing method	Average ash content [mf wt%]	Percentage of ash reduction [%]	Electrical conductivity of leachate [μS/cm]
Unwashed EFB	-	-	-	5.58	-	-
W36SSOATA1	120	0.75	soak	2.68	52.0	8200
W37SSOATA2	120	1.25	soak	2.18	60.9	4600
W38SSOATA3	120	2.25	soak	1.73	69.0	2600
W39SSOATA4	120	4	soak	1.38	75.3	1400

*The last letter begin with A denoted the amount of water that used for 100g feedstock, followed by the experiment sequence carried out at various water amount.

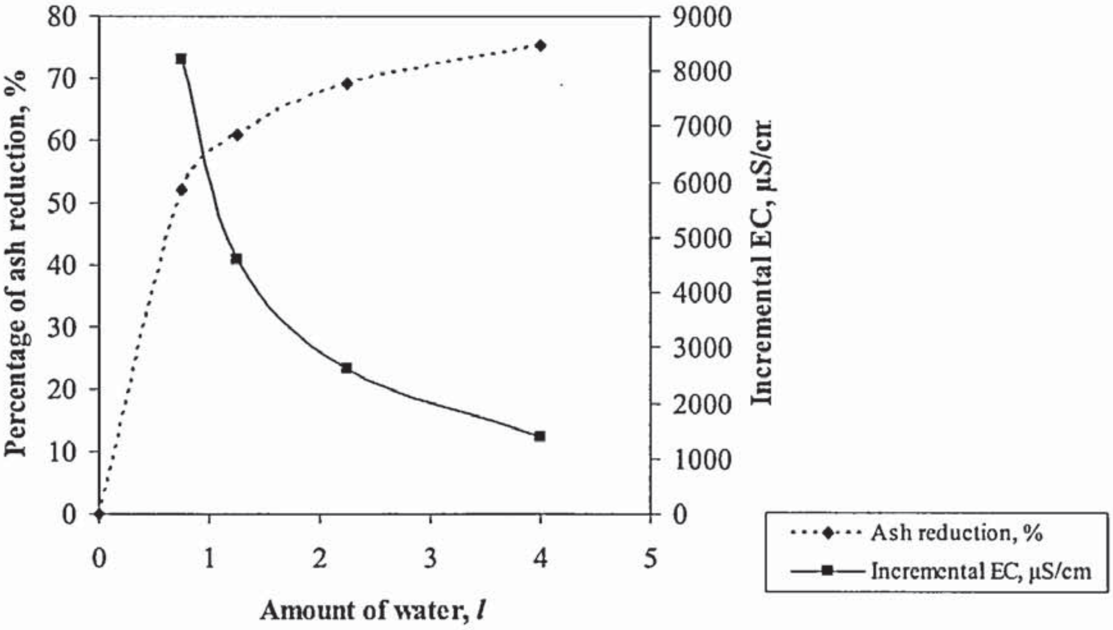


Figure 5.11: The percentage of ash reduction as the function of water amount by soaking the feedstock of size 250-355 μm

Table 5.8 summarises the run conditions together with the results of water washing test for particle of size 2-3cm using quick washing method on the feedstock at ambient temperature. Three of the tests were carried out at different residence time [0.5 min, 1 min, and 2 min] each with manual agitation and using a 100 mesh stainless steel sieve to filter the waste liquor. The fourth was carried out with a 1 minute residence time and using a Whatman No.1 filter paper to filter the waste liquor. Approximately 5*l* of distilled water were used per 100g of feedstock in all cases. Washing with 7*l* of water caused high ash reduction, therefore, the water amount was reduced to 5*l*. The average ash content for unwashed EFB was 5.43 mf wt%. The run number shown in Table 5.8 shows that the last letter begin with R denoted the residence time of feedstock in distilled water, followed by the experiment sequence carried out at various residence time.

Table **5.9** summarises the run condition for washing tests carried out by soaking the large feedstocks over residence times from 10 min to 180 min.

Figure 5.12 shows the percentage ash reduction by quick washing the feedstock of size 2-3 cm. The percentage ash reduction increased significantly in the first minute of washing and reached a constant after one to two minutes residence time, but increased again after 2 minutes of residence time. This may suggest that some ash, presumably close to the surface, can indeed be washed off very quickly and it makes virtually no difference whether the wash is one or two minutes. This figure also shows the increase of electrical conductivity of leachate in this washing test. This shows that the increase of ash reduction is mirrored by the increase in electrical conductivity of the leachate. This may suggest that the increase in ash reduction will affect the increase in alkali metal and organic ions, such as acetic acid, contain in leachate thus will increase the electrical conductivity of the leachate.

Table 5.8: **Run condition and mass balance summary by quick washing the feedstock of size 2-3cm over a range of residence time**

Run no.	Unwashed EFB	W40LSOATR1	W41LSOATR2	W42LSOATR3	W79LSOATR1
Residence time [min.]	-	0.5	1.0	2.0	1.0
Washing method	-	manual agitation	manual agitation	manual agitation	manual agitation
Size of filter	-	100 mesh	100 mesh	100 mesh	11 µm
Average ash content [mf wt%]	5.43	3.97	3.68	3.68	3.65
Ash content of sediment [mf wt%]	-	3.12	4.08	4.23	9.49
Ash content of leachate [mf wt%]	-	40.3	44.0	44.6	34.1
Percentage of ash reduction [%]	-	26.9	32.2	32.4	32.8
Electrical conductivity of leachate [µm]	-	715	840	860	not determined
In feed before washing					
Total ash [g, dry basis]	-	1.18	1.27	1.28	1.26
Total recovering after washing					
Total ash [g, dry basis]	-	1.17	1.21	1.22	1.19
Closure of ash balance	-	99.0	95.6	95.7	94.5
Before washing					
Feed [g, dry basis]	-	23.44	23.33	23.58	23.19
After washing					
Feed remaining [g, dry basis]	-	23.02	22.88	23.11	22.73
Sediment, [g, dry basis]	-	0.11	0.11	0.13	0.28
Leachate, [g, dry basis]	-	0.63	0.83	0.83	0.98
Difference [g, dry basis]	-	0.42	0.46	0.46	0.47
Percentage loss [mf wt%]	-	1.79	1.95	1.96	2.0
Closure of feed	-	101	102	102	103

Table 5.9: Run condition and ash reduction percentage by soaking the feedstock of size 2-3 cm over a range of residence time

Run no*	Residence time [min]	Amount of water [*l*]	Washing method	Average ash content [mf wt%]	Percentage of ash reduction [%]	Electrical conductivity of leachate [µS/cm]
Unwashed EFB	-	-	-	5.04	-	-
W43LSOATR1	10	5	soak	3.05	39.5	1000
W44LSOATR2	20	5	soak	2.14	57.4	1050
W45LSOATR3	30	5	soak	1.87	62.9	1090
W46LSOATR4	60	5	soak	1.78	64.7	1202
W47LSOATR5	120	5	soak	1.54	69.4	1265
W48LSOATR6	180	5	soak	1.44	71.4	1310

*The last letter begin with R denoted the residence time of feedstock in distilled water, followed by the experiment sequence carried out at various residence time.

From the results in Table 5.8, it is concluded that the ash content of sediment increased and the ash content of leachate decreased when using the smaller size filter. This may suggest that large amount of small biomass particles and insoluble soil particles collected as sediment, thus the ash content of sediment increased. It is, however, believed that there is no or negligible soil contamination on EFB.

Figure 5.13 illustrates the results of washing test that were shown in

Table 5.9. It was found that the percentage of ash reduction increased drastically for first 20 minutes and reached a constant value after about 120 minutes. This may suggest that greater gradient concentration would drive faster diffusion for first 20 minutes and then diffusion becomes slow once the wash water becomes saturated with minerals and reaches equilibrium. It was found that the ash reduced very slowly after 120 minutes of washing process, and the percentage of ash reduction reached 69.4%.

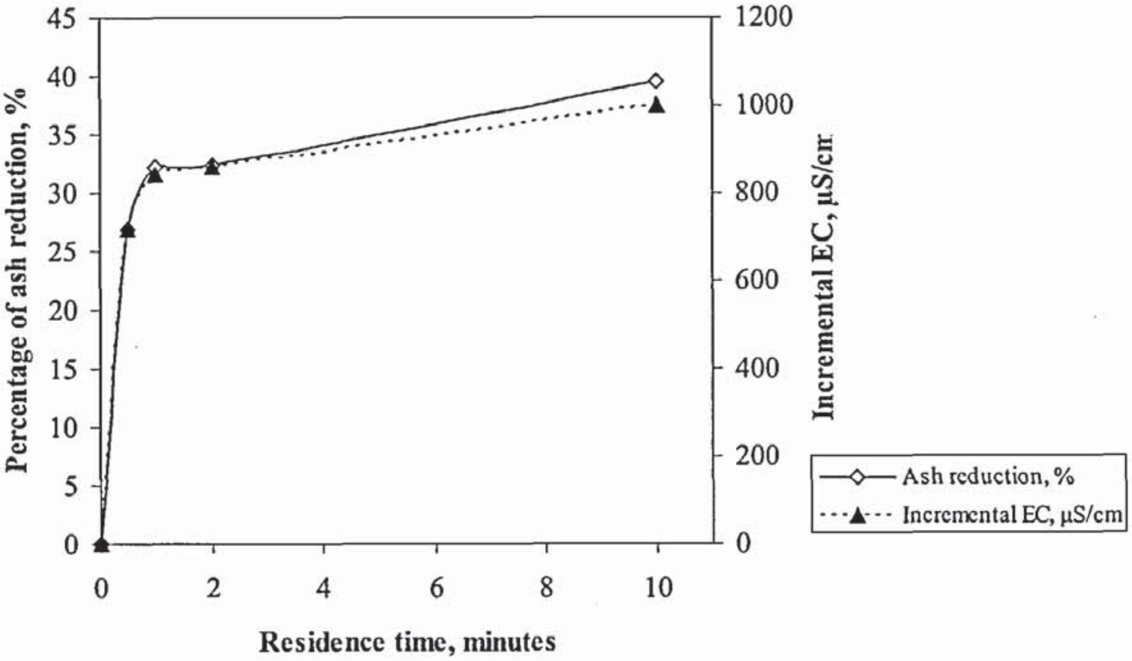


Figure 5.12: **The ash reduction percentage of feedstock and incremental electrical conductivity of leachate by quick washing the feedstock of size 2-3 cm**

Figure 5.13 also shows that the increase in ash reduction is accompanied by an increase in electrical conductivity of the leachate. This may be due to fact that the increase in ash reduction has an effect on the increase in alkali metal and organic ions contain in leachate consequently increase the electrical conductivity of the leachate.

Table 5.10 summarises the run conditions together with the results of three water washing for particle of size 2-3cm by soaking for 120 minutes at ambient temperature over a range of distilled water volume from 1.5*l* to 5*l*. Average ash content for unwashed EFB was 5.04 mf wt%.

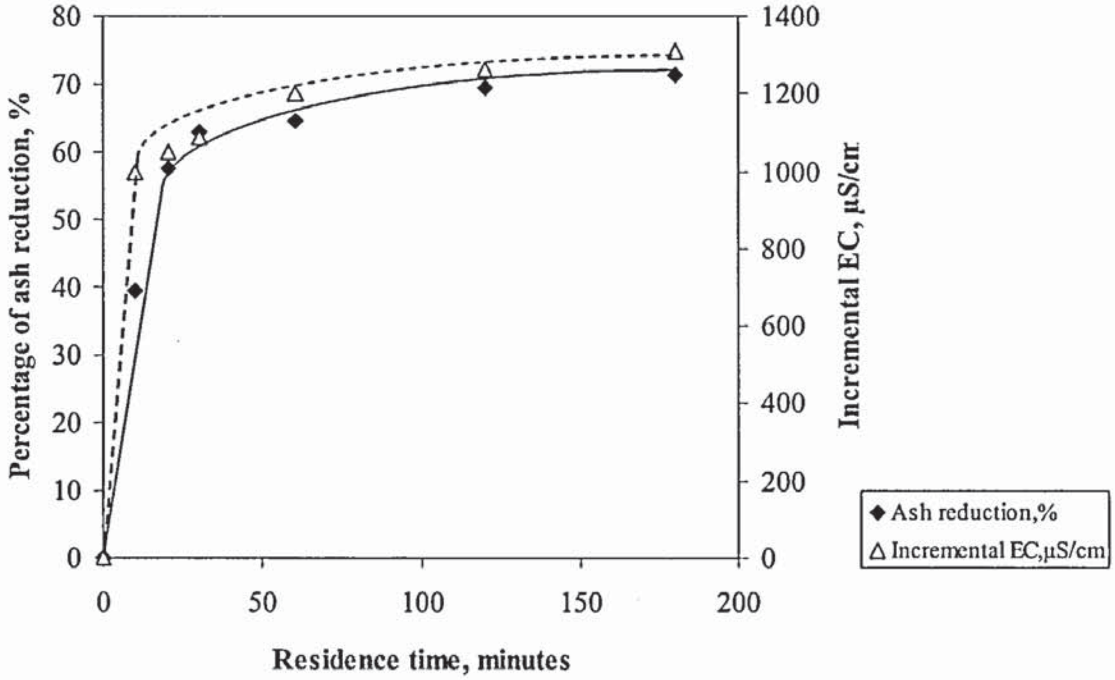


Figure 5.13: The ash reduction percentage of feedstock and incremental electrical conductivity of leachate by soaking the feedstock of size 2-3 cm

Table 5.10: Run condition and ash reduction percentage by soaking the feedstock of size 2-3 cm over a range of water amount

Run no*	Residence time [min)	Amount of water [*l*]	Washing method	Average ash content [mf wt%]	Percentage of ash reduction [%]	Electrical conductivity of leachate [µS/cm]
Unwashed EFB	-	-	-	5.04	-	-
W49LSOATA1	120	1.5	soak	1.9	62.3	3800
W50LSOATA2	120	3	soak	1.7	66.3	1500
W51LSOATA3	120	5	soak	1.54	69.4	1165

*The last letter begin with A denoted the amount of water that used for 100g feedstock, followed by the experiment sequence carried out at various water amount.

Figure 5.14 shows the results for washed feedstock of size 2-3 cm. It relates the percentage of ash reduction to the quantity of water. This figure shows that as the percentage of ash reduction increase, the electrical conductivity of the leachate decrease drastically with the increased amount of water. This may be because by increasing the water amount, the concentration of the leachate decreases, thus electrical conductivity of the leachate was reduced.

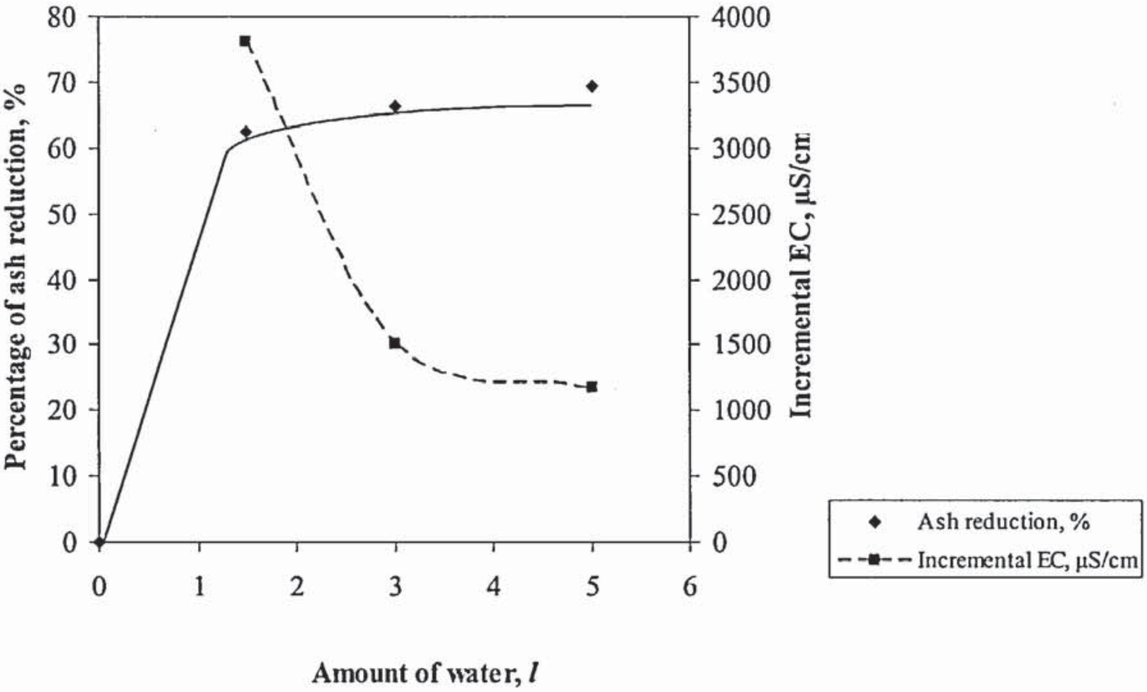


Figure 5.14: The percentage of ash reduction as the function of water amount by soaking the feedstock of size 2-3 cm

The ash reduction for smaller size particles is much greater than for the larger ones as shown in Figure 5.15. This may be due to the fact that the rate of ash removal for the smaller size are faster. It also shows that after 180 minutes, the percentage ash reduction for small size and large size is 72.3% and 71.4% respectively. As mentioned in Section 5.2.1, particle size does have significant impact after soaking for 24 hours 100g feedstock in 7*l* distilled water. However, it was found that soaking 100g large feedstock in 5*l* distilled water and 100g small feedstock in 4*l* distilled water does not have a significant impact on ash reduction. This may suggest that an equilibrium was established as early as after 180 minutes by soaking the feedstock with less water amount.

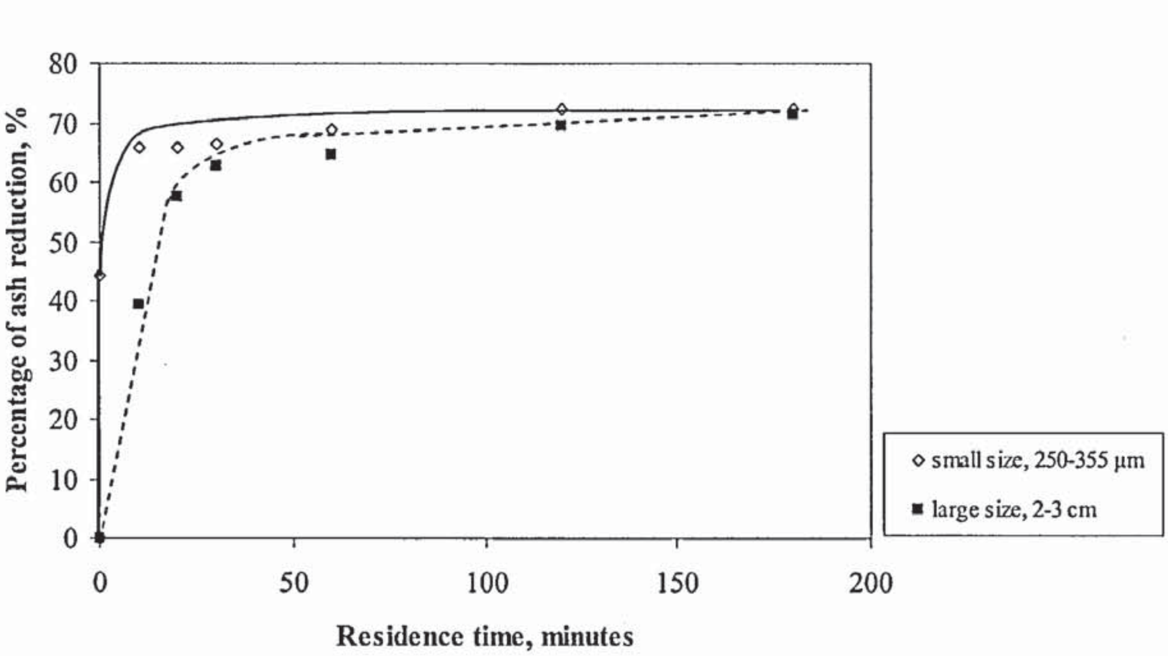


Figure 5.15: The percentage of ash reduction as the function of residence time for the feedstock of size 250-355 μm and 2-3 cm.

It was found that the percentage ash reduction was constant after soaking 100g of small feedstock for 120 minutes in 4*l* distilled water. By soaking the same quantity of large feedstock in more than 4*l* of distilled water and for more than 120 minutes does not show significant difference in ash reduction. It was also found that the percentage ash reduction was constant by soaking 100g of large feedstock for 120 minutes in 5*l* distilled water.

In order to determine the maximum ash content of feedstock which produces a homogenous bio-oil, a series of five pyrolysis experiments with feedstock of ash content 1.15, 2.14, 3.05, 3.68 and 5.29 mf wt% were carried out for the feedstock of run number W24LST90D, W44LSOATR2, W43LSOATR1, W41LSOATR2 and unwashed feedstock respectively. The results showed that the maximum ash content of feedstock which produced a homogenous bio-oil is 3.05 mf wt%. The results from fast pyrolysis experiments of washed feedstocks are presented, analysed and discussed in Chapter 7.

5.2.3 Impact of Feedstock Harvesting, Processing and Storage

Table 5.11, Table 5.12 and Table 5.13 summarise the run conditions and results for unwashed feedstock, quick washed feedstock and fresh feedstock respectively. A total of

27 tests were carried out and the washing tests were done on feedstock of size 250-355μm, 1cm and 2-3cm for each type of feedstock. Approximately *5l* of distilled water were used per 100g feedstock though in each case.

Table 5.11: Run condition and ash reduction percentage for unwashed feedstock of size 250-355 µm, 1 cm and 2-3 cm

Run no*	Temperature [°C]	Residence time [min]	Amount of water [*l*]	Size of feedstock	Average ash content [mf wt%]	Percentage of ash reduction [%]
Unwashed EFB	-	-	-	-	5.72	-
W52SSOAT	26-28	120	5	small	1.58	72.4
W53MSOAT	26-28	120	5	medium	1.73	69.8
W54LSOAT	26-28	120	5	large	1.81	68.4
W55SSO55	55	120	5	small	1.31	77.1
W56MSO55	55	120	5	medium	1.43	75.0
W57LSO55	55	120	5	large	1.50	73.8
W58SSO90	90	120	5	small	1.20	79.0
W59MSO90	90	120	5	medium	1.29	77.5
W60LSO90	90	120	5	large	1.34	76.6

*Example: W52SSOAT refers to washing test no.52, small size unwashed feedstock had been washed by soaking method at ambient temperature.

Figure 5.16 shows the percentage ash reduction for unwashed and quick washed feedstocks. It was found that the percentage of ash reduction is higher for quick washed feedstock that was treated by water washing for one minute [see Section 5.2.2].

Figure 5.17 shows the percentage ash reduction for unwashed and fresh feedstock. It indicates that the percentage ash reduction is higher for unwashed feedstock than for fresh feedstock. This may be due the fact that unwashed feedstock has already undergone sterilisation and strip processing in order to separate the sterilized oil palm fruit from the sterilised bunch stalks, therefore the cellular or molecular structure has been weakened, consequently, the ash were easier to remove. It can also be seen that the rate of ash reduction for small feedstock [less than 10000 μm] for fresh feedstock is higher than for unwashed feedstock. This may suggest that the structure of old feedstock [refer unwashed feedstock] was already destroyed, therefore, the ash reduction for small and large feedstock was quite similar.

Table 5.12: Run condition and ash reduction percentage for quick washed feedstock of size 250-355 μm, 1 cm and 2-3 cm

Run no*	Temperature [°C]	Residence time [min]	Amount of water [*l*]	Size of feedstock	Average ash content [mf wt%]	Percentage of ash reduction [%]
Quick washed EFB	-	-	-	-	5.43	-
W61WSSOAT	26-28	120	5	small	1.12	79.4
W62WMSOAT	26-28	120	5	medium	1.23	77.4
W63WLSOAT	26-28	120	5	large	1.31	75.9
W64WSSO55	55	120	5	small	1.05	80.7
W65WMSO55	55	120	5	medium	1.15	78.8
W66WLSO55	55	120	5	large	1.23	77.4
W67WSSO90	90	120	5	small	0.96	82.3
W68WMSO90	90	120	5	medium	1.07	80.3
W69WLSO90	90	120	5	large	1.15	78.8

*Example: W61WSSOAT refers to washing test no. 61, small size of quick washed feedstock had been washed by soaking method at ambient temperature.

Figure 5.18 shows the percentage ash reduction for fresh feedstock and quick washed. It shows that the ash reduction for quick washed feedstock is greater than for fresh feedstock. This may suggest that the quick washed feedstock is old feedstock and it is similar to unwashed feedstock which has already undergone stripping processing in order to separate the sterilised oil palm fruit from the sterilised bunch stalks, therefore the cellular or molecular structure has been weakened, consequently, the ash was easier to remove. It was found that the rate of ash reduction for small fresh feedstock [less than 10000μm] was also higher compared with quick washed feedstock. This may be due to the fact that structure of this feedstock already destroyed, therefore, the ash reduction for small and large feedstock was quite comparable.

Table 5.13: Run condition and ash reduction percentage for fresh feedstock of size 250-355 μm, 1 cm and 2-3 cm

Run no*	Temperature [°C)	Residence time [min]	Amount of water [*l*]	Size of feedstock	Average ash content [mf wt%]	Percentage of ash reduction [%]
Fresh EFB	-	-	-	-	5.3	-
W70FSSOAT	26-28	120	5	small	1.81	65.9
W71FMSOAT	26-28	120	5	medium	2.05	61.3
W72FLSOAT	26-28	120	5	large	2.23	57.9
W73FSSO55	55	120	5	small	1.66	68.7
W74FMSO55	55	120	5	medium	1.93	63.6
W75FLSO55	55	120	5	large	2.09	60.6
W76FSSO90	90	120	5	small	1.47	72.3
W77FMSO90	90	120	5	medium	1.66	68.7
W78FLSO90	90	120	5	large	1.78	66.4

*Example: W70FSSOAT refers to washing test no. 70, small size of fresh feedstock had been washed by soaking method at ambient temperature.

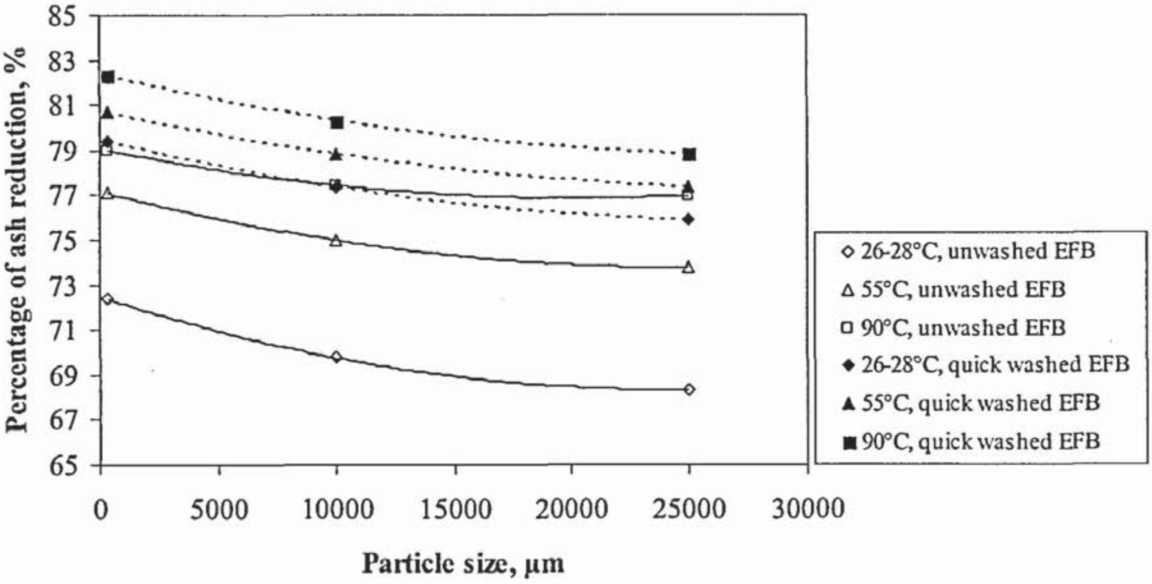


Figure 5.16: Diffusion of ash for unwashed and quick washed of feedstock*

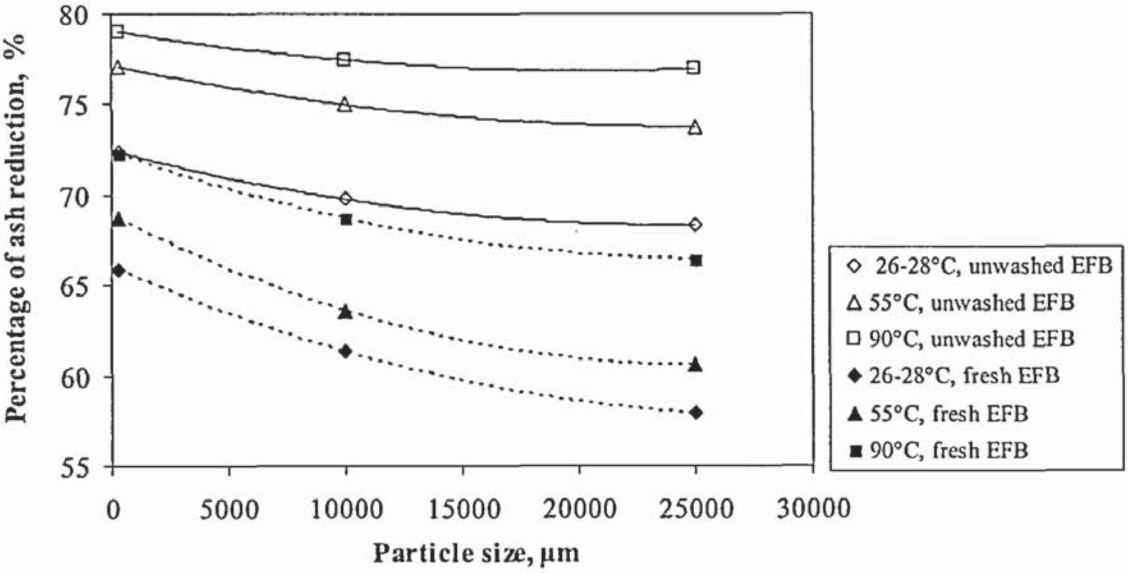


Figure 5.17: Diffusion of ash for unwashed and fresh of feedstock*

*"Unwashed" refers to aged feedstock (18 months old). See Section 4.6 for feedstock preparation.

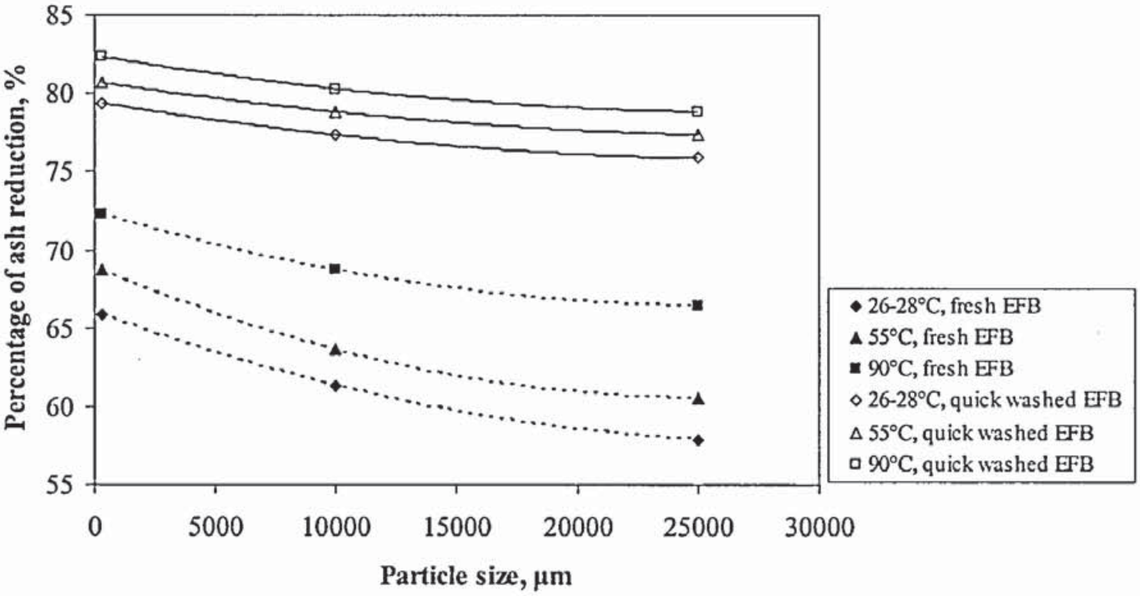


Figure 5.18: Diffusion of ash for fresh and quick washed of feedstock

Table 5.14 summarises the run condition together with the results of water washing test conducted at ambient temperature and 90°C for the unwashed feedstock [refer to sterilised feedstock] and fresh feedstock which had not undergone any sterilisation process.

Table 5.14: Run conditions and mass balance summary for unwashed feedstock and fresh feedstock

Run no.	W54LSOAT	W58SSO90	W60LSO90	W72FLSOAT	W76FSSO90	W78FLSO90
Temp. [°C]	26-28	90	90	26-28	90	90
Residence time [hour]	2	2	2	2	2	2
Type of water	distilled water	distilled water	distilled water	distilled water	distilled water	distilled water
Amount of water [*l*]	5	5	5	5	5	5
Average ash content [mf wt%]	1.81	1.20	1.34	2.23	1.47	1.78
Percentage of ash reduction [%]	68.4	79.0	76.6	57.9	72.3	66.4
In feed before washing						
Total ash [g, dry basis]	1.34	1.38	1.38	1.26	1.26	1.26
Total recovering after washing						
Total ash [g, dry basis]	1.31	1.35	1.31	1.21	1.23	1.24
Closure of ash balance	98.2	98.4	95.0	95.65	97.2	98.6
Before washing						
Feed [g, dry basis]	23.41	24.05	24.07	23.79	23.82	23.74
After washing						
Feed remaining [g, dry basis]	21.96	21.55	22.02	22.74	22.24	22.38
Total of feed and residue [g, dry basis]	23.42	24.06	23.7	24.03	23.98	23.92
Difference [g, dry basis]	1.45	2.5	2.06	1.05	1.58	1.36
Percentage loss [mf wt%]	6.19	10.4	8.55	4.43	6.62	5.72
Ash loss, g	0.94	1.11	1.08	0.75	0.93	0.86
Non-ash loss, g	0.51	1.39	0.98	0.30	0.64	0.50
Closure of feed	100	100.1	98.5	101	100.7	100.8

According to Effendi (151), no hemicellulose hydrolysis occurred by washing spruce with hot water. It was found that hemicellulose in biomass was lost by washing with acid. The feedstock used in this work was sterilised EFB, and as mentioned in Section 4.6, some hemicellulose may be hydrolysed during the sterilisation process. Therefore, it was expected that components of feedstock such as ash, extractives and hemicellulose were removed as well.

There is a difference in biomass loss when comparing sterilised [refer unwashed feedstock] and fresh feedstock as shown in Table 5.14. It shows that non-ash loss for the sterilised feedstock increased almost doubled compared to fresh feedstock for small feedstock by washing at ambient temperature and for large feedstock by washing at 90°C. It was also found that non-ash loss for sterilised feedstock more than doubled for small feedstock when washing at 90°C. This may be because the hydrolysed hemicellulose was sufficiently solubilised during washing, especially by washing the small feedstock at 90°C.

From the analysis done by Gil Garrote et al. (144), shown in Appendix G, it was estimated that for the fraction of hemicellulose for sterilised EFB, approximately 16% would be solubilised under typical sterilisation. As hemicellulose make up the biomass is 22.1 mf wt% [see Table 6.1], thus it was also estimated that the proportion of solubilised hemicellulose in EFB was approximately 3.5%. When comparing W58SSO90 and W76FSSO90 [Table 5.14], it was found that the difference of non-ash loss based on biomass dry basis was about 3.1%, which may be explained by solubilisation of hemicellulose.

5.2.4: Heating Value of Unwashed and Washed feedstock

The aim of bomb calorimetry experiment is to determine the high heating value [HHV] of feedstock for various ash content. The so-called high heating value, HHV, is the total energy content released when the fuel was burnt in air, including the latent heat contained in the water vapour, and therefore represent the maximum amount of energy potentially recoverable from a given biomass source. HHV is important when considering feedstock for fuel applications.

The bomb calorimetric technique had been used in this work in order to determine the HHV of the feedstock as explained in Section 4.8.1. This experiment was carried out in order to study how the changes of ash content in the biomass influence the values of HHV. Typical analysis errors for biomass samples are the range ±0.3% (146). Avicel cellulose which has heating combustion of 17.505 MJ/kg was used as a test to define the accuracy of bomb calorimeter experiment. The heat combustion of avicel cellulose derived from bomb calorimeter experiment was 16.9 MJ/kg, thus given an error of 3.45%. This may either be an indicator of the accuracy of the equipment utilised or possibly due to contamination of the cellulose or the benzoic acid used for calibration

According to McKendry (94), dependent on the ash content, the available energy of the fuel was reduced proportionately. Jenkins et al. (127) have previously studied how the changes of ash content in straws influence the HHV. They found that the high heating values has been correlated with ash content, and followed an inverse trend with respect to ash.

A total of 30 runs were carried out for bone dry and moisture feedstock of 5 mf wt%. Experiments for each sample of different ash content were carried out three times, and the averages of HHV were recorded. Table 5.15 gives the average high heating values of bone dry feedstock, average high heating value of feedstock with moisture content 5 mf wt % and average high heating value of bone dry feedstock in ash free basis. The standard deviations for these experiments are between 0.08-0.02 MJ/kg. It was found that the high heating value is inversely related to ash content, except for the feedstock with ash content 1.15 mf wt%. It was also found that this trend happened to the moisture feedstock as well, as shown in Figure 5.19. This may be because the feedstock with ash content 1.15 mf wt% has already undergone hot water washing at 90°C and some organics having large heating value were lost during washing.

Table 5.15: High heating values of unwashed and washed feedstock

Feedstock	Ash	Average HHV [MJ/kg]		
		Bone dry feedstock	5 mf wt% moisture content feedstock	Bone dry feedstock in ash free basis
Unwashed EFB	5.36	19.35	18.28	20.54
W41LSOATR2	3.68	19.80	19.07	20.56
W43LSOATR1	3.05	19.93	19.18	20.56
W44LSOATR2	2.14	20.11	19.41	20.55
W24LST90D	1.15	19.70	18.96	19.93

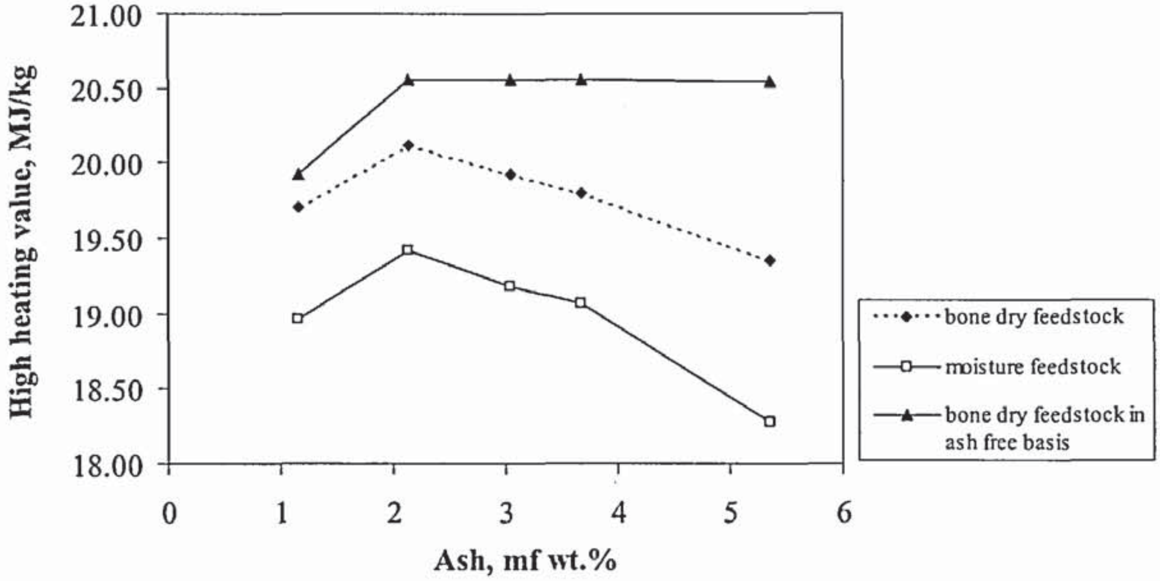


Figure 5.19: High heating value of unwashed and washed feedstock as the function of ash content

5.2.5: TGA Analysis for Unwashed and Washed Feedstock

Thermal degradation characteristics of unwashed and washed feedstocks are displayed in Figure 5.20 and Figure 5.21 by thermogravimetry [TG] and differential thermogravimetry curves [DTG] respectively. As shown in Figure 5.20 the TG curves show the weight loss of feedstock represented by fraction as a function of temperature. From 100 to 300°C it may show mainly the thermal degradation of extractives. The weight loss for all feedstocks was insignificantly changed from temperature 100-270°C. From 270-400°C the weight loss is the highest for all feedstocks, it may be due to the thermal degradation of polymer blocks of biomass [such as hemicellulose, cellulose and lignin]. Then above 400°C the loss can still be observed as the more difficult thermal degraded compounds present.

Figure 5.20 also illustrates that the total weight loss between 100-450°C is 77.4%, the highest for the feedstock of the lowest ash content. Table 5.16 lists the weight loss of all feedstocks for the temperature range. It was also found that the decomposition rate at the temperature higher than 450°C is faster for the feedstock of the lowest ash content, but it slower for the unwashed feedstock which has the highest ash content.

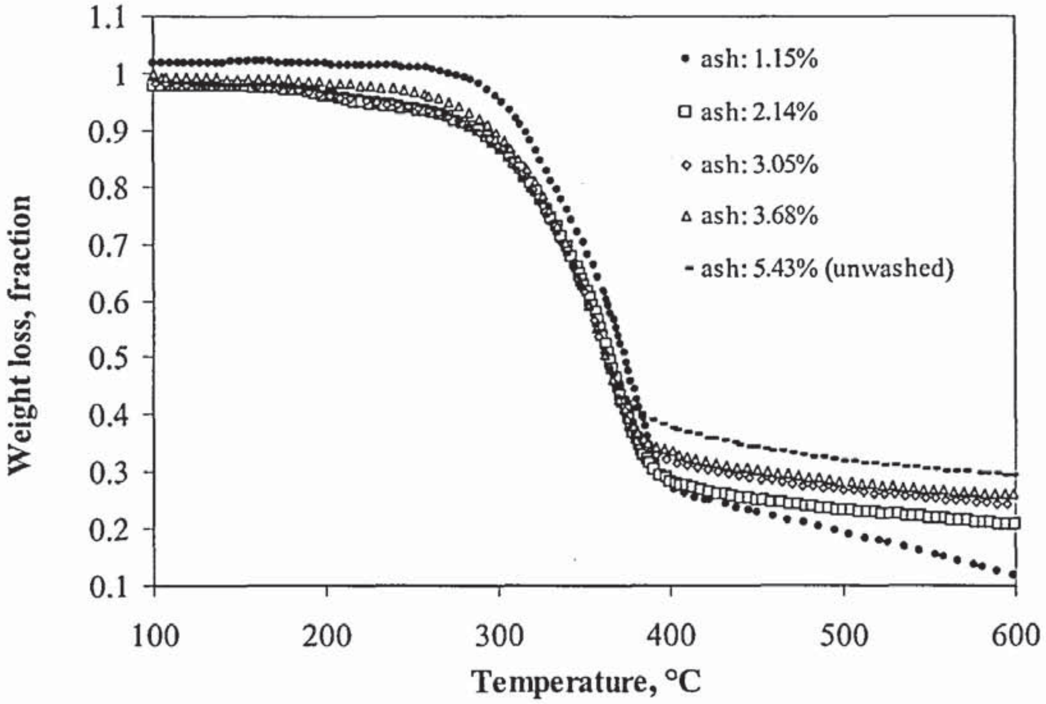


Figure 5.20: Thermogravimetric [TG] curves of unwashed and washed feedstock

Table 5.16: Weight loss in TGA between the temperatures of 100-450°C

Run no	Ash content [mf wt%]	Weight loss [%]
Unwashed feedstock	5.43	65.8
W41LSOATR2	3.68	69.4
W43LSOATR1	3.05	70.6
W44LSOATR2	2.14	74.4
W24LST90D	1.15	77.4

Figure 5.21 shows differential thermogravimetric curve represented by derivative weight loss as a function of temperature. The figure shows the peak maxima shifted to higher temperature as ash content in the feedstock was reduced by washing. It is well known that ash containing minerals exerted a catalytic action during thermal decomposition of polymer blocks (152), eased hemicellulose/cellulose decomposition to lower temperatures. Yang et al. (153) had previously studied that decomposition of hemicellulose, cellulose and lignin were from 220-300°C, 300-340°C and 750-800°C respectively. Based on this, the peak appeared from 250-400°C represent hemicellulose, cellulose and lignin degradation for the feedstocks. This result is in agreement with previous study done by Raveendran et al. (126,154) and Jensen et al. (155). They showed that clear temperature shifts were observed for several herbaceous biomasses by reducing inorganic content through water washing.

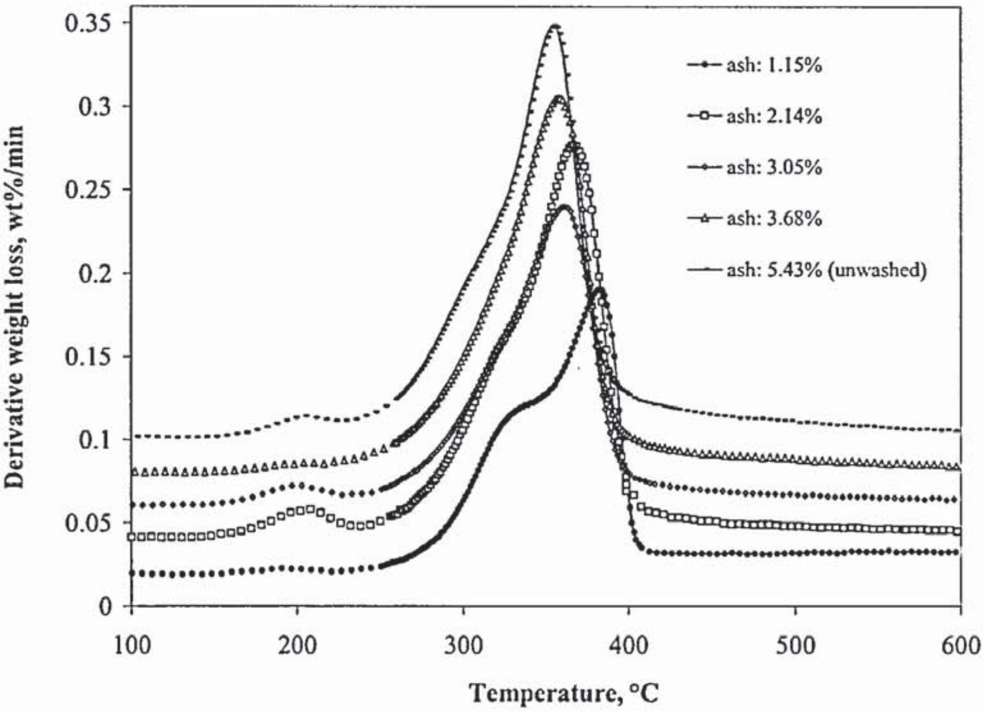


Figure 5.21: Differential thermogravimetric [DTG] curves of unwashed and washed feedstock

5.2.6: Surface Structure and EDX Analysis

Figure 5.22 and Figure 5.23 show the surface structure of unwashed and washed feedstock respectively. It was found that the surface for washed feedstock was clean and there were no dirt or particles on the surface. It is believed the unwashed feedstock of size 355-500μm could not feed easily into the feeder because the unwashed feedstock particles stick to each other, thus, making the feeding of the 150 g/h reactor difficult.

Figure 5.22: Surface structure of unwashed feedstock of size 355-500 μm

Figure 5.23: Surface structure of washed feedstock of size 355-500 μm

Table 5.17 shows the results of elemental analysis of unwashed feedstock, washed feedstock over a range of ash content and leachate for W79LSOATR1 using EDX. Note that hydrogen cannot be detected by this method. Elements such as Na, Al, P, S, Cl, K, Ti, Fe, Cu, were removed during the washing, however only Na, S and K decreased during the reduction the ash content of the feedstock. The EDX analysis results are gives in Appendix H. Stirring of the large feedstock at 90°C for 2 hours [W24LST90D] was found to be more effective in removing potassium, sodium and sulphur by 70.4%, 100% and 85.4% respectively. However, soaking the large feedstock at ambient temperature for 20 minutes [W44LSOATR2] was effective enough to remove potassium, sodium and sulphur by 67.2%, 100% and 25.0% respectively. As expected, an EDX analysis on leachate for run number W79LSOATR1 shows that the leachate has high potassium about 82.5 wt%. moreover, the ash content of leachate is higher [34.1 mf wt%].

Table 5.17: Elemental composition of unwashed and washed feedstock

Element	Unwashed EFB	W41LSOATR2	W43LSOATR1	W44LSOATR2	W24LST90D	W79LSOATR1 [leachate]
			[wt%]			
C	64.3	65.8	69	73.4	72.4	0.03
O	19.8	20.2	18.9	17.8	19.0	3.79
Na	0.33	0.41	0	0	0	0.63
Mg	0.19	0.25	0.29	0.35	0	1.68
Al	0.16	0.1	0.51	0.03	0	0
Si	1.95	1.87	1.34	2	1.72	0.1
P	1.06	0.43	0.8	1.39	1.71	5.39
S	0.48	0.55	0.39	0.36	0.07	1.54
Cl	1.37	0.37	0.5	0.19	0.36	3.48
K	8.61	9.1	7.68	2.82	2.55	82.5
Ca	1.43	1.47	1.76	1.56	1.53	1.06
Ti	0.13	0	0.06	0	0.29	0.03
Cr	0.15	0.25	0	0.55	0	0
Mn	0	0	0.06	0	0.05	0.02
Fe	0.29	0	0.48	0.08	0	0
Ni	0	0.26	0	0	0.59	0
Cu	0.31	0	0.28	0	0.23	0.04
Zn	0.12	0	0	0	0.66	0.06
Ash content [mf wt%]	5.43	3.68	3.05	2.14	1.15	34.1

5.3 CONCLUSIONS

Pre-treatment of EFB by water washing in order to remove some of the ash from the feedstock material was investigated. A total of 79 water washing experiments were carried out. These experiments were assessed by mass balances for ash and feedstock. Good mass balance closures for ash mostly above 95%, however, the mass balance closures for feedstock have been obtained between 95% and 104%.

Water wash experiments were carried out varying the following parameters: temperature of wash water, residence time, water amount and size of feedstock. Ash removal is enhanced by higher temperature of wash water, stirring, longer wash times and smaller particles. For small feedstock there is a breakdown of washing process into distinct phases: initial reduction extremely fast, then linear with time [between 10 min and 2 h], then static, and after six to eight hours some further reduction, perhaps from structural breakdown of the biomass or even beginning of bacterial attack.

Varying temperature of wash water, stirring rather than soaking, varying the residence time or particle size all had a small impact on ash removal, with virtually all experiments, apart from very short rinses or very low wash water amounts, showing ash removals of between 70-80%. However, small impact on ash removal may still be significant to the enhancement bio-oil yield.

Feedstock losses are significant during washing, in particular at high temperature. Moreover as near saturation is reached for ash removal, feedstock losses may still increase substantially in which organics losses increases at higher temperature, thus soaking at ambient temperature may be most economic option, subject to detailed economic study. For example, with refer to Table 5.2, the ash loss is 1.02g and 1.0g for W2SSOATD and W6SSO90D respectively, but the non-ash loss is 1.59g for W6SSO90D which is more than double compared to non-ash loss for W2SSOATD.

Feedstock losses easily doubling for the smaller feedstock compared to large feedstock through stirring at higher temperature [90°C].

In order to study the impact of feedstock harvesting, processing and storage, another three series of water washing tests were carried out on unwashed, quick washed and fresh feedstock. It can be concluded that the unwashed and quick washed feedstock are old feedstock where the bonding of components within the structure is already weak and the ash was easily remove. Freshly harvested EFB is more resistant to ash removal by washing. Furthermore, the unwashed and quick washed feedstocks were subjected to stripping and sterilisation at the oil palm mill in which the cellular or molecular structure has been weakened thus enhancing the diffusion process within the feedstock. Therefore, it shows that water washing is more significant on the EFB subjected to sterilisation and stripping process than on the fresh EFB.

A TGA was carried out on unwashed and washed feedstock under nitrogen at a flow of 100m*l*/min with a heating rate of 10°C/min in order to evaluate the qualitative compositions of feedstock such as hemicellulose, cellulose, lignin and their thermal degradation behaviour. The peak of TGA curve shifts to higher temperatures for washed feedstock which shows that loss of ash leads to less catalysis.

SEM and EDX analyses have been carried out on unwashed and washed feedstock for a range of ash content in order to study the surface structure and elements of unwashed feedstock and washed feedstock. The results showed that some element such as Na, Al, P, S, Cl, K, Ti, Fe, Cu, were removed during the washing, however washing with hot water at 90°C is more effective in removing potassium, sodium and sulphur.

6. EXPERIMENTAL SET-UP

The properties of EFB are described in this chapter. The received condition of EFB and any preparation methods used prior to pyrolysis are also described.

A 150g/h fluidised bed reactor was used in pyrolysis experiment, and the procedures for operating pyrolysis system are described in this chapter. A critical assessment of the mass balance and analytical procedures are explained in this chapter.

6.1 FEEDSTOCK INVESTIGATED

Malaysian Palm Oil Board [MPOB] from Malaysia supplied the Empty Fruit Bunches [EFB] used in this work. The material was received in November 2002 in the form of whole bunches and dry condition [i.e. less than 10 mf wt% moisture] as shown in Figure 6.1, and these samples were chopped and ground to get the feedstocks in correct sizes. EFB is very fibrous material, and the fibres stick together to form vascular bundles.

The bunches were chopped before being placed in the grass cutter in order to get into smaller size as shown in Figure 6.3. This results in the production of stringy strands of different lengths and sizes. A Fritsch grinder with a screen size of 500μm was used in order to get the size of feedstock less than 500μm as shown in Figure 6.4. Feedstock moisture content was also measured to ensure that it is less than 10 wt% on dry feed basis.

Properties of the EFB are given in Table 6.1. This table shows the component, elemental analysis, proximate analysis, ash and moisture contents of the EFB. The samples were tested using the hydrolysis method for cellulose, hemicellulose and lignin [supplied by Prof. Farid Nasir Ani of University Teknologi Malaysia]. The samples were sent to Medac Ltd on 27th November 2002 and tested using the combustion analysis method for carbon, hydrogen, nitrogen and sulphur, but oxygen content was determined by difference.

Figure 6.1: An EFB as received

Figure 6.2: EFB after chopping with a saw

Figure 6.3: EFB after cutting with a grass cutter

Figure 6.4: Ground EFB

The percentage of ash and moisture content of feedstock were obtained from the proximate analysis and were carried out by the author of this thesis. The sample as received had a moisture content of 7.95 mf wt% and ash content of 5.36 mf wt% determined using ASTM E871 and NREL [National Renewable Energy Laboratory] Standard Analytical Method LAP005 respectively. Volatile matter was analysed in accordance with ASTM E872-82.

The proximate analysis indicates that EFB is environment friendly, with a trace content of nitrogen and sulphur.

Table 6.1: Properties of EFB [mf wt%]

Component	
Cellulose	59.7
Hemicellulose	22.1
Lignin	18.1
Elemental Analysis	
Carbon	49.07
Hydrogen	6.48
Nitrogen	0.7
Sulphur	<0.10
Oxygen [by difference]	38.29
Proximate analysis	
Moisture	7.95
Volatiles	83.86
Ash	5.36
Fixed carbon	10.78

6.2 FEEDSTOCK PREPARATION

It is important that the feedstocks for pyrolysis have suitable particle size, particle range and of adequate dryness [less than 10% moisture by weight] for the feeder and reactor. The ground feedstocks as shown in Figure 6.4 were screened to a given particle size range. The size of feedstocks will be used for this experiment were small [less than 500μm], and for that, it is hoped that other properties, such as particle shape, regularity, surface area and surface area/volume ratio which may have an influence on the results of pyrolysis experiments will be negligible.

6.2.1 Size Reduction

The samples received from Malaysian Oil Palm Board were in a dry bunched form. In order to fit the feedstock into the grinder, their size had to be reduced in two stages; chop the bunches into small pieces and fit the feedstocks into the grass cutter as shown in Figure 6.2 and Figure 6.3 respectively. A cutting mill with an interchangeable screen was used to reduce the feedstock particle size. Screen sizes of 100μm, 250μm, 500μm and 1cm were available but in all cases a screen size of 500μm was used in order to get the size of feedstock less than 500μm.

However, as recommended by Hague (34), double grinding of the feedstock had been done to avoid any blockages in the feed tube aperture [Section 6.3.1] and the feed tube in the reactor [Section 6.3.2]. Some feedstock materials occasionally caused blocking in the feed tube aperture in the feeder and the feed tube in the reactor because those particles were bigger than the selected screen size. It is believed by double grinding of the feedstock the probability of pin-like particles remaining was reduced.

6.2.2 Screening

Feeding test for a 150 g/h reactor was carried out and it was found that only particles of a size less than 500μm would be suitable. It is desirable to have a particle size distribution as narrow as possible, therefore, feedstocks were sieved using standard test sieves of mesh size 150μm, 250μm, 300μm, 355μm and 500μm. Feedstock of six narrow ranges were obtained: less than 150μm, 150 – 250μm, 250 – 300μm, 300 – 355μm and 355 – 500μm.

From Table 4.12 [Section 4.6], it was found that the majority of particles were 355-500μm. However, the unwashed feedstocks for particles of size 250-355μm and the washed feedstocks of size 355-500μm had been used for the pyrolysis experiment. This is because the unwashed feedstocks of size 355-500μm could not be feed easily into the feeder compared to unwashed feedstocks of size 250-355μm. As mentioned in Section 5.2.6, it is believed the unwashed feedstocks stick to each other and making the feeding of the 150 g/h reactor difficult.

6.2.3 Moisture content

Biomass is a hygroscopic material which absorbs moisture in a humid environment and loses moisture in a dry environment. Therefore, the moisture content of feedstock should be measured at the time of performing the experiment and the feedstocks should be stored in a sealed container. If the feedstocks are left open to the atmosphere, improperly stored or stored for a long period of time, the moisture content may change. The moisture content of feedstock was carried out with the ASTM E871 method (156). Approximately 1g of sample was weighed [to 4 decimal places] and then placed in a pre-dried and weighed crucible; this was then placed in a fan oven at 105°C for at least 24 hours. From previous experiments involving repeated weighing of drying wood samples this was 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

The measurement of the ash contents was determined using NREL [National Renewable Energy Laboratory] Standard Analytical Method LAP005 (157). 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. This was in accordance to the ASTM E871 to determine the moisture content of the sample on a dry feedstock basis. The crucible was then placed in a muffle furnace at 575°C for a minimum of 6 hours before it was removed and cooled to room temperature in a desiccator 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 because the same crucible and pre-dried sample can be used. Furthermore, if this was done at a later time it can introduce an error in the calculation because ground biomass can rapidly gain or lose moisture when exposed to the atmosphere.

6.2.5 Drying

The feedstocks used for pyrolysis experiment must be in a relatively dry state, which is less than 10 mf wt% moisture as measured by the method as described in Section 6.2.3. The feedstocks were received in an acceptable moisture state [7.95 mf wt%]. Therefore, these feedstocks did not require drying as it was likely to lose moisture during grinding. However, the feedstocks were dried where necessary by storing in a fan oven at a constant 105°C for several hours to achieve the required moisture content.

6.3 PYROLYSIS SYSTEM

The 150 g/h fluidised bed system as shown in Figure 6.5 consists of three main parts, which are the feeder, reactor and products collection system. The following sections describe the approximate dimensions and operating methods of fluidised bed system.

Figure 6.5: 150 g/h fluidised bed system (adapted from 34)

6.3.1 Feeder

The feeder as shown in Figure 6.6 consists of a tubular storage hopper of size 63mm inside-diameter and 178mm inside-length, which was constructed from clear Perspex. The reasons for using clear Perspex to build the feeder was because Perspex is a strong and robust material, which can be quickly modified or make new designs, and Perspex is clear, which make it easy to observe the behaviour of the feedstock during an experiment. Therefore, action could be taken if any problem such as bridging or low levels of feedstock.

Biomass was slowly stirred by two paddles of length 60mm during a run. Feeding had been done by a tubular storage hopper, which was pressurised at the top with a small flow of nitrogen, which forces the feedstock through the 1.7mm feed aperture, into the feed tube of the reactor. Biomass was also entrained through the feed aperture by a continuous flow of nitrogen into the biomass entrain tube of size 3mm inside-diameter and 125mm length, which crosses the hopper at the bottom. After the biomass had been carried along the entrainment tube, it then passed into a flexible tube, which was connected to the feed tube at top of the reactor.

Figure 6.6: Schematic diagram of biomass feeder (adapted from 34)

The feeder can accommodate the desired feedrate of 100 – 150g/h. It is not recommended to run at higher or lower feedrates because at rates higher than 150g/h the feed tube in the fluidised bed was prone to blocking and at very low feedrates [less than 50g/h] the dilution of the pyrolysis vapours by the nitrogen gas makes gas analysis difficult, as discussed in Section 6.5.2.

The feedrate of biomass was controlled only by the feeder variables [paddle speed, entrain tube aperture size, feeder top pressure and entrainment flow] since the size and shape of feedstock, moisture content and preparation method as mentioned in Section 6.2 were fixed.

The feeder had mechanical paddles, which rotated slowly to prevent bridging of the feedstock and to maintain continuous flow of the feedstock. The speed of the feeder paddles were adjustable from 211, 290 and 365 rpm which correspond of setting 1, 1.5 and 2 respectively on scale of 1-10 of the instrument. Thus, allowing the feedrate to be altered during a run.

The top of the feeder was 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. The pressure in the feeder was increased by increasing the gas flow rate, thus increasing the biomass feedrate.

Entrainment gas helps the biomass to flow into the aperture more easily. Entrainment gas flow can be altered to increase or decrease the feedstock feed rate. However, this is not recommendable as entraining gas is part of the fluidising gas and should be kept constant during the run.

Figure 6.7 shows the influence of stirrer speed and feeder top flowrate to IEA poplar feedstock [295-600μm] feedrate (34). It is evident that for a 1.7mm feed tube aperture and an entrain gas flowrate of 1.5*l*/min, the feedrate is approximately twice as sensitive to stirrer speed than to feeder top flowrate. Hague (34) suggested that this general principle can be applied to other feedstock.

The influence of paddle speed and the feeder top flowrate are useful since they can be altered during a run to increase or decrease the flowrate. It was found that the feedrate reduces with the height of biomass in the feeder, therefore, the feedrate calibration was developed when the feeder was full.

Figure 6.7: Calibration relationship for feeder (34)

6.3.2 150g/h Reactor

The reactor as shown in Figure 6.8 consists of a 316 stainless steel cylinder with a length of 260mm and a diameter of 40mm. The top of the cylinder was threaded allowing the top of the reactor to be removed for cleaning and to add/remove the heating/fluidising medium. The top of the reactor has three apertures, one is for a thermocouple, which measured the internal of the reactor bed temperature, second is for the feed tube which transported the feedstock into the centre of the fluidised bed, and third is for an air-cooling line which prevented temperature sensitive feedstocks from being pyrolysed before they reach the fluidised bed.

The heating medium in the reactor is inert sand was sizes ranging between 355μm to 500μm, so that the fluidising velocity of the sand was sufficient to blow the pyrolysed biomass [char and vapours] completely of the bed while the sands remain in the bed. This is feasible, because the density of the char is approximately ten times lower than the density of sand. Consequently, a velocity that is sufficient to fluidise a bed of sand can be high enough for char of a similar size to be entrained from the bed. The sand fills the reactor to a depth of approximately 8cm and expands during fluidisation to 12cm. The sand was fluidised using nitrogen, which was 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 distributed by a sintered inconel plate with a 100μm pore size. The reactor was typically fluidised using 6-9*l*/min nitrogen [0.5 bar at 20°C]; this means that the bed was operating at approximately 3 times the minimum fluidising velocity [U_{mf}].

Figure 6.8: Schematic diagram of 150g/h fluidised bed reactor (34)

A stream of entrainment nitrogen carried the biomass to the reactor in the centre of fluidised bed. It begins to pyrolyse instantaneously producing pyrolysis vapour and char once it leaves the tube. Then it forms char particles which having similar dimensions to the original biomass once biomass reacted completely, but are only 10% of the original weight (34).

The fluidising velocity of the sand is enough to blow the char and vapours [pyrolysed biomass] completely out of the bed and a method known as 'blow-through' mode (53). They enter the first stage of product collection, which are the cyclone and the char pot. The cyclone was used to separate the char from the vapours. Due to density differences and centrifugal forces, the vapours then leave the cyclones at the top, while the char falls into the char pot.

The reactor, the cyclone and the char pot were placed into a furnace, which maintains the temperature at a set-point, which can be controlled to a fixed point between 400°C and 600^0C. The temperature of the reactor was measured by a K-type thermocouple located directly into the fluidised bed. The furnace set-point was approximately 20°C higher than the desired reactor temperature because energy was required by the reactor to heat up the fluidising nitrogen and the biomass feed to perform the pyrolysis.

The top of the furnace and the top of the reactor were insulated to prevent any heat losses. The outlet from the top of the reactor towards the second stage of products collection had been heated with trace heating tape to a temperature of 400°C. This pipe was also insulated to maintain temperatures above 400°C. If the temperature was below 400°C, the pyrolysis vapours would start condensing thus causing blockages in the transfer pipe between cyclone and second stage products collections, and the experiment would be terminated immediately.

6.3.3 Vapour Residence Time

Vapour residence time is the time that the pyrolysis vapours remain in the hot reactor system. There are two ways of calculating vapour residence time, one is total hot space residence time and second is reactor only residence time. 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 were still exposed to the furnace temperature. The reactor, cyclone and char pot were placed in the furnace, hence, the vapours were exposed to the temperature of the furnace. Consequently, vapours as well were kept at a constant temperature [which is that of the furnace or slightly lower] however, the vapours could undergo secondary reactions. Therefore, in all cases the residence time reported would be the total hot space residence time since this represents a more realistic view of the time/temperature, to which the vapours were exposed.

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 which affected the area above the distributor, cyclone, char pot and transfer line. The volume taken up by sand and char was discounted. The total hot space residence time as shown in Equation 6.1 was calculated from the volumetric throughput of the reactor system divided by the total hot space of the reactor.

$$\textbf{Residence time}_{\text{Total Hot Space}} = \frac{\left(Volume_{Totalhotspace} - \frac{W_{sand}}{\rho_{sand}}\right) * \; T_{Measurement} * Time}{1000 * T_{Reactor} * Volume_{TotalThroughput}}$$

Equation 6.1: Total hot space residence time (34)

Where:

$Volume_{TotalHotSpace}$ = Volume of reactor, cyclone and exit tube in cm^3

W_{sand} = Weight of sand used in g

ρ_{sand} = Particle density of sand in g/cm^3

$T_{Measurement}$ = Ambient temperature in K

$T_{Reactor}$ = Average reactor temperature in K

Time = Total run time in seconds

$Volume_{TotalThroughput}$ = Total volumetric output of system in litres

6.3.4 Liquid Collection System

Figure 6.5 also shows the product collection system. The product collection system can be divided into liquid products collection and gas products collection. The behaviour of the condensing pyrolysis vapours can be observed because all of the liquids collection system was constructed from glass. A reduction in vapour flowrate is an early indication of an operating problem, thus, indicates that a run has stopped. The presence of thick smoke on the other hand may indicate failure of the electrostatic precipitator. Therefore, the use of glass is a safety feature.

The liquid products collection consists of two cooled condensers, an electrostatic precipitator and cotton wool filter. Each unit of liquid collection system and gas collection are mentioned separately below.

6.3.4.1 Condenser 1

The first cooled condenser is a 'Davies type' double surface water condenser, which mounted at an angle 60° to facilitate liquid flow to the electrostatic precipitator [EP]. The pyrolysis vapours enter the condenser 1 which was cooled by circulated coolant [running tap water]. These pyrolysis vapours were then cooled from around 400°C to 50°C and starts the condensation process. The heavy ends of pyrolysis vapour condensed on the inner wall of the condenser and then dripped down to the electrostatic precipitator.

6.3.4.2 Electrostatic Precipitator

The electrostatic precipitator [EP] was very effective to capture vapours, which was present after the first condenser [condenser 1]. There is a circumferential stainless steel plate within the 50 mm diameter of glass housing of the EP, which was placed on the walls of the EP. This plate metal acts as a positive collection electrode. There is a thin stainless steel wire hanging down at the centre of the glass housing, which weighted with a bob and held in position with an external magnet. This thin wire acts as negative electrode and carries voltage of 15 kV. Therefore, the aerosols become negatively charged due to the presence of ions in the space between the electrodes. These negatively charge aerosols were then attracted to the positively charged plate on the walls of the EP. The pyrolysis liquid runs down the walls of the EP and accumulated at the bottom, which was attached to the oil pot 1. The pyrolysis liquid can be drained off during or after the run.

It takes a considerable amount of time to collect viscous pyrolysis liquids. Therefore, the collecting system has to be sealed in order to avoid the escape of volatiles from the liquid into atmosphere, in which a stopper was inserted into the opening of the glassware leading to the liquid collection system. The point, at which the metal transfer line from the reactor and cyclone connects to the glassware of the liquid collection system, needs to disconnect immediately after a run as it would otherwise become held very fast.

6.3.4.3 Condenser 2

The second condenser had a cold finger filled with dry ice and acetone and the temperature was approximately -80°C, thus, this further cools the pyrolysis vapours from around 50°C to 5°C. The light ends and water were condensed by this second condenser which collected on the inner wall and dripped down in oil pot 2. The oil pot 2 is a round bottom flask attached below condenser 2. While collecting all the pyrolysis liquid in condenser 2 into oil pot 2, the second condenser must be kept sealed after stopping a run in order to avoid loss of volatiles.

6.3.4.4 Cotton wool filter

The cotton filter is a glass column, which was densely packed with dry cotton wool to give protection to the down stream equipments, so that only clean non-condensable gases entered the gas meter and gas chromatograph system.

The introduction of the electrostatic precipitator [EP] has meant that the cotton wool collects only a small fraction of the total pyrolysis liquids and was now mostly used as a fail-safe to protect downstream equipment [gas meter and gas analysis equipment].

6.3.4.5 Gas meter

After the gas products exit the condenser 2 or go to the gas meter, the gas products should be non-condensable gases. The gas meter was located between the cotton wool filter and the gas chromatograph system. The gas meter measures the total volumetric throughput of gas through the system and was required to allow the gas to be analysed volumetrically for mass balance purposes.

6.4 MASS BALANCE

The products of pyrolysis were separated and collected in three distinct categories; char, gas, liquid. For mass balance purposes, these three categories will be defined below.

6.4.1 Mass Balance Reporting

A typical table which was used for mass balance reporting is shown in Table 6.2. The run number has the prefix EB denotes to Empty Fruit Bunches and then followed by a number. However, the run number for washed feedstock has the prefix EBW in which W denotes to empty fruit bunches which had subjected to washing process. The temperature is referring to the average reactor temperature which was the average recorded temperature from the in-bed thermocouple. The temperature was taken manually at 1 minute intervals throughout the course of a run. The total hot space residence time had been mentioned and calculated by the method described in Section 6.3.3.

The feedrate is the rate at which the feedstock was fed into the reactor and this was shown in grams per hour [g/h]. The feedrate should be kept between 50 and 150g/h to maintain consistency and accuracy during a run because 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 was calculated by weighing the feeder [±0.01%] before and after the run. The feedstock was not weighed alone since the small particle size means that it is difficult to handle, which could introduce inaccuracies. The feedrate was measured as the difference in feeder weights [before and after] divided by the total run time; hence it is an average. The moisture and ash content of the feedstock were calculated by the methods described in Sections 6.2.3 and 6.2.4 respectively. The particle size is referring to the size of feedstock that had been pyrolysed in this work, while run time is mentioned as the period of pyrolysis experiment has been completed.

The amount of feedstock used for each experiment is known as input. From Table 6.2, the wet feed is the weight of wet feedstock. This is the total feedstock for pyrolysis as this is the difference in weight of the feeder before and after pyrolysis. However, the weight of dry feedstock could be calculated from the weight of wet feedstock and from the feedstock moisture content. The weight of water in the wet feedstock can be calculated form the difference in weight of the wet feed and the dry feed. However, there was also some water added to the oil from the reaction which was not included in this category.

Table 6.2: Example of mass balance reporting

Run number	EB##
Temperature [°C]	Average of fluid bed temperature
Residence time [s]	Average total hot space residence time
Feedrate [g/h]	Average rate at which feedstock was fed into the reactor
Moisture [mf wt%]	Moisture content of feedstock
Ash [mf wt%]	Ash content of feedstock
Particle size [μm]	The size of feedstock
Run time, minutes	The period of experiment.
Input	Weight of feedstock before experiment in gram
Wet feed [g]	Weight of feedstock in wet basis
Dry feed [g]	Weight of feedstock in dry basis
Water in feed [g]	The amount of water in wet feedstock
Yields [mf wt%]	Major product yields [output] 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 6.5.1.1
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
Methane	Yield of methane
Carbon dioxide	Yield of carbon dioxide
Carbon monoxide	Yield of carbon monoxide
Hydrogen	Yield of hydrogen
Ethylene	Yield of ethylene
Ethane	Yield of ethane
Propane	Yield of propane
Propylene	Yield of propylene

The yields of the pyrolysis products were presented on a moisture free feedstock basis. The char, liquids and gas were calculated as described in Sections 6.4.2, 6.4.3 and 6.4.4 respectively. The details of the total liquids are described in Section 6.5.1.1, and it was measured by weighing which contains both organics and water of pyrolysis. The closure is the percentage of the original feedstock, which has been recovered or the percentage of the 'total mass out' to the 'total mass in'. It gives a measure to assess the quality of the experiment. If the value of closure is less than 90mf wt% or in excess of 100mf wt%, its indicates that something has not been measured correctly. However, in most cases the closure is in the region of 95-100 mf wt%.

The gas yields are further sub-divided into the uncondensable gases methane, carbon dioxide, ethylene, ethane, hydrogen, propylene, carbon monoxide and propane. Other gases n-butane and n-butylene were analysed but were rarely detected so they were not included in the mass balance reporting. All gas yields were given on a weight percent dry feedstock basis, which was calculated by dividing the weight of each gas with the weight of dry feedstock.

The contribution of each part of the 150g/h fluidised bed system to mass balance was illustrated in Table 6.3.

Table 6.3: Contributions of each part of the 150g/h reactor system to the mass balance

Input: Weight difference of feeder	Weight of wet feed			
Output:	Weight of:			
	Char	Organic	Water	Gases
Weight difference of whole reactor	▨			
Weight difference of condenser 1	▨	▨	▨	
Weight difference of EP, oil pot 1 condenser 2, oil pot 2 and cotton filter		▨	▨	
Volume difference of gas meter				▨

All measurement of weight for the 150g/h reactor system was to two decimal places and was accurate to ±0.01g. The weight difference of the feeder before and after run was claimed as the weight of wet feed consumed during the run. As nitrogen is the fluidising gas, therefore, the biomass fed into the reactor was the only item on the input side of the mass balance. The products of pyrolysis namely char, liquids and gas are mentioned separately below.

6.4.2 Char

The whole reactor includes the reactor top, the reactor body, the char pot, the cyclone, the connector [transfer tube] and the fluidising medium sand. As the whole reactor were assumed to remain at a constant weight, so any increase of weight after the run should be due to char. Char is a black substance collected in the char pot, as a residual coating on the sand, reactor, connector and cyclone and in the pyrolysis liquids, as some char was blown through the collection system. It was feasible that the sand will be worn away by attrition but this effect has been assumed to be minimal. It is possible that some of the sand was blown into the cyclone and hence char pot, but, since the sand was weighed before and after it would be accounted for. The char, which was blown into the condenser 1, tends to stick to the glass walls and can be filtered from the pyrolysis liquid washings [Section 6.4.3]. However, any char which gets into the liquids only be removed by diluting the pyrolysis liquids with a suitable solvent [methanol, ethanol or acetone] before they will pass through a filter.

6.4.3 Liquids

The collection of the liquid products begins in the condenser 1. They were collected on the walls of the condenser 1 and EP, and then they run down the walls into oil pot 1 which attached at the bottom of EP. There is the light part of the liquid drained down from the condenser 2 and was collected in oil pot 2. The liquid products collected in condenser 1 were very sticky and non homogeneous liquids were collected in the EP and oil pot 1, therefore, these liquid products were categorised into 3 types of liquids, and each type of liquid were further sub-categorised into organics and water. The liquid collected in condenser 2 and oil pot 2 was also sub-categorised into organics and water. It was found that only small fraction of the volatiles was trapped by the condenser 2 and the cotton wool filter as too little liquid collected for analysis. Therefore, it was assumed that the oil from the condenser 2, oil pot 2 and cotton wool filter had the same water content and zero char content. The liquids from the condenser 1, the EP, the oil pot 1 and oil pot 2 were placed into 4 separate storage containers for water content analysis.

The liquid which sticked on the glass walls of condenser 1 were washed out using methanol; this was 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 titration [Section 6.5.1.1] and were then stored as washings. As the liquid collected in the EP was a sticky liquid, it must be diluted using methanol before being analysed [Section 6.5.1.1]. The water came from the feedstocks original moisture content and also from water of pyrolysis which formed as a product of the pyrolysis reaction. The total water content of each of the pyrolysis liquid samples [condenser 1, EP, oil pot 1 and oil pot 2] was measured by Karl Fischer titration. The total water from the pyrolysis liquids which is the sum of water from the four pyrolysis liquid samples as mentioned above has the original feedstock water content subtracted from it. The water product quoted in the mass balance is the water of pyrolysis as it presented on a moisture free feedstock basis.

6.4.4 Gas

A Schlumberger Remus3 G1.6 total gas meter was used to measure the total volumetric throughput of the fluidised bed reactor system in cubic metres to three decimal places and it was accurate to ±2.0% of the total hourly flowrate.

The gas samples were analysed in the gas chromatograph [CP-4900 Micro Gas Chromatograph] every 5-10 minutes throughout the course of the run. The samples were analysed for their volumetric content of the major pyrolysis gases, which were carbon monoxide, carbon dioxide, hydrogen, methane, ethane, ethylene and propane. It was assumed that the remainder of the pyrolysis gas was nitrogen. From this analysis, the volume of the gas constituents was known and their weight can be calculated using their densities.

6.5 ANALYSIS METHODS

Analysis of pyrolysis products and accurate measurements are essential to any experimental based research. Several analytical techniques have been applied in order to quantify the major pyrolysis products and produce good quality reproducible mass balances. These following sections describe analytical techniques used in this work.

6.5.1 Pyrolysis Liquid Analysis

As mentioned in Section 6.4.3, the pyrolysis liquids were collected in 4 discreet samples from the pyrolysis system: condenser 1, EP, oil pot 1 and oil pot 2. Analysis techniques including Karl Fischer titration [to define water content of pyrolysis liquid] and char content of pyrolysis liquids had been done for all samples. However, only samples which produced by using the 1kg/hr rig was analysed for viscosity, stability, molecular weight, FTIR spectroscopy and lignin content of pyrolysis liquids. This sample had been produced from washed feedstock with ash content 1.06 mf wt% [run number of EBW09] which was a homogeneous pyrolysis liquid and have enough amount for these analyses. Although the quality of the pyrolysis liquid collected in oil pot 1 has been improved by the introduced washing technique as can be seen from its homogeneity. However, mixing liquids from oil pot 1 and oil pot 2 together was not totally achieved. This is probably because of the high water content of the mixture. According to Oasmaa and Peacocke (158), the liquid separates into two phases if the water content of pyrolysis liquid more than 30 wt%. Therefore, the samples produced from a 150g/h rig were not enough for other analyses.

6.5.1.1 Karl Fischer Titration

A Metrohm 758 KFD Titrino instrument that was accurate to ±0.01mf wt% was used to measure the water content of each of the pyrolysis liquid samples. Due to high viscosity of the pyrolysis liquids collected in condenser 1 and EP, the pyrolysis liquids were diluted using methanol before being analysed. Therefore, a small amount of these viscous pyrolysis liquids was first weighed into a vial. This was then diluted with a known weight of dry methanol. A known weight of the combined liquid was 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 was known the percentage water can be calculated. The moisture content of the original liquid can then be back calculated.

The watery pyrolysis liquids collected in oil pot 1 and oil pot 2 were not diluted in order to find the water content of these liquids. Therefore, a known weight of these pyrolysis liquids can be injected through a septum directly into the meter. The meter then determines a water content of this oil. The determination was repeated three times and the average value was reported. The standard deviation was required to be less than 0.3%. As the pyrolysis liquids produced from washed feedstock were homogenous [i.e. pyrolysis liquids collected in EP and oil pot 1 was in one phase], only the water content of pyrolysis liquids collected in condenser 1, oil pot 1 and oil pot 2 were measured.

6.5.1.2 Char content

A filtration method was used to define the char content in pyrolysis liquids. In order to enable the pyrolysis liquids to pass through the filter they were diluted with a suitable solvent either methanol, ethanol or acetone.

Approximately 1g of pyrolysis liquids was weight and then diluted by about 10g of methanol. This diluted solution then was filtered with a pre-dried and weight Whatman No. 1 qualitative filter paper. The filter was then placed in an oven at 105°C for a minimum of 6 hours before and then cooled in a desiccator for 1 hour before weighing. The char content was then calculated and an average of three samples taken. All measurement of weight was to four decimal places and was accurate to ±0.001g.

6.5.1.3 Viscosity

Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. For fuel, the viscosity is important because its effect on pumping and injecting of fuel (159).

Viscosity measurements were carried out by a colleague of the author of this thesis using glass capillary viscometers at a fixed temperature of 25°C. Only about 4 m*l* of sample required for the test for this type of viscometer. The viscosity was measured by determining the time taken for a fixed volume of pyrolysis liquids to flow between two marked points, and the viscosity was calculated using the equation V=Ct, which "V" is the viscosity in centistokes, "C" is the viscometer constant and was not affected by the temperature and "t" is the time taken for the liquid to fall from the first timing mark to second mark and the unit is seconds.

6.5.1.4 Stability

The Viscosity Index [VI] measures the relative change in viscosity with time and was used to provide a measure of stability. VI was calculated using the equation $VI=(\mu_f - \mu_i)/ \mu_i$,. The initial viscosity μ_i is referring to the viscosity of the fresh pyrolysis liquids which was tested at 25°C after 24 hours from it was produced. The final viscosity μ_f is referring to the viscosity of the pyrolysis liquids which was stored for 24 hours at 80°C which this pyrolysis is known as aged pyrolysis liquids as recommended by the Aston Viscosity Index. The viscosity was re-tested at 25°C as well. The lower the VI number, the more stable is the pyrolysis liquid. A VI of zero would be a completely stable liquid.

6.5.1.5 Fourier Transform Infra-Red Spectroscopy

Fourier Transform Infra-Red [FTIR] is a fast scanning, high resolution, high signal-to-noise ratio, non destructive analytical technique which was used to ascertain the presence of specific functional group composition in pyrolysis liquids. Analysis of FTIR spectra at wave numbers 4000 to 200 cm^{-1} of pyrolysis liquids provides a quick and simple qualitative technique by using the standard ir-spectra to identify the functional group of the components of the derived pyrolysis liquids.

6.5.1.6 Lignin content

The pyrolytic lignins were obtained from pyrolysis liquids by dropwise adding of the pyrolysis liquids to distilled water (160) under vigorous stirring [> 5000 rpm] using an ultra turrax. Pyrolysis liquids to water ratio of 1:50 were used in this work. After slowly adding the pyrolysis liquids to distilled water, pyrolytic lignin precipitated. After precipitation the liquid smoke [water soluble part of pyrolysis liquids] was dissolved in a large amount of distilled water. Subsequently the solid was filtered and washed thoroughly until the filtrate reached a neutral pH. Finally, the wet solids [pyrolytic lignins] were dried in vacuum at ambient temperature for 24 hours.

6.5.1.7 Gel Permeation Chromatography

Molar mass and molecular weight of pyrolytic lignins were determined by a colleague of the author of this thesis using a gel permeation chromatography [GPC]. The chromatography was set to 40°C and equipped with columns which have pore size of 50 and 100Å, and lengths of 300 and 600mm. The pyrolytic lignin sample was diluted in THF [tetrahydrofuran, Aldrich 99.5% + HPLC grade] to make 5 mg/ml solution. This sample solution was filtered using 0.2 μm pore size of a filter paper to remove insoluble impurities, and toluene was added into the sample solution acting as a flow marker. About 100μ*l* sample solution was injected into a mobile phase allowing the sample elution through the columns.

A series of polystyrene having molar mass from 161g/mol to 72200g/mol were used for calibrations standards. The Cirrus GPC software was used to determine the experimental data process with regards to molar mass and analysis. The number average molar mass [M_n], weight average molar mass [M_w], molecular weight at highest peak [M_p] and polydispersity index [PD=M_w/M_n] were calculated from refractive index [RI] signals using the software. Detectors consist of a differential refractive index and a photometer in UV range of 280nm.

6.5.2 Gas Analysis

Gas chromatography [GC] is an analytical technique for the separation and identification of chemical compounds. Gas samples were analysed for pyrolysis gases using gas chromatography and it were taken periodically during the course of a run. Two separate systems were used to detect the full range of gases which hydrogen, oxygen, nitrogen, methane and carbon monoxide were detected using a molecular sieve column, carbon dioxide, methane and C_1-C_4 gases were detected using a Poropak Q column. It was found that methane can be detected by both columns.

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 corresponds to that particular gas under the specific conditions for that gas chromatography system and column. Thus when a gas sample was injected only the gases that 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. The mass of pyrolysis vapours produced can then be calculated from the total volume measured by the gas meter.

The pyrolysis vapours were dilute because the fluidised bed reactor requires a high throughput of gas about 6-18*l*/min. nitrogen was typically used to keep the sand fluidised. About 2-3*l*/min of extra gas was also required to entrain the feedstock from the feeder and into the reactor. 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 increased to detect the low concentrations of gas. Gas chromatography are normally able to detect gas concentrations from 1.00% [total gas volume basis] for abundant gases such as carbon monoxide and dioxide, down to concentrations as low as 0.02% for minor gases such as n-butane and n-butylene.

6.6 EXPERIMENTAL ACCURACCY

The experimental results presented do not mean that they are accurate even though the author believed that is to be the best achievable from the equipment available at Aston University. This section describes the occurrence of errors, inaccuracy or non-quantification of a product which contributed to the incomplete closure. These were included the hygroscopic nature of feedstock, reactor temperature which effect to vapour residence time, product yield and analysis which had been done on product yield.

6.6.1 Hygroscopic Material

Feedstock is a hygroscopic material which naturally absorbs moisture from the air. Thus, although the moisture content of a feedstock may be correct at the time of the measurement, the moisture content may change if left open to the atmosphere, improperly stored or stored for a long period of time, and this will increase to the equilibrium moisture level. Therefore, the moisture content should be measured at the time of performing the experiment. Over measurement of the feedstock moisture content could result in reduced closure and when closure is high, it usually due to under measurement of the feedstock moisture content. The water in the pyrolysis liquid would be water of pyrolysis and the extra feedstock moisture.

The ash content was measured after the moisture content and was calculated on a dry basis; thus inaccuracies in the moisture content could have a compound effect on the ash content. However, the ash content does not have such significant effect on the feedstock mass balance. Ash does have a significant effect on the pyrolysis reaction on which water washing pre-treatment have been used to reduce the ash level and significantly increase the quality of pyrolysis liquids.

6.6.2 Reactor Temperature

The reactor temperature was measured directly from a K-type thermocouple placed in the fluidised sand. The reactor temperature was maintained by a furnace, which surrounds the reactor, cyclone and char pot. It was measured manually at set time intervals throughout a run and the average reactor temperature was hence calculated. This value, however, may not adequately describe the temperature profile within the reactor. As example, the run could have consisted of 15 minutes at 475°C followed by 15 minutes at 525°C, which was an average of 500°C. However, in most cases it was felt that the average reactor temperature provides a fair indication of the temperature the reactor was maintained at during a run.

The key reactor parameters are temperature and residence time. Therefore, it is important to know the total hot space residence time as this measures the amount of time the pyrolysis vapours will be exposed to the reactor temperature. The total hot space residence time as 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. Therefore, any error in measurement of any of the variables from which residence time was calculated would result in errors in the residence time. The volume of total hot space and the density of sand are constant. The weight of the sand is accurate to ± 0.01 g, therefore is not likely to introduce significant errors into the residence time calculation. The volumetric throughput of the reactor was assumed to be measured at 0°C. However, it is possible that the gases passing through the gas meter are hotter or colder than this since they were heated in the reactor and then cooled in the dry ice condenser.

The reactor temperature is an average which could also be a potential source of error. However, this value was used to calculate the total volume of gas at the reactor temperature. As an average volumetric throughput was calculated, therefore, it was best to use the average reactor temperature. The total run time was measured ±1s and because a run usually lasts at least 40 minutes there is virtually no error from this variable.

6.6.3 Products Yields

Products yields were categorised into char, liquids and gases, which closure is the sum of the product yields. As mentioned in Section 6.4.2, char was collected in the char pot and as a coating on the sand and inside the reactor. 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. The level of char in the liquid is generally very low which is about less than 2% on a pyrolysis liquid basis, therefore, it 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 were collected in the EP and oil pot 1 and oil pot 2 as described in Section 6.4.3. The liquids can be weighed directly, thus, it was unlikely that any error was introduced here. As mentioned above, some char may have blown into the liquids, thus giving a slightly inflated liquids yield; however this is minimal. Water content measurement of the liquids [Section 6.5.1.1] is accurate to ±0.01 wt% so it seems unlikely that this could introduce errors into the liquids 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 were used, the gas which acts as a carrier could carry a small percentage of the more volatile components out of the collection system and into downstream equipment. As each feedstock and reactor temperature will result in the production of a certain yield of volatile components, it is difficult to quantify on a general basis. 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.

The gas cannot be measured directly. Although the total volumetric throughput was known the amount of fluidising and entrainment nitrogen was not measured. This could be estimated from the rotameters, which were used to measure the nitrogen flows. However, sometimes these flows were altered during a run. If both the nitrogen input and total gas outputs where known, this only give an indication of total gas volume; the gas composition and therefore weight would still have to be determined.

6.6.4 Product Analysis

Product analysis can be divided into gas analysis and liquid analysis. There are several types of analysis methods that can be carried out on the liquid such as Karl Fischer titration, viscosity, stability, char content, lignin content, GPC, FTIR and GC-MS. Among these analyses, the Karl Fischer titration analysis only contributed to the mass balance calculation.

The Karl Fischer titration has been described previously in Section 6.5.1.1. As it is reproducible and accurate to ±0.01mf wt%; thus it is not believed that this is a source of inaccuracy or poor closure. However, in order to ensure consistency in the oil water analyses between different runs, some factors have been considered as below:

- The pyrolysis liquids were analysed at room temperature and 24 hours after production due to the oil water content changing with storage time and temperature.
- Calibration of the Karl Fischer apparatus was carried out every time before use. Solvent and Karl Fischer reagent may change with changing room moisture despite the use of desiccators. Accurate calibration must be carried out to ensure that the standard deviation is less than 0.3% preferably about 0.1%.
- All analyses results were based on an average of three analyses with a standard deviation of less than 0.3%.

7. PYROLYSIS OF UNWASHED AND WASHED FEEDSTOCKS

A series of unwashed and washed feedstocks have been pyrolysed over a range of temperatures from 399-610°C. In all cases, the maximum yield of organics has been determined along with the temperature at which the maximum yield occurs. A number of washed feedstocks with different ash content have been pyrolysed in order to determine the maximum ash level that produce the homogenous pyrolysis liquids. The results are compared to those from pyrolysis of various feedstocks with different ash contents.

7.1 OVERVIEW OF EXPERIMENTS

Pyrolysis experiments have been carried out on unwashed and washed feedstocks by using the 150 g/h fluidised bed bench scale fast pyrolysis unit operating at atmospheric pressure over a range of temperatures 399-610°C [see Section 6.3.2 for description of equipment]. In addition the washed feedstocks for the experiment of run number EBW09 [see Section 7.3.3] was carried out using the 1kg/h reactor in order to compare the effect of scale and obtain larger quantities of bio-oil characterisation.

The main objective of this experiment is to determine the best parameter of pyrolysis experiment that produce high yield of organics for unwashed and washed feedstocks. The pyrolysis experiments on unwashed feedstocks have been performed on feedstock with different ash contents, particle sizes, over a range of hot vapour residence times and temperatures. In addition, the washed feedstocks with different ash contents had been pyrolysed in order to determine the maximum ash level of the feedstock that can produce homogeneous pyrolysis liquids.

A total of 39 runs of pyrolysis experiments on unwashed and washed feedstocks were carried out, as shown in Appendix C. The results have been divided into two parts: pyrolysis of unwashed feedstock and pyrolysis of washed feedstock, which are discussed separately below.

7.2 PYROLYSIS OF UNWASHED FEEDSTOCK

The maximum quantity of the high quality liquid is dependent on the type of feedstocks as the composition for each feedstock is variable [see Section 2.3.1]. The maximum amount of pyrolysis liquid can be produced by determining the optimum temperature at which it occurs. The quality of the pyrolysis liquid as a fuel has been assessed by studing its stability, viscosity and heating value (158). The pyrolysis liquids produced from unwashed feedstocks were always in two phases -a heavy organic phase and a lighter aqueous phase. This liquid also known as the non-homogenous liquid, which contains of two liquids that exist in different form. One was in sticky form and very viscous and another one was very watery.

Figure 7.1 shows the product yields from a number of biomass feedstock types summarised by Toft (33). The author confirmed that each biomass feedstock has a maximum yield of organics and that the temperature at which this occurs depends on the feedstock type.

Figure 7.1: Yield of organics from pyrolysis of a range of feedstock types (33)

Results from a number of reactors gathered from a variety of published sources are shown in Table 7.1. This table also shows the maximum yields of organics and the temperature at which they were produced for a range of feedstocks pyrolysed. It is evident that woody feedstocks which has low ash content give the highest organics yields and non-woody feedstocks which has high ash content such as rape meal and miscanthus give the lowest. It can be seen that the maximum organic yields were produce from 429 to 600°C depending on the types of feedstock used.

Table 7.1: Organic yields comparison of pyrolysis technology from different sources

Kind of feedstock	Ash content, mf wt.%	Maximum yield of organics, mf wt%	Temp., °C	Source	Reference
IEA poplar	0.46	72	485	Aston	(34)
Pine wood	0.5	68	477	Aston	(34)
White spruce	0.5	66.5	500	Waterloo	(19)
Pine wood	0.5	65.9	602	Aston [ablative]	(161)
IEA poplar	0.46	65.8	500	Waterloo	(53)
Washed EFB	1.03	61.3	500	this work	
Pine wood	0.5	60	504	Aston [1kg/h FB]	(161)
Sweet sorghum bagasse	nd	58	515	Waterloo	(162)
Sugar cane bagasse	2.44	58	498	Waterloo	(19)
Miscanthus	5.7	55	458	Aston	(34)
Beech wood	0.6	54.2	555	Aston [ablative]	(163)
Rape straw	5.2	48	457	Aston	(34)
Rape meal	7.7	47	429	Aston	(34)
Wheat straw	4.6	43	582	Waterloo	(164)
Poplar bark	nd	43	500	Waterloo	(19)
Pine bark	1.79	38	505	Aston	(34)
Unwashed EFB	5.29	36.9	453	this work	

nd:not determined

The following sections present the results of pyrolysis experiment on unwashed feedstock which were assess by a mass balance obtained in this work [see an example of mass balance reporting in Table 6.2], and discuss any experimental points specific to the EFB feedstock.

7.2.1 Impact of Sieving on Pyrolysis

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, as shown in Table 4.12. Table 7.2 shows that for sieved feedstock the ash content is highest for the smallest particle size fraction. It was expected that a lot of inorganics soil fine particles could be found in the smallest particle size fraction. The sieved feedstocks of size ranges less than 150, 150-250, 250-300, 300-355 and 355-500µm have been pyrolysed over the temperature range 500-520°C. The mass balance results are summarised in Table 7.3.

Table 7.2: Ash content of EFB by size fraction

Feed particle size [µm]	Average ash [mf wt%]
Less than 150	8.49
150-250	7.46
250-300	6.70
300-355	5.91
355-500	4.83

As mentioned in Section 2.3.6, it was noted that as vapour residence time increased the liquid yields decreased (165). Therefore, the hot vapour residence times have been kept low in the pyrolysis experiments [between 1.04–1.66s] to minimise secondary reactions. The results are shown in Table 7.3. The experimental data from the runs are arranged in order of increasing feedstock ash content. EBI01 had a poor closure [89.8%], which was due to blockage in the feed tube of the reactor. This means that the feed could not flow into the reactor. Therefore, the run had to be stopped immediately so that the feed tube could be cleaned with a wire. For that reason, some feedstock was likely to be lost during the runs performed for this work, where blockage occurred. For the next run, a vibrator was placed to the feed tube of the reactor and all equipment was earthed to prevent electrostatic effects, and this solved the blockage problem. The closure for EBI05 is still low [91.0%]. This may be due to the failure of the electrostatic precipitator [EP], 8 minutes into the run, which required the reactor to be restarted. EBI01 is the first pyrolysis experiment in which several parameters were varied to get the optimum setting, thus gave the hot vapour residence time for this run slightly higher [1.66s] than for other runs and the feedrate was very low [17.1g/h].

Table 7.3: Mass balance of pyrolysis experiment on feedstock with variation ash content

Run number	EBI01	EBI05	EBI04	EBI02	EBI03
Reactor temperature [°C]	520	496	508	500	499
Hot vapour residence time [s]	1.66	1.07	1.08	1.04	1.04
Feedrate in wet basis [g/h]	17.1	46.8	69.9	57.3	45.2
Feed moisture [mf wt%]	8.9	0.21	0.57	0.87	0.29
Ash [mf wt%]	8.49	7.46	6.70	5.91	4.83
Particle size [μm]	< 150	150-250	250-300	300-355	355-500
Run time, minutes	217	162.4	121.6	107.1	120
Input					
Wet feed [g]	61.71	126.60	141.82	102.35	90.44
Dry feed [g]	56.67	126.34	141.01	101.48	90.18
Water in feed [g]	5.04	0.26	0.81	0.87	0.26
Yields [mf wt%]					
Char	22.43	20.74	24.86	20.88	24.26
Organics	29.83	38.64	38.83	40.54	38.17
Gas	20.91	18.36	21.26	19.50	17.33
Water	15.94	13.28	10.88	15.01	19.27
Total Liquids	45.33	51.92	49.71	55.55	57.44
Closure	89.8	91.0	95.8	96.0	99.0
Gas [mf wt%]					
Methane	0.60	0.84	0.91	0.64	1.21
Carbon dioxide	11.84	12.51	15.0	13.78	11.34
Carbon monoxide	2.70	4.46	4.93	4.55	4.14
Hydrogen	0.18	-	-	0.06	-
Ethylene	-	0.11	0.19	0.12	0.16
Ethane	5.60	0.23	0.28	0.21	0.26
Propane	-	0.13	-	0.14	0.21
Propylene	-	0.09	0.16	-	-

Figure 7.2 shows the results of the effect of feedstock ash content on organics yield. The results showed that as the ash content decreases the organics yield increases. However, it was found that the organics yield decreased for the feedstock of lowest ash content [4.83

mf wt%], and it can be claimed as not accurate since the feedstock composition such as lignin, cellulose and hemicellulose may be varies for different size of feedstock which influent the product yield. This means that although the ash content is low, the feedstock compositions can influence the product yields as well. The particles of size less than 150μm which contained the highest ash level had produced the lowest organics yield compared to the larger particle size which contains lower ash level. It might be because the low ash content promotes a reduction in catalytic cracking of primary liquid products, so that the formation of char is successively less favoured compared to volatile formation. Based on the literature review as shown in Table 7.1, it was found that the organics yield increased with decreasing ash content of biomass, which had been illustrated in Figure 7.2. Work by Raveendran et. al (126) is reviewed in Section 4.4, with particular emphasis on the removal of ash. They investigated the effect of ash on the products of pyrolysis from thirteen Bombay feedstocks. The results indicated that decreasing the ash content in biomass increased the volatiles yield, as shown in Table 4.11. It shows that ash present in biomass seems to have a strong influence on both the pyrolysis characteristics and product distribution, and this is relevant to the results.

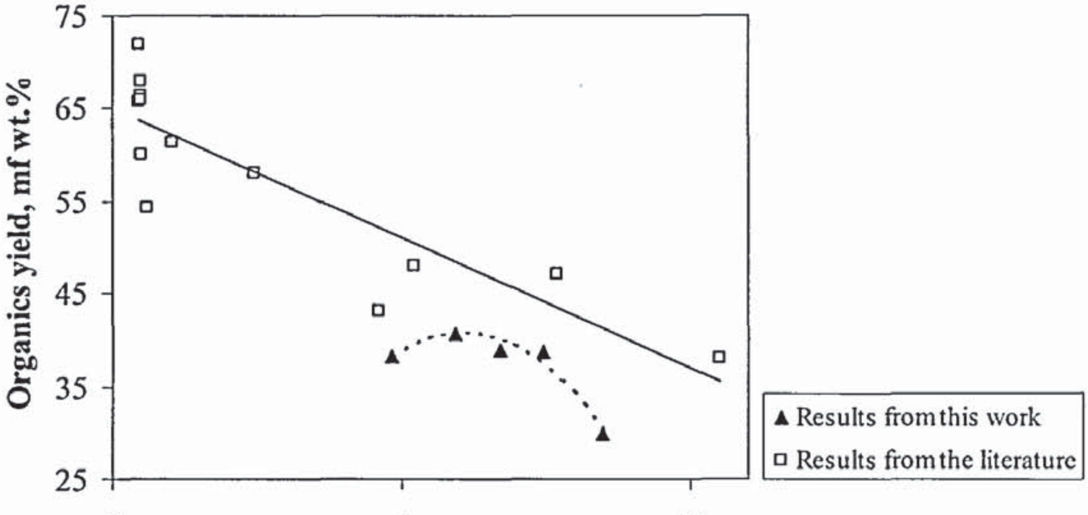


Figure 7.2: The effect of feedstock ash content on organics yield

Results for the effect of particle sizes on organics yield are shown in Figure 7.3. The results showed that the organics yield was maximum [40.5 mf wt%] for an average feed particle size of 328μm [average of 300-355μm], while the organics yield was minimum [29.8 mf wt%] for the particle of size less than 150μm. The particle of size 428μm [average of 355-500μm] produced organics yield about 38.2 mf wt%. It was observed that the maximum organics yields were obtained with the middle size of particle size [300-355μm]. This may be due to the fact that the smaller size particles were too quickly blown from the reactor before pyrolysis took place producing more char; and the larger particles were not adequately heated up causing incomplete pyrolysis. These results are similar to the work done by Nurul Islam et. al (20). They investigated fast pyrolysis of oil palm shell [2.3 mf wt% ash content] focussing on the effect of feed particles size [range from 150μm to 1mm], fluidisation gas flow rate and bed temperature on palm shell pyrolysis product distribution [liquid, char and gas]. The authors had not mentioned the capacity of reactor they used. It was expected that they used the reactor with capacity bigger than 150 g/h rig as the feedrate of feedstock was about 0.4-0.6 kg/h. They found that the percentage mass of liquid product was maximum [58 mf wt%] for an average feed particle size of 318μm [average of 212-425μm]. The particle of size less than 150μm produced liquid product of 28 mf wt% while the larger particle of average size 750μm [average of 500μm-1mm] produced liquid product of 42 mf wt%. The results of their works are shown in Figure 7.3.

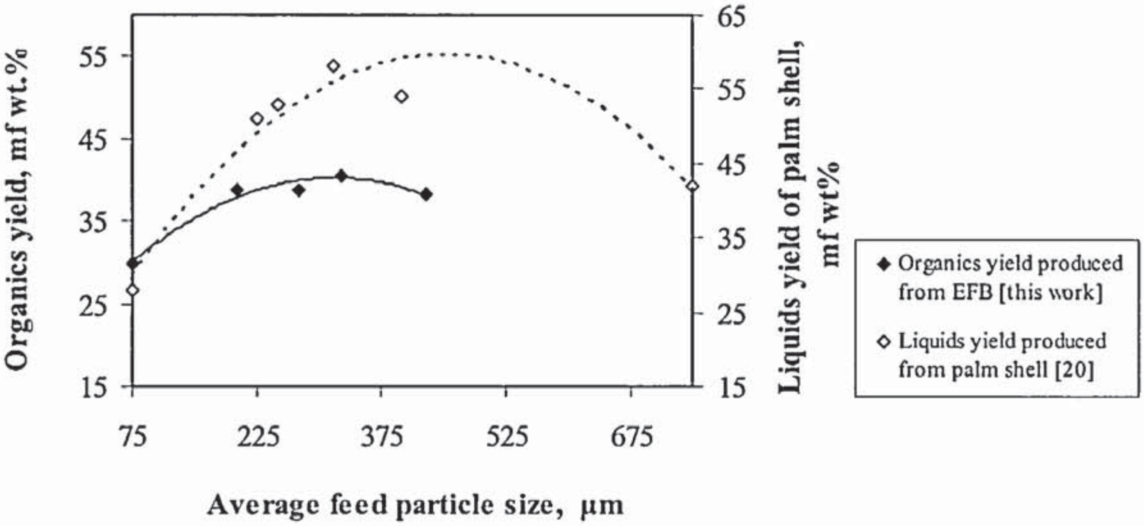


Figure 7.3: The effect of feed particle sized of organics yield

7.2.2 Effect of Vapour Residence Times on Product Yields

Pyrolysis experiments were conducted at a reactor bed temperature of 500°C over a range of vapour residence times on feedstock of size 300-355μm. The feedstocks of size 300-355μm were chosen because of their maximum organics yields. The results are shown in Table 7.4. A total of seven experiments were carried out, however only the best results have been included in Table 7.4.

Table 7.4: Mass balance of pyrolysis experiment with variation of vapour residence time

Run number	EB01	EB02	EB03	EB05	EB04
Reactor temperature [°C]	501	502	502	499	503
Hot vapour residence time [s]	0.79	0.96	1.03	1.16	1.23
Feedrate in wet basis[g/h]	109.02	106.67	86.46	107.24	74.92
Feed moisture [mf wt%]	7.86	7.58	7.04	8.53	7.41
Ash [mf wt%]	5.6	5.6	5.6	5.3	5.6
Particle size [μm]	300-355	300-355	300-355	300-355	300-355
Run time, minutes	70.5	81.23	88.87	107.24	119.95
Input					
Wet feed [g]	128.08	144.41	128.06	143.67	149.78
Dry feed [g]	118.74	134.24	119.64	132.37	139.45
Water in feed [g]	9.34	10.17	8.42	11.30	10.33
Yields [mf wt%]					
Char	27.08	26.30	23.81	25.73	27.34
Organics	35.26	36.83	40.53	34.94	33.46
Gas	17.79	17.61	18.48	18.92	22.24
Water	15.63	14.95	14.84	15.58	14.60
Total Liquids	50.89	51.78	55.37	50.52	48.06
Closure	95.8	95.7	97.66	95.18	97.64
Gas [mf wt%]					
Methane	0.62	0.51	0.73	0.57	0.65
Carbon dioxide	12.31	12.65	13.45	13.73	16.07
Carbon monoxide	4.47	4.10	3.82	4.29	4.95
Hydrogen	-	0.04	0.04	-	0.05
Ethylene	0.11	0.07	0.10	0.09	0.11
Ethane	0.21	0.18	0.24	0.19	0.23
Propane	0.06	0.06	0.08	0.06	0.09
Propylene	-	-	0.01	-	0.09

The experimental data from the runs are arranged in order of increasing vapour residence time from 0.79s to 1.32s. The ash content of this feedstock was obtained by measuring the ash content of the feedstock which was in the same bag. The feedstock was well mixed and sealed properly so that the dirt will not go into the feedstock to ensure that the ash contents for all subsequent tests were the same. However, the feedstock for the run number EB05 were taken from the different bag, therefore, the ash content is slightly different by 0.3 mf wt%.

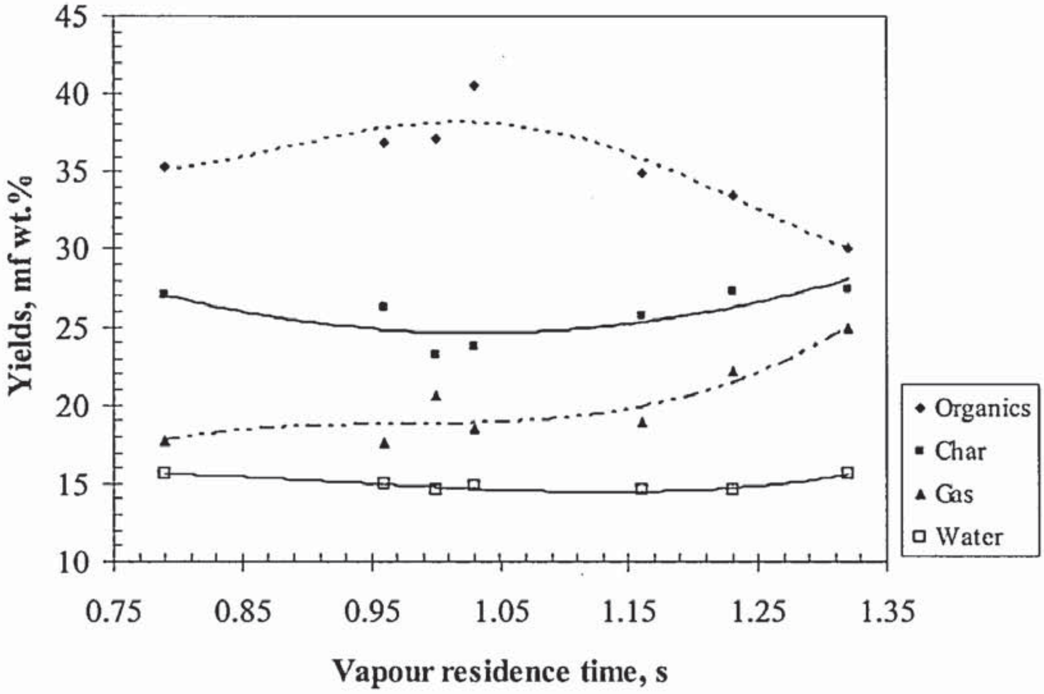


Figure 7.4: Product yields of a range of vapour residence time

All seven experiments are included in the graph of the major products plotted in Figure 7.4. The maximum organics yield was obtained at the vapour residence time of 1.03s. The organics yield decreased to a value of 35.26 mf wt% with the decrease of vapour residence time to 0.79s, but with the increase of vapour residence time up to 1.32s, the organics yield decreased to a value of 30.09 mf wt%. This may be due to the fact that at shortest vapour residence time the biomass was too quickly blown from the reactor before pyrolysis to take place producing more char. On the other hand, at longest vapour residence time contributed to the slightly lower organics yield by allowing more secondary reactions, thus, producing more gas and char yields. The results of this work are similar to the work done by Nurul Islam et. al (20). They investigated the efect of fluidisation flow rate on palm shell pyrolysis product distribution. They found that the maximum liquids yield was 36 mf wt% at a fluidisation gas flow rate of $0.8m^3h^{-1}$, however, the liquids yield decreased to a value of 28 mf wt% at fludisation flow rate of $1.2m^3h^{-1}$, while at fluidisation gas flow rate of $0.69m^3h^{-1}$, the liquids yield decreased to 22 mf wt% . The fluidisation gas flow rate is in inverse proportion to the vapour residence time [see Equation 6.1].

7.2.3 Effect of Reactor Bed Temperature on Product Yields

Pyrolysis experiments were carried out at a vapour residence time of 1.02-1.05s over the temperature range 399-610°C on feedstock of size 250-355μm. The mass balance reporting and the results are shown in Table 7.5.

Table 7.5: Mass balance of pyrolysis experiment with variation of reactor bed temperature

Run number	EB17	EB11	EB18	EB12	EB22	EB15
Reactor temperature [°C]	427	453	478	504	524	553
Hot vapour residence time [s]	1.02	1.02	1.02	1.02	1.05	1.05
Feedrate in wet basis [g/h]	69.27	107.34	124.92	123.56	115.0	159.58
Feed moisture [mf wt%]	8.96	7.48	8.85	7.91	8.56	8.96
Ash [mf wt%]	5.29	5.29	5.29	5.29	5.29	5.29
Particle size [μm]	250-355	250-355	250-355	250-355	250-355	250-355
Run time, minutes	106	73.63	70.7	69.74	80.45	52.43
Input						
Wet feed [g]	122.38	131.73	147.2	143.62	154.2	139.45
Dry feed [g]	112.32	122.56	135.24	133.09	142.03	127.98
Water in feed [g]	10.06	9.17	11.96	10.53	12.17	11.47
Yields [mf wt%]						
Char	26.77	25.74	25.13	24.52	23.78	23.28
Organics	35.05	36.89	35.09	34.71	34.20	32.55
Gas	19.25	19.81	20.76	22.31	24.90	27.62
Water	15.23	15.64	15.39	15.17	15.13	14.71
Total Liquids	50.28	52.53	50.48	49.88	49.33	47.26
Closure	96.3	98.1	96.4	96.7	98.0	98.2
Gas [mf wt%]						
Methane	0.47	0.67	0.68	1.0	1.13	1.75
Carbon dioxide	14.29	14.21	15.3	15.63	17.93	20.04
Carbon monoxide	4.13	4.49	4.37	4.93	5.25	4.83
Hydrogen	0.04	0.04	-	0.11	-	0.15
Ethylene	0.06	0.08	0.08	0.12	0.13	0.2
Ethane	0.18	0.23	0.23	0.3	0.32	0.42
Propane	0.08	0.07	0.10	0.09	0.15	0.22
Propylene	0.01	-	-	0.14	-	-

A total of nine experiments were carried out, however only the best results have been included in Table 7.5. Mass balance closures for all runs are greater than 95%.

The experimental data from the runs are arranged in order of increasing temperature and the pyrolysis temperatures were chosen to cover this range in approximately 25°C. The feedstock pyrolysed in the experiment had been taken from the same sealed bag. Thus, the ash content for all run is constant.

A graphical representation of products yield results is shown in Figure 7.5. Data from the nine experiments are included.

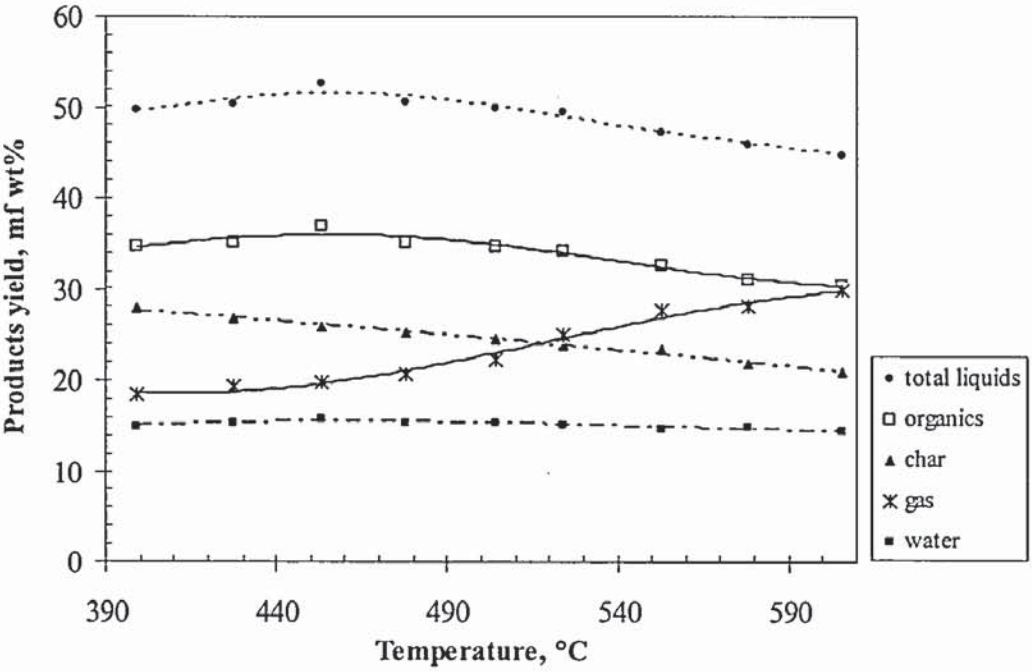


Figure 7.5: Effect of reactor bed temperature on products yield

The results from Figure 7.5 show that the yield of pyrolysis products follows similar trends to those described in Section 2.3.5, in which the yield of organic reaches a maximum at a temperature between 400 to 600°C; char yields decrease with temperature; gas yields increase with temperature and water remains relatively constant throughout. In this work, the results showed that maximum liquids yield was highest at about 453°C and this was 52.5 mf wt%, while the char and gas yields were 25.7 mf wt% and 19.8 mf wt% respectively. It was found that char yields decrease as temperature is raised, while gas yield increases as temperature increases. At temperature of 399°C, the liquid products yield was 49.6 mf wt%, while at a higher temperature of 606°C, the liquid products yield was only 44.7 mf wt% and the char yield was only 20.8 mf wt%. The water yields remain relatively constant through the temperature range investigated and the gas yields increase as temperature is raised. This is an indication that more secondary reactions are taking place as temperature increases, resulting in the formation of more carbon monoxide, carbon dioxide and more higher hydrocarbon [methane, ethylene, ethane, propylene and propane]. The increasing yield of carbon dioxide [CO_2], carbon monoxide [CO] and methane [CH_4] with temperature is shown in Figure 7.6. While carbon monoxide yield increases uniformly with temperature, the carbon dioxide yield increases up to about 550°C, but then appears to become relatively constant with further temperature increase.

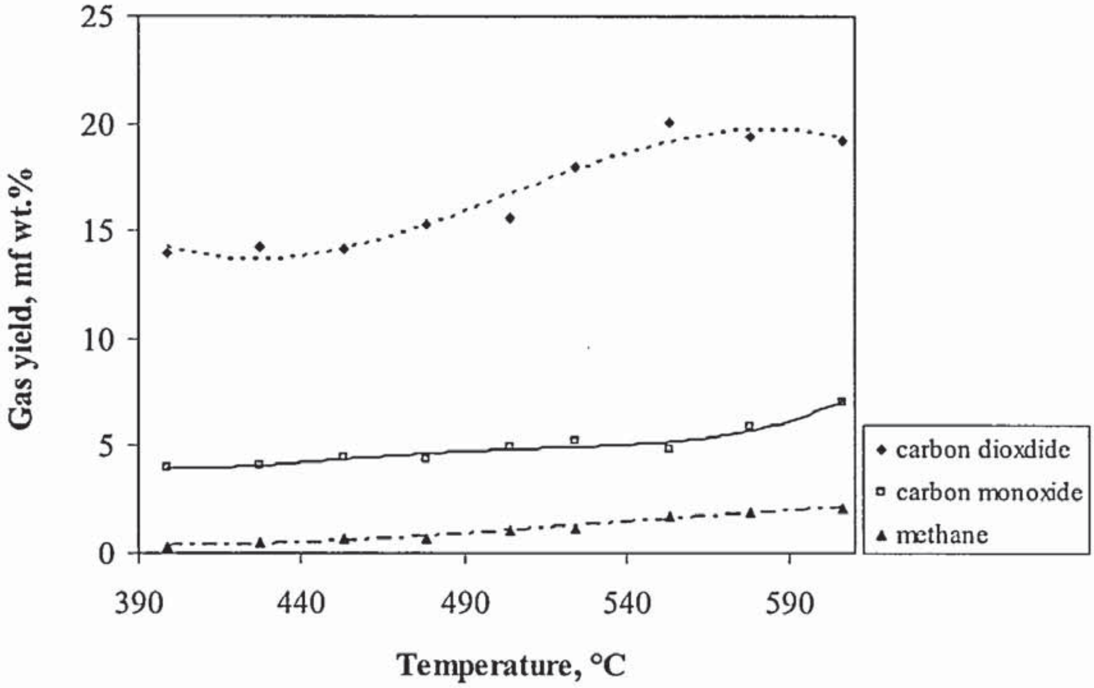


Figure 7.6: Gas yields as function of temperature for unwashed feedstocks

The pyrolysis liquids produced from pyrolysis experiments on unwashed feedstock separated into two phases, a phase predominated by tarry organics compounds and an aqueous phase. Therefore, this oil is unlikely to be suitable as a fuel in diesel engines and turbines. The high ash content promotes the second reaction of thermochemical biomass process which will tend more towards a phase separated oil and therefore of a lower quality (19,39). Pre-treatment of biomass such as water washing is one option. The pyrolysis experiment on the feedstock that were subjected to water washing as described in Chapter 4 will be discussed in the following section.

7.3 PYROLYSIS OF WASHED FEEDSTOCK

Fast pyrolysis of washed feedstock has been carried out using a 150g/h reactor except for pyrolysis of run number EBW09 which used a 1kg/h reactor. A number of washed feedstocks have been pyrolysed over a range of temperatures in order to determine the maximum yield of organics with the temperature at which this maximum occurs. The pyrolysis experiments were carried out on the washed feedstocks with different ash content in order to define the maximum ash level that can produce homogenous pyrolysis liquid. The characteristics of pyrolysis liquids from washed feedstocks had been studied to investigate the quality of these liquids and any possibility of applying these liquids for other application. The following sections present the results of pyrolysis experiments on washed feedstock which were assessed by a mass balance obtained in this work [see an example of mass balance reporting in Table 6.2], and discuss any experimental points specific to the washed EFB feedstock.

7.3.1 Effect of Reactor Bed Temperature on Product Yields

A number of washed feedstocks have been pyrolysed at a vapour residence time of 1.01-1.04s over the temperature range 439-551°C on feedstock of size 355-500μm. The ash content of feedstock used for all run was 1.03 mf wt%. The feedstocks used for all run were subjected to washing process by soaking them for 24 hours in distilled water of ambient temperature, with regard to washing test of run number W2SSOATD. This method was selected as it is easier to prepare the feedstock by soaking them for 24 hours at ambient temperature and it also gave the highest ash reduction [see Section 5.1.1]. The mass balance reporting and the results are shown in Table 7.6. A total of six experiments were carried out, however only the best results have been included in Table 7.6. Mass balance closures for all runs are greater than 95%. As discussed in Section 5.2.6 that the surface of washed feedstock was clean and free from any particle, which may explain the washed feedstock of size 355-500μm could be fed easily into the feeder. The experimental data from the runs are arranged in order of increasing temperature and the pyrolysis temperatures chosen to cover this range is approximately 25°C.

Table 7.6: Mass balance of pyrolysis experiment on washed feedstocks with variation of reactor bed temperature

Run number	EBW04	EBW06	EBW05	EBW07	EBW08
Wash method applied	W2SSOATD	W2SSOATD	W2SSOATD	W2SSOATD	W2SSOATD
Reactor temperature [°C]	449	473	500	526	551
Hot vapour residence time [s]	1.03	1.02	1.02	1.01	1.01
Feedrate in wet basis [g/h]	81.89	69.65	70.17	58.45	54.57
Feed moisture [mf wt%]	6.04	6.04	6.04	6.54	6.54
Ash [mf wt%]	1.03	1.03	1.03	1.03	1.03
Particle size [μm]	355-500	355-500	355-500	355-500	355-500
Run time, minutes	68.45	70.35	64.33	79.19	94.46
Input					
Wet feed [g]	93.42	81.66	75.23	77.15	85.91
Dry feed [g]	88.10	77.01	70.95	72.41	80.63
Water in feed [g]	5.32	4.65	4.28	4.74	5.28
Yields [mf wt%]					
Char	12.31	11.64	10.76	9.71	8.65
Organics	60.18	60.80	61.34	60.56	58.22
Gas	13.11	14.38	14.70	16.41	19.32
Water	10.89	10.83	11.01	11.08	10.92
Total Liquids	71.07	71.63	72.36	71.65	69.14
Closure	96.5	96.9	97.8	97.8	97.11
Gas [mf wt%]					
Methane	0.4	0.46	0.58	0.81	1.02
Carbon dioxide	8.17	8.20	8.17	8.01	8.73
Carbon monoxide	4.34	4.70	5.59	6.93	8.24
Hydrogen	0.00	0.00	0.07	0.08	0.00
Ethylene	0.06	0.09	0.17	0.28	0.46
Ethane	0.10	0.09	0.10	0.12	0.15
Propane	0.03	0.03	0.02	0.00	0.03
Propylene	0.00	0.00	0.01	0.18	0.01

All six experiments are included in the graph of the major products plotted in Figure 7.7. The yield of organics increased for washed feedstock which the results showed that maximum liquids yield is highest up to 72.4 mf wt% at about 500°C. The char yield is almost half that of unwashed feedstock, and as example at temperature about 453°C [see run number EB11 in Table 7.5], the char yield is 25.7 mf wt% for unwashed feedstock and it was reduced to 12.3 mf wt% [see run number EBW04 in Table 7.6] for washed feedstock. The yield of char and gas tends to be lower than that obtained for unwashed feedstock, which could be due to reduced secondary reactions, thus, producing less char and gas yields. Figure 7.8 shows that the yields of carbon dioxide appear to become relatively constant with further temperature increase while carbon monoxide yield increases uniformly with temperature. Overall it appears that the washed feedstocks gave higher yields of organics at the expense of char and gas. Table 5.17 in Section 5.2 had shown that potassium and sodium were the elements most easily removed by water washing, therefore, secondary reactions were decreased by the reduction of ash components, especially potassium.

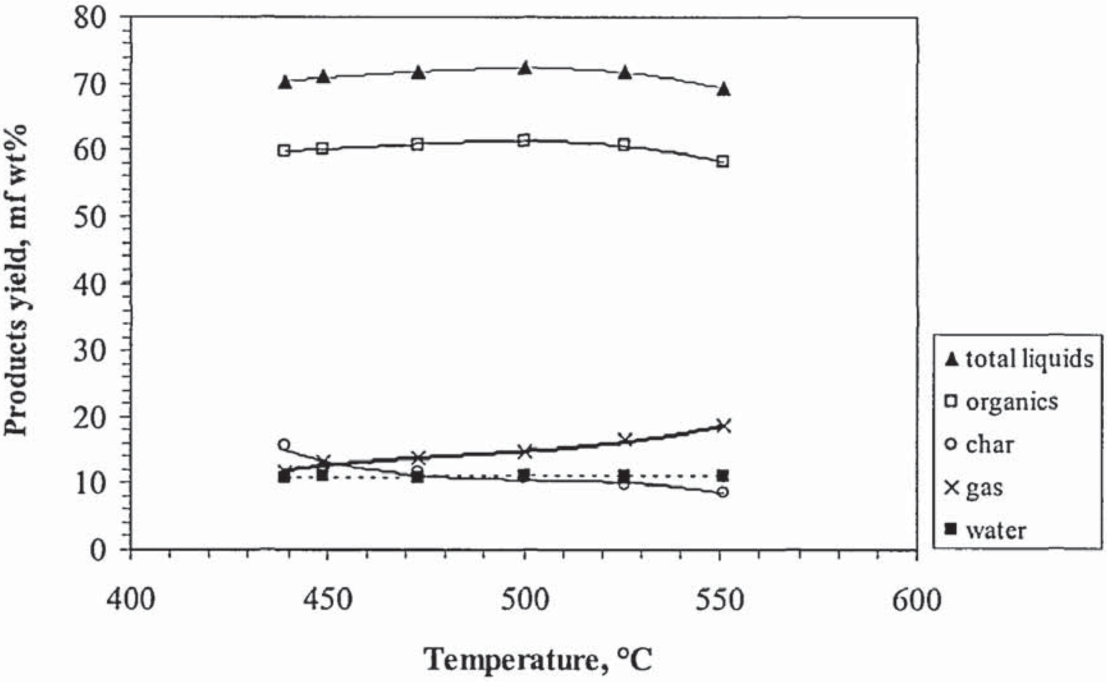


Figure 7.7: Products yield as function of temperature for washed feedstock

The results of products yield shown in Figure 7.7 have similar trend to those described in Section 2.3.5. However, the yield of organics for Figure 7.5 and Figure 7.7 were not significantly changed with increased of pyrolysis temperature. It is certainly possible that since EFB has already undergone sterilisation and stripping processing in order to separate the sterilised oil palm fruit from the sterilised bunch stalks, therefore the cellular or molecular structure has been weakened and this has made it easier to pyrolyse as it is more susceptible to thermal attack.

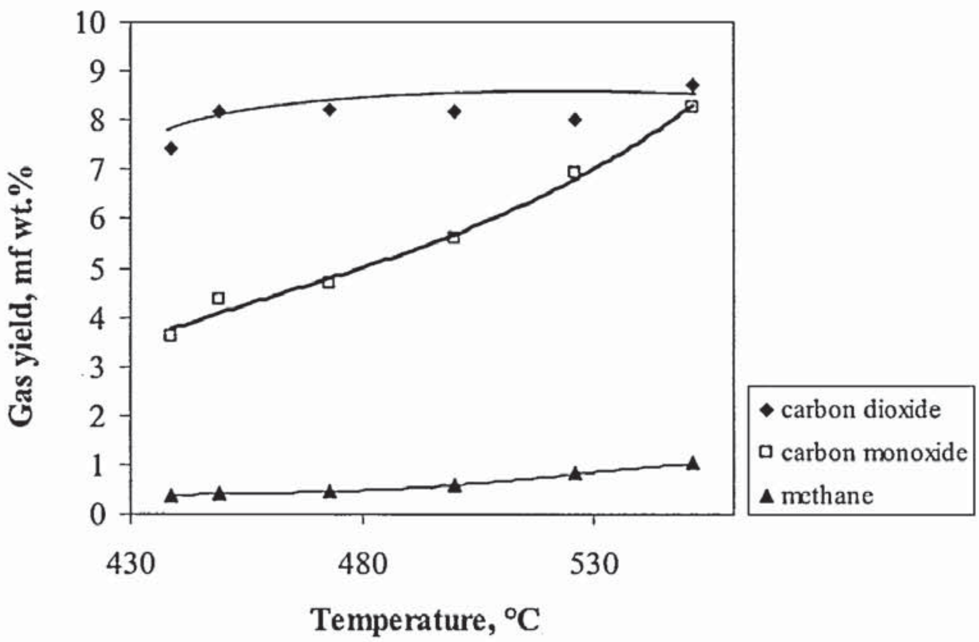


Figure 7.8: **Gas yields as function of temperature for washed feedstock**

7.3.2 Effect of Ash Content of Feedstock on Product Yields

A number of washed feedstocks with different ash contents from 1.03 mf wt% to 5.29 mf wt% have been pyrolysed at temperature from 500-504°C and at vapour residence time from 1.02s to 1.06s in a similar manner to all other experiments previously reported. Table 7.7 shows the mass balance reporting and the results of the experiments along with water washing methods applied for the feedstock. The method used to remove the ash from the feedstock was described in detail in Sections 5.1.1 and 5.1.2. The experimental data from the runs are arranged in order of increasing ash content of feedstock. It was found that the maximum ash content of washed feedstock that produce homogenous liquids is less than about 3 mf wt%.

Figure 7.9 shows that the organics yield achieved up to 61.3 mf wt% that brings the total liquids up to 72.4 mf wt% for the washed feedstock of ash content 1.03 mf wt%. Overall it shows that the yield of organics decreased while the char yields and gas yields increased as the feedstock ash content increased. This is probably because the increasing of ash promotes the secondary reactions, thus, producing more char and gas but producing less organics. The water yields remain relatively constant throughout the ash content range investigated.

Table 7.7: **Mass balance of pyrolysis experiment on washed feedstock with variation of ash content**

Run number	EBW05	EBW12	EBW10	EBW11	EB12
Wash method applied	W2SSOATD	W44LSOATR2	W43LSOATR1	W41LSOATR2	None
Reactor temperature [°C]	500	504	500	501	504
Hot vapour residence time [s]	1.02	1.05	1.04	1.06	1.02
Feedrate in wet basis [g/h]	70.17	58.65	50.61	52.35	123.56
Feed moisture,mf wt%	6.04	5.58	5.61	6.35	7.91
Ash, mf wt%	1.03	2.14	3.05	3.68	5.29
Particle size, µm	355-500	355-500	355-500	355-500	355-500
Run time, min.	64.33	97.64	98.04	96.08	69.74
Condition of liquids	homogenous	homogenous	homogenous	non-Homogenous	non-homogenous
Input					
Wet feed, g	75.23	95.45	82.69	83.83	143.62
Dry feed, g	70.95	90.40	78.30	78.83	133.09
Water in feed, g	4.28	5.05	4.39	5.00	10.53
Yields, mf wt%					
Char	10.76	16.86	19.53	20.15	24.52
Organics	61.34	44.32	41.09	34.78	34.71
Gas	14.70	24.50	25.67	27.83	22.31
Water	11.01	13.32	11.61	15.96	15.17
Total Liquids	72.36	57.64	52.70	50.74	49.88
Closure	97.8	99.0	97.89	98.71	96.72
Gas, mf wt%					
Methane	0.81	1.09	1.23	1.51	1.0
Carbon dioxide	8.01	15.46	16.81	16.38	15.63
Carbon monoxide	6.93	7.34	7.05	6.87	4.93
Hydrogen	0.08	0.00	0.09	0.11	0.11
Ethylene	0.28	0.18	0.16	0.48	0.12
Ethane	0.12	0.23	0.24	0.58	0.30
Propane	0.00	0.07	0.06	0.50	0.09
Propylene	0.18	0.10	0.02	0.29	0.14

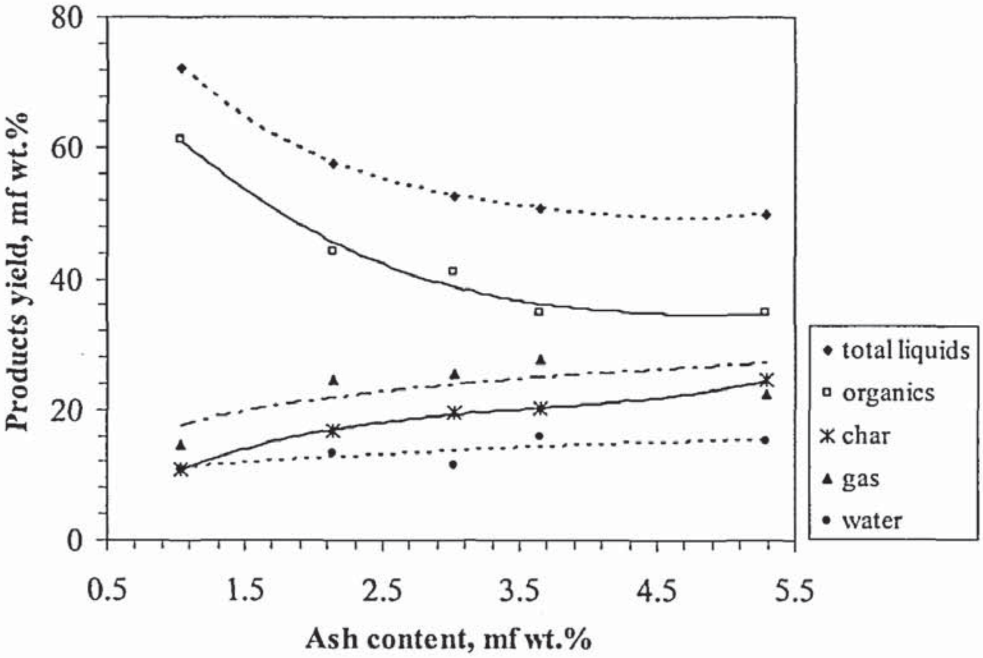


Figure 7.9: **Effect of ash content on products yield**

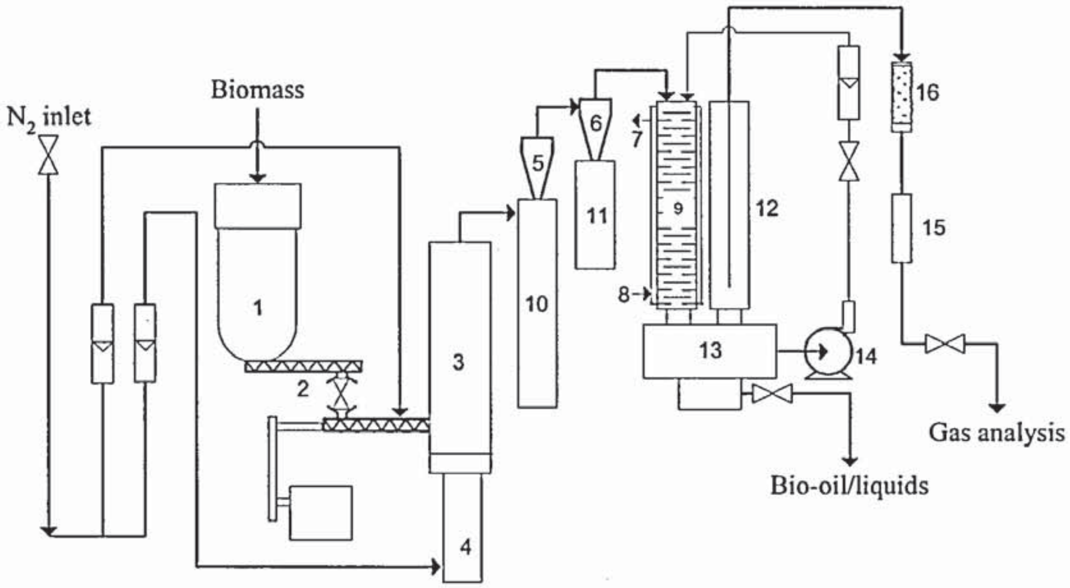
7.3.3 The Quality and Characteristics of Liquids Produced

Petroleum fuels differ significantly from pyrolysis liquids in both chemical composition and physical properties. "*Pyrolysis liquids are typically high in water and solids, acidic, have a heating value about half that of petroleum fuel or mineral oils, and are unstable when heated, especially in air*" (158). One of the main problems associated with the low heating value and physical/chemical instability of pyrolysis liquids is the high oxygen content. Typical pyrolysis liquids are highly polar containing 50 wt% oxygen which is about 40 wt% of dry matter, while petroleum fuel contains oxygen only in ppm levels (158).

In order to investigate the quality and characteristics of pyrolysis liquid of this work, the pyrolysis experiments were carried out at temperature about 500°C and at residence time of 1.1s on the washed feedstocks of size 355-600μm with ash content 1.06 mf wt% used the 1kg/h rig. As discussed in Section 6.5.1, the reason for this pyrolysis experiment using 1kg/h rig is because the amount of pyrolysis liquids which obtained from small rig [150g/h rig] is not enough for other analyses, and also to study the different product collection system of the 1kg/h rig. Even though most of the pyrolysis liquids from washed feedstock were homogenous, mixing liquids from oil 1 and oil pot 2 together was not totally achieved, thus, the liquids collected were not enough for other analyses.

Figure 7.10 shows the schematic diagram of the 1kg/h fluidised bed reactor consisting of a stainless steel reactor, a fluid bed gas heater chamber, a feed container with screw feeder, a solid-gas cyclone separator, a quench column and liquid collectors. Working principle of a 1kg/h rig is the same as the 150g/h rig which employ nitrogen as the fluidising gas and sand as the bed particles. The sand bed was heated to a desired temperature about 500°C. The washed feestocks of size 355-600μm were fed into the bubling hot sand in the reactor at a controlled feed rate. The reaction products [product vapours] were passed through two cyclones where the char was removed before being quenched with cooled recycle isopar. Once the vapours product passed through the quench column, the condensed liquid was collected by liquid collector [tank]. The vapours were finally passed through an electrostatic precipitator [EP] which is very effective to capture vapours. The EP is present after the quench column. The pyrolysis liquid runs down the walls of the EP and accumulated at the bottom which was attached to the tank as well. The isopar in the tank will be pumped into the quench column to cool and capture the vapours. The tank which was attached at the bottom of quench column and EP is the main liquid collection.

It was found that a dark brown sticky mass continues to stick on the wall of EP although the pyrolysis experiment was carried out using 1kg/h rig. The amount of dark brown sticky mass stick on the EP's wall and liquids collected in the tank is about 22.8% and 74% of total pyrolysis liquids produced from pyrolysis experiment respectively. Therefore, in the future, it is recommended a system that is capable of collecting the liquid in one single collecting point for the purpose of analysing the liquid quality should be used, and this will be discussed in Chapter 9. The liquid product collected in the tank was analysed for their properties as potential fuel in comparison to petroleum fuel or other application. However, only few analyses were carried out for the organics mass which sticks on the wall of EP as it was very viscous.



Legend:
1. Feed container
2. Screw feeder
3. Fluidised bed reactor
4. Gas heater
5. Cyclone 1
6. Cyclone 2
7. Cooling water out
8. Cooling water in
9. Quench column
10. Char pot 1
11. Char pot 2
12. Electrostatic precipitator (EP)
13. Tank
14. Pump
15. Cotton filter
16. Dry ice condenser

Figure 7.10: 1 kg/h fluidised bed system

Table 7.8 shows the results of EBW05 in comparison with the results of EBW09. Both experiments were carried out with similar run condition but on different capacity of reactor. Generally, the results from both experiments were comparable. However, for EBW09 the organics yield was slightly lower, the char yield and gas yield were slightly higher than for EBW05. It may be due to more secondary reactions occurred for EBW09, as the residence time for EBW09 was higher [1.1s] than for EBW05 [1.02s], thus, producing more char and gas yield.

Table 7.8: Comparison of pyrolysis liquid produced from 150g/h rig and 1 kg/h rig

Run number	EBW05	EBW09
Reactor	150g/h	1kg/h
Wash method applied	W2SSOATD	W2SSOATD
Reactor temperature [°C]	500	499
Hot vapour residence time [s]	1.02	1.10
Feedrate in wet basis[g/h]	70.17	1247.11
Feed moisture [mf wt%]	6.04	7.25
Ash [mf wt%]	1.03	1.06
Particle size [μm]	355-500	355-600
Run time, minutes	64.33	52.23
Input		
Wet feed [g]	75.23	1085.61
Dry feed [g]	70.95	1012.25
Water in feed [g]	4.28	73.36
Yields [mf wt%]		
Char	10.76	11.19
Organics	61.34	57.25
Gas	14.70	23.07
Water	11.01	6.96
Total Liquids	72.36	64.21
Closure	97.8	98.47
Gas [mf wt%]		
Methane	0.58	0.63
Carbon dioxide	8.17	13.17
Carbon monoxide	5.59	8.77
Hydrogen	0.07	0.03
Ethylene	0.17	0.27
Ethane	0.10	0.12
Propane	0.02	0.04
Propylene	0.01	0.01

Table 7.9 shows the characteristics of pyrolysis liquid from this work in comparison with pyrolysis liquid derived from olive bagasse and petroleum fuel. The high heating value [HHV] was calculated from the data of the elemental analysis using Channiwala and Parikh's formula (166) as below:

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \qquad \text{[MJ/kg]}$$

Formula 7.1: Channiwala and Parikh's formula for high heating value on dry basis (166)

Table 7.9: Comparison of characteristics pyrolysis liquid and petroleum fuel

Type of liquids	Pyrolysis liquid collected in EP's wall	Pyrolysis liquid collected in tank	Pyrolysis liquid of olive bagasse	Petroleum fuel
Reference	this work	this work	(167)	(168)
Water content, mf wt%	6.66	21.68	-	0.1
Elemental analysis, mf wt%				
C	56.47	41.86	66.9	85.2
H	7.85	7.82	9.2	11.1
O	35.46	33.94	21.9	1.0
N	0.22	0.1	2.0	0.3
S	0	0	0	2.3
HHV, MJ/kg [Channiwala and Parikh's formula]	25.29	20.32	31.9	42.94
Density, kg/m^3	1548	1206	1070	940
Viscosity, cP@25°C	not determined	46.31	51	180
pH	2.33	2.7	-	-
GPC analysis [g/mol]				
Mp	447	222	-	-
Mn	382	357	-	-
Mw	562	564	-	-
Polydispersity	1.47	1.57	-	-

Most of the pyrolysis liquid's characteristics in Table 7.9 are the results of liquids product analysis discussed as follows.

7.3.3.1 pH value

All the liquids produced from unwashed feedstocks and washed feedstocks gave pH of between 2 and 3 indicating higher acid contents which arising from organic acids such as acetic and formic acids. It shows that treated the feedstock by water washing had not increase the pH value of liquids.

7.3.3.2 Density

Referring to the run number EBW09, as expected, the density of liquids stick on the EP's wall which are more viscous and have much higher than the density of liquids collected in the tank. The density of liquids collected in the tank and the density of liquids stick on the EP's wall is 1206.1 kg/m^3 and 1548 kg/m^3 respectively. The density of typical pyrolysis liquid is 1230 kg/m^3 (168).

7.3.3.3 Water content

The water content changes with time and is a function of both storage temperature and storage duration. Therefore, the liquids water contents were tested at the same time after liquids produced. It was found that generally, the water content of liquid which stick on EP's wall for washed feedstock and unwashed feedstock are almost the same about 7-12 wt%. The water content for the liquid which collected in the tank [run number EBW09] is 21.7 wt% and the liquid which stick on the wall of EP is 6.9 wt%. However, it is expected that the water content of the liquids collected in the tank would be lower if the liquid were mixed with the tarry liquids from EP wall because the water content of the liquid stick on the EP's wall is lower.

7.3.3.4 Char content

Char is a coarse powder with particles sizes ranging from less than a micron to several millimetres which have similar size and shape characteristics as the feestocks. Overall, the char content of all liquids from unwashed and washed feedstocks is in the range of 0.2-2.0%.

7.3.3.5 Viscosity

As the liquids stick on the EP's wall for run number EBW09 is too viscous, therefore, the viscosity had been measured on the liquids collected in the tank only. It was found that the viscosity of fresh liquid and old liquid at 25°C is 46.31cp and 67.58cp respectively. The viscosity index and description of old liquid were discussed in Section 6.5.1.3. However, it is expected that the viscosity for the whole liquid of this run would be higher than 46.31cp if taking into account of the viscosity for the liquids stick on the EP's wall.

7.3.3.6 Stability

The stability of pyrolysis liquid was examined by monitoring the changes in viscosity, density and pH value. It was found that the density and pH of the pyrolysis liquid remained constant but the viscosity had changed with time. As discussed in Section 6.5.1.4 that the oil's stability can be measured by calculating the viscosity index. The Aston Viscosity Index [AVI] number for pyrolysis liquid produced from pyrolysis process on woody biomass at 500°C is about 2.2 (169). It was found that the AVI for the liquid of run number EBW09 is 0.46. Thus this liquid is quite stable as the AVI number is low. According to Salter (169), the lignin content of pyrolysis liquid greatly influenced the stability of the liquid because the more lignin in the pyrolysis liquid, the more stable the liquid is [the lower the AVI]. Investigation and understanding the nature of lignin content change in the pyrolysis liquids due to different ash content feedstocks is very interesting. This is probably because if the ash level in the biomass reduces it will reduce the catalytic effect in pyrolysis process and this might influence the amount of lignin in the pyrolysis liquid. Although this is beyond the scope of this work but it is recommended to do in the future.

7.3.3.7 Heating value

Typically pyrolysis liquid has a heating value of about 40-50% of the conventional petroleum fuel. It was found that the high heating value of the liquid collected in the tank and the liquid stick on the EP's wall for run number EBW09 is 20.32 MJ/kg and 25.29 MJ/kg respectively, thus, as average, the high heating value for these two liquids is 21.49 MJ/kg.

7.3.3.8 Functional group

The pyrolysis liquid stick on the EP's wall and pyrolysis liquid collected in the tank for EBW09 and pyrolysis liquid for EB12 [liquid produced from unwashed feedstock] were analysed using Fourier Transform Infra-red [FTIR] spectroscopy to determine the basic functional group of the compositions. The absorption frequency spectra representing the functional group of pyrolysis are shown in Appendix I. The C-H bend vibration between 1500 and 1450cm^{-1} indicates the presence of alkanes. The big absorption between 1750 and 1625cm^{-1} represents C=O stretching vibration indicates the presence of carboxylic acid, ketone and aldehyde. The absorbance peaks between 1675 and 1600cm^{-1} represent C=C stretching vibrations. The peaks between 1300 and 1000cm^{-1} are due to the presence of phenols and alcohols, and absorption peaks between 900 and 650cm^{-1} indicates the presence of single and polycyclic and substituted aromatic groups.

7.3.3.9 Pyrolytic lignin content

Lignin is one of the major wood components and pyrolytic lignin represents the water insoluble part of the pyrolysis liquids. Pyrolytic lignin can be obtained by precipitating pyrolysis liquid in excess of water. In this work, pyrolysis liquid collected in the tank derived from washed EFB [run number EBW09] was precipitated. It was found that the content of pyrolytic lignin in the pyrolysis liquid collected in the tank is 12.42w/w%, similar to pyrolytic lignin yielded from bio-oil derived from hard wood (170).

7.3.3.10 Molecular weight

Pyrolytic lignin of liquid collected in the tank for run number EBW09 prepared by precipitating this liquids in water have been studied with regard to the molar masses determined using GPC. It was found that average molar mass [M_w], average molar number [M_n] and molar mass at peak maximum [M_p] of the pyrolytic lignin is 886 g/mol, 588 g/mol and 660 g/mol respectively. The results of molar masses for both liquid of EBW09 [EP fraction and tank fraction] are mentioned in Table 7.10. The GPC spectra of the blank and pyrolytic lignin sample obtained from the liquid collected in tank for run number EBW09 is shown in Appendix J.

7.4 FEEDSTOCK COMPARISON

The results of pyrolysis experiment at range temperature of 400-650°C on unwashed EFB, washed EFB and other type of feedstocks from published sources is shown in Table 7.10.

Table 7.10: Comparison of pyrolysis products from a range of feedstocks at 500°C

Feedstock	Unwashed EFB [EB12]	Washed EFB [EBBW09]	Poplar aspen	Corn Stover	Wheat straw
Reference	this work	this work	(18)	(19)	(19)
Cellulose, mf wt%	59.7	not determined	42.3	31.0	32.4
Hemicellulose, mf wt%	22.1	not determined	31.0	43.0	41.8
Lignin, mf wt%	18.1	not determined	16.2	13.0	16.7
Moisture , mf wt%	7.48-8.96	6.04-6.54	5.0	6.5	9.0
Ash [mf wt%]	5.29	1.03	0.39	11.0	4.6
Yields [mf wt%]					
Char	24.52	10.76	11	42.2	22
Gas	22.31	14.70	14	13.7	19
Organics	34.71	61.34	58.9	27.3	37
Total Liquids	49.8	72.36	74.1	43.1	54

Poplar aspen is a wood, which has low ash content of 0.39 mf wt% and high cellulose content of 42.3 mf wt%, while EFB, corn stover and wheat straw are agricultural residues which have ash content of 5.29 mf wt%, 11.0 mf wt% and 4.6 mf wt% respectively. It is evident that a woody poplar aspen, which has low ash content, produced the best organics yield than non-woody such as corn stover, and wheat straw which has high ash content. It can be seen that washed EFB, which has ash content of 1.03 mf wt%, produced the organics yield of 61.34 mf wt% while organics yield of poplar aspen is 58.9 mf wt%. Figure 7.11 illustrates the yield of organics from pyrolysis for a range of feedstocks from different sources as mentioned in Table 7.10. The organic yield percentage of washed EFB is almost the same as poplar-aspen, while the organic yield percentage of unwashed EFB is almost the same as wheat straw and corn stover, which have high ash content. This showed that washed EFB with low ash content has similar properties as wood like poplar aspen. It is also evident that as ash content of the feedstock increases the yield of organics decreases.

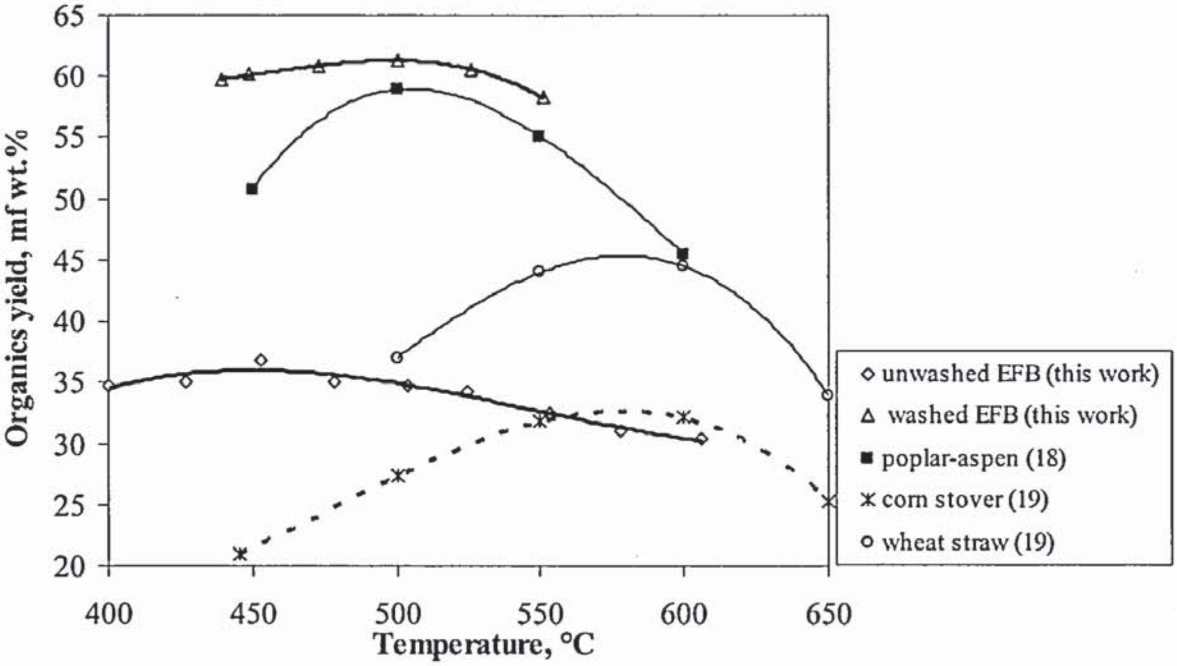


Figure 7.11: Yield of organics from pyrolysis of a range of feedstocks from different source

7.5 CONCLUSIONS

A series of unwashed and washed EFB have been successfully fast pyrolysed using a 150g/h fluidised bed reactor operating at atmosphere pressure. Figure 7.1 shows that each biomass will have a maximum yield of organics and that the temperature at which this occurs depends on the feedstock type. Table 7.1 shows the maximum yields of organics and the temperature at which they were produced for a range of feedstocks pyrolysed along with comparative results from other institutions.

The pyrolysis temperature has been varied over the range of temperatures in order to achieve the maximum organics yield at which it occurs. These have been found for unwashed and washed EFB and are shown in Table 7.5 and Table 7.6 respectively. The unwashed EFB were pyrolysed over a range of residence times to achieve the best of vapour residence time that produced the maximum organics yield. It is believed that by establishing the maximum organic yield, the pyrolysis temperature and hot vapour residence time at which this maximum occurs is the first part to achieve the optimisation of the pyrolysis process for liquids production.

The ash content of feedstock has been found to influence the yield of organics. The higher the concentration of ash in the feedstock the lower the yield of pyrolysis liquid as shown in Figure 7.9. It is showed in Figure 7.11 that the pyrolysis of agricultural residue tends to result in the lowest yield of organics as they have high ash content, whereas wood tends to give the highest yield of organics as they have low ash content. However, the results of pyrolysis on washed EFB which has ash content of 1.06 mf wt% showed that the liquids yield produced is almost the same as poplar aspen which has ash content of 0.39 mf wt%. This showed that washed EFB with low ash content has similar properties as wood like poplar-aspen.

Reduction of ash content to less than about 3 mf wt% required in order to produce homogenous liquids or to avoid phase separation of liquids.

Washed EFB has been successfully fast pyrolysed using a 1kg/h rig in order to get enough liquids product for analysis purposes and to compare result with the small rig. However, it was found that a dark brown sticky mass stick on the EP's wall whenever run the pyrolysis experiments either using the 150g/h rig or 1 kg/h rig. Therefore, a system that is capable of collecting the liquid in one single collecting point for the purpose of analysing the liquid quality is recommended to be used in the future and will be discussed in Chapter 9. It is hoped that more analyses can be done in order to investigate pyrolysis liquid properties as potential fuel in comparison to petroleum fuel or for higher value chemical applications

8. CONCLUSIONS

The EFB waste was pyrolysed to relate the organic fraction of the pyrolysis liquid yield to pyrolysis temperature, ash content and hot vapour residence time. The pyrolysis liquid was assessed as a fuel. The water washing experiments were designed and carried out at temperatures between ambient and boiling for a range of feedstock sizes and using soaking or stirring method, with the objectives to gain a better understanding of the basic factors impacting water washing of EFB. This would provide a basis for subsequent techno-economic optimisation.

8.1 WATER WASHING EXPERIMENT

- A total of 79 runs of water washing experiments were carried out in this work which can be divided into three sections: method of water washing, optimisation of water washing and diffusion process of ash. From 79 of water washing experiments, a total of 390 ashing tests were carried out, thus 5 ashing tests for each water washing experiment which included 3 ashing tests of washed feedstock, one ashing test of leachate and one ashing test of sediment. Good mass balance closures for ash mostly above 95%, however, the mass balance closures for feedstock have been obtained between 95% and 104%, as given in Section 5.2. It may suggest that there is an element of error, inaccuracy or non-quantification of a product as feedstock, sediment and leachate are the hygroscopic material which naturally absorbs moisture from the air, and the fact that feedstock and volatiles are easy to lose during the drying process, thus it is potential error on calculating the moisture content and contributed to the incomplete closure.
- The peak of TGA curve shifts to higher temperatures for washed feedstock which shows that reduction of ash leads to less catalysis.

- It was found that the high heating value of the feedstock is in an inverse trend with respect to ash, however it is not true for the feedstock of ash content 1.15 mf wt% which subjected to wash at 90°C.
- For small size of feedstock, there is a breakdown of washing process into distinct phases, initial reduction extremely fast, then linear with time (between 10 min and 2h), then static, and after six to eight hours indication of further reduction, maybe from structural breakdown of biomass or even beginning bacterial attack.
- Ash removal was enhanced by higher temperature of wash water, stirring, longer wash times and smaller particles of feedstock.
- Varying temperature, stirring rather than soaking, varying the time or particle size all had small impact on ash removal, with virtually all experiments, apart from very short rinses or very low wash water amounts, showing ash removal between 70-80%. However, small impact on ash removal may still be significant to enhanced bio-oil yield.
- Experiments indicate saturation levels at which longer residence time or particle size or stirring no longer make a difference.
- These saturation levels depend on temperature and wash water employed, for example while stirring has little beneficial effect at 55°C with tap water, changing over to distilled water or moving to 90°C means that stirring does again make a substantially positive difference.
- It was believed that there is no or negligible soil contamination on EFB.
- Freshly harvested EFB more resistant to ash removal by washing.
- Elemental analysis indicates that potassium more easily washed out than silicon.
- Feedstock losses are significant during washing which is higher at high temperature rather than ambient temperature. In particular, when near saturation is reached for ash removal, feedstock losses may still increase substantially in which organics losses increases at higher temperature, thus soaking at ambient temperature may be most economic option, subject to detailed economic study.

- Feedstock losses easily doubling for the smaller feedstock compared to large feedstock through stirring at higher temperature [90°C].
- For overall conclusion of water washing experiments, water washing fundamentals investigated in sufficient detail to provide a basis techno-economic analysis in the future.

8.2 PYROLYSIS EXPERIMENT

- A total of 39 fast pyrolysis experiments have been carried out on a 150 g/h fluidised bed bench scale rig, operating at atmospheric pressure. However, one of the fast pyrolysis experiments was carried out using the 1 kg/h rig in order to get ample amount of pyrolysis liquids for analysis purpose and to compare results with the small rig [150 g/h rig]. Generally, the results from both experiments are comparable as shown in Table 7.8. However, the organics yield was slightly lower for the experiment conducted with the 1 kg/h rig [refer to EBW09]. It may be due to more secondary reactions occurred for EBW09 as the residence time for EBW09 was higher [1.1s] compared to EBW05 [1.02s]. Good mass balance closures have been obtained, where the majority of the experimental results gave rise to mass balance closure greater than 95%, as given in Section 5.2.
- The effect of feedstock ash content on organic yield was found to be very important since the results showed that as the ash content decreases the organics yield increases. The particle of size less than 150μm which contained the highest ash level had produced the lowest organics yield compared to the larger particle size which contains lower ash level. It proves that ash has a significant influence on the pyrolysis reactions.
- Pyrolysis experiments were conducted on unwashed EFB, over a range of hot vapour residence times from 0.79 s to 1.32s. The longer hot vapour residence time will decrease the organic yields. This is believed to be due to secondary thermal cracking reactions of the organics into gases, water and smaller molecules.
- Pyrolysis experiments were carried out on unwashed EFB of ash content 5.29 mf wt% over a range of temperature from 399°C to 610°C and it was found that the organic

liquid yield is maximum up to 36.9 mf wt% at temperature about 453°C. While char yields decrease and gas yields increase with temperature but reaction water remains relatively constant throughout.

- The pyrolysis liquids produced from unwashed feedstock was separated into two phases; a phase predominated by tarry organics compounds and an aqueous phase. Therefore, this phase separated product is not suitable as a fuel in diesel engines and turbines.
- A large batch of washed EFB with ash content of 1.03 mf wt% were prepared and pyrolysed over the range of temperature from 439°C to 550°C, and it was found that maximum organics yield is highest up to 61.3 mf wt% at about 500°C. The yield of char and gas tends to be lower than that obtained for unwashed EFB, which could be due to reduced secondary reactions.
- The washed EFB of size 355-500μm were clean and free from any fine particles, thus, making the feeding of the 150 g/h reactor easier.
- The yield of organics produced from pyrolysis on unwashed and washed EFB [see Figure 7.5 and Figure 7.7] were not significantly changed with increased of pyrolysis temperature. It is certainly possible that since EFB has already undergone stripping and sterilisation process, therefore the cellular or molecular structure has been weakened and this has made it easier to pyrolyse as it more susceptible to thermal attack.
- A number of washed feedstocks with different ash content ranging from 1.03 mf wt% to 5.29 mf wt% have been pyrolysed in a similar manner to all other experiments previously reported. Overall result show that the yield of organics decreased while the char yields and gas yields increased as the feedstock ash content increased.
- Reduction of ash content to less than about 3 mf wt% required in order to produce homogenous liquids or to avoid phase separation of liquids.
- The results show that the washed EFB of ash content 1.03 mf wt% has similar property as wood like poplar-aspen since the organic yields of washed EFB is almost the same as poplar-aspen [61.34 mf wt % for washed EFB and 58.9 mf wt% for

poplar-aspen] (18,19). The unwashed EFB of ash content 5.29 mf wt% produced only 34.71 mf wt% organic yields and this is almost the same as wheat straw and corn stover which produced 37 mf wt% and 27.3 mf wt% organic yields respectively (18,19). The unwashed EFB, wheat straw and corn stover are agricultural residues which have high ash content.

- It was found that a dark brown sticky mass stick on the EP's wall whenever run the pyrolysis experiments either using the 150g/h rig or 1 kg/h rig. A dark brown sticky mass stick on the EP's wall and the liquids collected in the tank is about 22.8% and 74% of total pyrolysis liquids respectively for run number EBW09.
- Pyrolysis liquids derived from EFB has similar characteristics with other pyrolysis liquids derived from other feedstock. However it differ significantly from petroleum fuel in both chemical composition and physical properties as shown in Table 7.9. The average high heating value of pyrolysis liquids from this work is lower than those of petroleum fuels which is only 21.49 MJ/kg as compare to 40 MJ/kg for petroleum fuel due to water and oxygen content.
- The content of pyrolytic lignin in the pyrolysis liquid collected in the tank for run number EBW09 is 12.42w/w%. This value is similar to pyrolytic lignin yielded from pyrolysis liquid derived from hard wood and the average molar mass of this pyrolytic lignin is 886 g/mol.
- The Malaysian government initiated in targeting 500 MW of 'green energy' by the year 2005. There are compelling reasons for supporting the use of EFB as a source of fuel for Renewable Energy [RE] power generation [see Section 3.5]. Although Malaysia is the world's largest producer and exporter of palm oil, it also generates large quantities of oil palm wastes mainly EFB, are more than 20% of fresh fruit weight [see Section 3.5], and thus has created a major disposal problem. Fast pyrolysis is a thermo chemical process that converts biomass into high yields of liquid [bio-oil] with minimum of gas and char if this process is carefully controlled. The main product within the fast pyrolysis process is a fuel with a high heating value and a high density around 1.2 kg/litre. This product can be stored until required or readily transported to where it can be most effectively utilised (8). Therefore, this

process is perceived to offer logistical and hence economic advantages over other thermal conversion processes (13). Therefore, there are better financial gains with a number of other advantages when used the EFB as a fuel in the fast pyrolysis plant for RE power generation. However, if Malaysia would like to substitute the bio-oil [derived from EFB wastes] for fuel or diesel in many static applications including boilers, furnaces, engines and turbines for electricity generation, the EFB wastes need to be washed to achieve the ash content to less than about 3 mf wt% in order to produce homogenous bio-oil. EFB wastes are conveniently collected and available for exploitation in all palm oil mills. However, the palm oil mill is self-sufficient in energy, therefore, EFB wastes had been suggested to be used as a fuel in a proposed plan for the operational process and product of oil palm industry as shown in Figure 3.7.

9. RECOMMENDATIONS

The following recommendations have been made for the continuation of this work.

9.1 WATER WASHING PRE-TREATMENT

- During the sterilisation process, may be some hemicellulose loss occurred, hence hydrolysis of hemicellulose from biomass took place. Base on this, it is suggested to investigate the amount of hemicelulose loss by analysing the treated EFB compositions and compound analysis of washing solution.

- As mentioned above that may be hemicellulose hydrolysed during sterilisation process, thus, it is possible that the composition analysis to be carried out in the future to determine hemicellulose hydrolysis products [e.g sugar]. However, it is expected organic compounds that are soluble in water [e.g sugar] contained in the leachate as this compound washed out from biomass during washing. Therefore, it is recommended to study the fermentation process on the leachate for producing ethanol.

- It is recommended to study the preliminary economic on washing experiment i.e the cost of the washing and drying, and waste water disposal. Then, it would be beneficial to make comparison with the benefits from greater pyrolysis liquid production volume, or greater sales value due to higher bio-oil quality, or benefits from the production of by-products such as ethanol. The results of this preliminary analysis may be useful to design further water washing experiments. For example, if the results show that lower wash water volumes are more promising than greater wash water volume, then further water washing experiments may be useful to be carried out in order to find the optimum process conditions for lower wash water volumes.

- The average of dried EFB feedstock weight used for each water washing test is about 23g, thus given very little amount of dried sediment about 0.5g. It was expected that inorganics soil particles could be found in the sediment. Therefore, in order to study the chemicals contained in sediment beside to measure the ash content of sediment for a mass balance purpose, it is recommended to wash about 100g dry feedstock to get an ample amount of dry sediment about 2g.

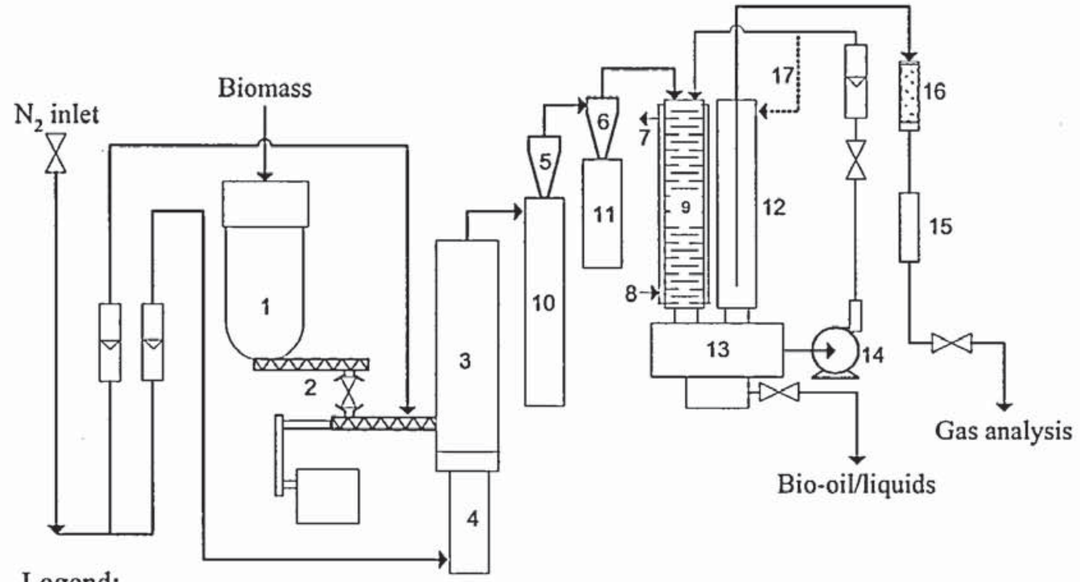
- The water washing pre-treatment proved reliable to remove ash by observing the percentage of ash reduction for each water washing test, however, in order to make more accurate, it is recommended to use i.e. ICP-AES [Inductively Coupled Plasma Atomic Emission Spectrometry] elemental analysis for determining ions in washed feedstock.

- Water washing tests were carried out using the distilled water to remove the ash in biomass. The relative acidity of distilled water may partially explain its greater washing effectiveness. As comparison to this work, it would be beneficial to study the effectiveness of water washing test using the de-ionised water which have pH of 7 due to no presence of ions in this water.

9.2 PRODUCTION OF PYROLYSIS LIQUIDS

- Ash has a significant influence on the pyrolysis reactions, thus, it may also give significant influence on the chemical composition of the pyrolysis liquid product which contains a number of potentially valuable chemicals such as levoglucosan and hydroxyacetaldehyde (34). Levoglucosan is an anhydrosugar with potential uses as a biodegradable polymer or plastic and high value speciality chemicals precursor. Hydroxyacetaldehyde can be used as a food flavouring, colouring agent and a tanning agent. It is recommended to find the economic recover from EFB wastes such as study the speciality chemical would be in the pyrolysis liquids [e.g levoglucosan and hydroxyacetaldehyde] by investigating the influence of ash on the chemical composition. HPLC [High Performance Liquid Chromatography] analysis is suggested to determine the concentration of some of the chemicals contained in the pyrolysis liquids.

- It is important to assess pyrolysis liquids quality in order to substitute pyrolysis liquid as fuel and also for higher chemical applications such as resins, fertilisers, food flavouring and colouring agent. However, a dark brown sticky oil continues to stick on the wall of EP although the pyrolysis experiment was carried out using 1kg/h rig as illustrates in Figure 7.10. Therefore, in the future, it is recommended to employ a system that is capable to collect the liquid in one single collecting point for the purpose of analysing the liquid quality as represents in Figure 9.1 as below.



Legend:
1. Feed container
2. Screw feeder
3. Fluidised bed reactor
4. Gas heater
5. Cyclone 1
6. Cyclone 2
7. Cooling water out
8. Cooling water in
9. Quench column
10. Char pot 1
11. Char pot 2
12. Electrostatic precipitator
13. Tank
14. Pump
15. Cotton filter
16. Dry ice condenser
17. Flushing system implement

Figure 9.1: 1 kg/h fluidised bed system with implementation of flushing system in EP

A pipe line will be installed to the EP as marked with number 17 in Figure 7.10. The purpose of installing this pipe line is to implement the flushing system in the EP. The isopar in the tank will be pumped into the quench column and the EP and all other mass that stick on the wall of EP will be flushed out into the tank which was attached at the bottom of quench column and EP as one single collecting point.

- The maximum quantity of good quality liquid is important for fuel applications. The maximum amount of pyrolysis liquid can be produced by knowing the maximum liquid yield and the temperature at which it occurs. However, this does not 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 reactor temperature, product collection system and fuel quality.

- Alternative application of pyrolysis liquid derived from EFB may be used for resin precursors. The pyrolysis liquid produced tends to have two phases when the ash content of feedstock is more than about 3 wt.% dry basis. Organic phase is considered to be the source of phenolics compounds, and these can be used as substitutes phenols in resole (phenol-formaldehyde) resin formulation used in wood adhesives. Present study showed that the content of pyrolytic lignin from pyrolysis of washed EFB (EBW09) was 12.42w/w%, similar to the pyrolytic lignin yielded from bio-oil derived from hard wood. The average molar mass of the pyrolysis liquids derived from washed EFB was 564g/mol. A low viscosity of pyrolysis liquid containing phenolic compounds with average molar mass of 400-600g/mol is desirable for resin precursor. Therefore, as a potential phenolics compound sources, it is suggested to have further investigation on pyrolysis liquid for resin applications.
- Pyrolysis of the moist feedstock increase the water content of the pyrolysis liquid. It may be beneficial as the viscosity of the pyrolysis liquids derived from moist feedstock is reduced due to the higher water content. However, the increased water content will also result in the pyrolysis liquid having a lower heating value. Therefore, further work should be carried out to determine whether heating value is more important than low viscosity for fuel applications.

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APPENDICES

Appendix A - Results Proforma of Pyrolysis Experiment

Aston Small Fluidised Bed Pyrolysis Reactor, 1 of 4

Experiment Data		
Run number		
Number		
Run Date		
Apparatus		
Feeder rate, g/h		
Fluidiser	**Sand**	
	Density, g/cm^3 :	
	Particle size, micrometer:	
Feedstock	**EFB**	
	Particle size, micrometer:	
Temperature attempted, °C		
Average temperature, °C		
Flow rate:	N_2 on line pressure, barr	
	Fluidising, *l*/min :	
	Entraining, *l*/min :	
	Feeder top, *l*/min :	
	Stirrer Speed:	
	Entrain tube size, mm :	
	Total input, l/min :	

Feeder calibration	Time, min	Mass, g	Flow rate, g/h
Run 1			
Run 2			
Run 3			

Feed water content

Samples	**crucibles (g)**	**crucibles + samples, before, g**	**crucibles + samples, after, g**	**Wet wood**	**Dry wood**	**Water**	**Moisture content (dry basis),%**	**Moisture content (wet basis),%**
1								
2								
3								
Average								

Feed ash content

Samples	**crucibles +samples, after, g**	**samples after, g**	**Ash content (dry basis), %**
1			
2			
3			
Average			

Aston Small Fluidised Bed Pyrolysis Reactor, 2 of 4

Date: / /	
Run number:	

Time	Min	Vol. outlet gas	Reactor temp.	Vol. inlet gas	Feeder, delta Pf inches of H_2O	Reactor, delta Pf inches of H_2O	Temperature outlet gas, °C
First reading	0						
	1						
	2						
	3						
	4						
	5						
	6						
	7						
	8						
	9						
	10						
	11						
	12						
	13						
	14						
	15						
	16						
	17						
	18						
	19						
	20						
	21						
	22						
	23						
	24						
	25						
	26						
	27						
	28						
	29						
	30						
	31						
	32						
	33						
	34						
	35						
	36						
	37						
Final reading							
Total time							

Run comments:

Aston Small Fluidised Bed Pyrolysis Reactor, 3 of 4

Weight Run number	Before run (g)	After run (g)	Difference (g)		Liquid 1 (organic phase)	Liquid 2 (organic phase)	Liquid 3 (aqueous phase)	Liquid 4 (aqueous phase)	Water
Feeder + feed									
Sand									
Reactor top + reactor body + char pot + sand									
Connector									
Char in condenser 1									
EP									
Condenser 1									
Liquid 1 in condenser 1									
Liquid 2 by separation process (in pot 1)									
Condenser 2									
Cotton + filter									
Pot 2 (liquid 4)									
Liquid 3 by separation process (in pot 1)									
Pot 1 (weight of liquid 2 & 3 in pot 1)									
Separation process									
Liquid 2 & liquid 3 (in pot 1)									
Burette									
Burette & liquid 2 (after separation)									
Liquid 2 left in burette									
Bottle									
Bottle & liquid 3									
Liquid 3									
Pot 1 after poured liquid in the burette									
Liquid 2 left in pot 1									
Total liquid 3									
Total liquid 2									
Washing method to extract char from condenser 1									
Condenser 1 with char, after washing (dried)									
Char left in condenser 1									
Char yield by filtration									
Total char by washing method									
Washing method to find the water content of liquid in condenser									
Condenser 1 with char, after washing (wet)									
Bottle + lid									
Bottle + lid +methanol + char + liquid 1									
Liquid 1									
Bottle + lid + char + methanol (after filtered - wet)									
Bottle + lid + char (after filtered - dried)									
Char left in the bottle (dried)									
Methanol left in the condenser (after filtered)									
Methanol in the bottle									
Total of methanol									
Total									
Total of liquid 1, liquid 2, liquid 3, liquid 4, char and water									
Total gas product									
Total product									
Feed									
Water in feed									
Dry feedstock									

Note:

Liquid 1 is in condenser 1, liquid 2 is in EP and oil pot 1, liquid 3 is in oil pot 1, and liquid 4 is in condenser 2, oil pot 2 and cotton filter.

Liquid 1, 2, 3 and 4 =water + a small amount of char + organic

Water content of liquid 1, liquid 2, liquid 3 and liquid 4 is analysed by Karl Fischer

Char content of liquid 1, liquid 2, liquid 3 and liquid 4 is analysed by filtration

Aston Small Fluidised Bed Pyrolysis Reactor, 4 of 4

Water and Char	
Run number	

Karl Fischer testing for water content measurement				
Sample	**1**	**2**	**3**	**Average**
Liquid 1 (organic phase), wt.%				
Liquid 2 (organic phase), wt.%				
Liquid 3 (aqueous phase), wt.%				
Liquid 4 (aqueous phase), wt.%				

Since the liquid 1 & 2 is too viscous, it had been diluted using methanol.

Weight of liquid 1, g	
Weight of methanol, g	
Total diluted solution, g	
Dilution ratio for liquid 1	

Weight of bottle, g	
Weight of bottle & liquid 2, g	
Weight of liquid 2, g	
Weight of methanol, g	
Total diluted solution, g	
Dilution ratio for liquid 2	

Char content by filtration				
Char content of liquid 2				
Sample	**1**	**2**	**3**	
Weight of dried filter paper, g				
Weight of sample, g				
Weight of dried filter paper + dried sample, g				
Average char content, wt.%				

Char content of liquid 3				
Sample	**1**	**2**	**3**	
Weight of filter paper, g				
Weight of sample, g				
Weight of filter paper + sample, g				
Average char content, wt. %				

Char content of liquid 4				
Sample	**1**	**2**	**3**	
Weight of filter paper, g				
Weight of sample, g				
Weight of filter paper + sample, g				
Average char content, wt. %				

Char yield by filtration of char which in the condenser 1	
Weight of dried filter paper, g	
Weight of dried filter paper and dried sample, g	
Weight of dried sample	

Appendix B - Excel Spreadsheets for Pyrolysis Experiment of EB05

Table B.1: Mass balance spreadsheets, Experimental tab 1 of 3

Experiment Data			
Run number	EB05		
Number	10		
Run Date	03/07/2003		
Apparatus	150g/h fluid sand bed		
Feeder rate, g/h	107.24		
Fluidiser	**Sand**		
	Density, g/cm^3:	2.67	
	Particle size, micrometer :	355-500	
Feedstock	**EFB**		
	Particle size, micrometer :	300-355	
Temperature attempted, °C		500	
Average temperature, °C		**499**	
Flow rate:	N_2 on line pressure, barr	0.5	
	Fluidising, *l*/min :	4.5	
	Entraining, *l*/min :	1.8	
	Feeder top, *l*/min :	0.36	
	Stirrer Speed:	2	
	Entrain tube size, mm :	1.7	
	Total input, *l*/min :	**6.66**	

Table B.2: Mass balance spreadsheets, Experimental tab 2 of 3

					Feeder, delta Pf	Reactor, delta Pf	Temperature
Time	Min	Vol. outlet gas	Reactor temp.	Vol. inlet gas	inches of H2O	inches of H2O	outlet gas, oC
First reading	0	688.534	501	146.468	20	15	28
	1		501				
	2		501				
	3		500				
	4		499				
	5		498				
	6		497				
	7		496				
	8		495				
	9		495				
	10		495				
	11		495				
	12		496				
	13		496				
	14		497				
	15		497				
	16		498				
	17		499				
	18		500				
	19		500				
	20		500				
	21		501				
	22		502				
	23		503				
	24		504				
	25		504				
	26		504				
	27		504				
	28		504				
	29		503				
	30		502				
	31		501				
	32		500				
	33		499				
	34		498				
	35		497				
	36		498				
	37		499				
	38		500				
	39		500				
	40		499				
	41		499				
	42		499				
	43		500				
	44		501				

Table B.3: Mass balance spreadsheets, Experimental tab 3 of 3

	45		502				
	46		503				
	47		503				
	48		503				
	49		503				
	50		502				
	51		502				
	52		502				
	53		500				
	54		500				
	55		499				
	56		498				
	57		497				
	58		495				
	59		495				
	60		495				
	61		495				
	62		495				
	63		495				
	64		495				
	65		495				
	66		495				
	67		496				
	68		497				
	69		498				
	70		498				
	71		498				
	72		498				
	73		498				
	74		498				
	75		497				
	76		496				
	77		495				
	78		495				
	79		495				
	80		495				
Final reading	**80.38**	689.067	495	146.819	50	50	28
Total time	**80.38**	**min**	**1.34**	**hour**	**4822.8**	**second**	
Total out let volume in m^3 at °C, 1 barr			0.533				
Total out let volume in litre at °C, 1 barr			533	litre			
Total in let volume in litre at 1barr+0.5barr = 1.5barr, 28°C			351	litre	1.50	barr	
Total in let volume in litre at 1barr, 28°C			526.5	litre	1.00	barr	

Table B.4: Mass balance spreadsheets, Weight tab 3 of 3

Weight									
Run number	**EB05**								
	Before run (g)	**After run (g)**	**Difference (g)**		**Liquid 1 (organic phase)**	**Liquid 2 (organic phase)**	**Liquid 3 (aqueous phase)**	**Liquid 4 (aqueous phase)**	**Water**
Feeder + feed	1063.55	919.88	143.67						
Sand	130.85								
Reactor top + reactor body + char pot + sand	3074.1	3105.38	31.28		0	0	0	0	0
Connector	22.69	23.01	0.32		0	0	0	0	0
Char in condenser 1			2.46		0	0	0	0	0
EP	741.62	744.43	2.81		0	2.81	0	0	0.25
Condenser 1	116.12	127.61	11.49						
Liquid 1 in condenser 1			9.03		9.03	0	0	0	0.44
Liquid 2 by separation process (in pot 1)			22.05		0	22.05	0	0	1.93
Condenser 2	581.18	581.45	0.27		0	0	0	0.27	0.19
Cotton + filter	254.18	258.21	4.03		0	0	0	4.03	2.89
Pot 2 (liquid 4)	23.4	37.4	14		0	0	0	14	10.02
Liquid 3 by separation process (in pot 1)			25.99		0	0	25.99	0.00	16.22
Pot 1 (weight of liquid 2 & 3 in pot 1)	56.3	104.35	48.05						
Separation process									
Liquid 2 & liquid 3 (in pot 1)			48.05						
Burette			61.30						
Burette & liquid 2 (after separation)			76.39						
Liquid 2 left in burette			15.09						
Bottle			58.74						
Bottle & liquid 3			84.73						
Liquid 3			25.99						
Pot 1 after poured liquid in the burette			63.26						
Liquid 2 left in pot 1			6.96						
Total liquid 3			25.99						
Total liquid 2			22.05						
Washing method to extract char from condenser 1									
Condenser 1 with char, after washing (dried)			117.94						
Char left in condenser 1			1.82						
Char yield by filtration			0.60						
Total char by washing method			2.46						
Washing method to find the water content of liquid in condenser									
Condenser 1 with char, after washing (wet)			124.98						
Bottle + lid			281.63						
Bottle + lid +methanol + char + liquid 1			310.76						
Liquid 1			9.03						
Bottle + lid + char + methanol (after filtered - wet)			282.79						
Bottle + lid + char (after filtered - dried)			281.67						
Char left in the bottle (dried)			0.04						
Methanol left in the condenser (after filtered)			7.04						
Methanol in the bottle			19.46						
Total of methanol			26.50						
Total					9.03	24.86	25.99	18.3	31.93
Total of liquid 1, liquid 2, liquid 3, liquid 4, char and water			112.24						
Total gas product			25.0439						
Total product			137.2839						
Feed	143.67	g							
Water in feed	11.30	g							
Dry feedstock	132.37	g							

Note:

Liquid 1 is in condenser 1, liquid 2 is in EP and oil pot 1, liquid 3 is in oil pot 1, and liquid 4 is in condenser 2, oil pot 2 and cotton filter.

Liquid 1, 2, 3 and 4 =water + a small amount of char + organic

Water content of liquid 1, liquid 2, liquid 3 and liquid 4 is analysed by Karl Fischer

Char content of liquid 1, liquid 2, liquid 3 and liquid 4 is analysed by filtration

Table B.5: Mass balance spreadsheets, Feed tab

Feed

Run no. EB05

Feed moisture

Samples are oven dried in the oven at 105°C for 24 hours to measure moisture content.

Samples	Weight of crucibles (g)	Weight of crucibles + samples, before (g)	Weight of crucibles + samples, after (g)	Wet wood	Dry wood	Water	Moisture content (dry basis),%	Moisture content (wet basis),%
1	21.5495	26.7898	26.3782	5.2403	4.8287	0.4116	8.52	7.85
2	22.3641	27.7843	27.3584	5.4202	4.9943	0.4259	8.53	7.86
3	22.1205	27.1249	26.7306	5.0044	4.6101	0.3943	8.55	7.88
Average							**8.53**	**7.86**

Ash

First dry: samples are oven dried in the oven at 105°C for 24 hours (as above)

Second dry: samples are burnt in the muffle oven at 575°C for 6 hours

Samples	Weight of crucibles +samples before second dry, g	Weight of samples after second dry, g	Ash content (dry basis), %
1	21.8125	0.263	5.45
2	22.6309	0.2668	5.34
3	22.3557	0.2352	5.10
Average			**5.30**

Table B.6: Mass balance spreadsheets, Water and char tab

Water and Char					
Run number	**EB05**				
Karl Fischer testing for water content measurement					
Sample	1	2	3	Average	
Liquid 1 (organic phase), wt.%	4.92	5.00	4.64	4.85	
Liquid 2 (organic phase), wt.%	8.73	8.79	8.69	8.74	
Liquid 3 (aqueous phase), wt.%	62.34	62.31	62.52	62.39	
Liquid 4 (aqueous phase), wt.%	71.53	71.64	71.61	71.59	
Since the liquid 1 & 2 is too viscous, it had been diluted using methanol.					
Weight of liquid 1, g	9.03				
Weight of methanol, g	26.50				
Total diluted solution, g	35.53				
Dilution ratio for liquid 1	3.93				
Weight of bottle, g	12.8038				
Weight of bottle & liquid 2, g	14.4367				
Weight of liquid 2, g	1.6329				
Weight of methanol, g	0.9960				
Total diluted solution, g	2.6289				
Dilution ratio for liquid 2	1.61				
Char content by filtration					
Char content of liquid 2					
Sample	1	2	3		
Weight of dried filter paper, g	0.1226	0.122	0.1228		*dried at 105°C for 5 hours*
Weight of sample, g	1.2078	1.3421	1.1744		
Weight of dried filter paper + dried sample, g	0.1321	0.1324	0.133		*dried at 105°C for 24 hours*
Average char content, wt.%	0.79	0.77	0.87	**0.81**	
Char content of liquid 3					
Sample	1	2	3		
Weight of filter paper, g	0.1209	0.1199	0.1178		*dried at 105°C for 5 hours*
Weight of sample, g	3.2343	3.213	3.2219		
Weight of filter paper + sample, g	0.1257	0.1243	0.1223		*dried at 105°C for 24 hours*
Average char content, wt. %	0.15	0.14	0.14	**0.14**	
Char content of liquid 4					
Sample	1	2	3		
Weight of filter paper, g	0.1171	0.1249	0.1211		*dried at 105°C for 5 hours*
Weight of sample, g	3.3126	3.467	3.2356		
Weight of filter paper + sample, g	0.1212	0.1303	0.1243		*dried at 105°C for 24 hours*
Average char content, wt. %	0.12	0.16	0.10	**0.13**	
Char yield by filtration of char which in the condenser 1					
Weight of dried filter paper, g	2.36				
Weight of dried filter paper and dried sample, g	2.96				
Weight of dried sample	0.60				

Table B.7: Mass balance spreadsheets, Gas tab

Gas										
Run number	**EB05**									
Gas products										
density of air=1200g/m^3										
Gas from GC	**Sample 1, %**	**Sample 2, %**	**Sample 3, %**	**Sample 4, %**	**Sample 5, %**	**Sample 6, %**	**Average volume, %**	**Density, g/l**	**Weight, g**	**Yield in dry basis, %**
Hydrogen										
Carbonmonoxide	0.7612	0.8137	0.8411	0.8719	0.8983	0.923	0.8515	1.25	5.6733	4.29
Methane	0.1274	0.1654	0.1876	0.2103	0.2361	0.2578	0.1974	0.717	0.7545	0.57
Carbon dioxide	1.547	1.6389	1.6966	1.7565	1.8194	1.8759	1.7224	1.98	18.1770	13.73
Ethane	0.0226	0.029	0.0326	0.0364	0.0405	0.044	0.0342	1.35	0.2460	0.19
Ethene	0.0136	0.0155	0.0165	0.0174	0.0185	0.0194	0.0168	1.26	0.1129	0.09
Propane	0.0052	0.0064	0.0072	0.008	0.0087	0.0096	0.0075	2	0.0801	0.06
Propene										
n-Butane										
Total gas product							**2.8299**		**25.0439**	

Table B.8: Mass balance spreadsheets, Residence time tab

Residence time	
Volume total hot space, cm^3	377.86
Total gas at temperature measurement, m^3	0.533
Total gas at average temperature reactor, m^3	1.366783
Temperature measurement, °C	28
Temperature measurement, K	301
Average temperature reactor, °C	499
Average temperature reactor, K	772
Carrier gas flow rate, m^3/s	0.000283
Volume occupied by sand, cm^3	49.007491
Net volume empty reactor, cm^3	328.852509
Net volume empty reactor, m^3	0.000329
Carrier gas flow, m^3/s	0.000283
Residence time, s	1.160381

Table B.9: Mass balance spreadsheets, Summary tab

Summary									
Date	03/07/2003								
Run number	EB05								
Number	10								
Feedstock	EFB								
Average temperature, oC	499								
Residence time,s	1.16								
Feedrate, g/h	107.24								
Particle size, micrometer :	300-355								
Fluidisation, l/min	4.50								
Run time, min.	80.38								
	Wet feed	**Dry feed**			**Water**				**Total**
Input, g	143.67	132.37			11.30				143.67
	Liquid 1	**Liquid 2**	**Liquid 3**	**Liquid 4**	**Water**	**Char**	**Organics**	**Gases**	**Closures**
Output, g	9.03	24.86	25.99	18.3	31.93	34	46.25	25.04	137.28
Yields in wet basis, %	6.29	17.30	18.09	12.74	22.22	23.71	32.19	17.43	95.56
Yields in dry basis, %					15.58	25.73	34.94	18.92	95.18
Water content liquid 1, wt.%	4.85								
Water content liquid 2, wt.%	8.74								
Water content liquid 3, wt.%	62.39								
Water content liquid 4, wt.%	71.59								
Char content liquid 2, wt.%	0.81								
Char content liquid 3, wt.%	0.14								
Char content liquid 4, wt.%	0.13								
Feed moisture, dry basis (wt %)	8.53								
Ash, dry basis (wt %)	5.30								
pH of liquid 2	2.35								
pH of liquid 3	2.75								
pH of liquid 4	2.44								
Calculated water content of bio-oil,%	40.84								
Gas From GC	**Yields in dry basis,%**								
Methane	0.57								
Carbon Dioxide	13.73								
Ethene	0.09								
Ethane	0.19								
Hydrogen	-								
Propene	-								
Carbonmonoxide	4.29								
Propane	0.06								
N-Butane	-								

Appendix C – List of Pyrolysis Experiment

Table C.1: List of pyrolysis experiments performed

No.	Run no.	Temperature, °C	Residence time,s	Size of biomass, µm
1	EBI01	520	1.66	Less than 150
2	EBI02	500	1.04	300-355
3	EBI033	500	1.04	355-500
4	EBI04	508	1.08	250-300
5	EBI05	496	1.07	150-250
6	EB01	501	0.79	300-355
7	EB02	502	0.96	300-355
8	EB03	502	1.03	300-355
9	EB04	503	1.23	300-355
10	EB05	499	1.16	300-355
11	EB06	503	1.00	300-355
12	EB07	504	1.32	300-355
13	EB08	451	1.33	300-355
14	EB09	450	1.12	300-355
15	EB10	451	1.03	300-355
16	EB11	453	1.02	250-355
17	EB12	504	1.02	250-355
18	EB13	500	0.96	300-355
19	EB14	504	0.92	300-355
20	EB15	553	1.05	250-355
21	EB16	399	1.02	250-355
22	EB17	427	1.02	250-355
23	EB18	478	1.02	250-355
24	EB19	528	0.96	250-355
25	EB20	578	1.01	250-355
26	EB21	606	1.02	250-355
27	EB22	524	1.05	250-355
28	EBW01	439	1.01	250-355
29	EBW02	462	0.98	355-500
30	EBW03	532	0.90	355-500
31	EBW04	449	1.03	355-500
32	EBW05	500	1.02	355-500
33	EBW06	473	1.02	355-500
34	EBW07	526	1.01	355-500
35	EBW08	551	1.01	355-500
36	EBW09	499	1.10	355-500
37	EBW10	500	1.04	355-500
38	EBW11	501	1.06	355-500
39	EBW12	504	1.05	355-500

Appendix D - Excel Spreadsheets for Water Washing Experiment of W4SSO55D

Table D.1: Mass balance spreadsheets, Weight tab

Run number:	**W4SSO55D**
Date:	**05/01/2004**
Temperature, °C:	**55**
Type of water:	**distilled water**
Concentration gradient, ml/g:	**70**
Period, hour:	**2**
Method:	**Soaking**
Note: 100 g biomass in 7 litre water	
Weight in gram.	
weight of biomass	25.72
weight of dry container 1	145.62
weight of water	1792.19
weight of dry drainer	64.25
weight of dry seive 1 (60 mesh =250micrometer)	72.46
weight of dry sieve 2 (100 mesh=150 micrometer)	15.46
weight of dry container 2	143.74
weight of wet drainer	64.7
weight of wet siever 1 + wet biomass	154.77
weight of long beaker	454.41
weight of wet long beaker + wet biomass	455.34
weight of wet biomass	83.24
weight of container 1 + leachate + sediment	1803.5
weight of container 2 + leachate	1794.05
weight of siever 2 + sediment	17.47
weight of wet drainer	64.5
weight of sediment	2.01
weight of leachate	1651.01

Table D.2: Mass balance spreadsheets, Moisture and Ash tab 1 of 2

Untreated biomass								
Feed moisture								
First dry: samples are oven dried to measure the moisture content with keep in the oven at 105C for 24 hours.								
Samples	**Weight of crubiles (g)**	**Weight of crucibles + samples, before (g)**	**Weight of crucibles + samples, after (g)**	**Wet wood**	**Dry wood**	**Water**	**Moisture content (dry basis),%**	**Moisture content (wet basis),%**
1	17.6489	22.6921	22.2979	5.0432	4.649	0.3942	8.48	7.82
2	19.9769	24.504	24.1476	4.5271	4.1707	0.3564	8.55	7.87
3	20.6457	24.5229	24.2126	3.8772	3.5669	0.3103	8.70	8.00
Average							**8.57**	**7.90**
Ash								
Second dry: samples are burnt in the muffle oven at 575C for 6 hours								
Samples	**Weight of crucibles +samples after second dry, g**	**Weight of samples after second dry, g**	**Ash content (dry basis), %**					
1	17.8935	0.2446	5.26					
2	20.1967	0.2198	5.27					
3	20.8338	0.1881	5.27					
Average			**5.27**					
Treated biomass								
Feed moisture								
Samples	**Weight of crubiles (g)**	**Weight of crucibles + samples, before (g)**	**Weight of crucibles + samples, after (g)**	**Wet wood**	**Dry wood**	**Water**	**Moisture content (dry basis),%**	
1	62.3449	119.528	77.0672	57.1831	14.7223	42.4608	288.41	
2	17.6497	34.8587	22.1127	17.209	4.463	12.746	285.59	
3	32.6348	35.1986	35.1391	2.5638	2.5043	0.0595	2.38	
4	33.5348	35.1999	35.0381	1.6651	1.5033	0.1618	10.76	
Average							**287.00**	
Ash								
Samples	**Weight of crucibles +samples after second dry, g**	**Weight of samples after second dry, g**	**Ash content (dry basis), %**					
1	21.6999	-40.645	-276.08					
2	17.7054	0.0557	1.25					
3	32.6655	0.0307	1.23					
4	33.5538	0.019	1.26					
Average			**1.25**					

Table D.3: Mass balance spreadsheets, Moisture and Ash tab 2 of 2

Sediment							
Feed moisture							
Samples	**Weight of crubiles (g)**	**Weight of crucibles + samples, before (g)**	**Weight of crucibles + samples, after (g)**	**Wet wood**	**Dry wood**	**Water**	**Moisture content (dry basis),%**
1	22.498	22.7252	22.5344	0.2272	0.0364	0.1908	524.18
Average							**524.18**
Ash							
Samples	**Weight of crucibles +samples after second dry, g**	**Weight of samples after second dry, g**	**Ash content (dry basis), %**				
1	22.5001	0.0021	5.77				
Average			**5.77**				
Leachate							
Feed moisture							
Samples	**Weight of crubiles (g)**	**Weight of crucibles + samples, before (g)**	**Weight of crucibles + samples, after (g)**	**Wet wood**	**Dry wood**	**Water**	**Moisture content (dry basis),%**
1	60.2255	2091.0455	61.8226	2030.82	1.5971	2029.223	127056.72
Average							**127056.72**
Ash							
Samples	**Weight of crucibles +samples after second dry, g**	**Weight of samples after second dry, g**	**Ash content (dry basis), %**				
1	61.3453	1.1198	70.11				
Average			**70.11**				

Table D.4: Mass balance spreadsheets, Summary tab

Run number		**W4SSO55D**					
Feedstock		**EFB**					
Average temperature, C		**55**					
Residence time,s		**7200**					
Type of water		**distilled water**					
		Wet feed	Dry feed	Water		Total	
Input, g		25.72	23.69	2.03		25.72	
Total ash in dry basis, g						1.25	
Output, g		Treated feed	sediment	leachate		Total	
Ash yields in dry basis, %		1.25	5.77	70.11			
Total ash in dry basis, g		0.27	0.019	0.91		1.20	
Closure,%						95.91	%
Output, g		Wet feed	Dry feed	Water			
		83.24	21.43	61.81			
Difference, g		2.26					
Percentage loss (wt.%, dry basis)		9.53					
Output, g		Treated feed	sediment	leachate		Total	
(Biomass + ash) dry basis, g		21.43	0.322025	1.60		23.35	
Closure,%						98.57	
biomass, ash +moisture free	22.44						
Ash out, g:							
in sediment	0.019						
in leachate	0.91						
total	0.929						
Non ash out, g:							
in sediment	0.303						
in leachate	0.687						
total	0.990						
Ash loss from washing	0.98						
Non ash loss from washing	1.28						
accounted for, %:							
ash	94.79						
non ash	77.49						
biomass loss before washing, g	0.92						
non ash loss not accounted for, g	0.29						

Appendix E – The Variables Used for Each Water Washing Experiment

Table E.1: List of water washing experiments from no.1 to 39

No.	Run No.	Residence time, min.	Amount of water per 100g biomass, litre	Temp. °C	Washing method	Feed particle size	Type of water
1	W1SSOATT	1440	7	26-28	soak	250-355μm	tap water
2	W2SSOATD	1440	7	26-24	soak	250-355μm	distilled water
3	W3SSO55T	120	7	55	soak	250-355μm	tap water
4	W4SSO55D	120	7	55	soak	250-355μm	distilled water
5	W5SSO90T	120	7	90	soak	250-355μm	tap water
6	W6SSO90D	120	7	90	soak	250-355μm	distilled water
7	W7SSTATT	120	7	26-28	stir	250-355μm	tap water
8	W8SSTATD	120	7	26-28	stir	250-355μm	distilled water
9	W9SST55T	120	7	55	stir	250-355μm	tap water
10	W10SST55D	120	7	55	stir	250-355μm	distilled water
11	W11SST90T	120	7	90	stir	250-355μm	tap water
12	W12SST90D	120	7	90	stir	250-355μm	distilled water
13	W13LSOATT	1440	7	26-28	soak	2-3cm	tap water
14	W14LSOATD	1440	7	26-28	soak	2-3cm	distilled water
15	W15LSO55T	120	7	55	soak	2-3cm	tap water
16	W16LSO55D	120	7	55	soak	2-3cm	distilled water
17	W17LSO90T	120	7	90	soak	2-3cm	tap water
18	W18LSO90D	120	7	90	soak	2-3cm	distilled water
19	W19LSTATT	120	7	26-28	stir	2-3cm	tap water
20	W20LSTATD	120	7	26-28	stir	2-3cm	distilled water
21	W21LST55T	120	7	55	stir	2-3cm	tap water
22	W22LST55D	120	7	55	stir	2-3cm	distilled water
23	W23LST90T	120	7	90	stir	2-3cm	tap water
24	W24LST90D	120	7	90	stir	2-3cm	distilled water
25	W25SSOATR1	0.2	4	26-28	soak	250-355μm	distilled water
26	W26SSOATR2	10	4	26-28	soak	250-355μm	distilled water
27	W27SSOATR3	20	4	26-28	soak	250-355μm	distilled water
28	W28SSOATR4	30	4	26-28	soak	250-355μm	distilled water
29	W29SSOATR5	60	4	26-28	soak	250-355μm	distilled water
30	W30SSOATR6	120	4	26-28	soak	250-355μm	distilled water
31	W31SSOATR7	180	4	26-28	soak	250-355μm	distilled water
32	W32SSOATR8	240	4	26-28	soak	250-355μm	distilled water
33	W33SSOSTR9	360	4	26-28	soak	250-355μm	distilled water
34	W34SSOATR10	420	4	26-28	soak	250-355μm	distilled water
35	W35SSOATR11	480	4	26-28	soak	250-355μm	distilled water
36	W36SSOATA1	120	0.75	26-28	soak	250-355μm	distilled water
37	W37SSOATA2	120	1.25	26-28	soak	250-355μm	distilled water
38	W38SSOATA3	120	2.25	26-28	soak	250-355μm	distilled water
39	W39SSOATA4	120	4	26-28	soak	250-355μm	distilled water

Table E.2: List of water washing experiments from no.40 to 79

No.	Run No.	Residence time, min.	Amount of water per 100g biomass, litre	Temp. °C	Washing method	Feed particle size	Type of water
40	W40LSOATR1	0.5	5	26-28	manual agitation	250-355μm	distilled water
41	W41LSOATR2	1	5	26-28	manual agitation	2-3cm	distilled water
42	W42LSOATR3	2	5	26-28	manual agitation	2-3cm	distilled water
43	W43LSOATR1	10	5	26-28	soak	2-3cm	distilled water
44	W44LSOATR2	20	5	26-28	soak	2-3cm	distilled water
45	W45LSOATR3	30	5	26-28	soak	2-3cm	distilled water
46	W46LSOATR4	60	5	26-28	soak	2-3cm	distilled water
47	W47LSOATR5	120	5	26-28	soak	2-3cm	distilled water
48	W48LSOATR6	180	5	26-28	soak	2-3cm	distilled water
49	W49LSOATA1	120	1.5	26-28	soak	2-3cm	distilled water
50	W50LSOATA2	120	3	26-28	soak	2-3cm	distilled water
51	W51LSOATA3	120	5	26-28	soak	2-3cm	distilled water
52	W52SSOAT	120	5	26-28	soak	250-355μm	distilled water
53	W53MSOAT	120	5	26-28	soak	1cm	distilled water
54	W54LSOAT	120	5	26-28	soak	2-3cm	distilled water
55	W55SSO55	120	5	55	soak	250-355μm	distilled water
56	W56MSO55	120	5	55	soak	1cm	distilled water
57	W57LSO55	120	5	55	soak	2-3cm	distilled water
58	W58SSO90	120	5	90	soak	250-355μm	distilled water
59	W59MSO90	120	5	90	soak	1cm	distilled water
60	W60LSO90	120	5	90	soak	2-3cm	distilled water
61	W61WSSOAT	120	5	26-28	soak	250-355μm	distilled water
62	W62WMSOAT	120	5	26-28	soak	1cm	distilled water
63	W63WLSOAT	120	5	26-28	soak	2-3cm	distilled water
64	W64WSSO55	120	5	55	soak	250-355μm	distilled water
65	W65WMSO55	120	5	55	soak	1cm	distilled water
66	W66WLSO55	120	5	55	soak	2-3cm	distilled water
67	W67WSSO90	120	5	90	soak	250-355μm	distilled water
68	W68WMSO90	120	5	90	soak	1cm	distilled water
69	W69WLSO90	120	5	90	soak	2-3cm	distilled water
70	W70FSSOAT	120	5	26-28	soak	250-355μm	distilled water
71	W71FMSOAT	120	5	26-28	soak	1cm	distilled water
72	W72FLSOAT	120	5	26-28	soak	2-3cm	distilled water
73	W73FSSO55	120	5	55	soak	250-355μm	distilled water
74	W74FMSO55	120	5	55	soak	1cm	distilled water
75	W75FLSO55	120	5	55	soak	2-3cm	distilled water
76	W76FSSO90	120	5	90	soak	250-355μm	distilled water
77	W77FMSO90	120	5	90	soak	1cm	distilled water
78	W78FLSO90	120	5	90	soak	2-3cm	distilled water
79	W79LSOATR1	1.0	5	26-28	manual agitation	2-3cm	distilled water

Appendix F – Experimental Procedure of Bomb Calorimeter

HEATS OF COMBUSTION - THE BOMB CALORIMETER

Objectives

1) To calibrate a bomb calorimeter by combustion of benzoic acid.
2) To use the calibrated calorimeter in measuring heats of combustion for other substances

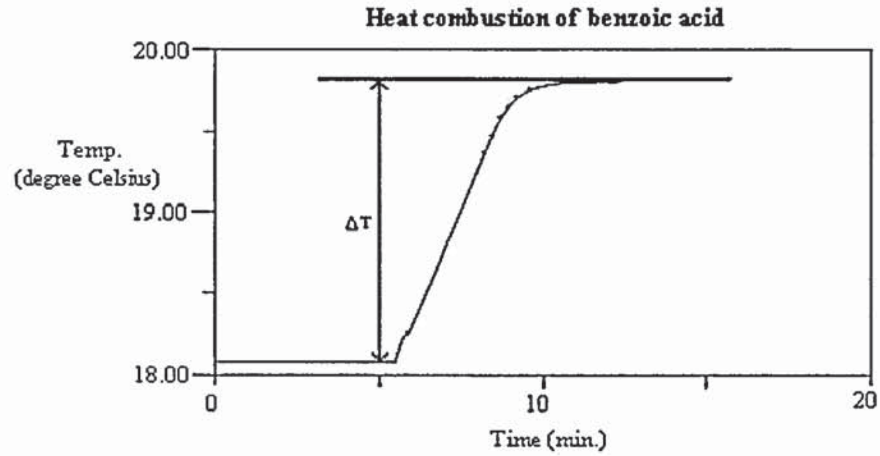
Background Theory

A calorimeter is an instrument for measuring heats of reaction by observing the temperature change in the calorimeter when a known amount of reaction occurs. The bomb calorimeter is principally used for measuring heats of combustion in oxygen to known products [CO_2 and H_2O if the substance contains only C, H, and O], e.g. for benzoic acid

$$C_7H_6O_2 + 7\tfrac{1}{2}O_2 \rightarrow 7CO_2 + 3H_2O\,\tfrac{1}{2}$$

A known weight of the substance is made 'to burn completely in an atmosphere of pure oxygen in a strong steel "bomb" [i.e. the reaction occurs at constant volume]. The bomb is immersed in a water-filled calorimeter and the temperature rise is measured.

The observed temperature rise must be corrected for heat losses in the calorimeter. Several methods may be used to make the correction; the basis of the simplest is shown in the diagram below.



Temperature readings are taken at regular intervals before firing and continued for some time afterwards until a linear fall in temperature with time is established. Extrapolation to the moment of firing as shown in the diagram allows the corrected temperature rise to be determined.

To convert the measured temperature rise to quantity of heat evolved, the calorimeter must be calibrated, i.e the heat capacity of the calorimeter determined. This may be carried out by observing the temperature rise produced by' an accurately measured input of electrical energy. However, a simpler method is to use the combustion of a known weight of pure benzoic acid as a calibrant [$\Delta U^{\circ}_{C,298} = -26.43$ kJ g^{-1}].

Since reactions in a bomb calorimeter are carried out at constant volume, the calculated quantities are $\Delta U^{\circ}_{C,298}$ and $\Delta \overline{U}\,^{\circ}_{C,298}$. Usually heats of reactions at constant pressure are tabulated [i.e $\overline{\Delta H}\,^{\circ}_{C,298}$] and the two quantities are related by

$$\overline{\Delta H}^{o}{}_{C,298} = \Delta\overline{U}^{o}{}_{C,298} + P\Delta V = \Delta\overline{U}^{o}{}_{C,298} + RT\Delta n$$

where Δn is the change in the number of gaseous moles in the reaction. The correction required to convert ΔU to $\overline{\Delta H}$ is usually small.

Experimental Procedure.

Always handle the bomb carefully. Ensure that the internal surfaces are clean before beginning each reaction.

Pour a measured quantity [about 2400 cm^3] of distilled water into the calorimeter. Then pipette 10 cm^3 of distilled water into the clean bomb [to absorb any corrosive gases which may be formed during the combustion].

Support the top of the bomb and connect a short length of tungsten wire across the two electrodes ensuring that good electrical contact is made; the wire should not be taut.

Tie a 3 inch length of cotton by its middle to the centre of the wire and ensure that the ends rest on the bottom of the crucible. Accurately weigh a pellet of benzoic acid [about 0.8 – 1g] and place in the crucible on top of the cotton.

Screw down the lid of the bomb tightly and fill with oxygen gas from a cylinder to a pressure of 25 atmospheres. Immerse the bomb in water to ensure that gas is not .leaking from it.

Place the bomb carefully into the calorimeter and attach the electrical leads to the bomb. Assemble the stirrer, thermometer and calorimeter cover [N. B calorimeter thermometers are fragile and very expensive, handle very carefully!] connect the firing circuit.

Start the stirrer and after about 15 minutes start to take temperature readings at half minute intervals. At the end of the fifth minute press the firing button. Continue to take temperature readings at half, minute intervals throughout the period of rapid temperature rise and afterwards until a regular decrease in temperature has been established for about 5 minutes.

Remove the bomb from the apparatus and carefully release the gas pressure via the gas valve. Open the bomb. [N.B. make quite certain that the gas pressure has been released before doing this]. Examine the contents of the bomb to ensure that combustion has been complete; the presence of carbon will indicate incomplete combustion.

Plot a graph of temperature against time and by extrapolation calculate the corrected temperature rise [ΔT]. Then determine the heat capacity of the calorimeter [C], defined by $q = C. \Delta T$ where q is the heat liberated by combustion of the weighed quantity of benzoic acid.

Repeat the experiment using between 0.5 and 0.7 g of naphthalene in place of the benzoic acid. From the observed temperature rise, and using the now known heat capacity of the calorimeter, calculate the heat of combustion of naphthalene.

Make a careful estimate of the experimental error in the calculated heat of combustion.

Use $\overline{\Delta H}^{o}{}_{C,298}$ measured to calculate the standard heat of formation of naphthalene and again estimate the experimental error in this quantity.

References

1. Shoemaker and Garland, "Experiments in Physical Chemistry"
2. Coleman and Pilcher, Trans-Faraday Soc., 62, 821 (1966)
3. A useful recent collection of data is "the Chemical Thermodynamics of Organic Compounds" by Stull, Westman, and Sinke (Wiley, 1966)

Appendix G – Mathematical Interpretation of Hydrolysis for The Severity Factor

The kinetic equation for a given reagent A participating in a typical irreversible reaction of n^{th} order with Arrhenius-type dependence on temperature,

$$-\frac{dC_A}{dt} = k_o e^{-(E_a/RT)C_A}$$

where C_A is the concentration of the reagent, t is the reaction time, k_o is the pre-exponential factor, E_a is the activation energy and T is the absolute temperature. The equation can be modified to give,

$$-\frac{1}{C_A^n} \times \frac{dC_A}{dt} = k_o e^{-(E_a/RT)}$$

Taking logarithms in both sides and developing (1/T) as a two-term Taylor series from a reference temperature T_r it can inferred that

$$ln\left\{-\frac{1}{C_A^n} \times \frac{dC_A}{dt}\right\} \cong ln\, k_o - \frac{E_a}{R \times T_r} + \frac{E_a}{RT_r^2}(T - T_r)$$

or

$$-\frac{1}{C_A^n} \times \frac{dC_A}{dt} = k_o e^{(-E_a/RT_r)} e^{(\frac{T-T_r}{\omega})}$$

where,

$$\omega = \frac{RT_r^2}{E_a}$$

After separation of variables and integration in which $C_A=C_{AO}$ at $t=0$ and $C_A=C_A$ at $t=t$, it can be followed that

$$\int_{C_{AO}}^{C_A} -\frac{dC_A}{C_A^n} = k_r \times R_o$$

where k_r is the kinetic constant measured at T_r and R_o is the severity factor defined by

$$R_o = \int_0^t e^{(\frac{T-T_r}{\omega})} dt$$

For first order reactions,

$$C_A = C_{AO} e^{(-k_r R_o)}$$

The contribution of less-reactive fraction to the overall xylan degradation is negligible, therefore:

$$C_A = (1-\alpha)\times C_{AO} + \alpha \times C_{AO}e^{(-k_r R_o)}$$

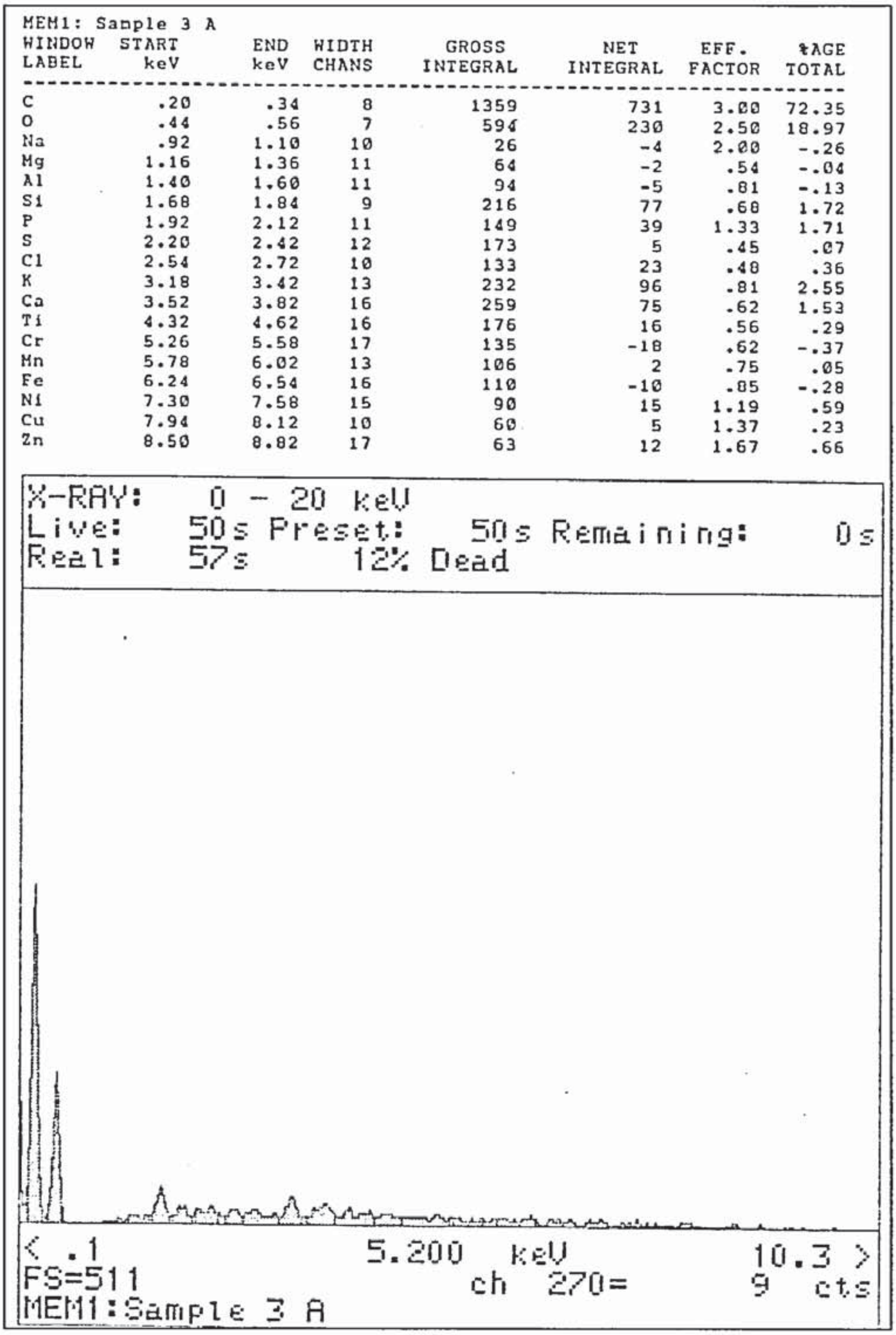
where α gives the weight fraction of susceptible xylan in the considered raw material. The percentage solubilised is determined as:

$$1-\left(\frac{C_A}{C_{AO}}\right)\times 100\%$$

By assuming that EFB is similar to hardwood, therefore α=0.879, E_a=121 kJ/mol and k_r=0.00602 min^{-1}. The condition of sterilisation process in which t=50 min., T=140°C. T_r=145°C because at this temperature, the conversion achieved at short reaction time is negligible. Therefore, the percentage of solubilised is 15.8%.

Appendix H – EDX Analysis Results

Table H.1: Elemental composition of W24LST90D

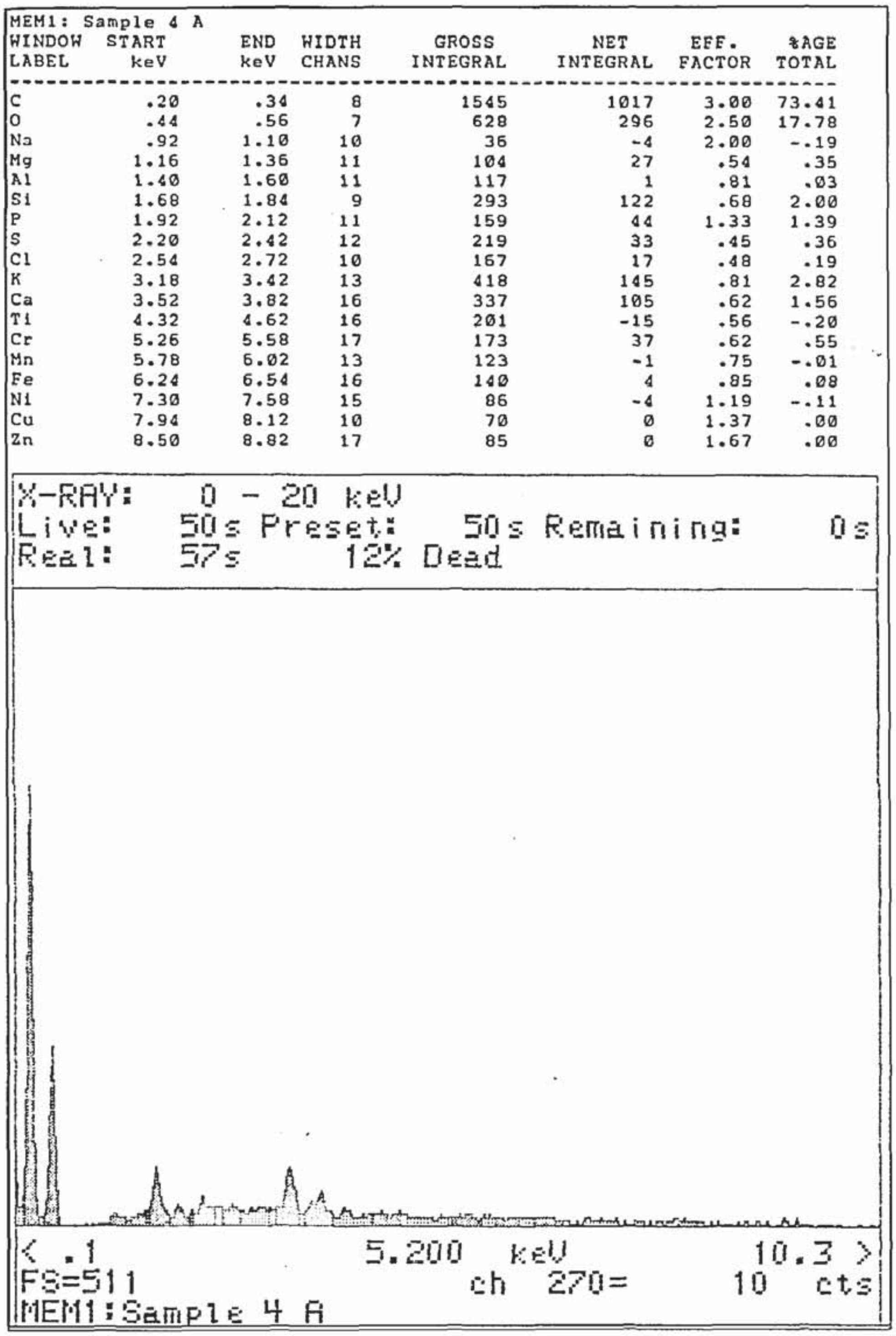


```
MEM1: Sanple 3 A
WINDOW  START        END  WIDTH       GROSS          NET    EFF.    %AGE
LABEL     keV        keV  CHANS     INTEGRAL    INTEGRAL  FACTOR   TOTAL
--------------------------------------------------------------------------
C         .20        .34     8        1359          731    3.00   72.35
O         .44        .56     7         594          230    2.50   18.97
Na        .92       1.10    10          26           -4    2.00    -.26
Mg       1.16       1.36    11          64           -2     .54    -.04
Al       1.40       1.60    11          94           -5     .81    -.13
Si       1.68       1.84     9         216           77     .68    1.72
P        1.92       2.12    11         149           39    1.33    1.71
S        2.20       2.42    12         173            5     .45     .07
Cl       2.54       2.72    10         133           23     .48     .36
K        3.18       3.42    13         232           96     .81    2.55
Ca       3.52       3.82    16         259           75     .62    1.53
Ti       4.32       4.62    16         176           16     .56     .29
Cr       5.26       5.58    17         135          -18     .62    -.37
Mn       5.78       6.02    13         106            2     .75     .05
Fe       6.24       6.54    16         110          -10     .85    -.28
Ni       7.30       7.58    15          90           15    1.19     .59
Cu       7.94       8.12    10          60            5    1.37     .23
Zn       8.50       8.82    17          63           12    1.67     .66

X-RAY:    0 - 20 keV
Live:     50s Preset:    50s Remaining:      0s
Real:     57s       12% Dead

< .1               5.200   keV          10.3 >
FS=511                ch  270=           9  cts
MEM1:Sample 3 A
```

Table H.2: Elemental composition of W44LSOATR2

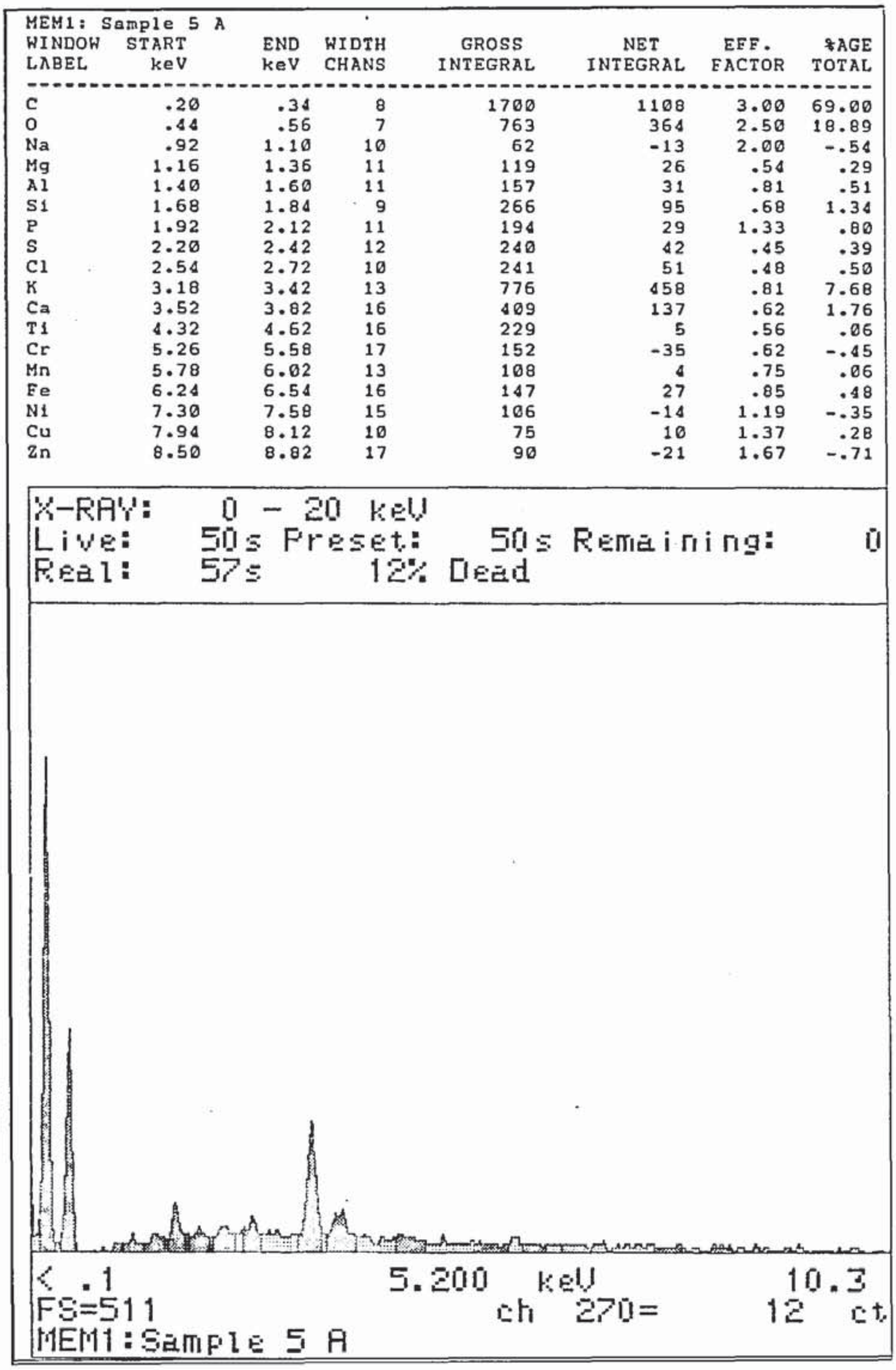


```
MEM1: Sample 4 A
WINDOW  START       END  WIDTH       GROSS          NET     EFF.    %AGE
LABEL     keV       keV  CHANS    INTEGRAL     INTEGRAL   FACTOR   TOTAL
------------------------------------------------------------------------
C          .20       .34      8       1545         1017     3.00   73.41
O          .44       .56      7        628          296     2.50   17.78
Na         .92      1.10     10         36           -4     2.00    -.19
Mg        1.16      1.36     11        104           27      .54     .35
Al        1.40      1.60     11        117            1      .81     .03
Si        1.68      1.84      9        293          122      .68    2.00
P         1.92      2.12     11        159           44     1.33    1.39
S         2.20      2.42     12        219           33      .45     .36
Cl        2.54      2.72     10        167           17      .48     .19
K         3.18      3.42     13        418          145      .81    2.82
Ca        3.52      3.82     16        337          105      .62    1.56
Ti        4.32      4.62     16        201          -15      .56    -.20
Cr        5.26      5.58     17        173           37      .62     .55
Mn        5.78      6.02     13        123           -1      .75    -.01
Fe        6.24      6.54     16        140            4      .85     .08
Ni        7.30      7.58     15         86           -4     1.19    -.11
Cu        7.94      8.12     10         70            0     1.37     .00
Zn        8.50      8.82     17         85            0     1.67     .00

X-RAY:     0 - 20 keV
Live:     50s Preset:     50s Remaining:        0s
Real:     57s          12% Dead

< .1               5.200  keV              10.3 >
FS=511                  ch  270=          10  cts
MEM1:Sample 4 A
```

Table H.3: Elemental composition of W43LSOATR1

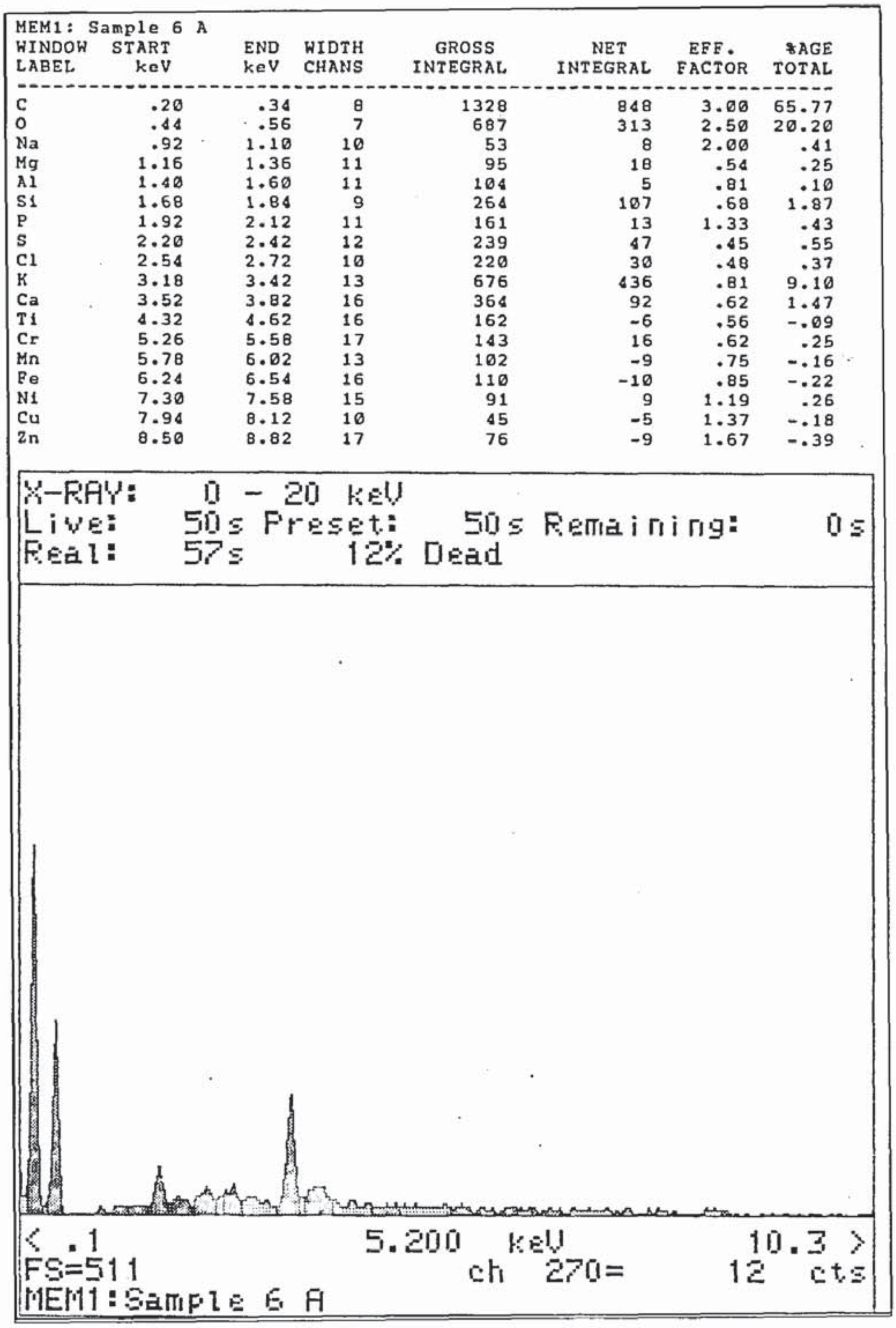


```
MEM1: Sample 5 A
WINDOW  START       END  WIDTH       GROSS         NET     EFF.    %AGE
LABEL     keV       keV  CHANS    INTEGRAL    INTEGRAL   FACTOR   TOTAL
-----------------------------------------------------------------------
C          .20      .34      8        1700        1108     3.00   69.00
O          .44      .56      7         763         364     2.50   18.89
Na         .92     1.10     10          62         -13     2.00    -.54
Mg        1.16     1.36     11         119          26      .54     .29
Al        1.40     1.60     11         157          31      .81     .51
Si        1.68     1.84      9         266          95      .68    1.34
P         1.92     2.12     11         194          29     1.33     .80
S         2.20     2.42     12         240          42      .45     .39
Cl        2.54     2.72     10         241          51      .48     .50
K         3.18     3.42     13         776         458      .81    7.68
Ca        3.52     3.82     16         409         137      .62    1.76
Ti        4.32     4.62     16         229           5      .56     .06
Cr        5.26     5.58     17         152         -35      .62    -.45
Mn        5.78     6.02     13         108           4      .75     .06
Fe        6.24     6.54     16         147          27      .85     .48
Ni        7.30     7.58     15         106         -14     1.19    -.35
Cu        7.94     8.12     10          75          10     1.37     .28
Zn        8.50     8.82     17          90         -21     1.67    -.71
```

```
X-RAY:    0 - 20 keV
Live:    50s Preset:    50s Remaining:     0
Real:    57s        12% Dead
```

```
< .1                  5.200  keV          10.3
FS=511                       ch  270=       12  ct
MEM1:Sample 5 A
```

Table H.4: Elemental composition of W41LSOATR2

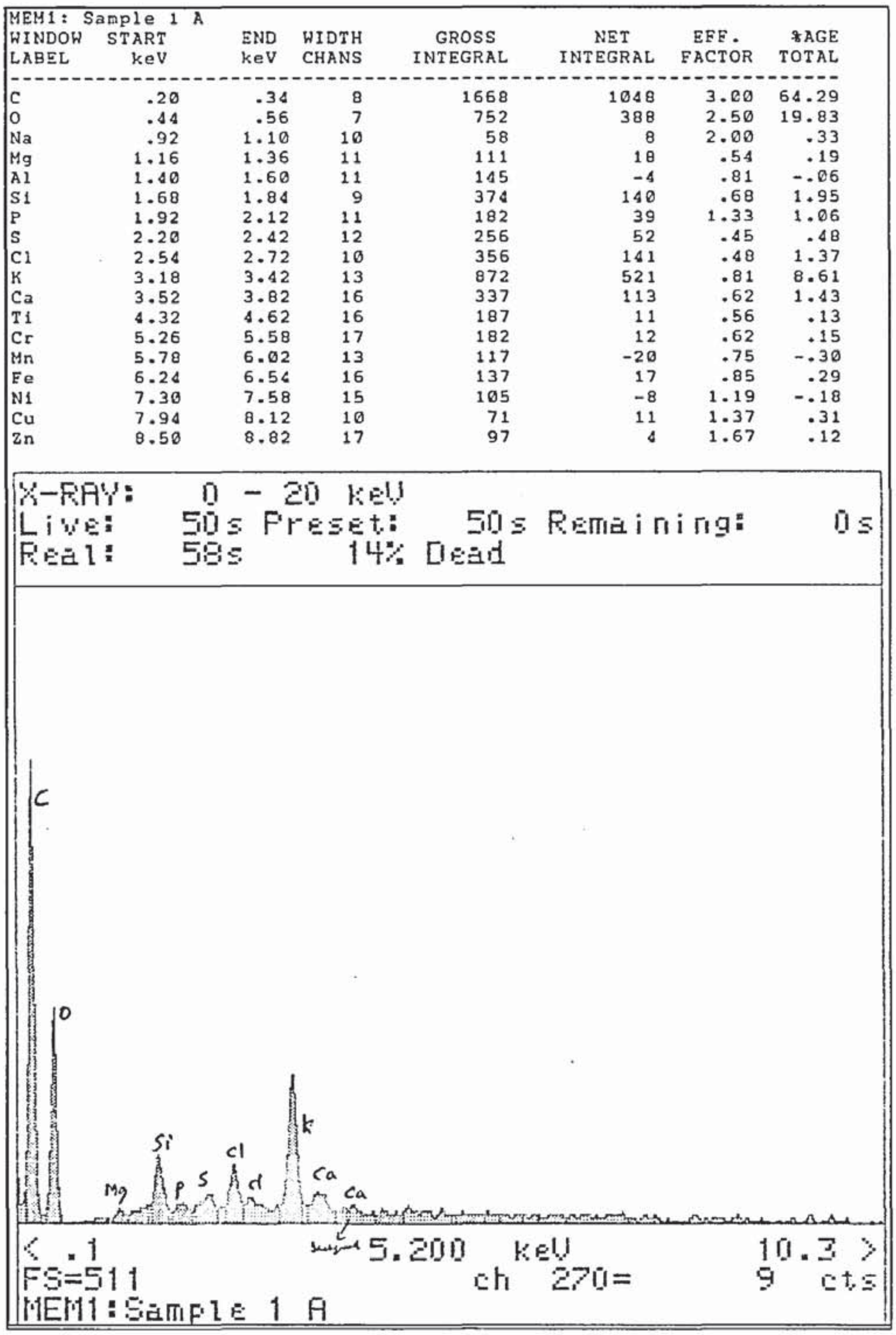


```
MEM1: Sample 6 A
WINDOW  START       END  WIDTH      GROSS          NET    EFF.    %AGE
LABEL     keV       keV  CHANS    INTEGRAL    INTEGRAL  FACTOR   TOTAL
-----------------------------------------------------------------------
C           .20      .34     8        1328         848    3.00   65.77
O           .44      .56     7         687         313    2.50   20.20
Na          .92     1.10    10          53           8    2.00     .41
Mg         1.16     1.36    11          95          18     .54     .25
Al         1.40     1.60    11         104           5     .81     .10
Si         1.68     1.84     9         264         107     .68    1.87
P          1.92     2.12    11         161          13    1.33     .43
S          2.20     2.42    12         239          47     .45     .55
Cl         2.54     2.72    10         220          30     .48     .37
K          3.18     3.42    13         676         436     .81    9.10
Ca         3.52     3.82    16         364          92     .62    1.47
Ti         4.32     4.62    16         162          -6     .56    -.09
Cr         5.26     5.58    17         143          16     .62     .25
Mn         5.78     6.02    13         102          -9     .75    -.16
Fe         6.24     6.54    16         110         -10     .85    -.22
Ni         7.30     7.58    15          91           9    1.19     .26
Cu         7.94     8.12    10          45          -5    1.37    -.18
Zn         8.50     8.82    17          76          -9    1.67    -.39

X-RAY:   0 - 20 keV
Live:   50s Preset:   50s Remaining:      0s
Real:   57s        12% Dead

< .1                 5.200  keV           10.3 >
FS=511                   ch  270=          12  cts
MEM1:Sample 6 A
```

Table H.5: Elemental composition of unwashed EFB

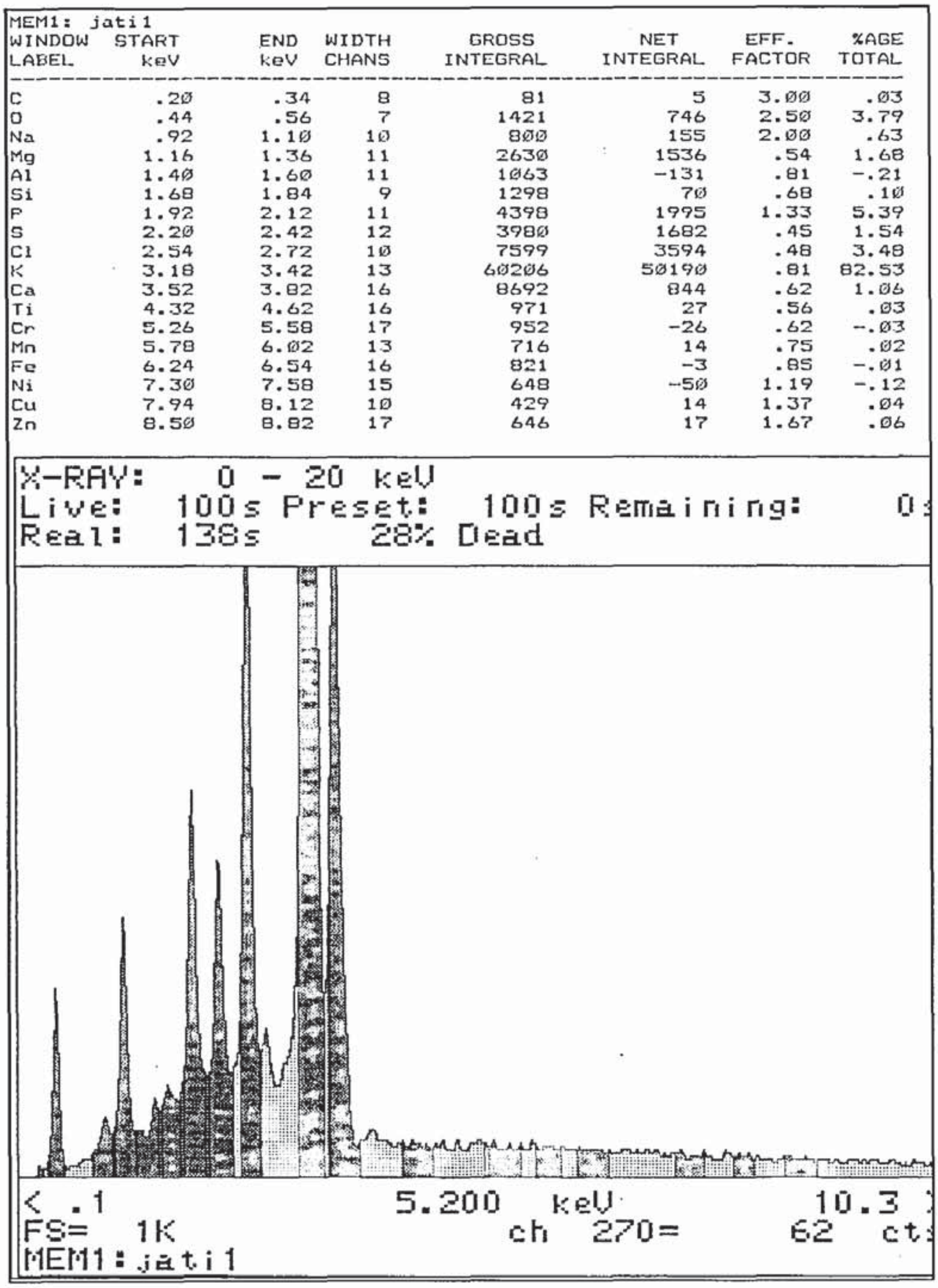


```
MEM1: Sample 1 A
WINDOW  START      END  WIDTH      GROSS          NET   EFF.   %AGE
LABEL     keV      keV  CHANS   INTEGRAL     INTEGRAL FACTOR  TOTAL
-------------------------------------------------------------------
C         .20      .34      8       1668         1048   3.00  64.29
O         .44      .56      7        752          388   2.50  19.83
Na        .92     1.10     10         58            8   2.00    .33
Mg       1.16     1.36     11        111           18    .54    .19
Al       1.40     1.60     11        145           -4    .81   -.06
Si       1.68     1.84      9        374          140    .68   1.95
P        1.92     2.12     11        182           39   1.33   1.06
S        2.20     2.42     12        256           52    .45    .48
Cl       2.54     2.72     10        356          141    .48   1.37
K        3.18     3.42     13        872          521    .81   8.61
Ca       3.52     3.82     16        337          113    .62   1.43
Ti       4.32     4.62     16        187           11    .56    .13
Cr       5.26     5.58     17        182           12    .62    .15
Mn       5.78     6.02     13        117          -20    .75   -.30
Fe       6.24     6.54     16        137           17    .85    .29
Ni       7.30     7.58     15        105           -8   1.19   -.18
Cu       7.94     8.12     10         71           11   1.37    .31
Zn       8.50     8.82     17         97            4   1.67    .12
```

```
X-RAY:    0 - 20 keV
Live:    50s Preset:    50s Remaining:     0s
Real:    58s      14% Dead
```

```
< .1              5.200   keV          10.3 >
FS=511                 ch  270=         9  cts
MEM1:Sample 1 A
```

Table H.6: **Elemental composition of leachate of W79LSOATR1**



```
MEM1:  jati1
WINDOW   START        END  WIDTH      GROSS         NET     EFF.    %AGE
LABEL      keV        keV  CHANS   INTEGRAL    INTEGRAL   FACTOR   TOTAL
-------------------------------------------------------------------------
C          .20        .34      8         81           5     3.00     .03
O          .44        .56      7       1421         746     2.50    3.79
Na         .92       1.10     10        800         155     2.00     .63
Mg        1.16       1.36     11       2630        1536      .54    1.68
Al        1.40       1.60     11       1063        -131      .81    -.21
Si        1.68       1.84      9       1298          70      .68     .10
P         1.92       2.12     11       4398        1995     1.33    5.39
S         2.20       2.42     12       3980        1682      .45    1.54
Cl        2.54       2.72     10       7599        3594      .48    3.48
K         3.18       3.42     13      60206       50190      .81   82.53
Ca        3.52       3.82     16       8692         844      .62    1.06
Ti        4.32       4.62     16        971          27      .56     .03
Cr        5.26       5.58     17        952         -26      .62   --.03
Mn        5.78       6.02     13        716          14      .75     .02
Fe        6.24       6.54     16        821          -3      .85    -.01
Ni        7.30       7.58     15        648         -50     1.19    -.12
Cu        7.94       8.12     10        429          14     1.37     .04
Zn        8.50       8.82     17        646          17     1.67     .06

X-RAY:    0 - 20 keV
Live:   100s Preset:   100s Remaining:     0
Real:   138s       28% Dead

< .1             5.200  keV           10.3
FS=  1K             ch  270=          62  ct
MEM1:jati1
```

Appendix I – FTIR Results

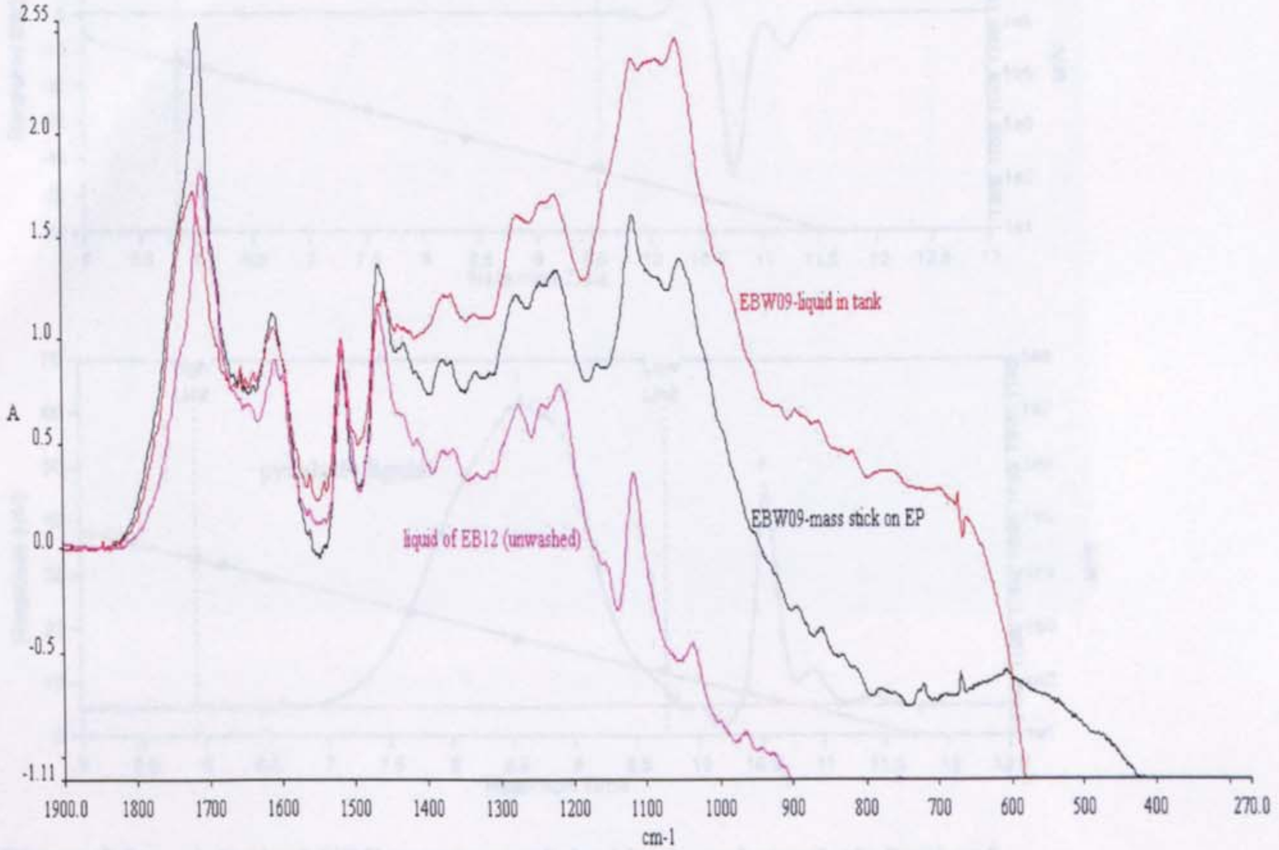


Figure I.1: **FTIR spectra of pyrolysis liquid of EB12 [unwashed feedstock] and EBW09 [washed feedstock]**

Appendix J – GPC Analysis

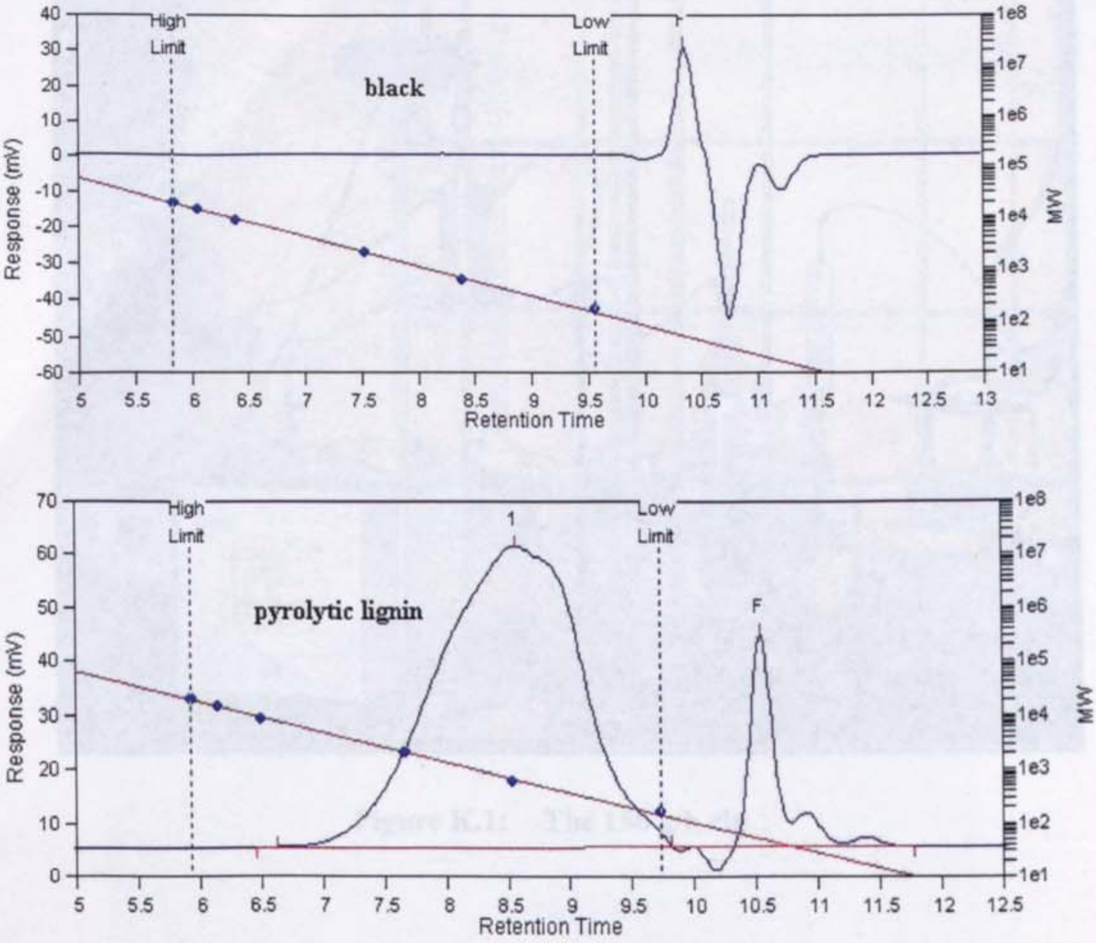


Figure J.1: A typical GPC spectrum of the blank and pyrolytic lignin of pyrolysis liquid collected in the tank for EBW09

Appendix K – Picture of 150 g/h Rig and 1 kg/h Rig

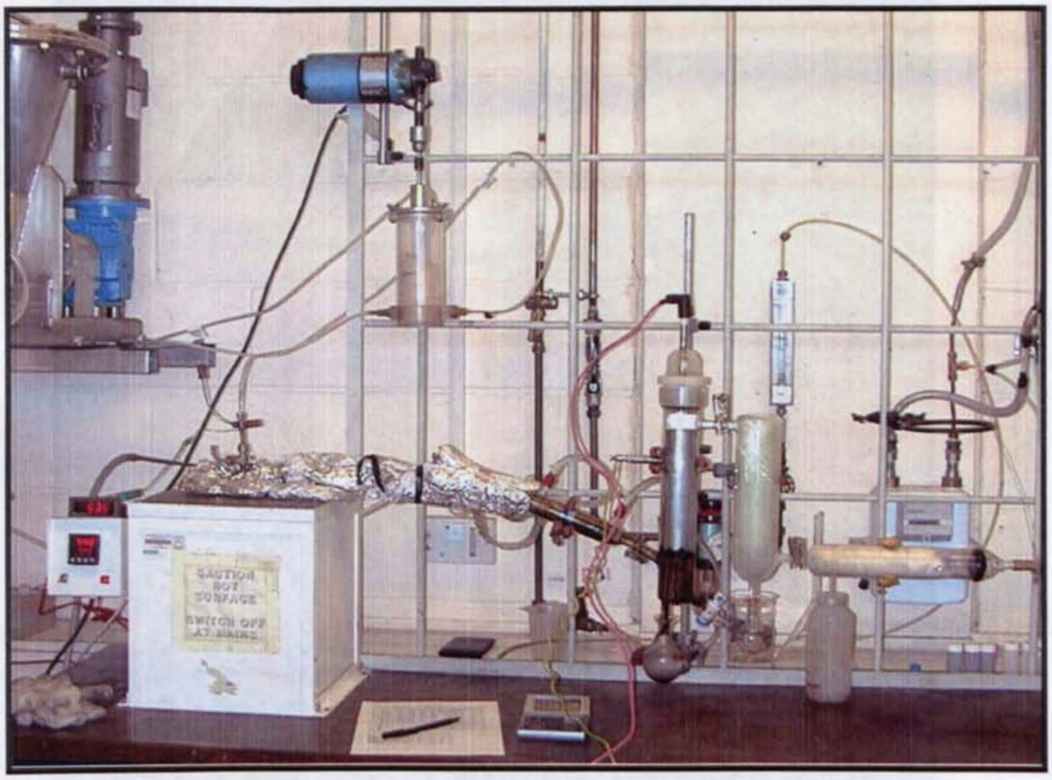


Figure K.1: The 150 g/h rig

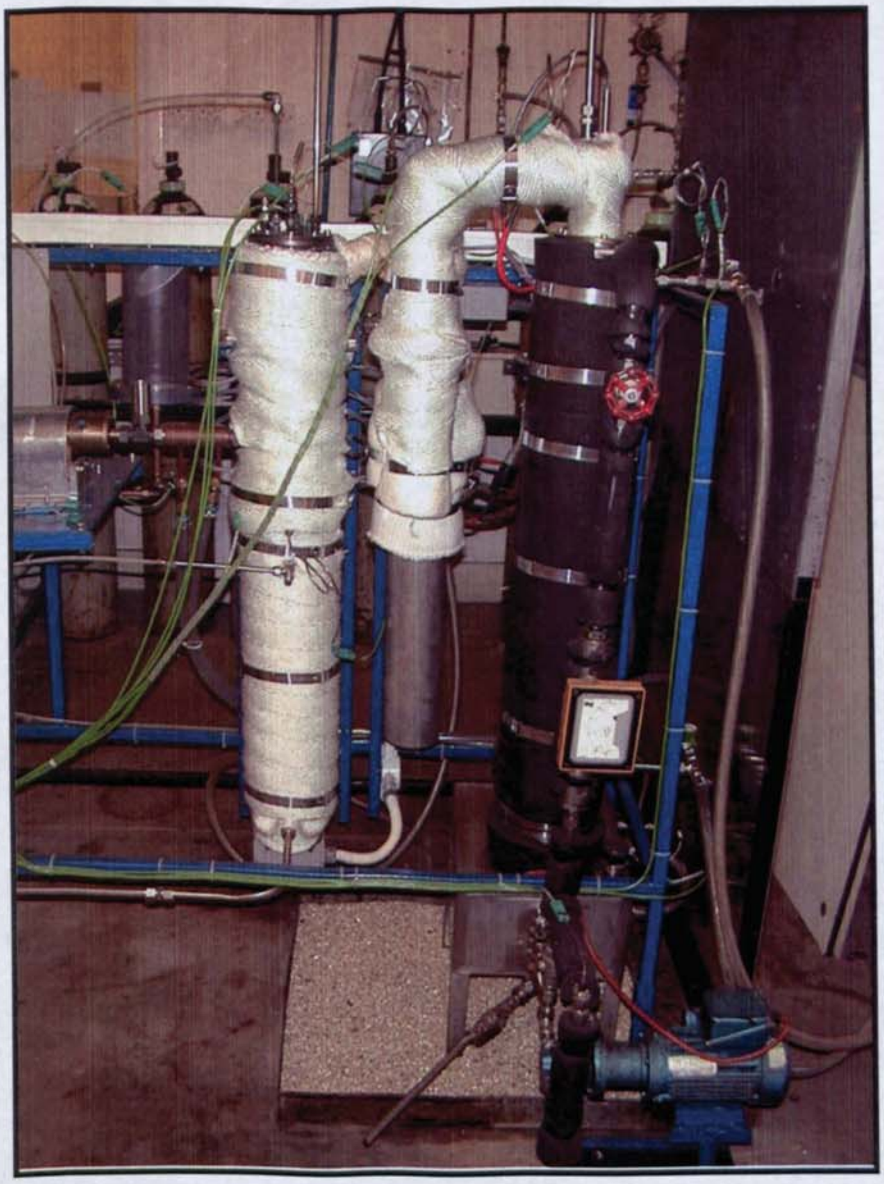


Figure K.2: The 1 kg/h rig