IMPROVEMENT OF BIO-OIL STABILITY IN WOOD PYROLYSIS PROCESS

Peiyan Liu

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Aston University

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SUMMARY

Pyrolysis is one of several thermochemical technologies that convert solid biomass into more useful and valuable bio-fuels. Pyrolysis is thermal degradation in the complete or partial absence of oxygen. Under carefully controlled conditions, solid biomass can be converted to a liquid known as bio-oil in 75% yield on dry feed. Bio-oil can be used as a fuel but has the drawback of having a high level of oxygen due to the presence of a complex mixture of molecular fragments of cellulose, hemicellulose and lignin polymers. Also, bio-oil has a number of problems in use including high initial viscosity, instability resulting in increased viscosity or phase separation and high solids content. Much effort has been spent on upgrading bio-oil into a more usable liquid fuel, either by modifying the liquid or by major chemical and catalytic conversion to hydrocarbons

The overall primary objective was to improve oil stability by exploring different ways. The first was to determine the effect of feed moisture content on bio-oil stability. The second method was to try to improve bio-oil stability by partially oxygenated pyrolysis. The third one was to improve stability by co-pyrolysis with methanol.

The project was carried out on an existing laboratory pyrolysis reactor system, which works well with this project without redesign or modification too much. During the finishing stages of this project, it was found that the temperature of the condenser in the product collection system had a marked impact on pyrolysis liquid stability. This was discussed in this work and further recommendation given.

The quantity of water coming from the feedstock and the pyrolysis reaction is important to liquid stability. In the present work the feedstock moisture content was varied and pyrolysis experiments were carried out over a range of temperatures. The quality of the bio-oil produced was measured as water content, initial viscosity and stability. The result showed that moderate (7.3-12.8 % moisture) feedstock moisture led to more stable bio-oil.

One of drawbacks of bio-oil was its instability due to containing unstable oxygenated chemicals. Catalytic hydrotreatment of the oil and zeolite cracking of pyrolysis vapour were discussed by many researchers, the processes were intended to eliminate oxygen in the bio-oil. In this work an alternative way oxygenated pyrolysis was introduced in order to reduce oil instability, which was intended to oxidise unstable oxygenated chemicals in the bio-oil. The results showed that liquid stability was improved by oxygen addition during the pyrolysis of beech wood at an optimum air factor of about 0.09-0.15.

Methanol as a postproduction additive to bio-oil has been studied by many researchers and the most effective result came from adding methanol to oil just after production. Co-pyrolysis of spruce wood with methanol was undertaken in the present work and it was found that methanol improved liquid stability as a co-pyrolysis solvent but was no more effective than when used as a postproduction additive.

Keywords: Biomass, pyrolysis, bio-oil, stability, viscosity, moisture content.

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CHAPTER 1 . INTRODUCTION

Fast pyrolysis of biomass at moderate temperatures (400-600°C) produces three products; pyrolysis liquid (also known as bio-oil), char and gas. The pyrolysis liquid can be combusted as an alternative to fuel oil. However, the pyrolysis liquid has its drawbacks compared with petroleum and hence considerable upgrading of the product is required to obtain a liquid that is suitable for use as a fuel. Unfortunately the methods used for upgrading have problems associated with them. This work investigated the effect of water in the bio-oil on its stability and explored new upgrading methods.

This work was conducted in three parts: Firstly, an investigation of the effects of feed moisture content on bio-oil yields, viscosity and water content was carried out to determine the optimum feed moisture content for stable bio-oil; secondly a new method was explored to improve bio-oil stability by partially oxygenated pyrolysis; thirdly co-pyrolysis with methanol was investigated to improve bio-oil stability.

1.1 INTRODUCTION

Biomass (harvest and process residues in forestry and agricultural operations, specific terrestrial or aquatic crops grown for fuel, animal waste streams, refuse derived fibre, etc.) represents an important energy resource in the world. In recent times depletion on fossil fuels and pressures on the global environment have lead to calls for an increased use of renewable energy sources.

Biomass, as an energy source, has two striking characteristics. Firstly, biomass is the only renewable organic resource and is also one of the most abundant resources. Secondly, biomass fixes carbon dioxide in the atmosphere by photosynthesis.

Kaltschmitt and Dinkelbach [1] have concluded that in general, biomass can be regarded as an environmentally and climatically sound option for energy provision due to its:

- Almost closed carbon dioxide cycle (i.e. no impact on the greenhouse effect),
- Low sulphur dioxide emissions (no impact on acid rain),
- Good opportunities for ash utilisation (i.e. the produced waste can be used with a certain benefit on the area where the biomass was grown),
- Potential to save fossil energy resources (i.e. the fossil energy resources last for a longer period).

Biomass is also a source of energy, which is hardly affected by crises being:

- An indigenous energy carrier (i.e. biomass is, in most cases, produced close to the place where it is used),
- Characterised by short supply chains,
- A form of stored solar energy (i.e. no storage problems as they occur using wind power or photovoltaics).

The production and utilisation of biomass is widely accepted and offers benefits for rural areas related to employment, rural infrastructure, the conservation of cultivated areas and hence the attractiveness of rural regions.

Despite the undisputed environmental and social benefits of biomass utilisation, biomass is generally poorly suited for direct energy use, with pre-treatment often necessary for altering its physical and chemical form. Moisture content can be in excess of 50%, so costs of collection, transportation, and energy conversion become relatively inefficient. Further, biomass availability (e.g., from row crops) is sometimes seasonal, so storage is necessary. As biomass can spoil, it has to be covered and processed soon after receipt.

Fortunately, thermal conversion processes are somewhat insensitive to type, form and shape, and can convert biomass into stable, storable and transportable energy forms, and in physical or chemical forms that can be used in higher efficiency energy conversion processes developed for liquid petroleum, coal and natural gas.

As reported by Bridgwater [2], there is a wide range of processes available for converting biomass and wastes into more valuable and usable fuels such as fuel gas and fuel oil or higher value products for the chemical industry. In general, this upgrading may be achieved by *physical, biological* (anaerobic digestion and fermentation), *chemical* or *thermal* methods to give a solid, liquid or gaseous fluid. In contrast to other renewable energy sources, biomass is a source of liquid, solid and gaseous fuels. Of the variety of technologies available, thermochemical processing has received most attention for converting biomass into more useful and valuable products.

The thermochemical methods for converting biomass into energy directly, or into another form suitable for the provision of energy are the following:

1. *Direct combustion of the solid material* to provide heat for steam production for use in processes such as the driving of a turbine in electricity generation [3,4]. Bridgwater and Diebold [5] have highlighted that combustion implies the addition of air or oxygen directly to the reactor in sufficient quantity to completely oxidise the biomass (stoichiometric), usually with an excess of oxygen to ensure burnout. During combustion of biomass, the latter is first

pyrolysed to gases and organic vapours, which are then burned in flaming combustion. The char burns in glowing combustion after the pyrolysis step.

2. *Gasification* to provide a fuel gas that can be combusted for use in an engine or, as for direct combustion, for the generation of heat for steam production for use in processes such as electricity generation [4]. Gasification is designed to produce non-condensable gases, usually with the addition of a small amount of oxygen or air (sub-stoichiometric) directly to the reactor to provide the process heat required for the gasification reactions.
3. *Pyrolysis* to produce a mixture of solid char, liquids and condensable vapours by heating the biomass in the absence of oxygen [5]. Fast pyrolysis, in particular, is a process designed to maximise the formation of condensable vapours, with minimum of gas and char. It thereby provides a liquid fuel that can substitute fuel oil in any static heating or electricity generation application [4]. The advantage of pyrolysis is that it can directly produce a liquid fuel, which is beneficial when biomass resources are remote from where the energy is required; hence the liquid can be readily stored and transported [6]. The liquid can also be used to produce a range of speciality and commodity chemicals [7].

As direct combustion, gasification, pyrolysis, the thermochemical technology has been researched and developed for the economic production of fuel products that may be readily integrated into the energy infrastructures of both industrialised and developing countries [2].

Amongst the thermochemical processes, pyrolysis has received increasing attention, since this process provides the greatest quantity of the liquid product bio-oil. Bio-oil offers substantial potential as a liquid fuel for many direct firing applications and as a source of chemicals and derived products. Combustion tests performed using different scale burners [8, 9, 10] and internal combustion engines [11, 12] have demonstrated that the oils could be burnt efficiently in standard or slightly modified equipment. These test also identified several challenges in the bio-oils applications resulting from their properties.

Bio-oil has a lower heating value in the range of 14-18 MJ/kg, which is similar to that for biomass and is only 40-45% of that for hydrocarbon fuels. This low value results from both the high oil water content (15-25 wt %) and high oxygen content (30-40 wt % on dry basis) of the bio-oils (see section 3.2 and section 3.3). High oil water content contributes to the increase of ignition delay and the decrease of combustion rate compared to diesel fuels.

Bio-oils also contain substantial amounts of organic acids, mostly acetic and formic acid, which result in a pH of 2-3. For this reason, the oils are corrosive to common construction materials such as carbon steel and aluminium.

In addition, it contains unstable oxygenated compounds that, during storage or handling, can react with themselves to form large molecules. The main chemical reactions observed are polymerisation of double bonded compounds, as well as ethers formation and esterification occurring between hydroxyl, carbonyl, and carboxyl group components, in which water is formed as a by product [13, 14] (see section 3.4).

A small amount of char ranged from 0.1 to 3% is also present in bio-oil (see section 3.3.3). In most cases these char are highly undesirable because they tend to settle at the bottom of the vessel in a form of sludge, hence can cause erosion, and block injection nozzles.

Bio-oil has poor phase stability due to its high oil viscosity and high water content (see section 3.3.2 and section 3.3.5); phase separation over long storage time is therefore a definite handicap for fuel application.

It seems that the quality of bio-oil is inferior to those of petroleum-based fuels (see section 3.5.3). However, the advantage of bio-oils is that they are generated from renewable resources and do not contribute to the net release of greenhouse gases (see section 3.5.2). In addition, some undesired characteristics of bio-oils could be improved by exploring upgrading methods.

Hot vapour filtration (see section 3.6.1.1) method has been used to separate char (especially size below 10 μm) in the bio-oil, as char in the oil degraded the oil quality (see section 3.3.3), but hot vapour filtration has not yet proved his worth over long term process operation.

Solvent addition means has also been used to homogenize and to reduce viscosity of bio-oils. The addition of methanol showed a significant effect on oil stabilization (see section 7.1). Considering the simplicity, the low cost of methanol and its beneficial effect on the oil properties, this method seems to be the most practical approach for bio-oil quality upgrading.

Emulsification of bio-oil with diesel oil with the aid of surfactants showed promising ignition characteristics of bio-oil. The drawback of this approach is the cost of surfactants and a large amount of energy required for emulsification.

Deoxygenation processes based on catalytic hydrotreatment or catalytic vapour cracking have been proposed to increase oil-heating value with extensive changes to oil chemical structure, but they significantly decrease the oil yields and are very capital intensive (see section 6.1).

Bio-oil has many unusual characteristics and drawbacks compared to petroleum based fuel (see section 3.5). Its advantage, however, may make it an important energy carrier in the future, especially when taking into account environmental considerations. Extensive research into bio-oil upgrading options therefore appears justified. The upgrading methods mentioned above are too much concerned with bio-oil after its production. The main objective of this project is therefore to develop a better understanding of the effects of water in bio-oil on bio-oil stability and how stability may be improved by modifying the pyrolysis process, so that the addition of a supplementary step to the pyrolysis process is not required.

The effect of water in the oil is complex as water in the oil gives a controversial affects to oil. Water in the oil decrease oil heating value but lowers oil viscosity; More water in the oil increase oil stability but too much water in the oil leads to oil phase separation. The pH of the oil increases but the oil density increases too if water is removed from oil. Water in the oil comes from pyrolysis process and feedstock moisture as well, thus the effect of feedstock moisture content is very important on bio-oil stability. High feedstock moisture gives high water yields during the pyrolysis, this leads to high oil water content. The water in the oil reduces oil viscosity, but water content in some range does not affect oil stability. The optimum oil water content, which gives most stable and least viscous oil, comes from moderate moisture feedstock (see chapter 5).

The presence of numerous and various oxygenated functions gives bio-oil unwanted characteristics (see section 3.4) and while heating or in air unstable chemically reactive carbonyl functions in the oil are thought to facilitate polymerisation reactions that yields an overall increase in the viscosity and decrease in the stability of the oil. Catalytic hydrotreatment or catalytic vapour cracking has been proposed to increase oil-heating value by decreasing of unstable oxygenated chemicals in the oil, but they are not practical economically. An alternative route partially oxygenated pyrolysis was introduced here in order to improve bio-oil stability by decreasing of unstable oxygenated chemicals in the oil. Partially oxygenated pyrolysis decreases unstable oxygenated chemicals in the oil and increase water in the oil, the former will increase oil stability and the latter will lower oil viscosity, but too much water in the oil will make oil phase separation, thus an optimum airfacor in partially oxygenated pyrolysis gives an most stable oil (see Chapter 6).

The additions of methanol showed a significant effect on oil stabilization but this still is a supplementary step followed pyrolysis. Co-pyrolysis with methanol means to combine two steps in one, this method was aroused by Diebold's [14] suggestion that methanol used shortly after the pyrolysis oil is produced is most effective in reducing oil viscosity. Copyrolysis did improve the oil stability but it is not as effective as methanol as an additive (see chapter 7).

1.2 STRUCTURE OF THE THESIS

The thesis is arranged into the following chapters:

Chapter 2. Fast Pyrolysis for Bio-oil

Fast pyrolysis uses moderate temperatures [400-600°C] to break down biomass into liquid, char and gas. The yields of these products are controlled by process and feedstock parameters. This chapter describes the fast pyrolysis process and investigates parameters, which affects on pyrolysis liquid – bio-oil. This chapter forms the basis for the experimental work described in Chapters 4-8.

Chapter 3. Bio-oil and upgrading

This chapter reviews bio-oil characteristics. The advantages and disadvantages of bio-oil are discussed by comparison with petroleum and petroleum products. The unusual characteristics of bio-oil are also discussed in this chapter. The present investigation into the improvement of bio-oil stability has been designed to overcome some of the drawbacks associated with the use of bio-oil.

Chapter 4. Experimental

The pyrolysis experiments used to produce bio-oil were carried out in an existing 150g/h reactor system. This chapter describes the equipment used and procedures for operating the existing pyrolysis system. A critical assessment of the mass balance and analytical procedures has been included. This chapter includes a discussion of the problems encountered when using the existing system, the resulting improvements that were made, and possible future work in this area.

Chapter 5. Effect of feed moisture content on the stability of liquids from fast pyrolysis of spruce wood

The presence of water in biomass influences its behaviour during pyrolysis and impacts on the physical properties and quality of the pyrolysis liquid. The presence of water reduces the oil-heating value, lowers oil viscosity and increases instability as very high water content leads to oil phase separation. Little work on the effects of feed moisture content on pyrolysis liquid stability has been carried out previously. The effects of varying feed moisture content on pyrolysis liquid stability were investigated in this chapter.

Chapter 6. Partially oxygenated pyrolysis of Beech wood to improve the stability of pyrolysis liquid

The presence of numerous and various oxygenated functional groups gives bio-oil-unwanted characteristics that need to be overcome. Zeolite cracking of pyrolysis vapour is effective in eliminating oxygen but gives low liquid yields. Catalytic hydrotreatment of pyrolysis liquid requires hydrogen or hydrogen donors at considerable cost. An alternative method, partially oxygenated pyrolysis, was investigated in the present work and discussed in this Chapter.

Chapter 7. Co-pyrolysis of spruce wood with methanol

The use of methanol as a postproduction additive to bio-oil has been investigated previously by many research groups. It was found that methanol was the least expensive and most effective additive used, provided that the addition was made relatively quickly after the pyrolysis oil had been produced. This chapter discusses the co-pyrolysis of spruce wood with methanol to determine the effect on pyrolysis yield and bio-oil stability.

Chapter 8. Conclusions

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

Chapter 9. Experimental inaccuracy and further recommendation

This chapter gives recommendations for further work related to using of this existing small rig in order to get more accurate experiment result.

CHAPTER 2 . FAST PYROLYSIS FOR BIO-OIL

This Chapter illustrates the principles and characteristics of fast pyrolysis technology. It also describes the technological requirements of a fluidising bed reactor used for this purpose. Fast pyrolysis technology was fundamental to the experiment work conducted in this project.

2.1 FAST PYROLYSIS PRINCIPLES

Fast pyrolysis is a high temperature process in which the biomass is rapidly heated in the absence of oxygen. As a result, it decomposes to generate mostly vapours, aerosols and some charcoal [4]. It is an advanced process that can be carefully controlled to give high yields of liquid – bio-oil [5], which can be used as a substitute for liquid fossil fuels in some applications [4].

In the period 1980-1984, it was found in work done by the pyrolysis research group at the University of Waterloo [15,16,17], that if certain reaction conditions were met, a maximum yield of organic liquid product could be obtained from wood and from most lignocellulosic materials. These conditions, which have been defined as those of fast pyrolysis, require atmospheric pressure operation at temperatures from 450-550 °C with a very short volatiles residence time and a very rapid biomass heating rate. This requirement of rapid heating rate limits the reactor configurations, since only those capable of such performance can be used, and also mandates a relatively small particle size [18].

Bridgwater *et al.* agreed that most wood gives maximum liquid yields of up to 80 wt. % on a dry feed basis at 500-550 °C with vapour residence times of not more than 1 s, and summarised the essential features of the process [3, 4, 6].

- Very high heating rate and very high heat transfer rates >1000°C/s at the reaction interface.
- Short vapour residence times of typically less than 2 seconds.
- Carefully controlled pyrolysis reaction temperature of around 500°C.
- Carefully controlled pyrolysis vapour phase temperatures of 400-500°C
- Rapid cooling of pyrolysis vapours.

2.2 THE POSSIBLE PATHWAY OF PYROLYSIS PROCESS

Fast pyrolysis is not an equilibrium process. Biomass is a complex polymeric and its thermal decomposition is multistage complicated process. Many pathways and mechanisms have been proposed to explain the fundamental steps in pyrolysis [19, 20, 21]. Shafizadeh type kinetic models [23] are perhaps the most widely used for cellulose pyrolysis but they can be also applied to the whole biomass, which are shown as Figure 2-1 [22].

2.3 HOW TO MEET FAST PYROLYSIS REQUIREMENTS

Fast pyrolysis can be carried out in a number of reactor types; a thorough review of technologies has recently been completed by Bridgwater [6]. There are three main methods of achieving fast pyrolysis, namely ablative pyrolysis, fluid bed and circulating fluid bed pyrolysis. However, most workers have been in agreement that, providing all criteria mentioned above are met, fast pyrolysis can be carried out in most type of reactor. In this work a fluidised bed reactor was employed for the production of bio-oil, and therefore the following discussion focuses on the requirements of the fluidised bed reactor technology for fast pyrolysis.

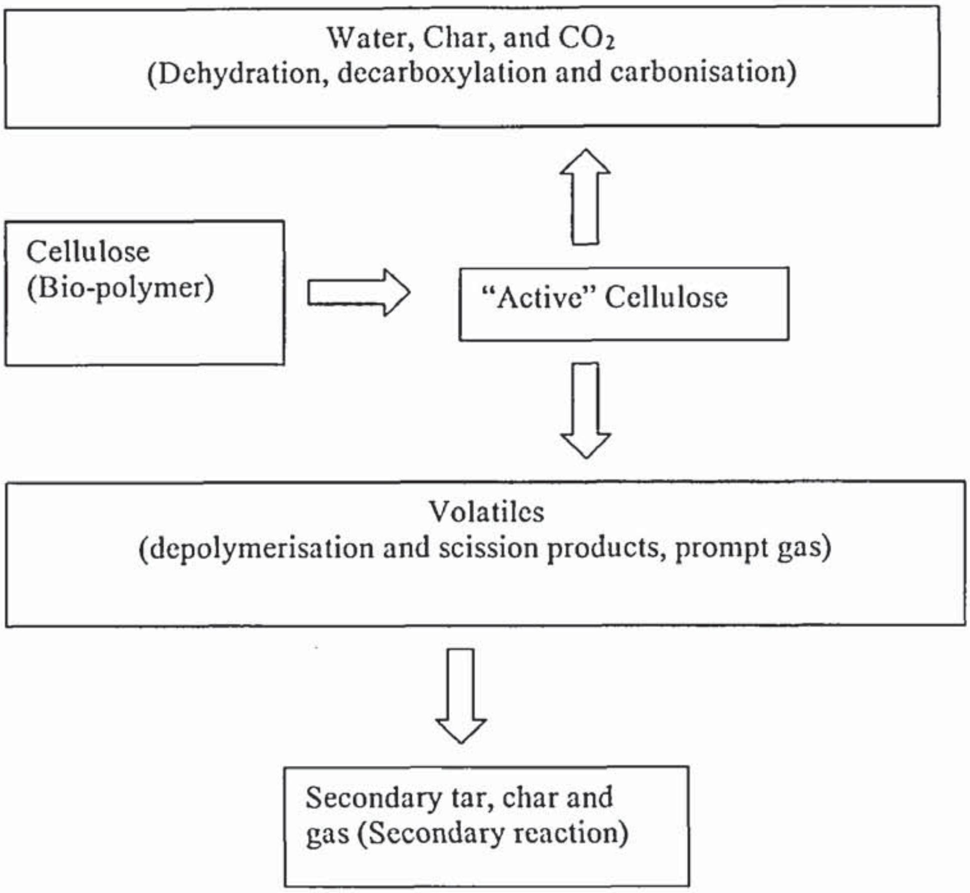


Figure 2-1. Typical cellulose decomposition model [22]

2.3.1 Very high heating rate and heat transfer rate

The pyrolytic reactions proceed over a wide range of temperatures and the products formed earlier undergo further transformation and decomposition reactions. Furthermore, as these materials are heated to higher temperatures, the availability of sufficient energy to overcome the activation energy requirements of various side reactions results in a variety of products. Long heating periods allow the sequence of consecutive reactions to take their course. Rapid or flash pyrolysis can reduce the secondary reactions (Section 2.4.7) and prevent further degradation of products [23]. For this reason very high heating and heat transfer rates are preferred.

With regard to heat transfer, Bridgwater *et al.* [4] discussed two important requirements for heat transfer in a fast pyrolysis reactor:

1. Transfer to the heat transfer medium (gas and solid in fluid bed reactors)

2. Transfer from the heat transfer medium to the pyrolysing biomass.

In order to obtain a high transfer rate the following methods were adopted for use in Aston's bench scale fluidised bed reactor.

2.3.1.1 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% [4].

2.3.1.2 Fluidising medium

Fluidised 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. The sand particle size for the Aston 150g/h reactor (Section 4.2) was similar to the feed stock particle size in order to ensure good solids mixing [4]. For large reactors however, the sand particle size is smaller than both the biomass particle size and the average char particle size. The main reason for not using a smaller sand particle size in the present work was the likelihood of sand entrainment in the gas stream and its subsequent loss from the small reaction vessel.

2.3.1.3 Finely ground biomass feed

Biomass has a low thermal conductivity and hence the time taken for the centre of the particle to reach the reaction temperature increases with particle size. Fine particle sizes for the feedstock accelerate heat exchange and therefore speed up the reaction. In other words, the particles have to be very small to fulfil the requirement of rapid heating.

2.3.2 Short hot vapour residence time

The hot vapour residence time (Section 4.2.3) 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. Although the yields of pyrolysis products are a function of reactor temperature, the history of the vapour phase will also influence the amount of secondary reactions (Section 2.4.7) that occur. Secondary reactions (Section 2.4.7) lead to the production of low molecular weight products and gas and should be avoided for the production of liquid.

Therefore, in conjunction with vapour product temperature, residence time is seen as having a significant effect on product yields and the properties of pyrolysis products (see section 2.4.6).

2.3.3 Controlled reaction temperature around 500 °C

It is believed that establishing the maximum organic yield and the temperature at which the maximum occurs is the first part to optimization of the pyrolysis process for fuel production. The effect of temperature is well understood in terms of total product yield with a maximum at typically 500 °C for most woody biomass. Reaction temperature is seen by most fast pyrolysis workers to be the main controlling factor on product yields and also the yield of chemicals in the pyrolysis liquid (see section 2.4.5). In Aston's bench scale fluidised bed, reactor temperature can be controlled by manual operation and it was affected by feed rate, flow of cooling air, heating rate of furnace (See Chapter 4).

2.3.4 Pyrolysis vapour temperature 400 °C to 500 °C

Long vapour residence times and higher temperature (>500 °C) cause secondary cracking of primary products, reducing yields of specific products and organic liquids. Lower temperatures (<400 °C) lead to condensation reactions and the subsequent formation of lower molecular weight liquids, which can also react [24].

2.3.5 Rapid quenching of the vapours

The process of pyrolysis is complex, but the most accepted theory is that primary vapours are first produced, the characteristics of which are most influenced by heating rate. These primary vapours then further degrade to secondary tars and gases if held at high temperature for long enough for secondary reactions (Section 2.4.7) to occur. 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. The primary liquid products tend to have lower viscosity, be more stable under ambient conditions, less sensitive to water contamination and more homogeneous. Efficient cooling and product collection appear to be difficult but important. An electrostatic precipitator (Section 4.2.4.2) is effective and was used in this work.

2.4 THE PARAMETERS WHICH AFFECT PYROLYSIS PRODUCTS

The main feedstock, reactor and product recovery parameters have been discussed by many researchers [25, 26, 27]. In this chapter, only those parameters that have a significant effect on yields and properties of pyrolysis products will be reviewed.

2.4.1 Feedstock type

Biomass composition relates to two main areas, that is, the amount of each of the biomass chemical components and the composition of each component for a particular biomass type. Table 2-1 shows 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 [28]. Each biomass type (e.g. beech and spruce) will have different amounts of each of the main biomass components. Every biomass type when fast pyrolysed produces different yields of liquid, char and also different chemicals in the liquid.

Table 2-1. Analysis of typical biomass feedstocks [29]

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

Meier [30] carried out the study on chemicals from pyrolysis of different wood. The liquids were produced at Aston, BTG and IWC. Aston liquid was produced from pine in a 1kg/h fluidised bed reactor, BTG liquid from softwood cones in a rotating cone reactor and IWC liquid from beech wood in a fluidised bed reactor. The quantitative results are shown as Table 2-2. The cellulose-derived chemicals make up the largest proportion of the analysed liquids. The hemicellulose and lignin derived chemicals make up only a small proportion of the total analysed liquid. There are a large number of different chemicals but they are only present in small concentrations. The chemicals derived from the cellulose component were present in high concentrations and were also present in the liquids from all biomass species.

Hague [27] has successfully fast pyrolysed a number of feedstocks, pine bark, rape straw, rape meal, miscanthus, pine and poplar using a 150g/h fluidised bed reactor. It was 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. Agreement results also found by Agblevor, the total liquid yields (61 %) obtained from pyrolysis of switchgrass feedstock were lower than those obtained for woody biomass feedstock (68%) pyrolysed under similar condition [31]. Switchgrass bio-oils were stickier than wood bio-oils and tended to stick more tenaciously to the glass condensers [32]. Woody bio-oil were easily washed from the glassware with acetone after each run, whereas switchgrass bio-oils did not readily dissolve in acetone when dry, but readily dissolved in an alcoholic potassium hydroxide solution. The total char yield from the switchgrass was significantly higher than from woody biomass [33]. Similar result was also found in this work, bio-oil produced from pyrolysis of miscanthus (elephant grass) was very sticky compared to bio-oil gained from woody (Beech and Spruce). Bio-oil yields of 60.8% for miscanthus, 76% for Spruce wood and 78% for beech wood at the same pyrolysis condition. Partly because grass included leaves as well as stems and the ash content (see section 2.4.2) of the leaves are usually several fold that of the stems [34].

The present work was aimed at optimising the pyrolysis process for fuel production using two types of biomass, beech wood (hardwood) and spruce wood (soft wood) as feedstock.

2.4.2 Feedstock ash content

The inorganic content of plant fibres is known as ash [35]. The most common elements in ash are calcium, potassium and magnesium; and these are contained as carbonates, phosphates, silicates and sulphates [36]. During fast pyrolysis the ash tends to be incorporated into the char; also, there is usually a small amount of char in the pyrolysis liquid. The ash component will influence the pyrolysis reaction and hence the yield of chemicals as these inorganic in the ash, especially potassium and calcium, catalyse biomass decomposition and char-forming reaction. [25]. The switchgrass and miscanthus mentioned in section 2.4.1 gave very poor oil quality and yields due to their very high ash content. Switchgrass has a very high ash content compared to woody biomass feedstock as switchgrass feedstock included leaves as well as stems and switchgrass is fertilized with potassium chloride. [32]

The ash content of wood is usually between 0.2-2.0% (e.g. pine 0.23%, poplar 0.46% and pine bark 1.94%). Beech and spruce wood, which were the main feedstock used in this work, had low ash content of 0.5% and 0.4% (see Table 2-1), so the effect of ash content on pyrolysis products was neglected in this work.

2.4.3 Feedstock moisture content

The presence of water in the biomass will influence how the biomass behaves in the reactor, as well as the physical properties and the heating value of the recovered pyrolysis liquid. Drying is usually essential as the presence of water in the feedstock delays the onset of pyrolysis [37, 38]. Wetter biomass takes longer to reach pyrolysis temperature. Consequently, the extent of secondary reactions (Section 2.4.7) could be increased, which would lead to a reduction in liquid yield. Furthermore, all the feed water is included in the liquid product and this water cannot be removed by conventional methods such as distillation [15]. The effect of water is complex in that it affects stability, viscosity, pH, corrosiveness, and other liquid properties (Section 3.3.1).

Since feed moisture content (Section 4.5.4) is altered by processing prior to entering the pyrolysis reactor it is discussed as part of the process parameters.

Little work has been done on the effects of feed stock moisture content on the stability and physical properties of pyrolysis liquids. By increasing the moisture content of the feedstock it will be possible to produce liquids with higher water contents; however, although the increased water content lowers the viscosity of the liquid it also lowers the heating value. The effects of feed moisture content on product yields and liquid property will be addressed in Chapter 5.

Table 2-2. Quantitative GC analysis of pyrolysis liquids [39]

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

* - indicates chemical identified but not enough to quantify

2.4.4 Feedstock particle size

Heat is transported to the surface of the particle by conduction. 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. Fig. 2 [40] below shows the processes that govern the biomass particle pyrolysis.

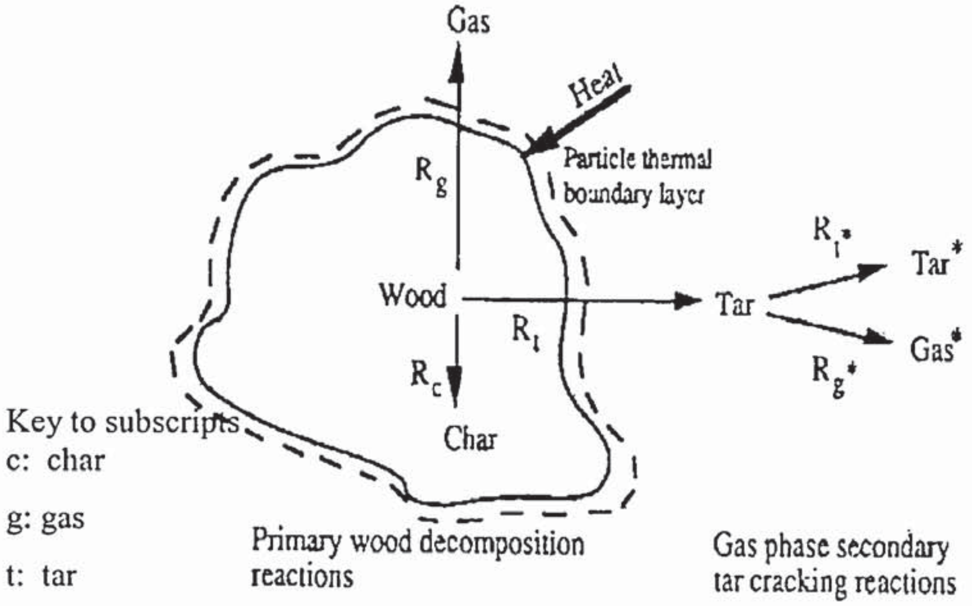


Figure 2-2. Decomposing wood particle including reactions involved [40]

The size of the biomass particles will therefore influence the rate at which they can be heated [41, 42, 43]. As particle size increase, the heat conducted into the biomass interior will be reduced. Nik-Azar et al. [44] studied the pyrolysis behaviour of beech-wood and found that the yield of bio-oil for particles with a diameter of 53-63 μm was 53%, the yield for the particles with diameter of 270-500 μm was only 38%. The liquid yields reduce with particle size increase. The reason for this is that secondary reactions within the particle become increasing significant with particle size increasing. Scott et al. investigated the effect of particle size on organic liquid yields from a 100g/h fluidised bed reactor at 500°C [15]. Using aspen poplar of particle sizes 44-105μm, 105-250μm and 250-500μm, they found that the best organic liquid yield was obtained using 105-250μm. Organics yields of 51.0, 58.9 and 53.0 mf wt.% were obtained for each size fraction respectively. Unfortunately char yields were not accurate due to the char being blown out of the reactor, before complete reaction. Thus the char could have been a mixture of unreacted wood, partially reacted wood and char. It may be that higher organic liquid yields would have been obtained if all of the wood had reacted. Results obtained by Scott et al. reported later have organic liquid yields of 66 mf wt.% for poplar at 500°C [15].

The liquid and gas yields increased with the heating rate increasing from 20 to 100 °C/ min at maximum temperature of 600 °C [45]. The influence of pyrolysis reaction parameters such as heating rate has been shown to determine the yield and composition of the products.

2.4.5 Reaction temperature

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

The influence of reactor temperature on the fast pyrolysis of various biomass types has been investigated by most researchers [46, 47, 48, 49]. A kinetic model result for the production of liquids from fast pyrolysis of biomass is illustrated in Figure 2-3 [50].

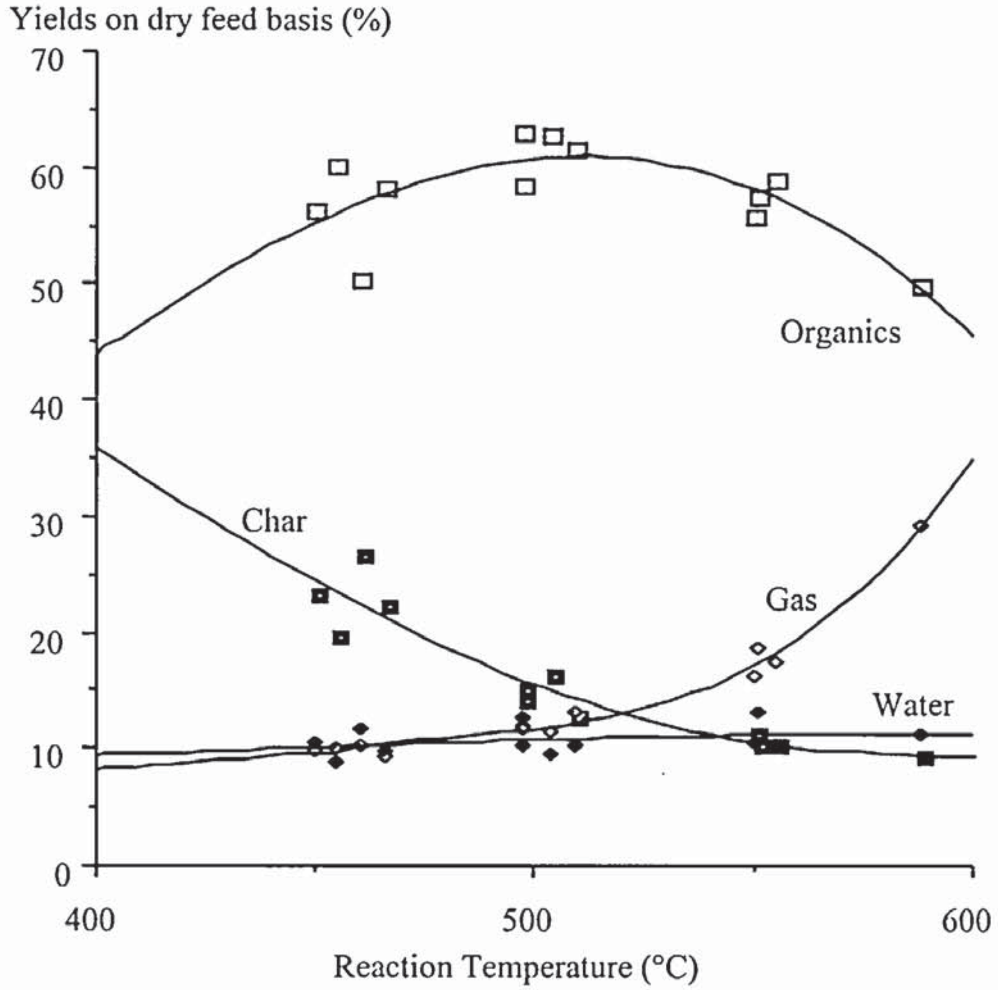


Figure 2-3. Fast pyrolysis product yields versus temperature [50]

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 wt.% at 450°C for cellulose [46], to 85 wt.% for sweet gum hardwood at 627°C [51]. 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 [52, 53, 54]. Gas and water yields remain relatively stable up to around 500°C. Above 500°C, gasification and secondary reactions tend to increase, which leads to increased cracking of the larger molecules resulting in the production of smaller molecules such as water and gas [55, 56].

Toft [26] analysed the product yields from a number of biomass feedstock types. He confirmed that each biomass feedstock would have a maximum yield of organics (see

Figure 2-4) and that the temperature at which this occurs depends on the feedstock type.

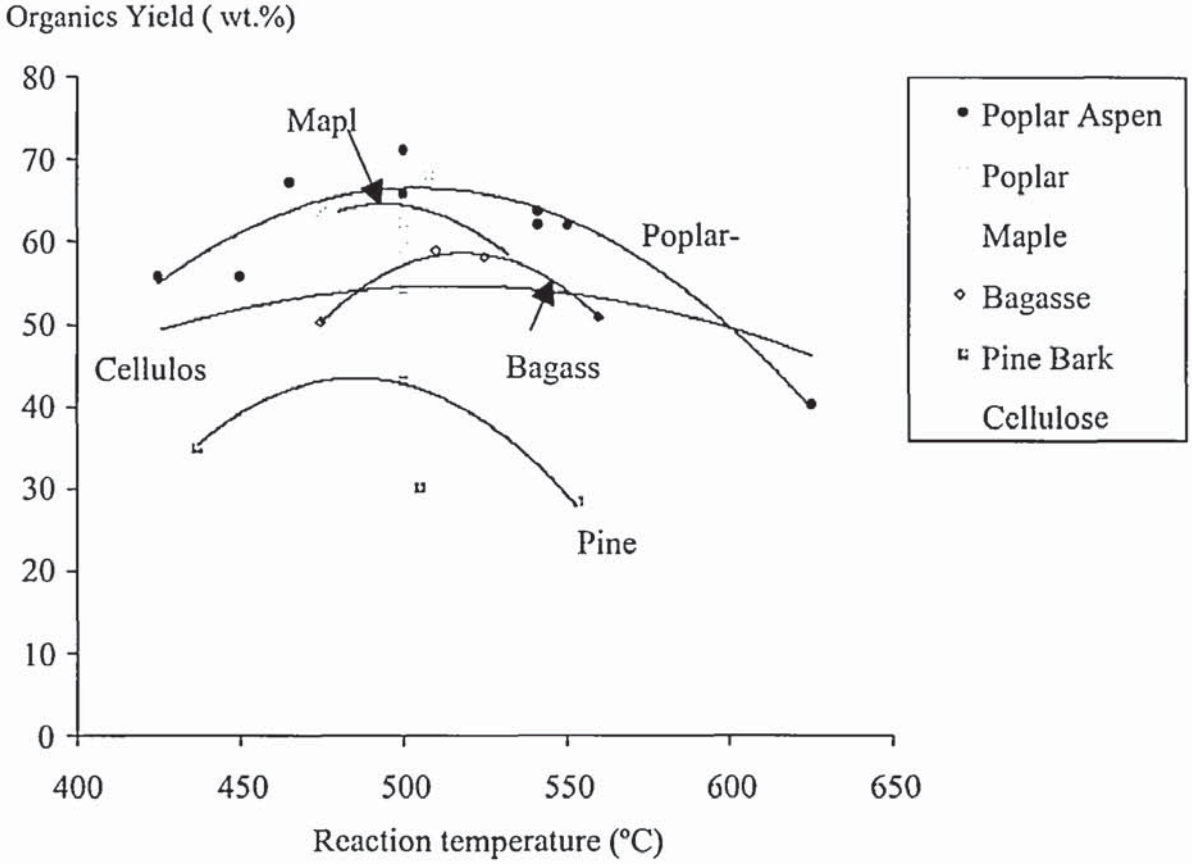


Figure 2-4. Variation of organics yield with feedstock type [26]

Toft modelled the pyrolysis products for a generic wood type, i.e. designed a model, which was applicable to any biomass type over any fast pyrolysis temperature. He compiled data for many feedstock types over the temperature range 400-650°C and derived relationships by regression analysis as shown in equations 2-1 to 2-4, which are plotted in Figure 2-5.

Organics % $= -16.4\times 10^{-6}(T)^2 + 0.0164(T) - 3.47$ **Equation 2-1**

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

Char % $= 8.60\times 10^{-6}(T)^2 - 0.0099(T) + 2.95$ **Equation 2-3**

Water % $= 4.70\times 10^{-6}(T)^2 - 0.0049(T) + 1.20$ **Equation 2-4**

where T = Reactor temperature, °C

These equations adequately model any wood type; however, care should be taken in their use since some feedstocks may perform significantly worse (or better) than the equations and therefore could produce poorer (or better) results than expected. It would appear that there is a mistake in equation 2-4, since analysis gave negative yields of water. However, correspondence with Toft has found that the equation is correct for the data that he used. It should be noted that, in subsequent modelling work, Toft found that it is best to calculate the water by difference; this also has the advantage that 100% closure is always achieved. The water yields shown in Figure 2-5 are calculated by difference.

Toft differentiated the organics equation 2-1 to determine the temperature at which the maximum yield of organics occurred. He found the maximum yield of organics was 63.0 wt.% at 500°C.

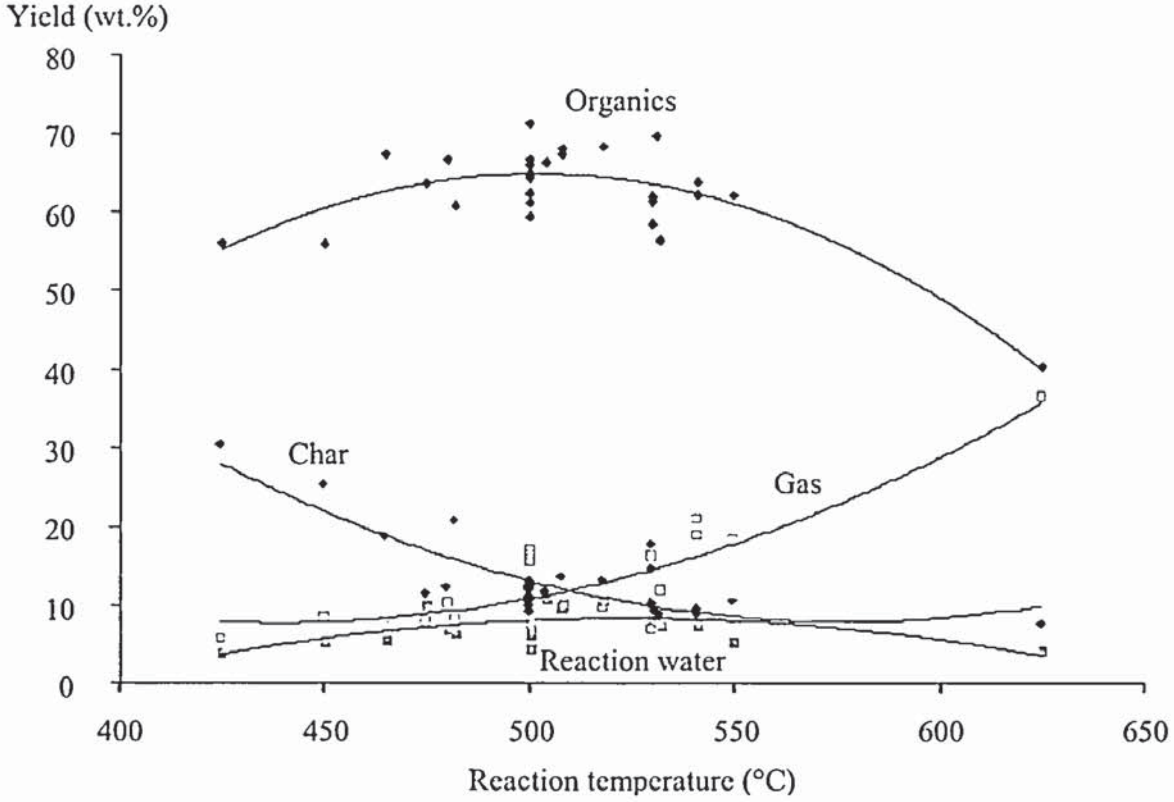


Figure 2-5. Fast pyrolysis yields from generic wood [26]

Scott et al. [46] pyrolysed cellulose and eastern red maple using two different reactor configurations at two institutions to assess the influence of temperature on the yield of products. Good agreement was achieved between both reactor systems for both feedstocks. Their conclusions were that, if less than 10% of the particle weight was lost before the particle temperature reached 450°C, and then the yields of char, oil and gases will be determined by the reactor temperature. Scott calculated, using kinetic and heat transfer modelling of Lidén [57] and kinetic data produced by Thurner and Mann [58], that for a 2mm diameter hardwood particle in a fluidised bed reactor the above criterion would be satisfied.

Thus for any reactor, providing the vapour residence times (see Section 2.4.6) are the same, the product distribution will be a function of reactor temperature alone. For fluidised bed reactors, providing particles of less than 2mm are used, the pyrolysis temperature will determine the product yields. The final product distribution and composition will then depend on the history of the vapour phase and secondary vapour kinetics.

2.4.6 Vapour residence time

Vapour residence time is a measure of how long the pyrolysis vapours remain in the hot reactor environment (see section 4.2.3). Although the yield of pyrolysis products is a function of reactor temperature, the history of the vapour phase will also influence the amount of secondary reactions (see section 2.4.7) that occur. To avoid secondary reactions the pyrolysis vapours should be removed from the reactor environment as quickly as possible.

The effect of vapour residence time was investigated by Scott and Piskorz [16]. These workers studied the organic liquid yield from the fast pyrolysis of poplar wood. The wood had a particle size of less than 595μm and was pyrolysed at 500°C. The results, shown in Figure 2-6, show that short vapour residence time increases the yield of organic liquids.

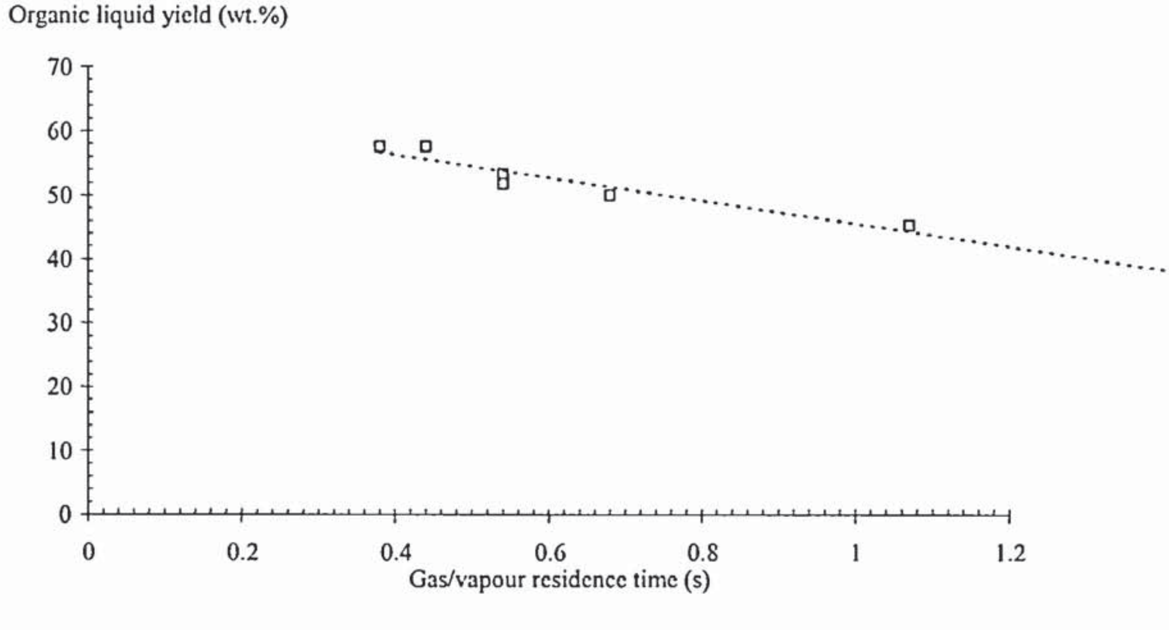


Figure 2-6. Organic liquid yield with gas/vapour residence time [16]

Peacocke investigated the effect of gas/vapour residence times from 1 to 10s on the yields of organics and water from ablative pyrolysed pine wood [59]. He found that as the gas/vapour residence time increased, the yields of water increased up to an asymptotic maximum of 24 wt.% after 10s (shown in Figure 2-7). He also suggested that the yield of organics reached an asymptotic minimum of 47 wt.%. It may be that the high yields of water are due to the low gas vapour temperatures (280-420°C) present in his reactor, which may have initiated condensation reactions before the products left the reactor. Peacocke does suggest that in future work the temperature of the product gas/vapour should be increased by preheating the carrier gas and increasing the flowrate to reduce gas/vapour residence time and hence water yields.

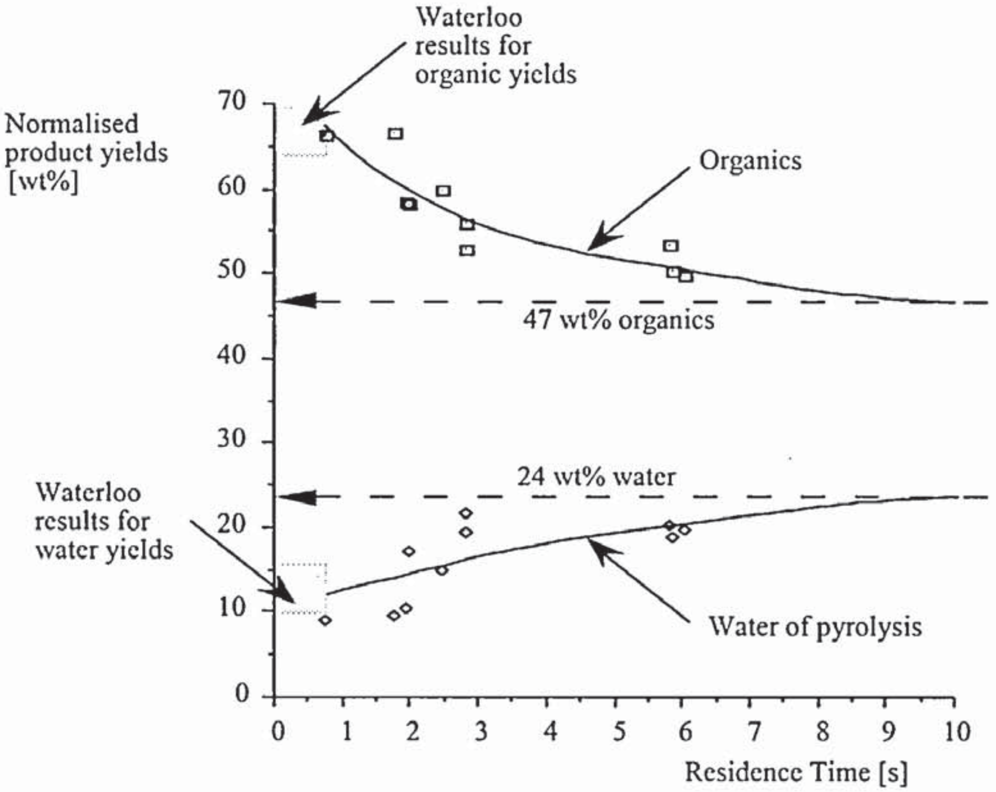


Figure 2-7. **Yields of organics and water versus vapour residence time [59]**

Thus the residence time should be kept as low as possible to avoid lowering of the organic liquid yield. Most fluidised bed reactors tend to operate on high gas throughputs to maintain fluidisation; this also helps to maintain low residence times. Thus it is unlikely that high vapour residence times will be a problem in this work since all pyrolysis reactions are carried out using a fluidised bed reactor (Chapter 4).

2.4.7 Secondary reaction

Broido Shafizadeh model was expected to be the most general chemical pathway of biomass pyrolysis (See section 2.2).

If the volatiles or vapours are rapidly cooled, they condense to give pyrolysis oil; the 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 are maintained at high temperature above 500 °C they will further crack to small molecular or permanent gases, those are so-called secondary reaction in pyrolysis process.

A longer residence time can cause secondary cracking of primary products at temperature above 500 °C and condensation reactions at vapour product temperatures below 400 °C. Secondary reactions lead to the production of low molecular weight products and gas and should be avoided for the production of speciality chemicals [25]. To avoid secondary reactions the pyrolysis vapours should be removed from the reactor environment as quickly as possible.

Both residence time and temperature control are important to 'freeze' the intermediates of most chemical. Research has shown 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 [24].

2.4.8 Product recovery parameters

Most workers have used some system of rapid cooling of the vapours in order to collect the pyrolysis liquids. Graham specified rapid cooling of the product vapours (<40ms) to preserve speciality chemicals [60]. The rate of cooling depends on the system employed, with direct cooling offering the best heat transfer characteristics, but possible problems in subsequently removing the coolant. Indirect heat exchange gives low temperature gradients and could fractionate the larger molecular weight components, which collect first. Further discussions see section 4.11.

2.5 SUMMARY:

The process parameters, which affect fast pyrolysis product yields, have been reviewed and discussed in this chapter.

The process parameter, which has the largest influence on product yields, is reactor temperature. It has been found by most fast pyrolysis workers that fast pyrolysis of the vast majority of biomass feedstocks will result in a maximum yield of liquids at 500°C. Thus the temperature range of 450–550°C was chosen to determine the maximum liquids yield in this work.

It is likely that the way in which the pyrolysis liquids are collected will have a substantial effect on the liquid quality, especially for fuel applications. The collection system used in this work will be described and discussed in Section 4.11.

Many researchers have found that feed moisture content has an effect on the pyrolysis process, but little work has been done regarding the effects of feed stock moisture content on the stability and physical properties of pyrolysis liquids; this topic will be addressed in Chapter 5.

Beech and spruce wood were chosen as the main types of feedstock in this work, as wood gives one of the largest liquid yields and as it has a very low ash content compared with other types of feed stock, thus the effect of ash content on pyrolysis products was neglected in this work.

CHAPTER 3 . BIO-OIL AND UPGRADING

The oil's unusual characteristics are discussed in this chapter. The advantages and disadvantages of bio-oil are discussed by comparison with petroleum and petroleum products. The drawbacks of bio-oil are the reason why upgrading has been considered by many research groups and improvement of bio-oil stability is going to be investigated in this work.

3.1 BIO-OIL

Bio-oil consists of water and organic compounds that are condensed and collected after the pyrolysis step, usually after char is removed from the hot gas and vapour stream (Section 3.6.1.1). Bio-oil is a black or cloudy brown, thick but flowing, acidic liquid that is a very complex mixture containing molecular fragments of the cellulose, hemicellulose and lignin polymers that were able to escape the pyrolysis environment by volatilization or by being part of a liquid droplet small enough to be entrained in the gas stream [61]. The physical properties of bio-oil as well as the methods for their measurements have been described in several publications [30,5,62,63,64,65].

3.2 CHEMICAL COMPOSITION

Bio-oil is a free flowing liquid with about 40 significant chemical components greater than 0.1% of the wet oil, plus more than 1000 additional compounds in trace quantities [66, 67,68,69]. Table 3-1 shows the main components of the liquid.

Table 3-1. The main composition of the bio-oil [67,68,69]

Major Components	*Percent by mass*
Water	15-30
Lignin fragments: insoluble pyrolytic lignin	15-20
Aldehydes: formaldehyde, acetaldehyde, hydroxyacetaldehyde, glyoxal, methylglyoxal	10-20
Carboxylic acids: formic acid, acetic acid, propionic acid, butyric acid, pentanoic, hexanoic, glycolic acid, (hydroxy acetic)	10-15
Carbohydrates: cellobiosan, α- D- glucose, fructose levoglucosan, oligosaccharides, 1.6 anhydroglucofuranose	5-10
Ketones: acetol (1-hydroxy-2-propanone), cyclo pentanone	1-5
Phenols: phenol, furfural, methyl furfural,	2-5
Alcohols: methanol, ethanol, ethylene glycol.	2-5

3.3 BIO-OIL UNUSUAL CHARACTERISTICS

Bio-oil has some unusual behaviour due to some properties tend to change with time and temperature.

3.3.1 Water content

Water in the bio-oil comes from moisture in the biomass feed and is also a product of the pyrolysis reactions. The water content of pyrolysis oil is commonly around 15-30% [64]. The water content in the oil increased with the length of oil storage and high storage temperature resulted in greater changed in the oil water content [70].

The reason of oil water content increased with temperature and storage time was discussed by many researchers [64,70], they suggested that condensation or dehydration reactions occurred during oil storage, especially when oil is exposed to the higher temperature (see section 3.4).

Oil water content is the main factor for a number of other characteristics.

- Water in the oil reduces its viscosity. 1.9–2.6% of volatiles were kept in the bio-oil due to water in the oil. Water dissolves volatiles then makes lower average molecular weight. Thus leading to lower oil viscosity [65].
- Water in the oil also affects its pH value, the pH of the oil increases if water is removed, as oil can be considered as mixtures of water and water-soluble organic compounds with water insoluble materials [65].
- The density increases with a decrease in the water content.
- Water in the oil lowers its heating value. The heating value of the bio-oil decreases as the oil water content increases.
- High oil water content leads to phase separation.

Water in the oil is difficult to remove. Evaporation or distillation at normal temperatures of around 100°C or higher can cause significant and potentially deleterious physical and chemical changes in the bio-oil liquid. Lower-temperature drying is not successful due to the nature of the relationship between water and the organic component to which the water seems to be chemically combined. Water may be present as water of hydration, or may be in the form of an emulsion. Furthermore, a number of the volatiles in the bio-oil escape more easily than water during drying [71].

3.3.2 Oil viscosity

The oil viscosity increased with the length of oil storage and high storage temperature resulted in greater change in the oil viscosity [70].

A wide range of viscosities have been reported for bio-oil that reflect differences in the average molecular weight or extent of cracking of the oligomers and monomers to monomer fragments.

Molecular weight increase with storage time is the main reason for higher oil viscosity. Czernik [70] found that with progress of storage of the oil, the proportion of low-molecular-weight material decreased while that of high-molecular-weight material increased. This effect is more distinctive for oil stored at higher temperatures. The increase in the amount of the high-molecular-weight fraction resulted in an increase in the weight average molecular weight (Mw) of the oil. The increase was faster over the initial period of storage at high temperatures, that is, the weight average molecular weight increase obtained after storage for 12 weeks at 37 °C was comparable to the increase that occurred after 4 days at 60°C or 6 hours at 90°C before levelling off occurred.

Char fine in the oil are believed to be another reason for increasing oil viscosity as char accelerate the polymerisation reactions [72].

Viscosity is one of the most important parameters in the characterisation of fluids in general and of bio-oils in particular. It is crucial for the design of supply facilities and storage tanks. It is a very important quantity for the plant designer for the calculation of pump requirements because of the exponential dependence of viscosity on temperature. A small increase in temperature can substantially change the viscosity.

High viscosity leads to high pressure drops in pipelines, which may potentially lead to an increased risk of leakage or even pipe rupture with consequence of higher equipment costs.

Some research has been done on reducing oil viscosity:
The addition of alcohol such as methanol to pyrolysis oils decreases the viscosity [20]. Adding water to pyrolysis oils decreases the viscosity about as effectively as methanol on a volume basis. Further discussion can be found in chapter 7.
Removal of ash and micro char through hot filtration seems to have a large influence on viscosity [72] (Section 3.6.1.1).

3.3.3 Char content

Char is a coarse powder with particle sizes ranging from 40 to 50 μm to several millimetres; the particles are mainly needle-shaped and have similar size and shape characteristics as the feed. A fraction of the char commonly bypasses the char removal equipment such as cyclones and passes through to the liquid collection system. The char content of the pyrolysis liquid is in the range of 0.1 to 3% depending on the pyrolysis technology and on the efficiency of char removal from pyrolysis vapours.

Char is highly undesirable because:

- Char tends to settle at the bottom of vessels in the form of sludge, can obstruct the flow and cause erosion of injection nozzles.
- Char is also a source of alkali present in bio-oil at a level too high for certain applications (Section 2.4.2).
- Char in the bio-oil probably lead to oil ageing characteristics, as char appear to catalyse polymerisation reactions during storage; this results in viscosity increases and possibly agglomeration of the suspended char [72,73].
- Char and ash may lead to a less pleasing appearance of the oil.

Separation of char from the liquid is poorly researched and reliance is usually placed on primary separation in the vapour phase, generally using one or two cyclones (Section 4.2.2). Hot-gas filtration has also been tried in some cases to remove the char fines (Section 3.6.1.1).

3.3.4 Lignin content

Lignin is one of major component of wood; roughly content of lignin in wood is 20-30% by weight. Lignin is a random three-dimensional branched polymer composed of phenolic units [74], due to the aromatic content of lignin, it degrades slowly on heating (i.e. decomposition takes place over a wide temperature range), hence the apparent thermal stability of lignin during pyrolysis; it contributes to a major fraction of char formation. Cleavage of principal bonds in lignin requires oxidation. [75,76].

It is well known that water addition to the fast pyrolysis liquid leads to separation into an aqueous and an organic phase. The latter is a sticky brown tar containing the high molecular weight compounds derived from lignin. Pizkorz et al were the first to record a ^{13}C spectrum from this tar and as it looked similar to that of lignin, the material was given the name "Pyrolytic lignin" [77,78].

The pyrolytic lignin represents the water-insoluble part of the pyrolysis liquids. The yield of pyrolytic lignin is in the range of 25%, the exact yields being unavailable. Meier analyzed the pyrolytic lignin by using techniques common to lignin chemistry and found that the elemental composition and hydroxyl contents were similar to that of lignin isolated from wood. However, the methoxyl contents were drastically reduced through pyrolysis. Pyrolysis lignin has very high weight-average (Mw = 896-2431g/mole) and number-average (Mn = 136-309g/mole) molecular weights [77].

Such large molecules existing in the liquid can be the reason for several undesirable properties of bio-oil such as phase separation and high viscosities. One of possible solutions is finding feedstock, which have lower lignin content, as pyrolytic lignin seems to be similar to traditionally isolated lignin [77]. Changing process conditions to reduce the nature of the pyrolytic lignin will be explored in this work (See section 6.8).

3.3.5 Stability

The stability of bio-oil was examined by monitoring the changes in its density, viscosity and pH. It was found that the pH and density of the bio-oil remained almost constant with time [65], thus changes in the viscosity of the bio-oil are the most important factor that needs to be monitored to assess its stability. The viscosity became the most commonly used property for determination of the oil's stability [79, 80, 81, 82]. Aston University has developed the AVI method for this purpose (See section 4.9.2.3).

The other unusual aspect of these oils is their carboxylic acid content, e.g. formic and acetic acids, which causes the oils to have acidity which causes the pyrolysis oils to be corrosive to mild steel, aluminium, etc. Aldehyde also contributes to the low pH of 2-3.

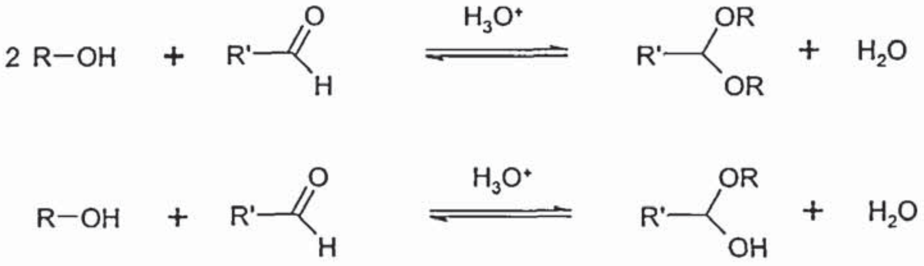
3.4 SOURCE OF INSTABILITY OF BIO-OIL

The liquid contains several hundred different chemicals in widely varying proportions. It is an ill-defined mixture of water, char and oxygenated organic compounds.

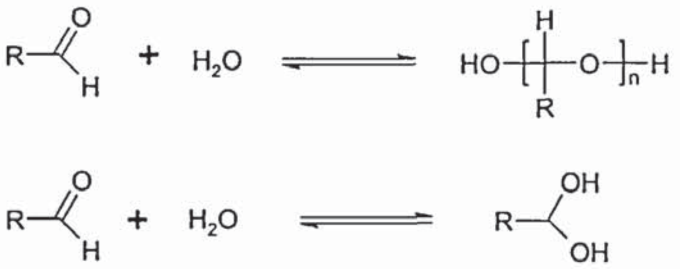
Pyrolysis liquids are inherently unstable, due to the reactions occurring within the complex mixture of several hundred chemicals including phenols, acids, aldehydes, ketones and other oxygenated hydrocarbons in varying concentrations [83]. The pyrolysis oils are chemically reactive with them and will polymerise with time, usually with the formation of additional water as a by-product of the reactions. After prolonged storage, the oils tend to increase their molecular weight as the result of chemical reactions [83].

♦ The reaction of alcohols with organic acids forms esters and water.

♦ Aldehydes and alcohols react to form acetals or hemiacetals as shown by the following reaction:



♦ The aldehyde groups are also very reactive and can react with each other to form polyacetal oligomers and polymers, this is the reason for viscosity increasing.



These reactions result in an unwanted increase in viscosity and a decrease of volatility.

The polar nature of many of the oxygenated compounds allows a very significant amount of water to dissolve in the oils. The viscosity is rapidly reduced as the water content is increased. However, too much water in the oil causes the biocrude to separate into a thinner aqueous-rich phase and a thicker organic-rich phase. This phase separation is temperature dependent and can be difficult to detect visually, because the phases are both quite dark.

3.5 COMPARISON TO PETROLEUM FUEL

The concept of classification of pyrolysis liquid was proposed by Diebold [5], but as yet, no ASTM (American Society for Testing of Materials) Boiling Point or Cetane Number has been found for pyrolysis liquid. All those properties result from the chemical composition of the oil, which is significantly different from that of petroleum-derived fuels. A comparison with three petroleum products is used to illustrate the differences and similarities for a range of physical properties in table 3-2 [84].

Table 3-2. Physical Properties of Petroleum and Pyrolysis Liquid

	Motor Gasoline [a]	*No. 2 Petroleum Fuel* [a]	*No. 6 Petroleum Fuel* [a]	*Pyrolysis Liquid* [b]
Fuel Type	Transport Fuel	General purpose heating in burners	Heavy oil requiring pre-heating for burning and handling	Fuel oil for static applications
Density (kg/m^3) @ 15°C	0.712-0.748	0.806-0.922	0.934-1.064	0.826
Kinematic Viscosity (mm^2/s)	0.4-0.6 @ 38 °C	2.0-3.6 @ 38 °C 1.9-3.4 @40 °C	200-2000 @ 38 °C	233 @ 25 °C 134 @ 40 °C
Pour Point (°C)		-6		-23
ASTM Boiling Range (°C)	40-225	170-145	170-500	-
Ash Content % by weight	0	0	0.01-0.5	0.1

Notes: [a] Figures taken from Perry [85], [b] Figures taken from Bridgwater [86].

3.5.1 Economic assessment of bio oil-compared with petroleum

According to Bridgwater [87], the economics of fast pyrolysis to produce pyrolysis oil have been extensively studied and reported. A review [87] of these independent studies with different assumptions revealed conclusions that pyrolysis oil can be produced for between US$0.13 and $0.16 per litre of wet oil ($6.50 to $7.0/GJ – LHV), with feedstock costing between $44 and $60 per dry tonne [88, 89, 90].
With congregation, the cost dropped to $0.11 per liter ($6.00/GJ) with feedstock costing $44 per dry tonne [91].

Assigning zero cost to feedstock as in the case of waste biomass, the predicted production costs decreased to between $2.00 and $3.00/GJ [5].

The production of pyrolysis oil for fuel application would be economically attractive with low cost, waste feedstocks. If fuel taxes can be avoided, the economics for pyrolysis oil appear to be excellent in many site-specific cases, especially if the oil can be a replacement for a better fuel oil. Finally, the projected cost of bio-oil is related to feed cost and size of unit [92].

3.5.2 Advantages

A major advantage is that pyrolysis liquids are carbon dioxide neutral, on combustion only releasing carbon dioxide less than or equal to that taken up by growing the biomass [93]. A secondary advantage is that bio-oil is a clean and consistent fuel free from potentially environmentally damaging substances such as sulphur, chlorine and to a lesser extent nitrogen, which is beneficial as sulphur present in combustion gases contributes to acid rain. Thus they contribute very little to the greenhouse gases or other regulated air pollutants. This is favourable from an environmental point of view. Neither does bio-oil contain vanadium and nickel [94]. It can therefore be considered "environmentally friendly" in terms of carbon dioxide recycling and sulphur emissions.

The sulphur content of bio-oils is naturally low, due to the low sulphur content of biomass. This low sulphur content is one of the positive aspects of bio-oils.

One of the variables with bio-oils will be the nitrogen content of the oil, which will reflect the variable protein content possible with biomass. Biomass that has a significant content of green, living plant cells (e.g. green grasses) will have a higher nitrogen content than biomass having a large content of dead plant cells (e.g. straw and wood). The nitrogen contained in the bio-oils will contribute to NO_x emissions.

Many lower cost raw materials or industry wastes could be utilised to produce bio-oil [95]:

- Trees, naturally occurring or originally planted for timber, which no longer have any value due to poor form, storm damage, neglect or normal silvicultural processes.
- Trees, which were planted especially as a fuel crop, e.g. short rotation coppice or forestry.
- Forest residues are likely to be a source of woody biomass fuel as the raw materials are available on site at very low cost.
- Industry wastes can be used as source materials of bio-oil. There are a whole variety of industries processing wood into high value products such as timber, paper, particle and fibreboards etc. Many of these production processes are unable to use all of the woody materials imported to the plant. These residue materials could be slabwood, sawdust, offcuts and shavings.

Bio-oils from biomass are particularly interesting as energy because they have, in comparison to gases and solids, a high energy density and offer advantages in transport, storage, flexibility of use and retrofitting. Another important point is the possibility to use these liquids in existing facilities such as boilers, diesel engines or turbines.

3.5.3 Disadvantages

In contrast to petroleum fuels, bio-oils contain a large amount of oxygen. The oils produced by the pyrolysis of biomass, due to high levels of oxygen, may be highly viscous and corrosive, relatively unstable, and may exhibit a poor heating value [96,82,97].

Bio-oil contains 10-15% carboxylic acids including formic acid, which make the bio-oil acidic and give it a pH of usually less than 3, which may give corrosion problems. Bio-oil contains a large number of oxygenated compounds in polar and non-polar form. The polar nature of many of the oxygenated compounds allows a very significant amount of water to dissolve in the liquid to give a micro-emulsion form that makes the bio-oil unstable especially with time and elevated temperature. In addition to this, double bonds in oxygenated compounds readily polymerise and form long molecules, which increase the viscosity of the liquid. Water in bio-oil results in low energy density and micro-fine char makes bio-oil dark.

Although bio-oil experiences a rapid growing in its utilisation, there are perceived and real problems in handling and storage associated with its propensity to degrade over time, notably viscosity and phase separation.

3.6 BIO-OIL UPGRADING

Improvement of the principle physical and chemical characteristics is often referred to as "Upgrading".

As economic studies revealed, liquids obtained from biomass by flash pyrolysis processes have the potential to enter the market of liquid fuels [98]. However, bio-oil has a number of special features and characteristics, such as instability, acidity, and high oxygen content, which require consideration in any application including production, storage, transport, and utilisation. The properties that negatively affect bio-oil fuel quality are foremost low heating value, incompatibility with conventional fuels, solids content, high viscosity, and chemical instability. The conclusion was that some undesired characteristics could be improved using simpler methods and some are more intractable but none are insoluble while each has its own drawbacks. The upgrading methods are reviewed below.

3.6.1 Physical upgrading of bio-oil

The properties, which are considered capable of being improved by physical means, are solids content (char, other solids), pH, ash content (metals), viscosity, sediment, water content and heating value.

3.6.1.1 Hot-gas filtration for char removal

In the pyrolysis process a residual char is formed. A positive aspect of the char in the pyrolysis oil product is that it increases the overall energy yield and the heat of combustion of the oil. However, there are several negative aspects of having the char in the oil, including sedimentation and sludge formation during storage, increased viscosity, plugging of small orifices, higher alkali content in the char and different burnout rates for the char compared to the oil droplets. In addition to these problems, Agblevor et al. found that the presence of char in the oil adversely affects oil stability [99] (See section 2.4.2).

Much of the char can be separated in cyclone separation in which centrifugal forces cause the separation.

Important considerations in the cyclone design are that the efficiency of solids removal decreases with decreased solids diameter and increases with the square of the velocity. Overall there is poor efficiency of separation of particles less than 10 µm so that a small but significant portion of pyrolysis char is not removed from the pyrolysis oil in cyclone separations.

One option for removing the char is to filter the oil product after condensation [100] but this has not been very successful. This step forms cleaner oil but oil also tends to agglomerate around the particles and to form sludge, which leads to high-pressure drops developing across the filter and oil losses due to removal of some of the oil with the char sludge. The submicron char present tends to pass through the liquid filters. In addition, this cleanup allows the acids in the condensate to leach alkali from the char in to the oil product. Filtration will remove only the solids, and dissolved alkali would remain in the oil product [84].

An effective method of solids removal during the pyrolysis process is to filter the oil product before condensation. This hot vapor filtration [101] is a better option in which char is filtered prior to condensation so that no leaching of alkali into the oil occurs.

Such filtration has been performed using sintered metal and flexible ceramic fabric elements. The filters were operated at about 400-420 °C, a range that avoided oil condensation and minimized the oil yield losses caused by thermal cracking [102]. Hot gas filtration resulted in an oil yield of 50-55%, which is 10% less than that obtained in the same reactor system using cyclones. However, the ash content of the hot-filtered oil was less than 0.01% and the alkali content was less than 10 ppm. This is much lower than reported for biomass oils produced in a system using only cyclones. Removing solids also lowered bio-oil viscosity and reduced its rate of increase during storage.

The thermal cracking of pyrolysis vapours during hot filtration improved oil quality. Cracking reduced the size of oligomeric molecules, which not only decreased the oil viscosity but also affected its combustion chemistry. Diesel engine tests performed on crude and on hot filtered oil showed a substantial increase in burning rate and a lower ignition delay for the latter, due to the lower average molecular weight for the filtered oil [103]. The ablative vortex pyrolysis reactor was used to produce a pyrolysis stream, from which the char was removed using a hot-gas filter at NREL. The results showed that total alkali metal levels of around 10 ppm were reproducibly obtained, thus the hot gas filtering was effective in removing the char to very low levels, but the oil yields were lower due to excessive cracking of vapors in the baghouse [104]. This yield reduction may have been due to the fact that a hot char layer on the filter has a pronounced catalytic effect for cracking the vapours to gases in the hot zone of the reactor [105]. Hot-gas filtration has not yet been demonstrated in a long-term operation. Experiments performed to date revealed difficulties with effective removal of char cake from the filter surface when using traditional back-flush methods [106].

3.6.1.2 Emulsions

Pyrolysis oil is not miscible with hydrocarbon fuels, but with the aid of surfactants they can be emulsified with diesel oil. A process for producing stable micro-emulsions with 5-30% of bio-oil in diesel has been developed at CANMET [107]. The resultant emulsions showed promising ignition characteristics. A drawback of this approach is the cost of surfactants and the large amount of energy required for emulsification [106].

3.6.1.3 Solvent addition

Raw pyrolysis liquid contains a complex mixture of chemicals. Identification and manipulation of those functional groups that create the dynamic nature of the liquid provides an alternative route to stabilising the liquid after its production. This can be done using selectively reactive chemical reagents. The topic will be further reviewed and discussed in chapter 7.

3.6.2 Chemical/Catalytic upgrading of bio-oils

The quantity of oxygen contained in pyrolysis oils is considerably greater than the oxygen content of any other material, which could be used as fuel or raw materials to produce it [108]. This affects the energy content, and the heating value is rather low. The chemical/catalytic upgrading processes aim to remove oxygen, which is the main cause of instability and other unwanted characteristics of bio-oils. They are more complex and expensive than physical methods, but they offer improvements ranging from simple stabilisation to high quality fuel products [84]. More details will be discussed in chapter 6.

3.7 SUMMARY

Bio-oil has many unusual characteristics and drawbacks compared to petroleum fuel. Its advantages, however, may make it an important energy carrier in the future, especially when taking into account environmental considerations. Extensive research into bio-oil upgrading options therefore appears justified. Many physical and chemical methods have been discussed by other researchers. All of them have been found to have significant drawbacks. In this work new methods for improving bio-oil stability are explored. The effects of feed moisture content on bio-oil stability, partially oxygenated pyrolysis of beech wood to improve the stability of bio-oil and copyrolysis of spruce wood with methanol to improve the stability of bio-oil will be discussed in the following chapters.

CHAPTER 4 . EXPERIMENTAL

This chapter describes the equipment used and the procedures for operating the existing pyrolysis system. Problems encountered with the operation of this 150g/h system were overcome by modification of the equipment. A critical assessment of the mass balance and analytical procedures is included.

4.1 INTRODUCTION:

An existing small bench scale fluid bed, with a maximum feed rate of 150 g/h was used in this work. The procedures used in the operation of this apparatus were those employed by Hague and Salter [27]. The following modifications were implemented in order to allow experiments to be conducted under different pyrolysis process conditions.

1. Modification of the liquid collection system in order to obtain more consistent experimental results (See section 4.11).
2. Entraining gas pipeline changes were carried out in order to use it for partially oxygenated pyrolysis (See section 4.6).
3. An additional feeding tube was incorporated in the reactor for co-pyrolysis with methanol (see section 4.7).

4.2 150 g/h REACTOR DESCRIPTION AND MODIFICATIONS USED TO OVERCOME OPERATIONAL PROBLEMS

The 150g/h fluidised bed system (Figure 4-1) consisted of three sections: feeder, reactor and products collection system. The approximate dimensions and operating methods are described in the following sections.

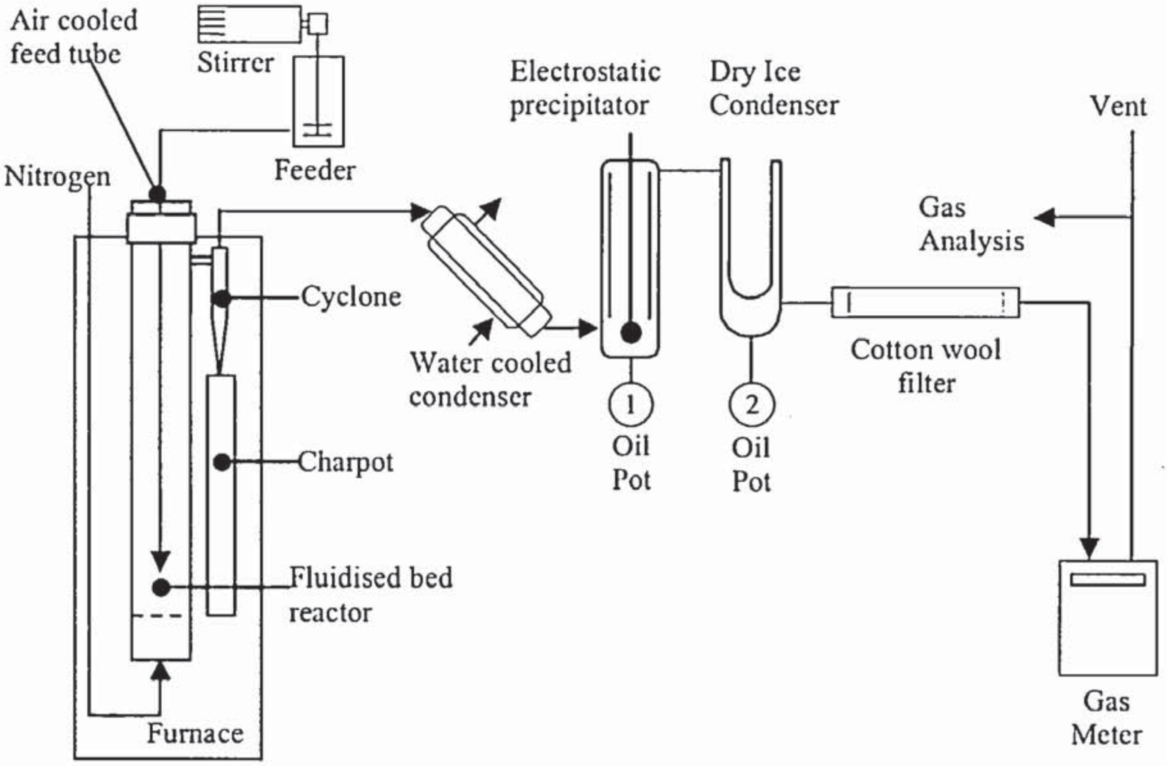


Figure 4-1. Schematic diagram of 150g/h fluidised bed reactor

4.2.1 Feeder

A detailed diagram of the feeder is shown in Figure 4-2. The feeder consisted of a tubular storage hopper (63mm inside-diameter), which could be charged from the top and sealed in order to build up a head of nitrogen over the feed stock. The biomass is slowly stirred by two paddles (60 mm length) during a run to prevent bridging of the feedstock and to maintain continuous flow of the feedstock. Biomass is entrained through the feed aperture (1.7 mm diameter hole) by a continuous flow of nitrogen into the biomass entrain tube (3mm inside-diameter and 60 mm length), which crosses the hopper at the bottom. The biomass then passes into a flexible tube linking it to the feed tube in the reactor. This feeder was designed to supply approximately 100 –150 grams per hour of biomass feed to the reactor.

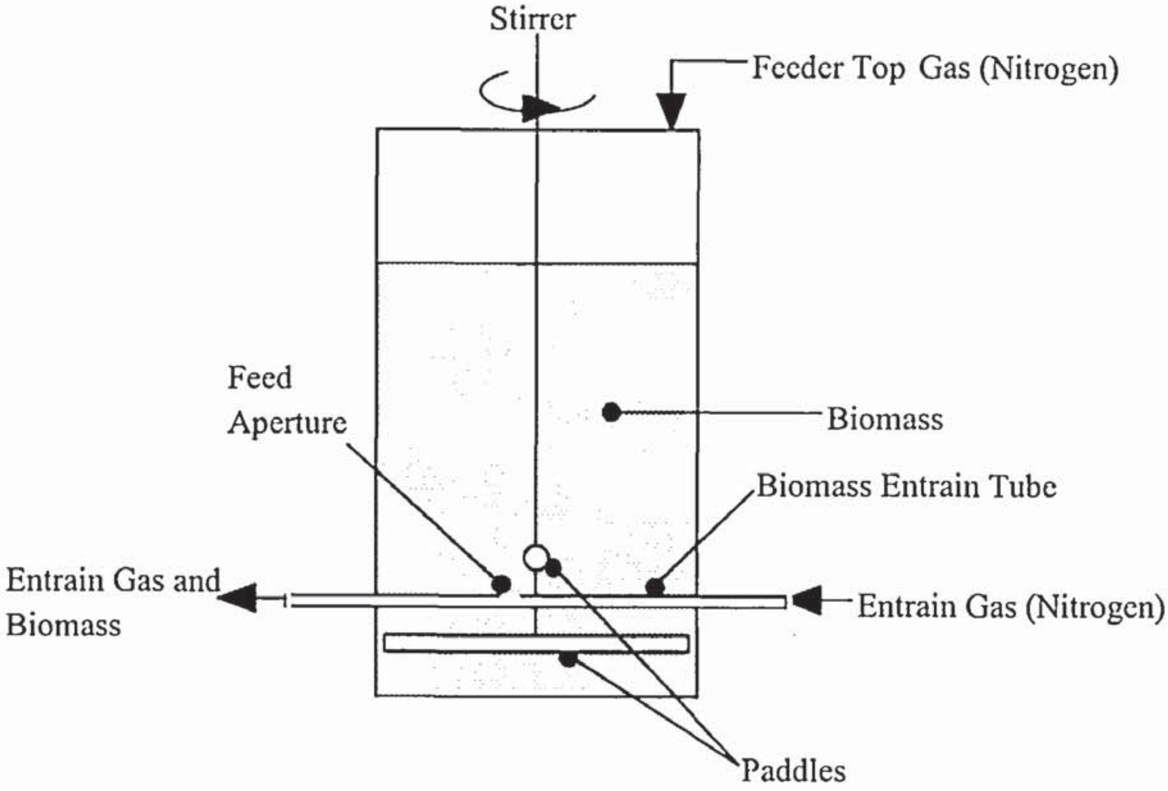


Figure 4-2. **Schematic diagram of biomass feeder**

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

The rate at which the feedstock is fed into the reactor was measured in grams per hour [g/h]. The feed rate was measured as the difference in the weight of the feeder before and after a run divided by the total run time; That is, an average feed rate was given. The total weight of the feeder rather than the weight of the feedstock alone was measured because of the nature of the biomass particles (sawdust). Their fine structure makes them difficult to pour without loss to the atmosphere, and static electricity effects add to the handling difficulties. Although the feeder could be weighed to ±0.01%, only, as this is the tolerance of balances used to weigh objects of this size and weight, this was more accurate than measuring the weight of biomass alone using a smaller balance with a tolerance of ±0.001%. In this work the feed rate was maintained at between 100 and 150g/h to maintain consistency and accuracy during a run. Low feed rates can result in poor gas analysis, and high feed rates can result in overloading of the reactor and collection system, which may lead to blockages.

The factors that affect the biomass feed rate are the following variables: feedstock particle size, moisture content, shape, preparation method and the feeder entrain tube aperture size, paddle speed, entrainment flow and feeder top pressure. The feed rate of biomass changes when one of these factors changes and must therefore be reset.

The biomass type, the speed of the stirrer, the entraining nitrogen flow-rate and the feeder top nitrogen flow rate were all able to be manipulated to alter the flow rate of biomass to the reactor and the pressure across the feeder. These are discussed separately below.

4.2.1.1 Effects of biomass type on feed rate:

The feed rate was a function of biomass type. Table 4-1 shows that the feed rate changed when a new biomass was introduced while simultaneously holding all other variables, such as paddle speed or nitrogen entrain flow rate. This result perhaps was due to different particle density of feed stock. Thus it is necessary to recalibrate the feed rate when a new biomass type is used. All results took from an average of triple experiments.

Table 4-1. Feed rate of hardwood and softwood under the same feeding conditions

Feed stock	Feed rate	Particle size	Moisture content	Entrain flow	Feeder top flow
Beech (hard wood)	137g/h	355-500 µm	Bone dry	1.5 l/min	1.2 l/min
Spruce (soft wood)	169g/h	355-500 µm	Bone dry	1.5 l/min	1.2 l/min

4.2.1.2 Effects of paddle speed on feed rate:

The feeder had mechanical paddles, which slowly rotated to prevent bridging of the feedstock and also to maintain accurate and continuous flow of the feedstock. The speed of the feeder paddles was adjustable, the normal settings being 211, 290 or 365 rpm. These corresponded to settings 1, 1.5 and 2 respectively on the 1-10 scale on the instrument. This allowed the feed rate to be altered during a run, with the rate increasing with increasing paddle speed.

4.2.1.3 Effects of feeder top pressure on feed rate:

The top of the feeder was pressurized with a small flow of nitrogen, which forces the feedstock through the feed aperture into the feed tube. This flow could be changed to either increase or decrease the biomass feed rate. By increasing the gas flow rate the pressure in the feeder is raised, thus increasing the feed rate.

4.2.1.4 Effects of entraining gas flow rate on feed rate:

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

When the feedstock is light and does not easily pass through, the entraining gas flow rate needed to be increased. 1.5 l/min entraining gas flow was enough to make normal wood, whether soft or hard, go through easily. However, for miscanthus the entraining gas flow needed to be higher than 3 l/min as miscanthus has very low particle density.

4.2.1.5 Adjustment of feed rate:

There are three main factors that require consideration in feed rate adjustment, namely feed top pressure, entraining gas flow rate, and paddle speed. Other factors such as feedstock particle size, moisture content, feed stock shape, feeder entrain tube aperture size and preparation method are fixed. The procedure for calibration was to fix two of the three main factors and to change the third one. The feeder change in weight was noted every 5 minutes, with three measurements taken for each factor, and finally an average weight change was calculated.

Figure 4-3 shows that for a IEA poplar (295-600µm) feedstock, a fixed 1.7 mm feed tube aperture, an entraining gas flow rate of 1.5l/min and a feeder top gas flow rate of 0.25 l/min, the feed rate is approximately twice as sensitive to stirrer speed than to feeder top flow rate. The influence of pedal speed and feeder top flow rate are useful since they can be altered during the run to increase or decrease the feed rate [27].

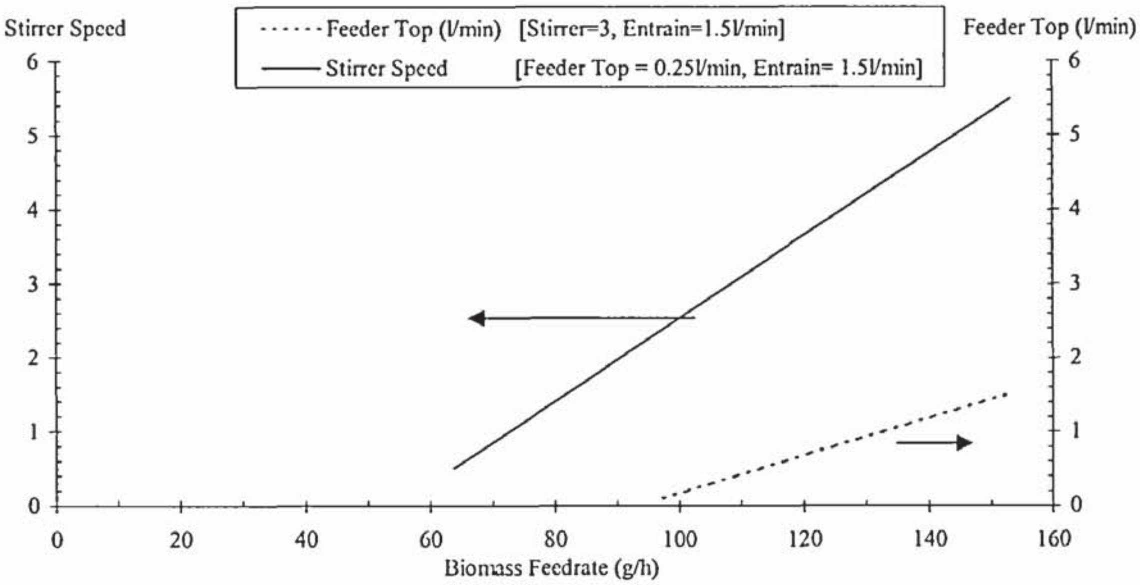


Figure 4-3. Calibration relationship for feeder [27]

4.2.2 150g/h Reactor

Figure 4-4 shows the schematic diagram of 150g/h fluidised bed reactor. The reactor consisted of a 40mm internal diameter 316 stainless steel tube with a length of 260mm. The top of the tube was threaded allowing the top of the reactor to be removed for weighing, cleaning and to add/remove the heating/fluidising medium (sand). The top of the reactor had two apertures, one for a thermocouple and the other for the feed tube with the air-cooling line.

A K-type thermocouple was used to monitor the reactor internal bed temperature. This temperature was controlled by altering the furnace temperature. The reactor temperature, the furnace temperature and set point temperature of the furnace were all monitored throughout a run by taking meter readings every minute. The set point was manipulated to produce the desired reactor temperature. To assist with temperature control and reduce heat losses, the top of the furnace, through which the reactor assembly was suspended, was lagged.

The feed tube transports the feedstock into the centre of the fluidised bed. This feed tube is not solid but has a hollow metal coat that allows cooling air through. It is air-cooled by a pressurised flow of air, which prevents temperature sensitive feedstocks from being pyrolysed before they reach the fluidised bed (which is referred as to prepyrolysis).

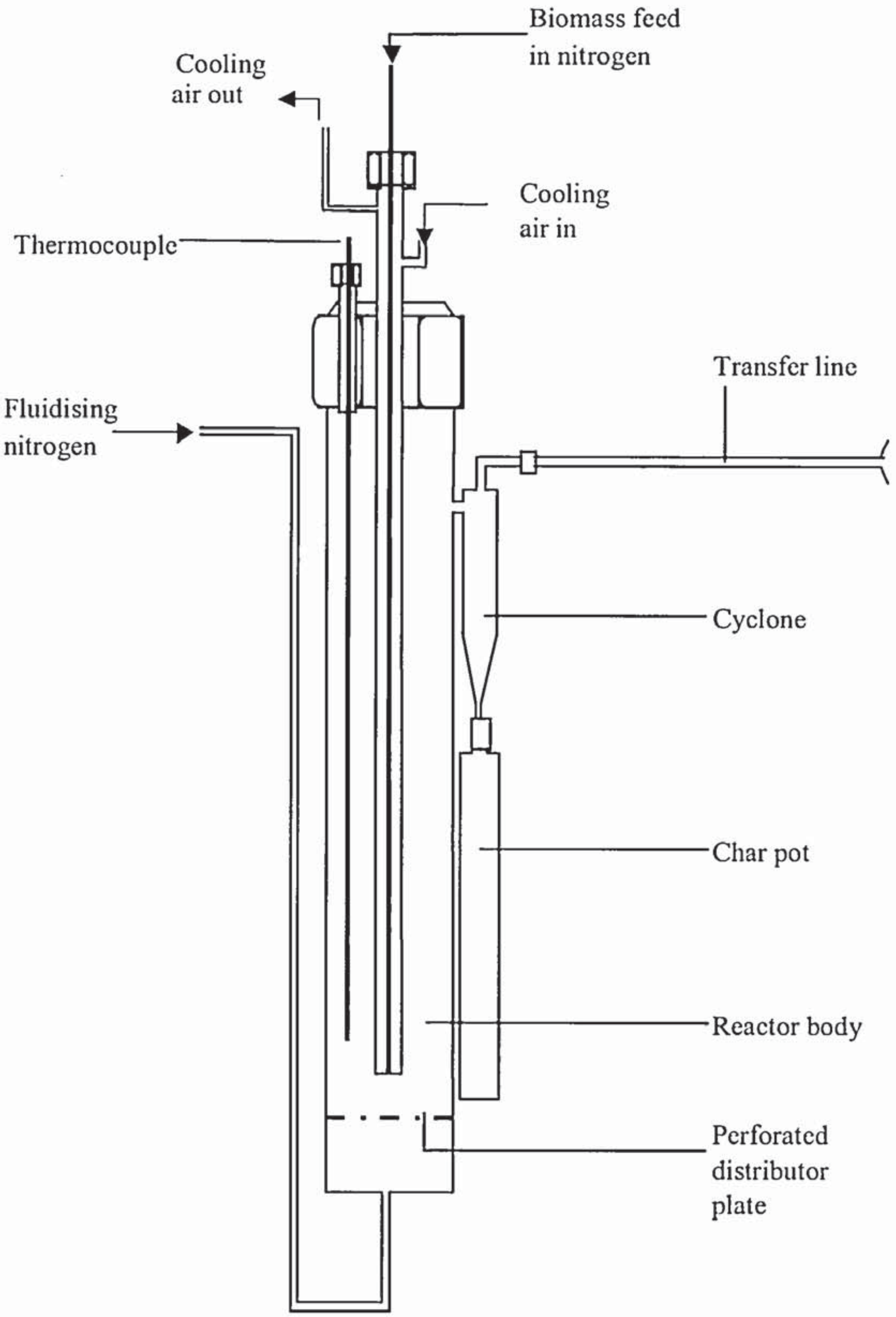


Figure 4-4. Schematic diagram of 150g/h fluidised bed reactor [27]

The heating medium in the reactor is inert sand with a particle size of 355-500μm. This particle size range is used so that the reactor operates on blow-through mode. This means that the fluidising velocity of the sand is enough to blow the pyrolysed biomass (char and vapours) completely out of the bed while the sand remains in the bed. The sand fills the reactor to a depth of approximately 8cm and expands during fluidisation to 12cm [27]. No sand loss found during experiments as the weight of sand before and after a run was constant when measured. Bed expansion was measured by cold flow model work. Also tests were done using the 150kg/h unit with just the bottom section. As increase of the fluidising gas flow rate the bed will gradually increase in size until it reaches its maximum volume just before becoming fully fluidised. The bed remains in its expanded state until it is knocked and will then drop down to its original volume with the reducing of the fluidising gas flow rate.

The sand is fluidised using nitrogen, which is preheated by the furnace in the line prior to entering the base of the reactor. The nitrogen then passes into the base of the reactor and is distributed by a sintered inconel plate with a 100μm pore size. The reactor is fluidised using nitrogen (0.5 bar, 20°C nitrogen, which is preheated by the furnace in the line prior to entering the base of the reactor). The biomass is carried down the reactor feed tube in a stream of entrainment nitrogen into the centre of the fluidised bed. Once it leaves the tube it begins to pyrolyse almost instantaneously, producing pyrolysis vapours and ultimately char. Once the biomass has reacted completely it forms char particles having similar dimensions to the original biomass, but having only approximately 8 - 15% of the original weight (See mass balance result in section 4.10.4). This char is then carried out of the fluidised bed by the fluidising gas flow.

The vapours and char then pass into the first stage of product collection, which is the cyclone and char pot. The cyclone is used to separate most of the char from the pyrolysis vapours. The pyrolysis vapours pass out of the cyclone via an outlet in the top and the char falls to the bottom of the cyclone where it passes into the char pot. The reactor, cyclone and char pot sit in a vertical tube furnace, which maintains the temperature of the furnace at a set point between 400 and 600°C. The temperature of the reactor is measured by a K-type thermocouple placed directly into the fluidised bed. The furnace set point is approximately 20°C higher than the desired reactor temperature; this is because energy is constantly required by the reactor to heat the nitrogen and biomass and perform the pyrolysis. There is also heat loss from the reactor that must be compensated for. Thus to maintain a constant reactor temperature there must be enough excess heat available from the furnace to meet these requirements. The furnace uses a proportional controller linked to a thermocouple, which is independent of the reactor, to maintain the set point to within ±5°C. The furnace thermocouple is mounted in the furnace wall at approximately 100mm from the top.

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

4.2.3 Hot Vapour Residence Time

Vapour residence time is a measure of how long the pyrolysis vapours remain in the hot reactor environment. There are two methods of vapour residence time measurement, namely reactor only residence time and total hot space residence time. The reactor, cyclone and char pot are all situated in the furnace and are exposed to the temperature of the furnace. Thus the vapours are kept at a constant temperature (which is that of the furnace or slightly lower) and could undergo secondary reactions (see section 2.4.7). The reactor only residence time is not a realistic view of the time/temperature exposure of the vapours, since once the vapours leave the reactor they are still exposed to the furnace temperature. In all cases the residence time reported would be the total hot space residence time since this represents a more realistic view of the time/temperature, which the vapours are exposed to. Hot vapour residence time is defined as the time between vapour formation and the time that the temperature of the vapours falls to that below which secondary reactions (see section

2.4.7) cannot occur. This is usually the first cold point in the reactor system. (The cold point started on the first water cooled condenser)

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 collective volumes of the reactor (above the distributor), cyclone, char pot and transfer line as far as the glass connector to the water condenser. The volume taken up by sand and char is discounted.

The total hot space residence time was calculated from the volumetric throughput of the reactor system divided by the total hot space of the reactor [27].

$$\text{Residence Time}_{\text{Total Hot Space}} = \frac{\left(Volume_{TotalHotSpce} - \dfrac{W_{sand}}{\rho_{Sand}(1-\varepsilon)}\right) * T_{Measurement} * Time}{1000 * T_{Reactor} * Volume_{TotalThroghput}}$$

Equation 4-1

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

ε = 0.39 [109]

$T_{measurement}$ = 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

4.2.4 Liquid Collection System

The liquid products collection system consists of two cooled condensers, an electrostatic precipitator and a cotton wool filter (see Figure 4-1). All of the liquid collection system is constructed from glass for easy cleaning and also so that the behaviour of the condensing pyrolysis vapours can be observed. A reduction in observed vapour flow rate or the cessation of vapour production is an early indicator of an operating problem. Also, the absence of smoke indicates that a run has stopped.

The presence of thick smoke on the other hand may indicate failure of the electrostatic precipitator (see section 4.2.4.2). The use of glass is therefore a safety feature.

4.2.4.1 Condenser 1:

The first cooled condenser was a 'Davies type' double surface water condenser, which was mounted at an angle of 60° to facilitate liquid flow to the electrostatic precipitator (see section 4.2.4.2), which was attached to oil pot 1. This pot collected the bulk of the liquid product. The cooling liquid used in condenser 1 was tap water. The heavy ends of pyrolysis vapour condensed on the inner wall of the condenser and then dripped down to the electrostatic precipitator.

The rate of cooling was important, with slow cooling leading to preferential collection of the lignin derived components. This is a viscous liquid that can lead to blockage of the heat exchange equipment. Initially, tap water was used as cooling liquid in condenser 1, Water temperatures were 10 – 25 °C, with the variation depending largely on the season. A few experiments on the effects of temperature variation were performed and it was found that the temperature of condenser 1 seriously affected oil stability, with lower temperatures giving much better results (see section 4.11).

It was necessary to use the same temperature for condenser 1 in different runs in order to make experimental results comparable in a series of runs. It was quite difficult to keep tap water temperature unchanged in different seasons, and when there was a substantial period of time between different runs in the same season. Therefore, a chiller that provided refrigerated cooling water of a constant temperature was employed instead of tap water in condenser 1 when temperatures became excessive. The chiller considerably improved temperature control of condenser 1 and provided more comparable experimental results.

4.2.4.2 The electrostatic precipitator (EP):

The EP is used to capture aerosols and particulates from the vapours that are present after the first condenser. Within the 50 mm diameter glass housing of the EP is a circumferential metal tube that acts as a positive collection electrode. Hanging down the centre is a thin metal wire, weighted with a bob and held in position with an external magnet. This acts as the negative electrode and carries 15 KV. The aerosols become negatively charged due to the presence of ions in the space between the electrodes. The aerosols are attracted to the positive metal tube, where they give up their charge, coalesce, and run as a liquid to the bottom of the EP. The liquid drains into oil pot 1 during or after the run. A round bottom flask attached below the EP constitutes oil pot 1.

Some of the liquid in condenser 1 and in the EP is rather viscous and takes a considerable amount of time (several hours to one day depending on the viscosity of the product) to drain into oil pot 1. Therefore, for that period of time, the collection system has to be kept sealed to avoid the escape of volatiles from the liquid into the atmosphere. However, the point at which the metal transfer line from the cyclone and reactor connects to the glassware of the liquid collection system needs to be disconnected immediately after a run, as it would otherwise become held fast. To keep the system sealed a stopper is inserted into the opening of the glassware leading to the liquid collection system.

4.2.4.3 Condenser 2 and oil pot 2:

The second condenser has a cold finger filled with dry ice and acetone (approximately -80°C). The light ends and water are condensed on the inner wall of the secondary condenser, and drip down to collect in oil pot 2. This is a round bottom flask attached below condenser 2.

As for condenser 2, the system must be kept sealed after stopping a run to avoid loss of volatiles while allowing time for all the liquid in condenser 2 to collect in oil pot 2. The amount of liquid collected by condenser 2 depends on the amount of condensable vapours bypassing condenser 1. When the temperature of condenser 1 was lower, very small amounts of oil were collected by oil pot 2 (see section 4.11).

4.2.4.4 Cotton wool filter:

The cotton wool filter is a glass column, which is densely packed with dry cotton wool. This forms a dense filter, on which the pyrolysis vapours coalesce. The introduction of the electrostatic precipitator [EP] has meant that the cotton wool collects only a small fraction of the total pyrolysis liquids [see Section 4.11]. It is used mainly as a fail-safe device to protect downstream equipment, namely the gas meter and gas analysis equipment. That is, it ensures that only clean non-condensable gases enter the gas meter and gas sampling/analysis system. Considerably less cotton wool is required and the pressure drop over the cotton wool is much lower than would be expected in the absence of an EP, at the start and during a run. In that regard, it was found helpful to leave a void area between the cotton wool and the inlet.

4.2.4.5 Gas meter:

A gas meter was located after the cotton wool filter. The gas meter measures the total volumetric throughput of non-condensable gas through the system for mass balance purposes.

4.2.5 Problems encountered and methods by which these were overcome:

There were some unexpected problems encountered during pyrolysis runs. Table 4-2 shows the problems encountered in this work. Some of these were serious enough to stop a run, mainly because they were of a nature that would have presented insurmountable problems in establishing a credible mass balance. Some problems, however, were resolved without interruption of the experiment.

Table 4-2. Problems encountered using 150g/h rig in Aston

Problem	Reason
1. Change in feeder top pressure	Feeder top or entraining tube jammed; feeding problems.
2. Fluctuation of inside pressure of pyrolysis system	Cotton wool packed too tightly or jammed; collection system leakage due to bad connection.
3. Rapid increase in reactor temperature	Feeding tube jammed due to pre-pyrolysis or stop of feeding.
4. Thick smoke in the EP	EP does not work or a short circuit has occurred.

Methods for resolving these problems:

1. When the feeder top pressure changed, the feeder top and the feeder entraining tube required checking. The feed aperture was particularly likely to be the source of the problem, if the feeder top pressure gauge showed a pressure drop. This problem occurred when the feed particle shape was not suitable for easy passage through the aperture or the feed particle density was very low, e.g. with miscanthus grass. The former could be dealt with by screening feed particle size carefully and the latter could be resolved by increasing entraining gas flow rate.
2. The liquid collection system was checked with particular attention being paid to ascertain that there was no leakage from the tube connecting to condenser 1 or that the cotton wool had not become jammed. The latter could usually be noticed by the fluidising pressure gauge indicating a pressure drop change.
3. A sudden rise in reactor temperature was generally indicative of feeder malfunction or of pre-pyrolysis in the feeder tube that prevented the free flow of biomass into the fluidised bed. Pre-pyrolysis of the feedstock in the feeding tube occurred due to a higher reactor temperature. Cooling air was employed for high temperature pyrolysis (greater than 500 °C) in order to prevent the feeding tube temperature from rising too high.
4. The negative electrode in the EP needs to be positioned very accurately by magnet connection to avoid arcing and to keep the EP working efficiently.

4.3 FLUIDISING MEDIUM – SAND PREPARATION

Sand requires cleaning before being used as the fluidising medium to remove any impurities. Sand was sieved to 355 –500 μm particle size and soaked in 10 M H_2SO_4 for about two days in order to eliminate impurities, then washed by fresh water and dried in an oven. The mass of sand used was 120.0 g in every run in order to make the results more comparable. After each run, the sand was placed in a Muffle furnace at 750 °C in order to burn off the char coating within 24 hours.

4.4 FEED STOCK TYPE

In this work, the main feed stocks used were Beech wood (hard wood) and Spruce wood (soft wood) although other feed stock types such as miscanthus (elephant grass) was also used as part of the experimental work.

4.4.1 Beech wood (main feed stock for chapter 6 partially oxygenated pyrolysis)

Beech wood (lignocel - Grade: HBK 750-2000) was the main feedstock for partially oxygenated pyrolysis and was supplied by J. Rettenmaiert & Söene, Rosenburgh, Germany.

Beech wood elemental analysis varies depending on the location of its growth. Therefore, an elemental analysis (determined on a moisture-free basis as a percentage accurate to ± 0.01 %) was carried out on the beech wood. Based on this analysis, the empirical formula of this wood was determined to be $C_6H_{10}O_5$, which was referred to as the Biomass formula. The elemental analysis results are shown in Table 4-3.

Table 4-3. Elemental Analysis of Beech Wood (Medac Ltd)

Element	Beech wood (wt% dry)
Carbon	45.55 %
Hydrogen	6.04 %
Oxygen	48.05% by difference
Nitrogen	< 0.1 %
Sulphur	Not reported

4.4.2 Spruce wood (main feed stock for Chapter 5 moisture content and Chapter 7 co-pyrolysis)

Spruce wood was employed for runs aimed at determining the effect of moisture content and was supplied by Kielder. Table 4-4 shows the elemental analysis results for spruce wood.

Table 4-4. Elemental analysis of spruce wood (dry)

Elements	Spruce wood (wt% dry)
Carbon	50.19 %
Hydrogen	6.10 %
Oxygen	43.54 %
Nitrogen	0.16 %
Sulphur	Not reported

4.5 FEEDSTOCK PREPARATION

Feedstocks were usually received in a ground and sized form. However, some additional size reduction, screening or drying was carried out in some cases in order to make the feedstock suitable for use in the feeder and pyrolysis reactor.

4.5.1 Biomass feed particle size:

Since the thermal conductivity of biomass is very poor, reliance on gas-solid heat transfer means that biomass particles have to be very small to fulfil the requirements of rapid heating to achieve high liquid yields. Feed particles that are too large will lead to lost yields of liquid due to the removal of char prior to the completion of pyrolysis. (Section 2.3.1.3)

However, there is a point where even lower feed particle sizes will no longer be beneficial for liquid yields. Feed particles that are too small produce very fine char that may pass through the cyclone and be collected in the liquid. In this work, a fixed entrain tube of aperture size 1.7 mm and a feed particle size in the range 355 –500 μm was used based on results obtained previously in work using this apparatus.

It was found that the feed rate could be maintained within the optimum range of 100-150g/h by using particle sizes in the range 355-500μm [25]. It was sometimes possible to obtain this size range solely by direct screening of a large amount of feedstock with a wide size range. However, this procedure has the disadvantage that different particle sizes may vary in their compositions, which means that the sample in the correct size range may not be representative of the feedstock as a whole. In this work the following steps were carried out.

4.5.2 Size reduction

A Fritsch cutting mill with an interchangeable screen was used to reduce the feedstock particle size. Screen sizes of 100, 250, 500μm and 1mm were available.

In all cases a screen size of 500μm was used, since this was found to separate out most of the particles in the 355-500μm range. Some undersized particles were produced, but these were removed by screening. Choosing a suitable screen size for the grinding operation was complicated by the fact that grinding resulted in heat production and thus some feed drying. The longer the grinding time, the drier the feedstock; indeed, combustion of the feedstock sometimes occurred after long grinding times. Consequently, the feed moisture content (see section 4.5.4) required measuring after the grinding operation.

4.5.3 Screening

By means of sieving, the following were achieved.

- Narrow particle range
- Undersized particles produced by screening were minimised.

A feedstock size distribution of 355-500 μm was decided according to existing rig requirement [25]. However, it was considered useful to collect particles of smaller sizes as well, in case there were problems with the feeding. Therefore, feedstock was sieved using standard test sieves of mesh size 251, 295, 355 and 500 μm. This procedure provided feedstock of three narrow size ranges:

- 251-295 μm.
- 295-355 μm.
- 355- 500 μm.

Some feedstock materials occasionally caused blocking in the feed tube aperture and the feed tube in the reactor. It was found that this occurred due to the nature of the size reduction and screening processes, which allowed particles through that were larger than the selected screen size. This can occur since the sieve will allow particles through, which have a smaller dimension in a particular orientation, than the mesh size. Thus a rectangular particle could pass through a screen in a particular orientation, but may not in another orientation (Figure 4-5). This problem was eradicated by double grinding of the feedstock to remove long thin rectangular or "pin like" particles, and by controlling sieving time according to the volume of feedstock in the sieve to reduce the chance for these particles to pass through. It is purely a matter of chance, which way a particle is orientated; by double grinding the feedstock the probability of pin-like particles remaining is reduced. Feedstock that had been ground once was found to occasionally block; however, double ground feedstock did not block the feeder aperture or reactor feed tube.

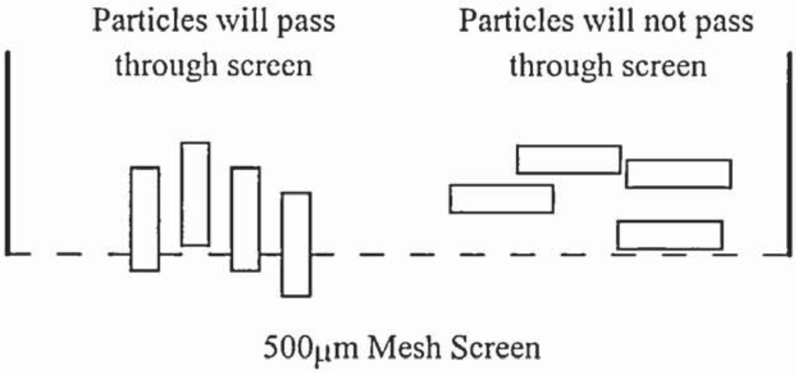


Figure 4-5. Particle orientation on a sieve

4.5.4 Moisture content

Moisture content mentioned here is equilibrium moisture content. Under constant conditions of temperature and humidity, wood is neither gaining nor losing moisture. The equilibrium moisture content represents a balance point where the wood is in equilibrium with its environment.

The moisture content of wood is defined as the weight of water in wood given as a percentage of dry weight. In equation form, moisture content (MC) is expressed by Equation 4-2 [110].

$$MC = \frac{Moist\ weight - Dry\ weight}{Dry\ weight} \times 100\%. \qquad \textbf{Equation 4-2}$$

Biomass is a hydroscopic material that absorbs moisture in a humid environment and loses moisture in a dry environment. As a result, the moisture content of wood is a function of atmospheric conditions and depends on the relative humidity and the temperature of the surrounding air. Thus, although the moisture content of a feedstock may be correct at the time of measurement, if left open to the atmosphere, improperly stored or stored for a long period of time, the moisture content may change. Thus the moisture content should be measured at the time of performing the experiment. Also, the feedstock should be kept in a sealed container for storage.

The method used for measuring the feedstock moisture content was drying [111]. After the feedstock was prepared to the correct size distribution, approximately 1g was weighed (to 4 decimal places) and then placed in a pre-dried and weighed crucible; this was then placed in an oven at 105°C for at least 24 hours. From previous experiments involving repeated weighings of dried 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 was always carried out in triplicate and an average taken.

4.5.5 Drying

Fast pyrolysis required feedstocks in a relatively dry state, that is, 10 % dry feed basis moisture content as measured by the method in section 4.5.4. Feedstocks were dried where necessary by storing in a fan oven at a constant 110°C for 24 hours. Most feedstock was received in an acceptable moisture state (10 –15 % dry feed basis moisture) in our laboratory. This material did not require drying, as it was likely to lose moisture during grinding. However, for bone-dry feedstock, three days of drying in the fan oven at 110°C were required.

4.6 MODIFICATION OF THE RIG FOR PARTIALLY OXYGENATED PYROLYSIS

The original rig only employed nitrogen as the fluidising gas, however, for oxygenated pyrolysis some oxygen was required. The modification work focused on the gas pipelines. Figure 4-6 shows the new pipeline layout after modification.

4.7 MODIFICATION OF THE REACTOR FOR THE CO-PYROLYSIS OF SPRUCE WITH METHANOL

The equipment that was previously used for the wood pyrolysis experiments was appropriately modified to accommodate the addition of a liquid.

An additional port at the top of the reactor was added to allow feeding of the liquid. Figure 4-7 shows the reactor modified for co-pyrolysis.

A peristaltic pump was used to supply the liquid to the reactor. The peristaltic pump was calibrated with water. For the calibration, different speed settings were fixed and the quantity of water flowing during a particular period of time was measured. This correlation allowed the determination of flow rates for each setting. The quantity of methanol or ethanol could be estimated approximately using this flow rate. After pyrolysis, it was measured accurately by weighing the methanol or ethanol container and determining the quantity used by subtraction from the original weight. Water can only be used to calibrate different speed settings roughly as the inside pressure of the pyrolysis system was different from atmospheric pressure. This led to different flow rates even for the same solvent.

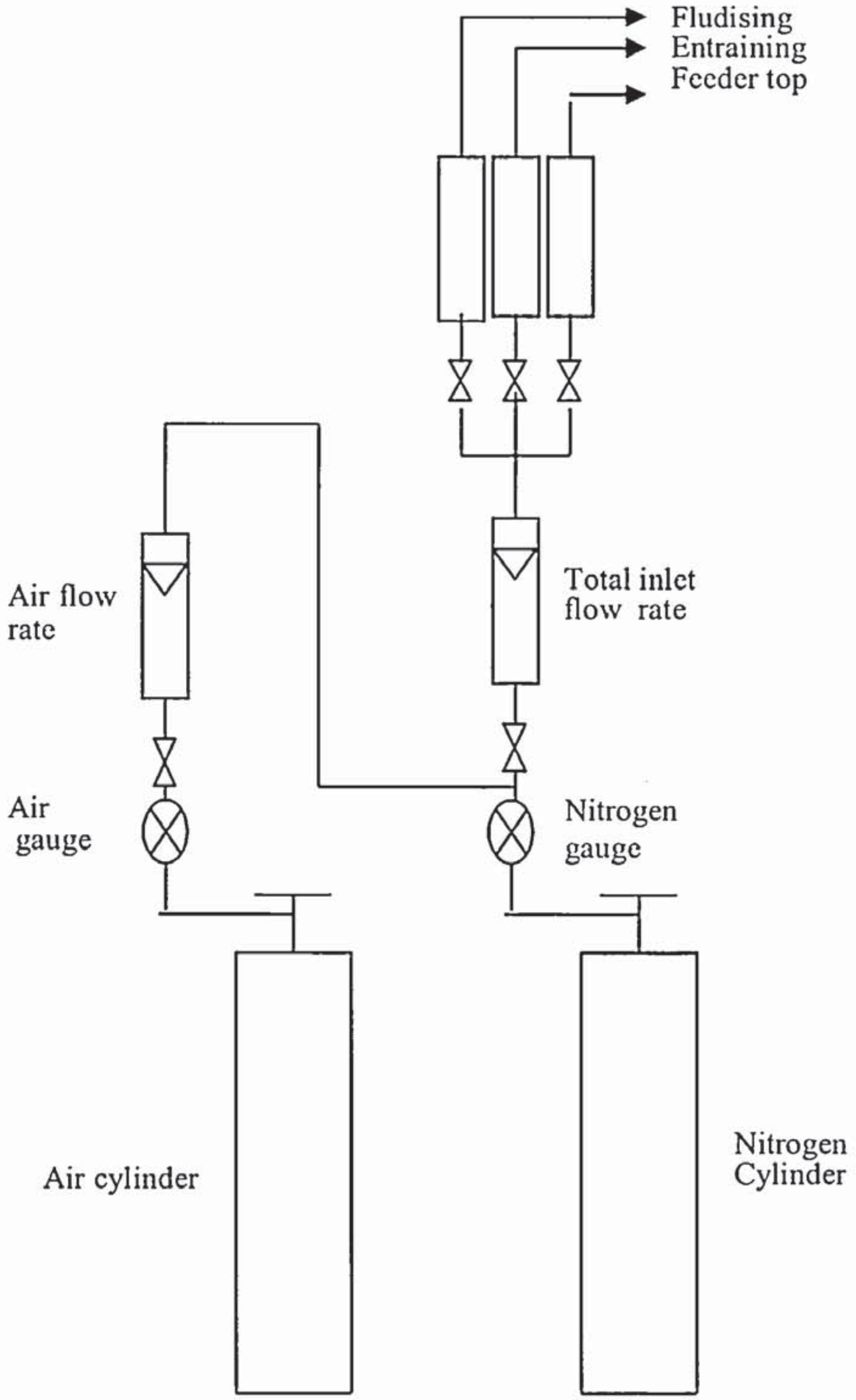


Figure 4-6. New pipeline layout for the fluidising gas

4.8 MODIFICATION OF THE OIL COLLECTION SYSTEM FOR HIGHER QUALITY AND MORE COMPARABLE RESULTS

The quality of oil in pot 1 was affected by the temperature of condenser1 (See 5.1.4.1). Thus, changes in the temperature of condenser1 led to inaccurate comparisons between oil obtained in different runs. A chiller unit was introduced instead of tap water, as changes in the temperature of the tap water with the seasons had previously led to considerable inaccuracies in comparisons between different runs.

4.9 ANALYSIS METHODS

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

4.9.1 Gas Analysis

Gas samples were taken periodically (every 5 minutes) during the course of a run. These samples were analysed for pyrolysis gases using gas chromatography. Three separate systems were used to detect the full range of gases. Hydrogen, oxygen, nitrogen and carbon monoxide were detected using a molecular sieve column, carbon dioxide using a Poropak Q column, and C_1-C_4 gases using a picric acid column. The detector used is Thermal Conductivity Detector (TCD), which is also known as a Katharometer Detector. This type of detector can be used to analyse for all of the gases above listed including oxygen.

Gas chromatography is an analytical technique that 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 GC system and column. Thus when a gas sample is 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. From the total volume measured by the gas meter, the mass of pyrolysis vapours produced can then be calculated.

The pyrolysis vapours are dilute because the fluidised bed reactor requires a high throughput of gas (6-18 l/min. nitrogen was typically used) to keep the sand fluidised. Extra gas is also required to entrain the biomass from the feeder and into the reactor (2-5 l/min). 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 chromatographs 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.

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

4.9.2 Pyrolysis Liquid Analysis

The pyrolysis liquids were collected as two discrete samples from the pyrolysis system, one from oil pot 1 with electrostatic precipitator and condenser1 and another from oil pot 2 (See Figure 4-1). These samples were analysed for water content (see section 4.9.2.1) and also chemicals content (HPLC and GC, Section 4.9.2.4 and 4.9.2.5).

4.9.2.1 Karl Fischer for oil water content

A Karl Fischer volumetric titrator was employed for testing the water content of the oil. A Metrohm, 758 KFD Titrino instrument that was accurate to 0.01 wt% was used. This method can generally be used for the determination of the water content of samples without previous blank value determination and with all samples in their original forms. The determination was repeated three times and the average value was reported. The standard deviation was required to be less than 0.3 %.

The Karl Fischer reagent was Hydranal Composite 5K purchased from Riedel-deaden Sigma-Aldrich Laborchemikalien. The solvent was prepared by mixing of chloroform and methanol in the ratio of 70% to 30% by volume dry solvent.

4.9.2.2 Viscosity measurement

Viscosity measurements were carried out using capillary viscometers at a fixed temperature of 25°C. This type of viscometer was chosen because of the small sample required for the test (4ml). The viscosity was measured by determining the time taken for a fixed volume of bio-oil to flow between two marked points. The viscosity was calculated using Equation 4-3:

$$V = C * t \qquad \textbf{Equation 4-3}$$

Where:

V is the viscosity in centistokes (cS),

C is the viscometer constant C and is unaffected by temperature,

t is the time taken for the liquid to fall from the first timing mark to the second (in seconds).

4.9.2.3 Stability:

The Viscosity Index (VI) measures the relative change in viscosity with time and is used to provide a measure of stability. The viscosity of the fresh pyrolysis liquid was tested at 25±0.5 °C by capillary viscometer 24 hours after production. The liquid was maintained at room temperature prior to viscosity measurement. This was the initial viscosity μ_1. The liquid was then stored for 24 hours at 80°C and after cooling, which is recommended by The Aston Viscosity Index, the viscosity was re-tested at 25°C, which is μ_2. As volatiles may evaporate with time, it was necessary to store the sample in a sealed container. This oil is known as aged oil. The lower the VI number, the more stable is the pyrolysis liquid. A VI of zero would be a completely stable liquid. VI is calculated using Equation 4-4:

$$\mathbf{VI = (\mu_2 - \mu_1) / \mu_1} \qquad \textbf{Equation 4-4}$$

4.9.2.4 HPLC for chemical analysis of the oil

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

A 0.05 wt.% sulphuric acid solution was used as the mobile phase in this work. The mobile phase is constantly pumped through the column and carries the sample to be analysed. Hence only water-soluble compounds in the pyrolysis liquids can be analysed. The samples were prepared by weighing out about 0.1 to 0.2 g (to 4 decimal places) pyrolysis liquid, depending on its viscosity, into a pre-weighed plastic vial. A known weight of mobile phase was then added to the vial to dilute the pyrolysis liquid (about 4 part mobile phase to 1 pyrolysis liquid in weight). The sample was shaken and the water insoluble fraction formed a precipitate known as pyrolytic lignin. The plastic vial was centrifuged for 5 minutes at 4000rpm to remove all the precipitate. The water-soluble pyrolysis liquid fraction was then poured out of the vial and filtered using a Gelman Acrodisc PTFE filter (0.2μm pore size) to remove any remaining lignin. The filter was used as a precautionary measure to prevent lignin entering the HPLC system and damaging the analytical columns. The precipitate remaining in the sample vial and on the filter was dried (115°C, 4h) and weighed. This material is classified as pyrolytic lignin.

The HPLC system used a Bio-rad column, which was linked to a refractive index detector. The filtered water-soluble sample was injected into the column and after approximately 50 minutes a trace showing the chemicals detected and the areas under their HPLC peaks was produced. The software package then integrated these areas and compared them with the standard; thus, the concentrations of the water-soluble compounds in the pyrolysis liquids were found. This technique enabled the effect of different pyrolysis conditions on liquid composition to be determined.

4.9.2.5 Gas Chromatography- Mass Spectroscopy and Gas Chromatography

Gas Chromatography - Mass Spectroscopy and Gas Chromatography analysis were carried out by the institute for Wood Chemistry (IWC) in Hamburg, Germany.

Gas chromatography – flame ionization detection (GC-FID) and gas chromatography – mass spectrometry (GC-MS) were used to obtain chromatograms and mass spectra of chromatographic peaks, respectively. A capillary column (Chrompack 60 m column containing an organic component with oxygen) was used for separation of the complex mixture of chemicals present in pyrolysis liquid. The detector temperature was 280°C and the injector temperature was 250°C.

Only 30-40% of the component chromatographic peaks were detectable by the GC-MS system. The rest were too fast or did not have enough functional groups.

GC-FID was employed for routine analysis whereas GC-MS was used to establish the identity of certain chromatographic peaks. FTIR (Fourier Transform Infrared Spectroscopy) was also used to identify the presence of functional groups.

4.9.2.6 Lignin content in the oil

The oils were diluted with HPLC mobile phase water (1:10), agitated thoroughly, and then centrifuged. The water-soluble fraction was removed by filtration and the residue was dried (115°C, 4h) and weighed. The latter was mainly pyrolytic lignin.

4.9.2.7 Char content of the oil

The char content in pyrolysis oil was measured by a filtration method but the pyrolysis liquid required dilution with a suitable solvent (ethanol, methanol or acetone) to enable it to pass through the filter.

Approximately 1g of oil was weighed (to 4 decimal places) and then diluted by about 10g of ethanol. After ensuring that all the oil was diluted thoroughly in the ethanol by shaking until the liquid was clear, it was filtered with a pre-dried and weighed (to 4 decimal places) glass micro fibre filter (GF/B 4.7 cm). The filter was then placed in an oven at 115°C for a minimum of 6 hours before and then cooled in a desiccator for 1 hour before weighing (to 4 decimal places). The char content was then calculated and an average of three samples taken.

4.10 MASS BALANCE

4.10.1 Contribution to mass balance

The products of pyrolysis were separated and collected into three distinct categories, char, pyrolysis liquid (organic, water and a small amount of char) and gas.

The contribution of each part of the 150g/h bench scale reactor system to the mass balance is illustrated in Table 4-5.

Table 4-5. Contributions of the different parts of the rig to the mass balance

Total inlet	Feed			
Difference of feeder	Wet feed			
Total outlet	Char	Organic	Water	Gases
Difference of Whole Reactor	√	-	-	-
Difference of Condenser1, EP and Oil pot 1	√	√	√	-
Difference of condenser 2, oil pot 2 and cotton wool filter	-	√	√	-
Difference of Gas meter	-	-	-	√
Mass Balance	Total outlet in weight/total inlet in weight (dry basis)			

4.10.2 Total input:

The difference in weight of the feeder before and after pyrolysis is the weight of wet feed consumed. The weight of dry feed was calculated from the weight of wet feed and the moisture content. The biomass fed into the reactor was the only item on the input side of the mass balance for standard pyrolysis (see section 4.10.2.1). As nitrogen does not react with the biomass, and as little nitrogen from the biomass itself enters the gas stream, it was neglected in the mass balance. In partially oxygenated pyrolysis and when adding methanol or ethanol in co-pyrolysis, oxygen or the liquid that is being co-pyrolysed are further items on the input side of the mass balance.

4.10.2.1 Blank run (Standard pyrolysis)

This consisted of pyrolysis without any additives such as oxygen or methanol, and with nitrogen as the only fluidising gas. Therefore, wood was the only item that entered the mass balance on the input side.

4.10.2.2 Copyrolysis with methanol

Wood and methanol were both inputs for the mass balance and need to be taken into account in yield calculations.

4.10.2.3 Partially oxygenated pyrolysis

Both wood and oxygen occur on the input side of the mass balance and therefore require consideration in yield calculations. The mass of oxygen added was calculated by multiplying the average oxygen percentage (GC result) in the inlet nitrogen stream with the total inlet gas volume and the density of oxygen at room temperature. The mass of oxygen leaving the process was calculated by multiplying the average oxygen percentage in the outlet gases with the total outlet gas volume and the density of oxygen at 0°C. The difference between the two was the oxygen consumed in pyrolysis.

4.10.3 Total output:

4.10.3.1 Difference of whole reactor:

The whole reactor includes the reactor itself, the char pot, the cyclone, the transfer tube and the fluidising medium sand. The reactor, cyclone and sand were assumed to remain at a constant weight, so any increase in weight was due to char. Char is a black substance that was collected in the char pot, and also as a residual coating on the sand, reactor, char pot, cyclone and transfer tube.

The reactor and cyclone were weighed before and after a run (±0.01%) and the difference was assumed to be char. The coating on the sand was quantified by weighing the sand before and after a run, the difference again being char. The contents of the char pot were also classed as char and again were weighed. In both cases the weighing was to 2 decimal places and was accurate to ±0.01g. It is possible that some of the sand was blown into the cyclone and char pot, so using the weight difference of the whole reactor was more accurate than the weight differences for the individual parts.

4.10.3.2 Difference of Condenser1, EP and Oil pot 1:

The collection of the liquid products began in the first condenser. These were condensed on the walls of the first condenser and then ran down the walls into oil pot 1. They were also collected in the EP, where again they run down the walls to be collected in oil pot 1. Oil pot 1 was weighed [to an accuracy of ±0.01g] before and after the run and the difference was the main pyrolysis liquid. Condenser 1 and the EP were also weighed before and after the run (to an accuracy of ±0.01g).

The liquid from oil pot 1 was placed into separate storage containers for subsequent water and chemicals content analysis at 24 hours after production.

Any liquids remaining on the glassware were washed off using ethanol; this was then filtered to remove char using pre-dried and weighed Whatman No. 1 qualitative filter paper. This was done for the first 50 runs and very low char content in the oil (0.05%) was found. HPLC analysis results showed that the remaining oil in condenser 1 and inside EP had the same chemical composition as the oil in oil pot 1. After that it was assumed for all further runs that the liquid in condenser 1, the EP and oil pot 1 had the same water content as the liquid that drained into condenser 1 and the EP within 24 hours.

The pyrolysis liquids were further sub-categorised into organics and water. About 90 % of the liquid was collected in oil pot 1 and the water content for this main fraction of the pyrolysis liquid ranged from 15 to 30 %.

4.10.3.3 Difference of condenser 2, oil pot 2 and cotton wool filter:

The light part of the liquid drained down from condenser 2 and was collected in oil pot 2. It constituted about 10% of the pyrolysis liquid. According to the water content the liquid was also sub-categorized into organic and water. Its water content was about 50-60% and no char was detected. Only a small fraction of the volatiles was trapped by condenser 2 (the amount of liquid was too little to be collected for analysis) and the cotton wool filter. Therefore, the assumption was made that the oil from the three parts (oil pot 2, condenser 2 and cotton wool filter) had the same water content and zero char content.

4.10.3.4 Difference of Gas meter and GC analysis results:

The total volumetric throughput of the fluidised bed reactor system was measured using a Schlumberger Remus3 G1.6 total gas meter. This measured the total gas throughput in cubic metres, to three decimal places. After the gas meter, an on line GC was used to analyse samples every 5 minutes throughout the course of the run; the samples were analysed for their volumetric content of the major pyrolysis gases, namely carbon monoxide, carbon dioxide, hydrogen, methane, ethane, ethylene, propane, propylene, n-butane and n-butylene. It was assumed that the remainder of the pyrolysis gas was made up of nitrogen. From this analysis the volumetric constituents of the pyrolysis gas were calculated and the weight of gas deduced.

4.10.4 Mass Balance Reporting

Table 4-6. Example of Mass Balance Reporting

Summary of Mass Balance		
Run Number		100
Run Date		18/07/2001
Feedstock		Beech
Feed Moisture Content [wt% dry] (see section 4.5.4)		8.09
Average Reactor Temperature [°C] (see section 4.2.2) *		475.4
Total Hot Space residence time [s] (see section 4.2.3)		0.59
Feed rate [g/h] **		145.14
Input Oxygen by GC result [v/v %] (see section 4.10.2.3)		1.28
Outlet Oxygen by GC result [v/v] (see section 4.10.2.3)		0.28
Temperature of condenser 1 [°C] (see section 4.2.4.1)		0
Airfactor (see section 6.2)		0.064
Input in Weight		
Wet Feed [g]	77.41	
Dry Feed [g]	71.62	
Water in feed [g]	5.79	
Oxygen [g] ***	5.42	
Total inlet [g]	82.83	
Output	**In weight (g)**	**In yields (wt% dry)**
Total outlet	82.28	99.29
Oil (organic + total water)	58.61	68.56
Water including water in feed	16.47	13.86
Organic	42.14	54.70
Char	8.19	10.63
Total Gases	15.48	20.10
Methane	0.37	0.47
Carbon Dioxide	11.34	14.72
Ethylene	0.07	0.10
Ethane	0.03	0.04
Hydrogen	0.02	0.03
Propylene	0.01	0.01
Carbon monoxide	3.64	4.72

* The reactor temperature is measured manually at one-minute intervals throughout a run and noted. At the end of a run the average reactor temperature is calculated.

** The federate is measured by feedstock (in weight) consumed in total pyrolysis divided by a total run time.

*** The oxygen here is calculated by input oxygen – output oxygen (in weight), thus it actually is oxygen consumed in pyrolysis.

Each entry in the table is explained below:

Input in weight:

- **Wet Feed [g]:** The weight of wet feed is the difference in weight of the feeder before and after pyrolysis. This is the total feedstock for pyrolysis.
- **Dry Feed [g]:** The weight of dry feed could be calculated from the weight of wet feed and from the feed moisture content.
- **Water in feed [g]:** The weight of water in the feed can be calculated from the difference in weight of the wet and the dry feed. There was also some water added to the oil from reaction, which was not included in this category.
- **Input Oxygen [g]:** The weight of input oxygen was calculated by multiplying the oxygen percentage in the fluidising nitrogen (obtained from GC analysis) by the total nitrogen volume (which was obtained from the inlet gas volume meter).

Output in weight [g]: For the contributions of each part see Table 4-5.

- **Oil:** The weight of oil was obtained from the weight difference before and after pyrolysis of condenser 1, EP, oil pot 1, condenser 2, oil pot 2 and cotton wool tube.
- **Water:** The total water in the oil was calculated from the mass of oil and its water content. The oil water content was analysed by the Karl Fischer process (see section 4.9.2.1) so that the weight of total water in the oil = (water content of oil pot1) × total weight of oil (in condenser1, oil pot1 and EP) + (water content of oil pot 2) × total weight of oil (in condenser 2, oil pot 2 and cotton wool)
- **Organic species:** The total weight of the organics was obtained from the total mass of oil minus the mass of water in the oil. The small amount of char in the oil (section 4.9.2.7 and section 4.10.3.2) was neglected.
- **Char:** The total weight of the char is the difference in weight of the reactor before and after pyrolysis.
- **Output oxygen:** The total weight of oxygen leaving with the outlet gases was calculated by multiplying the oxygen percentage in the total outlet gases by the total volume of those gases.

- **Total Gases:** Total weight of Methane, Carbon Dioxide, Ethylene, Ethane, Hydrogen, Propylene and Carbon Monoxide. The total weight of each gas in the outlet gases was calculated by multiplying the gas percentage in the total outlet gases by total gas volume

4.11 THE EFFECT OF CONDENSER 1 TEMPERARURE ON COLLECTION SYSTEM PRODUCT YIELDS

The product of fast pyrolysis is vapours, aerosols and gases from the decomposition of wood, together with carrier gases from fluidisation. The vapours require rapid cooling to minimise secondary reactions and to condense the true vapours. Once the pyrolysis vapours leave the hot space and enter the liquids collection system (condenser 1), condensation starts and the liquid products start to collect. Tap water was used as cooling water in condenser 1 (see section 4.2.4.1) for the existing 150g/h reactor (Figure 4-1). During the course of the work here reported it was found that the experimental results could be influenced by the season of the year, as the temperature of the tap water would change. Therefore, only a series of runs performed over a short period of time gave results that could be usefully compared. The mechanism by which the temperature of condenser 1 affected the properties of the oil collected in pot 1 is discussed below.

Table 4-7, Table 4-8 and Table 4-9 give the results of four runs that were performed with different temperatures for condenser 1. Run 44 and Run 98 were both partially oxygenated pyrolysis of beech wood at a pyrolysis temperature of 475 °C and an airfactor of 0.035 and 0.037; the only significant difference between theses two runs is that the temperature of condenser 1 was 20 °C for Run 44 and 0 °C for Run 98. Run 45 and Run 96 were pyrolysis of spruce wood at a pyrolysis temperature of 500 °C; the temperature of condenser 1 was 20 °C for Run 45 and 0 °C for Run 96.

Table 4-7. Total liquid distribution among different part of collection system (%)

	Run 44	Run 98	Run 45	Run 96
Condenser 1 temperature	20 °C Airfactor 0.035	0°C Airfactor 0.037	20 °C	0°C
Condenser1	6.1	3.49	5.1	2.8
EP	13.2	5.36	14.2	6.9
Pot1	60.1	80.3	59.8	80.5
Condenser 2	0.9	0.99	0.8	1.04
Pot2	11.9	5.65	11.7	5.12
Cotton wool	7.7	4.18	8.4	3.56

Table 4-7 shows the total liquid product distribution in terms of weight among the different parts of the oil collection system. The results show that a lower temperature in condenser 1 leads to more oil being collected in oil pot 1, and less oil being left in condenser 1 and the EP. Furthermore, less oil was collected in oil pot 2 and in the cotton wool. This can be explained by the fact that molecules with a greater molecular weight can be condensed more easily than those with a lower molecular weight. Therefore, a lower temperature in condenser1 would lead to a greater fraction of low molecular weight chemicals, including water, being condensed there. A greater fraction of water and other chemicals with a low molecular weight would lower the viscosity of the liquids in condenser1 and consequently would allow them to drain more easily from condenser 1 and the EP into oil pot 1. If more of the oil is condensed in oil pot 1, less will pass through to condenser 2 and to the cotton wool. In other words, it is clear that the temperature of condenser 1 will affect the chemical composition of the oil collected in pot 1. As this was the oil that was used as the main liquid to be analysed for water content, viscosity and chemical composition in this work, the temperature of condenser 1 will seriously affect the experimental results.

Table 4-8. Pot 1 oil water content and viscosity and product yields versus condenser 1 temperature

Condenser 1 temperature	Oil in pot1				Oil in pot 2	Mixed oil of pot1 and pot 2
	Water content	Fresh oil viscosity	Aged oil viscosity	Viscosity index	Water content	Water content
20 °C for Run 45	12.48%	242.07 mm^2/s	821.81 mm^2/s	2.39	64.41%	20.96%
0°C for Run 96	18.87%	52.25 mm^2/s	148.66 mm^2/s	1.85	52.39%	20.87%
	Product yields (%) on dry feed basis for Run 45 and Run 96					
	Oil	Water	Char	Organic	Gases	Closure
20 °C for Run 45	75.88	10.72	11.48	65.16	12.39	99.74
0°C for Run 96	76.91	10.72	11.17	66.19	11.41	99.49

Table 4-8 and Table 4-9 show product yields and the oil viscosity and water content for Run 44, Run 45, Run 96 and Run 98. The results show that a lower temperature in condenser1 gives higher water content in pot1 oil and lower water content in pot 2 oil, which can be explained by the fact that more water was condensed and collected at a lower condenser1 temperature. Furthermore, a lower temperature in condenser1 will lead to the collection of more chemicals with a small molecular weight in oil pot 1, thereby reducing the viscosity of the oil collected there. The results obtained for the viscosity index show that a lower temperature in condenser1 led to more stable bio-oil in pot 1. This was in agreement with the results obtained for the influence of oil water content on oil viscosity and oil stability (see Chapter 6). The liquid obtained by mixing the oil collected in both pot1 and pot 2 gave the whole oil water content, which was nearly identical in runs with differing temperatures in condenser 1. This means that the temperature in condenser 1 did not affect the liquid as a whole. The results also show that product yields did not change with different condenser 1 temperature. Similar results are also shown in Table 4-10.

Table 4-9. Pot 1 oil water content and viscosity and product yields versus condenser 1 temperature

Condenser1 temperature	Oil in pot1				Oil in pot 2	Mixed oil of pot1 and pot 2
	Water content	Fresh oil viscosity	Aged oil viscosity	Viscosity index	Water content	Water content
20 °C for Run 44	17.42%	135.51 mm^2/s	381.69 mm^2/s	1.82	70.76%	26.27%
0 °C for Run 98	23.76%	34.48 mm^2/s	86.96 mm^2/s	1.52	46.66%	25.27%
	Product yields (%) on dry feed basis for Run 44 and Run 98					
	Oil	Water	Char	Organic	Gases	Closure
20°C for Run 44	72.62	14.36	10.49	58.26	16.43	99.54
0°C for Run 98	71.53	13.05	10.72	58.48	16.91	99.16

Table 4-10. Effect of temperature of condenser 1 on oil quality

Tap water flow	Oil in pot1				Oil in pot 2
	Water content	Fresh oil viscosity	Aged oil viscosity	Viscosity index	Water content
Slow	8.5%	1263.31mm^2/s	4778.26 mm^2/s	2.78	47.5%
Fast	9.2%	925.03 mm^2/s	3499.42 mm^2/s	2.78	46.3%
	Mixed pot 1 and pot 2 oil together				
	Water content	Fresh oil viscosity	Aged oil viscosity	Viscosity index	
Slow	11.8%	391.16 mm^2/s	1369.06 mm^2/s	2.50	
Fast	12.1%	349.6 mm^2/s	1222.89 mm^2/s	2.50	
Product yields on dry feed basis for run 86 and 87					
Oil	Water	Char	Organic	Gases	Closure
75.85	10.73	11.71	65.12	11.32	98.88
74.71	10.42	11.49	64.29	11.02	97.23

Spruce wood with moisture content 0.07% at 500 °C

Table 4-10 gives some further information about the way that the temperature in condenser 1 affected the water content of the oil collected in pot 1 oil. The actual variable investigated was the flow rate of the tap water; the temperature of condenser 1 was not actually measured. The difference was found to be small for oil viscosity and no difference could be found for oil stability, presumably as the flow rate of the water only had a fairly small impact on the temperature in condenser 1.

It was therefore concluded that the temperature in condenser 1 affected the distribution of the pyrolysis liquid among the different components of the oil collection system. The temperature of the liquid condenser had a definite effect on the properties of the oil product. Lower temperature led to more volatile organic vapours and water being condensed to become the pyrolysis oil product. These volatiles can be considered solvents as they had very low viscosities and thus had a very beneficial impact on lowering the viscosity of the oil, even at low concentrations. Higher collection temperatures minimized water condensation in the production then result in high oil viscosity and lower oil yield.

It is suggested that using cooling water with a constant and adjustable temperature instead of tap water, or employing a collection system that only has one pot for the oil to accumulate in, would be potential solutions to the problems described above. A chiller that provided refrigerated cooling water of a constant temperature was employed from Run 80 onwards.

CHAPTER 5 . EFFECT OF FEED MOISTURE CONTENT ON THE STABILITY OF LIQUIDS FROM FAST PYROLYSIS OF SPRUCE WOOD

The presence of water in biomass influences its behaviour during pyrolysis and affects the physical properties and quality of the pyrolysis liquid. This water becomes part of the bio-oil product in addition to that produced in the pyrolysis reaction. Water in the oil reduces oil-heating value, lowers oil viscosity, and increases oil instability. Feed moisture was also found to affect the pyrolysis process and the yields of pyrolysis product. Few references to work on the effects of feed moisture content on pyrolysis liquid stability appear in the literature. The effects of varying feed moisture content on pyrolysis liquid stability were investigated in this chapter.

5.1 INTRODUCTION

Pyrolysis of wood is a complex phenomenon, even if the wood stock is dry. It involves heat transfer to and through the feed particle, chemical reaction within the particle, and escape of volatiles through and from the particle.

Feedstock moisture content affects the pyrolysis process, product yields and product characteristics. If the feedstock is wet, as it is initially in most cases of interest to industry, the whole process is delayed. Additional heat must be supplied for water evaporation, before pyrolysis temperatures are reached. This study investigates the effects of that water on pyrolysis and also seeks to optimise the amount of drying that should be undertaken before the pyrolysis reaction. There are two significant reasons for drying the biomass prior to pyrolysis.

1. Drying prior to pyrolysis can be carried out with waste low-grade energy (i.e. less than 150°C) whereas evaporation of water from moist biomass in the pyrolysis reactor takes place at 500°C. This is more costly energetically and will consume more by-product char and gas, possibly leading to a process with an energy deficit.
2. All the water in the feed becomes part of the liquid product, together with water produced in the pyrolysis process. A high water content in the product lowers the bio-oil heating value and can lead to phase separation.

For economic optimisation it is necessary to weigh the increase in capital costs associated with drying against the increased value of the bio oil. That value, however, depends on more than just the heating value of the fuel; it is also determined by bio-oil yield and quality, notably viscosity and stability.

Of these factors, the most investigated is the effect of water on bio oil viscosity, a higher water content generally leading to a lower viscosity [70]. Little work has been found on the effects of water content on the stability of pyrolysis oil. A few studies have investigated the influence of feed moisture content on bio oil yield. Kelbon [112] studied the effect of moisture content by pyrolysing feedstock with different moisture contents. The experimental results showed that when moisture is present during pyrolysis, the temperature rises to 100 °C where it remains on a plateau as heating continues until the water has evaporated. The temperature then rises more slowly and attains a somewhat lower ultimate temperature than found in drier wood particles under the same conditions. The duration of the 100 °C plateau and the time to reach ultimate temperature are prolonged, the greater the initial moisture content of the particles. This means that the increase in water content delayed the onset of pyrolysis due to moisture vaporisation. The pyrolysis of large moist wood particles was also undertaken in that work to investigate the synergistic influence of particle size, heating intensity and feed moisture. It was found that optimum moisture content can facilitate tar production. The greatest tar fraction was obtained for intermediate moisture content.

Gray found that pyrolysing wood at a slower rate (5°C/s) than that usually experienced in fast pyrolysis, at a moisture content of 16%, raised the char yield from 31 to 36% and the organic yield from 26 to 28% compared with bone dry material [113]. These yields were on a dry ash free feed basis and the reaction temperatures ranged from 320-460°C.

Maniatis and Buekens investigated pyrolysis over a higher temperature range of 600-800°C at a minimum heating rate of 100°C/s [114]. They found that increasing the feed moisture content from 0% to 10% resulted in less char, less oil and more gas, that is the exact opposite of the results obtained by Gray. Both temperature ranges were outside the range commonly employed for fast pyrolysis of biomass for liquid production, which is 450-550°C.

Moisture in biomass will slow down the rate of heating of the biomass particle and increase the mass flow of pyrolysis degradation products through the reacting particle. The higher water partial pressures in the escaping volatiles might be expected to react with char on the particle surface, thereby reducing char yields and increasing gas yields as reported by Maniatis [114]. However, this effect would not be expected to be as pronounced at fast pyrolysis temperatures.

The results reported here address the results of work on the effect of water content on yields and liquid product stability over the temperature range studied. A range of moisture contents of spruce wood has been investigated from bone dry to 15.2% over a reactor temperature range of 450 to 550°C. All data are presented on a dry feed basis and most of them are the average of two or three runs.

5.2 PRODUCT YIELD:

5.2.1 Char and gas yields versus feed moisture content

Figure 5-1 and Figure 5-2 show that over the temperature range of 450°C to 550°C, the yields of char decreased and the yields of gases increased, a trend not affected by feed moisture content. These results are in very close agreement with those of Scott that showed that char yields decreased rapidly as the temperature was increased to 500 °C and then decreased very slowly for temperatures up to 800°C. That work also showed that total gas yields increased at higher temperatures [115]. Similar observations have been made by other workers (see section 2.3.3). The decrease in the char yield with increasing pyrolysis temperature could be due to greater primary decomposition of the wood at higher temperature or to secondary decomposition of the char residue at higher temperature. The increase in yields of gases is thought to be due to secondary cracking of the pyrolysis vapours at higher pyrolysis temperature. Also, the secondary decomposition of char at higher temperature may also give non-condensable gas products.

These results shown in Figure 5-1 and Figure 5-2 are in agreement with those of Maniatis, which showed that moist samples produced significantly higher gas and lower char yields [114]. There is also agreement with the results of Girard [116], which suggested that charcoal yields decreased with higher moisture content. That work involved the determination of charcoal yields from pressurized pyrolysis for feedstock of different moisture contents (0, 20% and 40%). However, Girard expressed concern about the effect of experimental error on the results of that work. Saito [117] studied combustion characteristics of waste material containing high moisture and found that char combustion rates increased slightly with increasing water content since part of the char is burned during the long volatile matter combustion.

The same result was obtained by Minkova *et al.* [118] in work on steam pyrolysis. The lower yields of char and the high yield of volatiles obtained in pyrolysis under a flow of steam are related to the water vapour. During pyrolysis, some of the pores in the solid materials may be blocked by deposition of carbonaceous materials and this contributes also to higher yields of the solid residue, char. Higher moisture results in higher water vapour pressure during pyrolysis, with greater vapour penetration of the solid materials. This assists with adsorption, distillation and efficient removal of the volatile products from the solid.

There is disagreement, however, between the results of the present work and those reported by Gray on the pyrolysis of woodex in the temperature range 300 °C - 460 °C [113]· Gray found that pyrolysing wood with a moisture content of 16% compared with bone dry material, raised the char yield from 31 to 36%. This may have been due to the lower temperatures and/or the nature of the raw material (woodex pelletised biomass) and/or the rate of pyrolysis used. More importantly, the reactor temperature range was different, with little overlap with the temperatures investigated in this study. As lower reactor temperatures lead to increased char yields, it may also be that the cooling effect of the evaporation of the biomass moisture explains Gray's contrary result of an increase of char yield with feed moisture content.

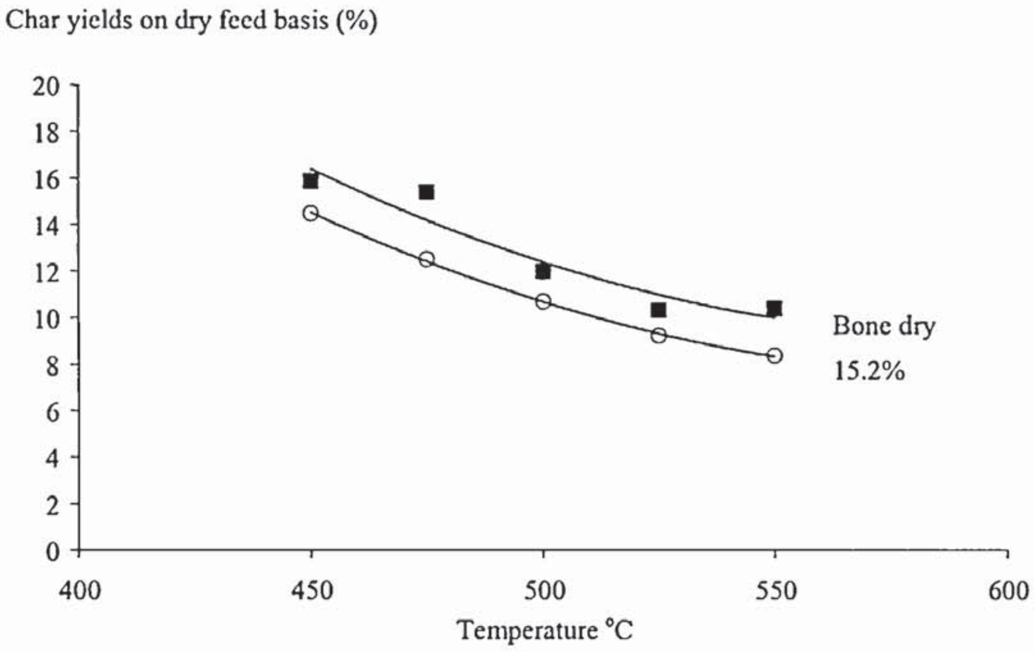


Figure 5-1. Char yields versus reactor temperature for spruce with different moisture content

The equations of curves are shown as Equation 5-1 and 5-2, their R-squared value is above 0.94 and 0.99.

Char % = 0.0003 (T)^2 - 0.382(T) + 123.85 for bone dry feed Equation 5-1

Char % = 0.0003(T)^2 - 0.3567(T) + 115.33 for 15.2% moisture feed Equation 5-2

Where T is reaction temperature.

5.2.2 Liquid yields versus feed moisture content

Figure 5-3 shows that total liquid yield from wood pyrolysis had an optimal yield temperature of 500 °C for bone dry and 7.3% moisture content spruce, which is in agreement to the result of Scott and Piskorz [16, 78]. However, for high moisture content spruce (12.8%) the optimal yield temperature was at 475 °C. This result showed that optimal yield temperature was affected by wood moisture content, with higher feed moisture content leading to a lower optimal yield temperature. This result is in agreement with Kelbon [112], who performed pyrolysis of large moist particles and found that the yields of tar produced from pyrolysis of moist wood were higher than from dry wood particles. Kelbon speculated that the reason for the high tar yields from moist feed was a combination of a lower average pyrolysis temperature, and a reduced extent of cracking reactions as the volatiles left the cooler particle.

The results also show that liquid yields were greater for high moisture content spruce. Experiments conducted with feeds having the higher moisture contents of 15.2 and 18.6% resulted in phase separation at 500 and 450°C respectively. The results of these experiments have been omitted because further analysis cannot be conducted accurately due to liquid phase separation. This might be due to high feed moisture content leading to an increase in reaction water. Similar results were found by other authors [118, 119, 120, 121] in studies of water vapour in the steam pyrolysis of biomass. They found that the water vapour strongly influenced the distribution of products. In a flow of steam, the yields of liquid products dramatically increased, and the liquid product obtained in steam separated into a tar and a water-soluble fraction, which was quite similar to the phase separation encountered in this work. The largest part of the liquid product from steam pyrolysis was found in the water-soluble fractions. For all samples, the total yield of liquid product obtained in steam pyrolysis was 2-4 times higher than in an inert atmosphere.

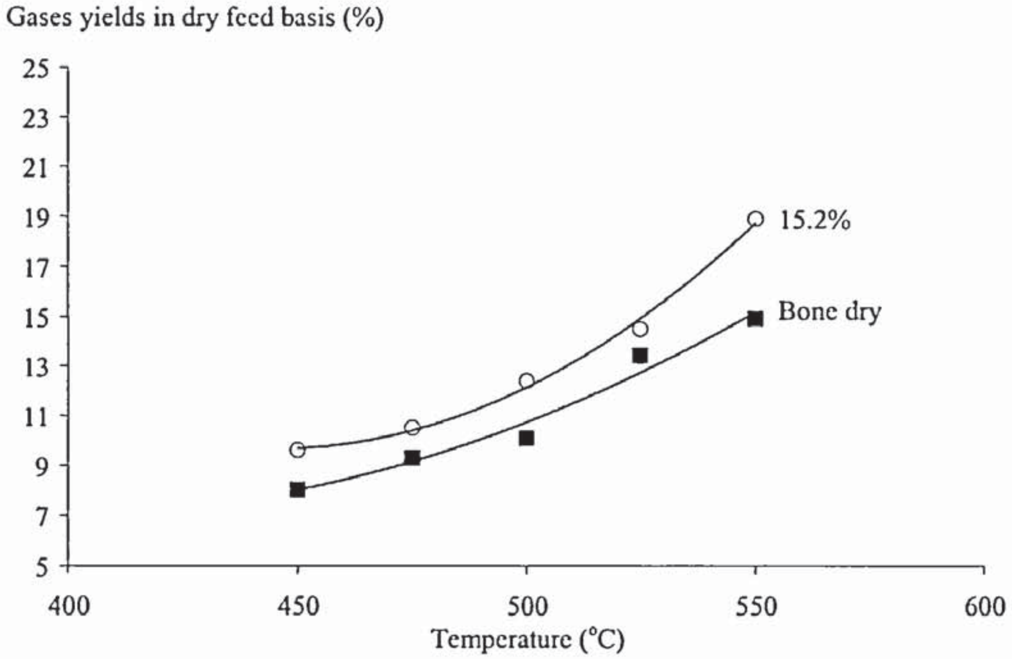


Figure 5-2. Gas yields versus reactor temperature for spruce with different moisture content

The Equations of curves are shown as Equation 5-3 and 5-4, the R-squared value is above 0.98 and 0.95.

$$\textbf{Gas \%} = 0.0008(T)^2 - 0.7325(T) + 172.67 \text{ (for 15.2\% moisture feed)} \quad \dots \text{ Equation 5-3}$$

$$\textbf{Gas \%} = 0.0003(T)^2 - 0.2699(T) + 60.304 \text{ (for bone dry feed)} \quad \dots \text{ Equation 5-4}$$

Where T is reaction temperature.

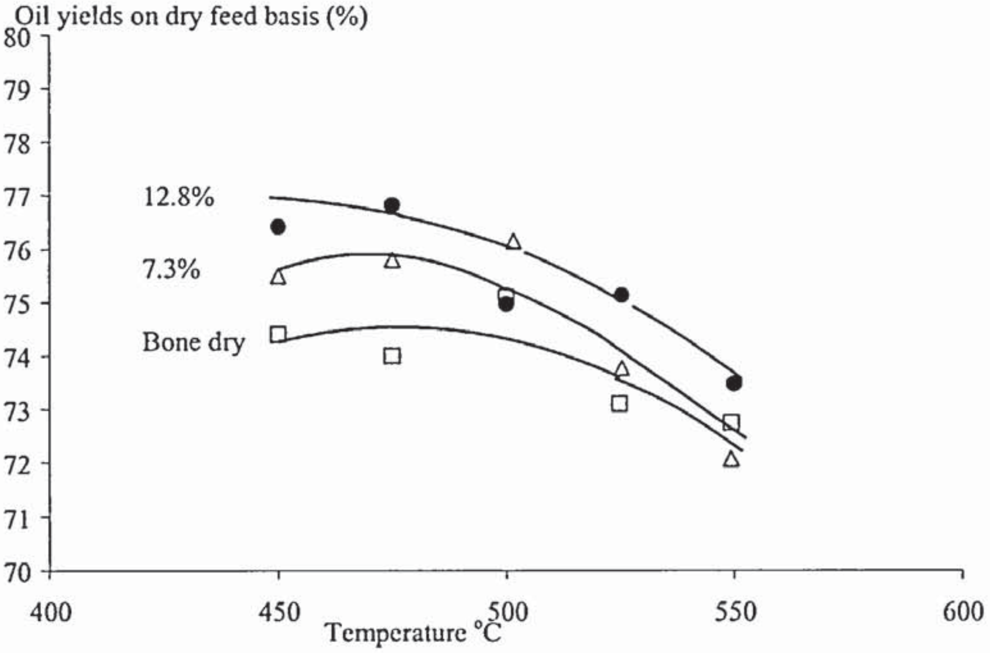


Figure 5-3. Oil yields Total liquid yield versus reactor temperature for bone-dry spruce and spruce with 7.3%, 12.8% moisture content.

The Equations of curves are shown as Equation 5-5, 5-6 and 5-7.

Oil % $= -0.0002(T)^2 + 0.2107(T) + 30.544$ (for 12.8% moisture feed)

... Equation 5-5

Oil % $= -0.0007(T)^2 + 0.7003(T) - 88.648$ (for 7.3% moisture feed)

... Equation 5-6

Oil % $= -0.0004(T)^2 + 0.3812(T) - 16.28$ (for bone dry feed)

... Equation 5-7

5.2.3 Organic yields versus feed moisture

Figure 5-4 shows that organic yields from the pyrolysis of spruce with different moisture contents decreased slightly when the pyrolysis temperature increased from 450 °C to 550 °C, however, feed moisture content seemed to have no effect on organic yields.

5.2.4 Water yield versus feed moisture content

Water present in the oil comes from the evaporation of feedstock moisture and from dehydration reactions during pyrolysis. In the case of the pyrolysis of bone-dry spruce water in the product was derived from reaction only.

Figure 5-5 shows that water yields increased with feed moisture content and decreased slightly with pyrolysis temperature. Here the water yields are on dry feed basis, so all yields shown are reaction water. The results show that high feed moisture leads to high reaction water yields.

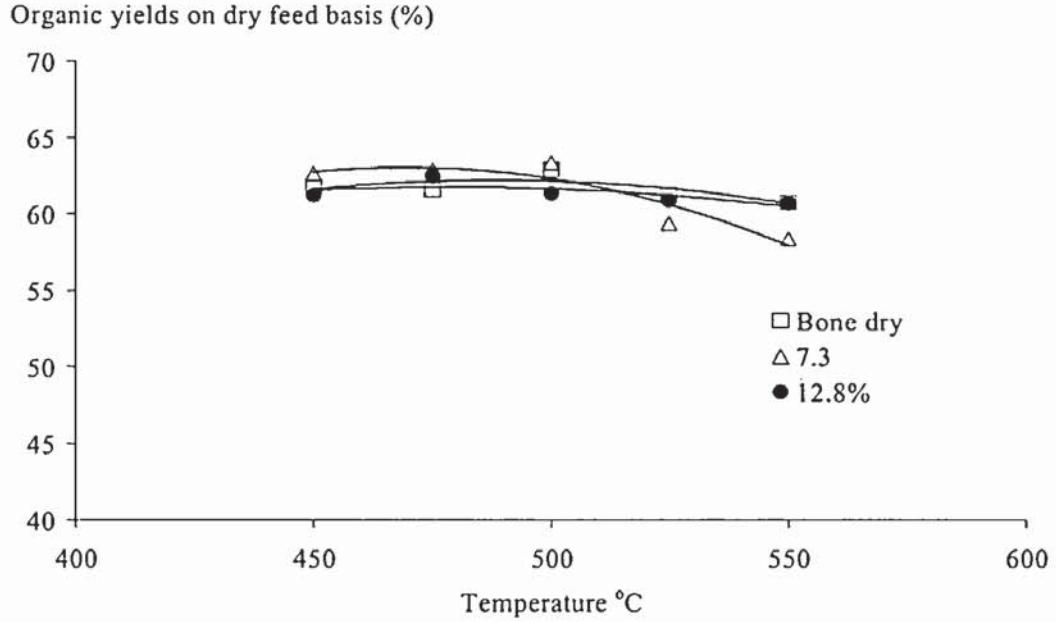


Figure 5-4. Organic yield versus reactor temperature for spruce with different moisture content

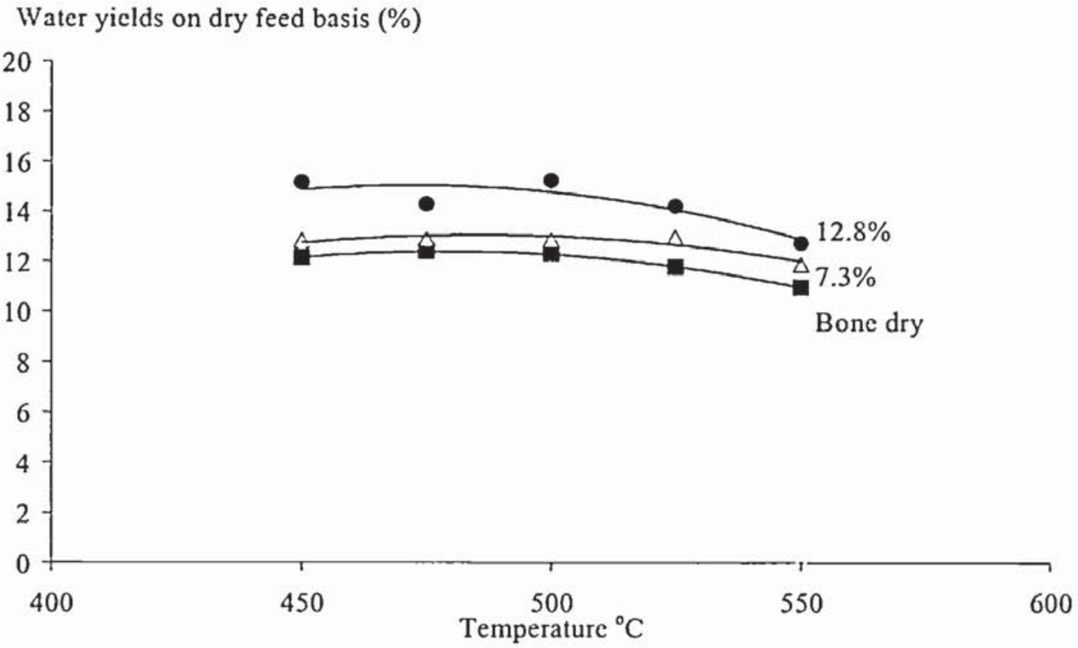


Figure 5-5. Water yields (water from reaction) versus reactor temperature for spruce with different moisture content

The Equations of curves are shown as Equation 5-8, 5-9 and 5-10, the R-squared value is above 0.9.

Water % = $-0.0004(T)^2 + 0.3414(T) - 65.622$ (for 12.8% moisture feed)

Equation 5-8

Water % = $-0.0003(T)^2 + 0.2481(T) - 47.177$ (for 7.3% moisture feed)

Equation 5-9

Water % = $-0.0003(T)^2 + 0.2811(T) - 54.963$ (for bone dry feed)

Equation 5-10

5.3 BIO-OIL PROPERTY

5.3.1 Water content of bio-oil:

The water content of pyrolysis oil is typically between 15 and 30 wt% and originates from the water present in the biomass feedstock, and reaction water that is dependant on the process conditions [64,122]. The water content changes with time and is a function of both storage temperature and storage duration (section 3.3.1). All oil water contents were therefore tested at the same time after oil production. Figure 5-6 shows oil water content versus reactor temperature and feed moisture content. The oil water content experienced a slight decrease at higher reactor temperatures. A similar result was obtained by Horne et al [123] in an investigation of mixed wood waste pyrolysis over the 400 to 550 °C temperature range. These workers found that the oil water content was 28 wt% at 400 °C and 26.8 wt% at 550 °C although they thought this change was experimental error and pyrolysis temperature did not influence on oil water content.

Figure 5-6 shows that increased feed moisture content led to higher oil water content. Water was also formed as a product of the pyrolysis reactions. Indeed, in the case of bone dry spruce all of the water contained in the pyrolysis oil must have come from reaction. Considering the complexity of the pyrolysis process, it was to be expected that the amount of reaction water should depend on the process conditions and therefore also on the feed moisture content. The water in the oil can be considered an advantage because it reduces the viscosity of the liquid, but phase separation is likely to occur at water concentrations greater than a threshold value, which will be discussed in section 5.3.4.

5.3.2 Oil char content

In this work, spruce wood was employed as feedstock, which has very low ash content of 0.5% (see Table 2-1); it was presumed that this may be one of the reasons explaining the very low char content of the oil, which generally ranged between 0.05 wt% to 0.15 wt%. The test was so delicate for such low char contents in the oil that even a small change in the fourth decimal place was enough to make the result inaccurate. Therefore, only typical samples were chosen for the char content test. The results are illustrated in Figure 5-7, which shows the char content in the oil obtained in the pyrolysis of bone dry spruce at different reaction temperatures, and Figure 5-8, which shows the char content in the oil derived from the pyrolysis of spruce at different moisture contents and at a reaction temperature of 500°C. The oil char content increased at higher reaction temperatures, in spite of the fact that the total char yield became smaller at increased reaction temperatures. A simple explanation for this is that high reaction temperature leads to lower char yields, as high temperature is beneficial for char benefited for decomposition. This decomposition makes the char particle size much smaller than that obtained at lower temperatures. Very small particle size char was more easily blown into the collection system. Therefore, higher temperatures gave high oil char contents. High feed moisture content led to lower oil char content at the same reaction temperature, which is in agreement with the results obtained for total char yield as moisture is beneficial for vapour to penetrate the solid materials and reduce the deposition of inside pores.

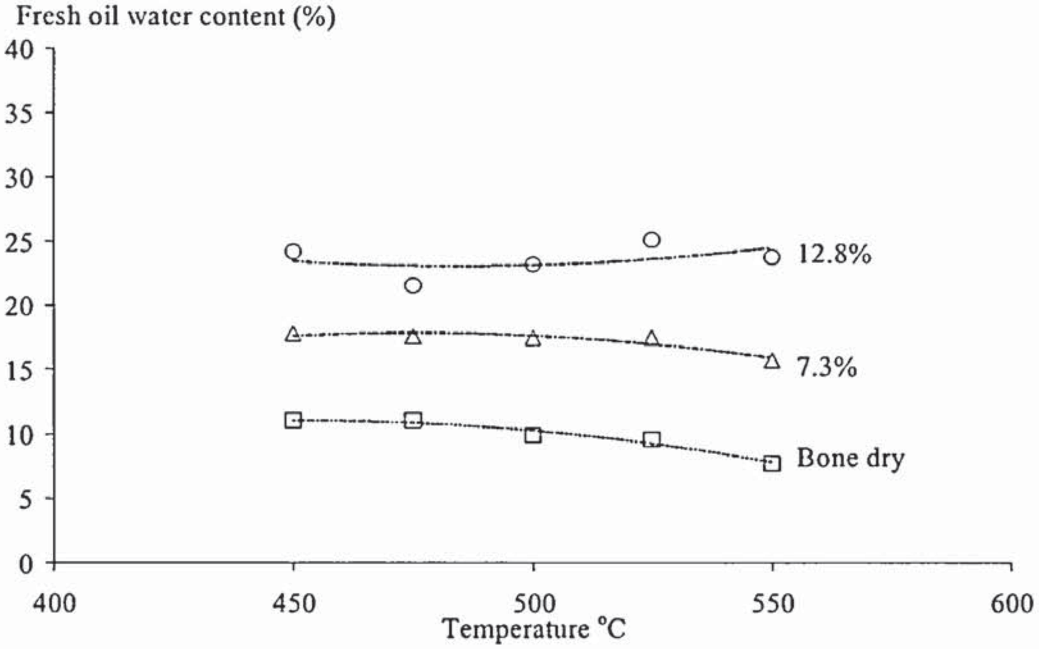


Figure 5-6. Fresh oil water content versus reactor temperature for spruce with different moisture content

5.3.3 Bio-oil viscosity:

The viscosity of the oil increased with the length and temperature of storage leading to the need to test all oil after the same conditions had been experienced. Figure 5-9 and Figure 5-10 show the viscosity of fresh and aged oil versus reactor temperature and feed moisture content. A high reactor temperature leads to high oil viscosity, which is also the case for low moisture content; both phenomena are presumed to be due to reduced water content in the oil produced.

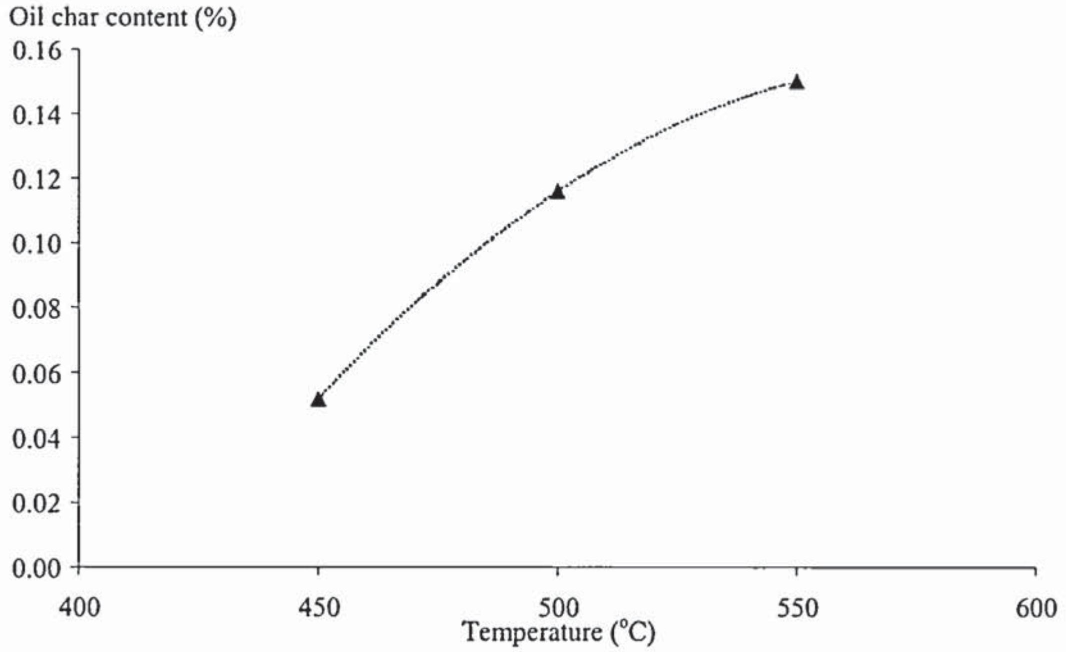


Figure 5-7. **Oil char content versus reactor temperature**

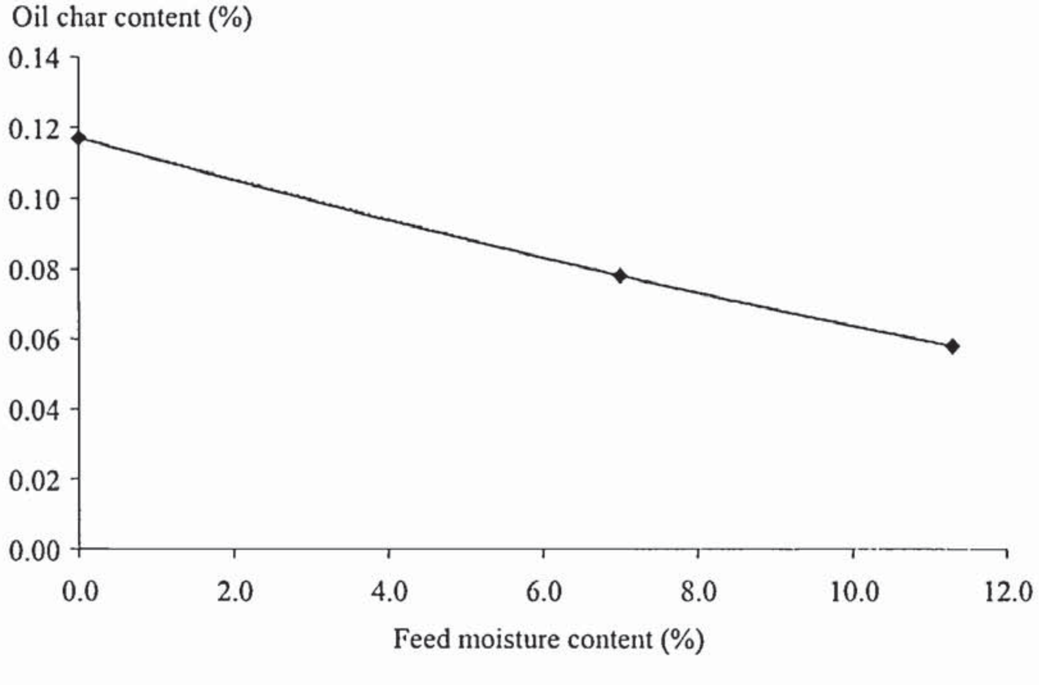


Figure 5-8. **Oil char content versus feed moisture content at same reactor temperature 500°C**

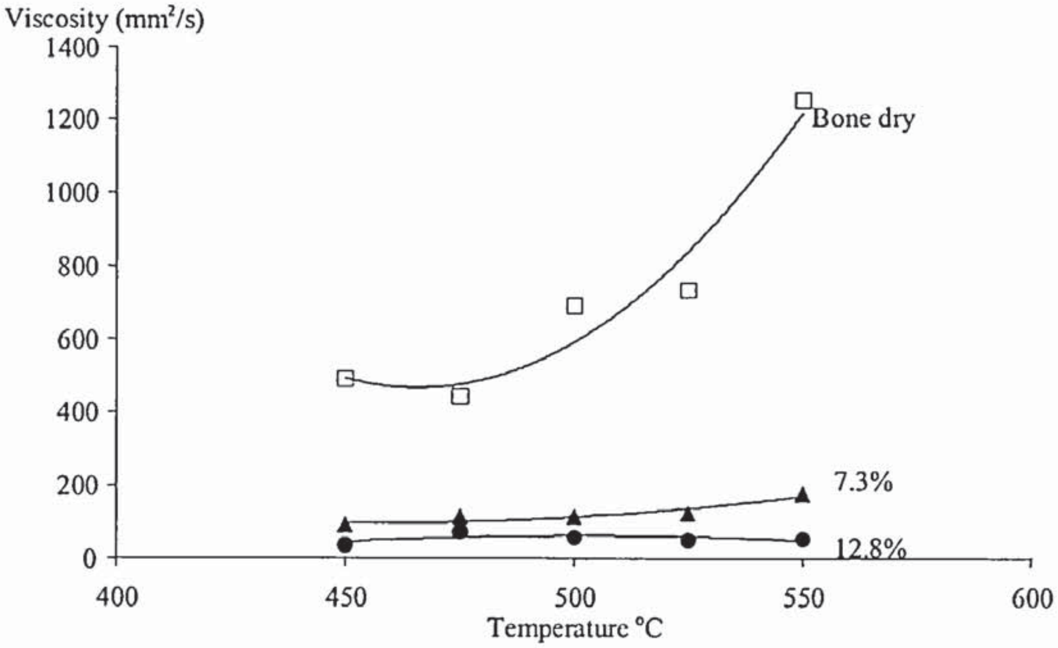


Figure 5-9. Fresh oil viscosity versus reactor temperature for spruce with different moisture content

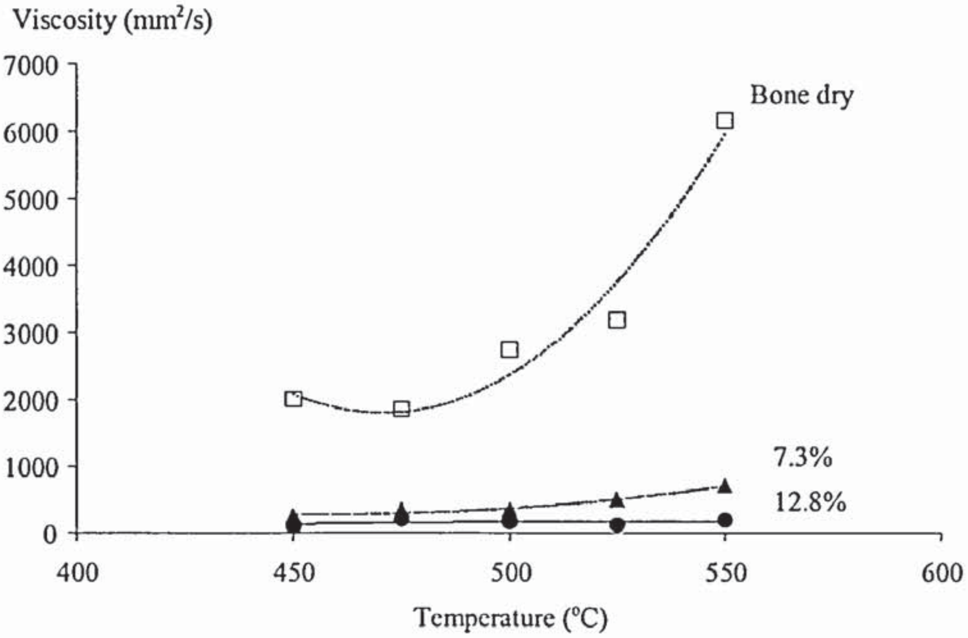


Figure 5-10. Aged oil viscosity versus temperature for spruce with different moisture content

5.3.4 Bio-oil stability:

Figure 5-11 shows the VI value for different moisture contents. The higher moisture content spruce gives unstable bio-oil, with phase separation occurring at high reactor temperatures. This occurred at 500°C for 15.2% moisture spruce and 450°C for 18.6 % moisture spruce. Wood with a moisture content of 12.8% pyrolysed at above 500°C resulted in an oil that displayed phase separation after aging (which is required as part of measuring the viscosity index). Phase separation makes the determination of the viscosity index impossible. For the lowest moisture content spruce (bone dry spruce) the VI was also relatively high, particularly at higher reactor temperatures. Figure 5-7 also shows that oil derived from pyrolysis carried out at a high reaction temperature had high char content. This may have been one of the reasons for the poor stability of this oil, with the char in the oil accelerating the polymerisation reactions. Moderate feed moisture contents (approximately 7.3-12.8%) gave better stability, but this effect became reduced at higher reaction temperatures. The stability of bio-oil therefore appeared to decrease with increasing reactor temperature. The most stable bio-oils appeared to be made at temperatures below 500°C and with moderate water contents of 7.3-12.8% on a dry basis.

An important characteristic of bio-oil is that water can be tolerated up to around 30% wt of the bio-oil, but above this figure, it becomes increasingly unstable and can more easily undergo phase separation. Water in the bio-oil may be considered to be a mixture of water, water-soluble organic compounds and water-insoluble materials. The amount of water that can be dissolved in the oil before phase separation occurs depends on the type of feedstock. Elliott [100] found that phase separation occurred when the oil water content was greater than 35% for oak oil and 25-30% for pine oil. Czernik [70] found that birch oil phase separated when the oil water content reach to 27 %, and for pine and poplar oil, phase separation occurred when the water content was 25% and 31% respectively. This work showed that spruce oil phase separated at water contents greater than 28%.

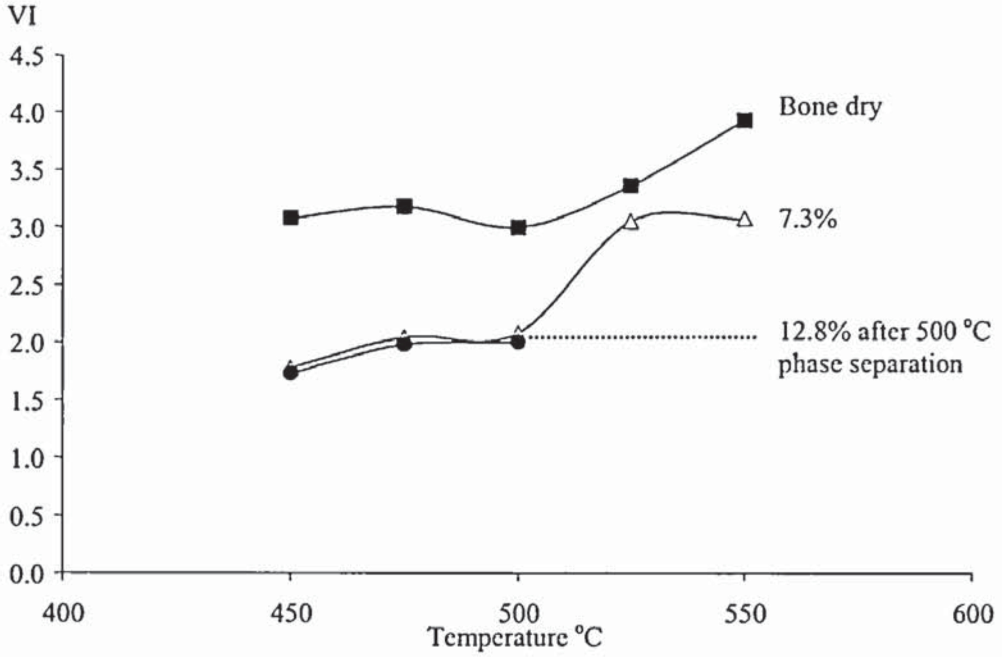


Figure 5-11. Viscosity index versus reactor temperature for spruce with different moisture content

5.3.5 The relationship between viscosity and water content

The viscosity of bio-oil strongly depends on its water content, dilution with water making the oil less viscous [70]. Figure 5-12 and Figure 5-13 illustrate that relationship clearly both for fresh and aged oil. The oil samples were derived from the pyrolysis of spruce with the same feedstock moisture content at different reaction temperatures. It should be noted that the differences in water content in the two figures were the result of differing reactor temperatures, which affects pyrolysis oil viscosity through other means besides water content. Nevertheless, the effect of dilution with water was clearly apparent. It would not have been straightforward to illustrate this relationship by direct dilution of the pyrolysis oil, that is addition of water to the condensed oil, because there would have been mixing problems potentially leading to phase separation. The other three moisture contents examined led to similar graphs. The effect of dilution therefore appears to be independent of feed moisture content. Meier *et al* studied oil characteristics for four oil samples derived from different feedstocks and different pyrolysis reactors, namely softwood (rotating cone), hardwood (circulating fluid bed), poplar (bubbling fluidised bed) and eucalyptus (vortex). These workers found that a high oil water content did not necessarily result in a low viscosity [77]. This result can be explained by the fact that water content is not the only reason for different oil viscosities. The viscosity of the pyrolysis liquid also has a direct relationship to liquid average molecular weight. Other factors are the oil char and lignin content. As the four liquid samples used were derived from different feedstocks, and were produced by different pyrolysis processes, it was assumed that there were differences in the chemical composition of the oils. The differences in average molecular weight were probably the principal factor explaining the observed liquid viscosity. A similar result was found in this work. Figure 5-14 shows that aged oil had a much higher viscosity than the corresponding fresh oil, however, as can be seen in Figure 5-15, aged oil had higher water content than fresh oil. An explanation for this fact may be that bio oil contains compounds that, during storage or handling, can react to form larger molecules that impede shear movements across the liquid, that is, increase the viscosity. Furthermore, the loss of volatiles during aging at high temperature may also lead to oil viscosity increases. At the same time dehydration reactions take place, resulting in the formation of water during the aging process. The water released during the aging process is rather small, however, and its effect is overcompensated by the increase of viscosity related to the formation of larger molecules.

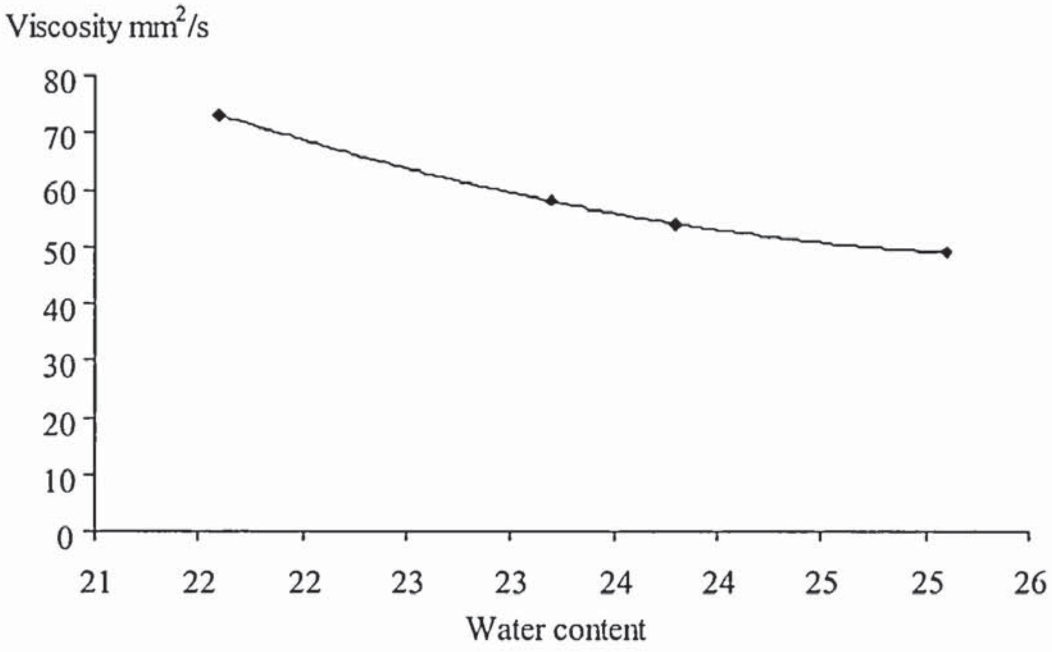


Figure 5-12. Fresh oil viscosity versus its water content

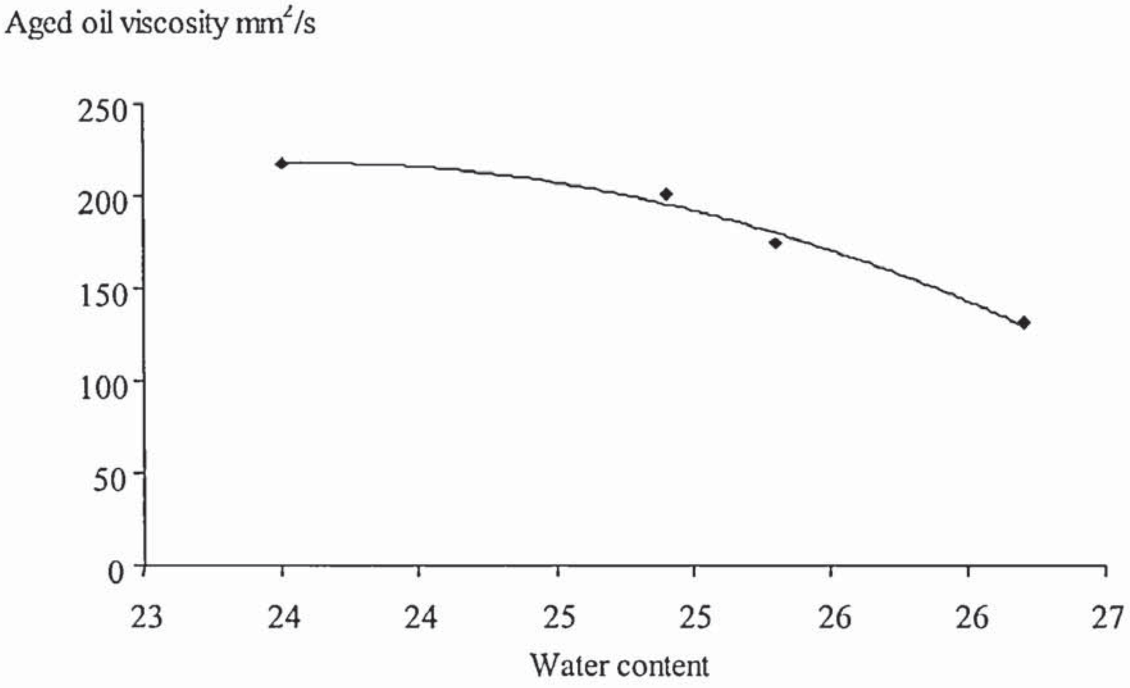


Figure 5-13. Aged oil viscosities versus its water content

The equation of fresh oil viscosity versus oil water content is as Equation 5-11, the R-squared value is 0.99 and for aged oil is as Equation 5-12, the R-squared value is 0.9.

Viscosity (mm^2/s) = $1.33\ W\%^2 - 69.0\ W\% + 943.5$ **Equation 5-11**

Viscosity (mm^2/s) = $-12.8\ W\%^2 + 605.2\ W\% - 6921.5$ **Equation 5-12**

Where W% is oil water content.

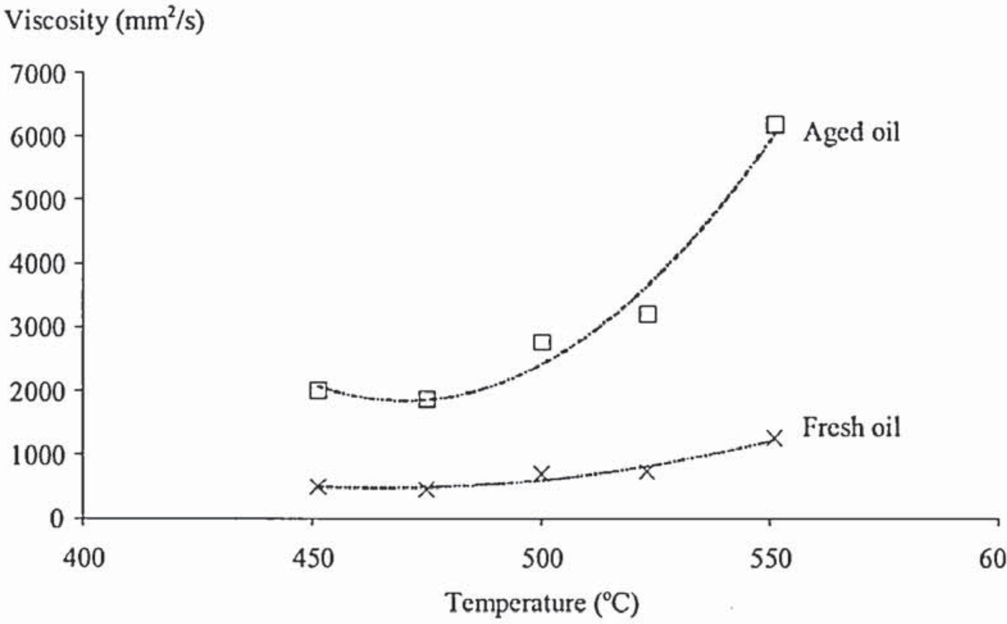


Figure 5-14. Fresh and aged oil viscosity versus reactor temperature for bone dry spruce

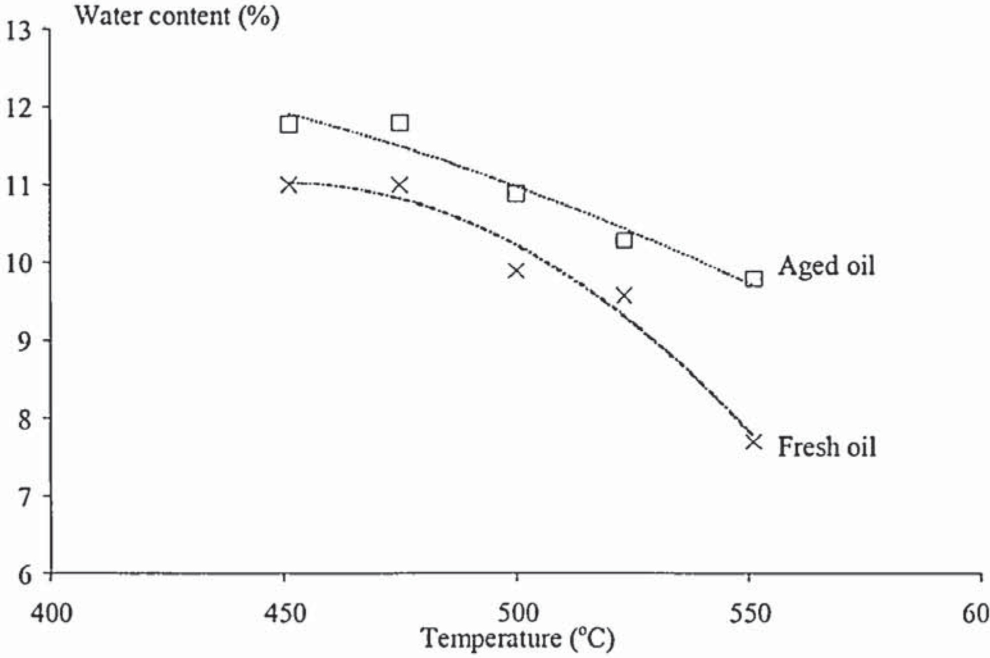
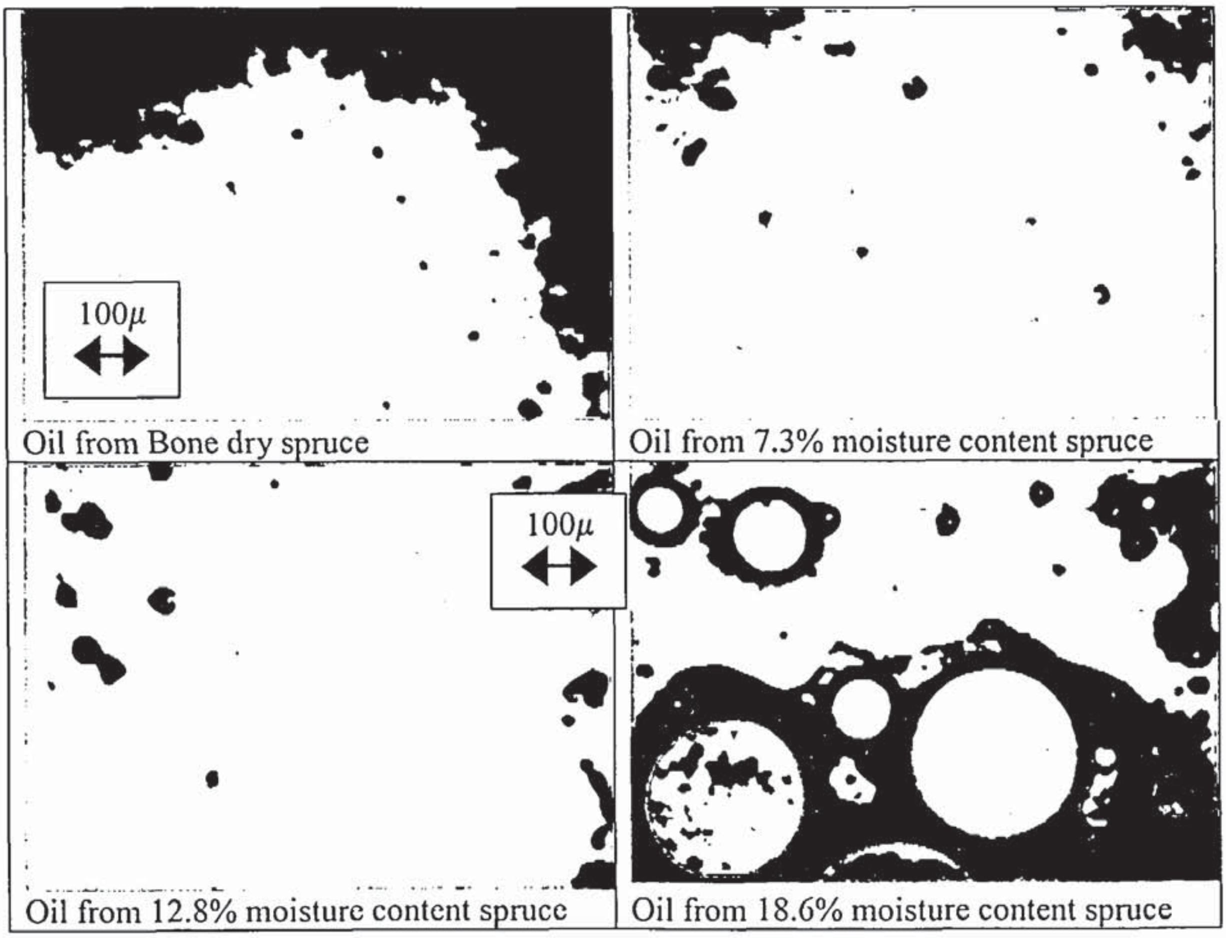


Figure 5-15. Fresh and aged oil water content versus reactor temperature for bone dry spruce

5.3.6 Observation

Figure 5-16 shows optical microscope pictures of the bio-oil made at the same reactor temperature with different moisture content feeds from bone dry to 18.6%. These suggest that an emulsion is formed in the oil with increasing emulsion droplet sizes at increasing water contents. For high moisture oil (15.2% and 18.6%), the emulsion (w/o) formed contained large and easily breakable droplets that contributed to making the oil unstable. Micro-emulsions (w/o) formed in oil obtained in the pyrolysis of spruce with a more moderate moisture content (approximately 7.3-12.8%) showed better stability. For bone dry spruce, little visual evidence of emulsions was found in the oil, but lower water contents gave a higher viscosity bio-oil that was less stable and gave higher viscosity indexes. Thus the overall effect of feed moisture content on bio-oil stability was partly due to the reactions of water in the pyrolysis process and partly due to the feed moisture affecting the product water content and hence stability.



Oil from Bone dry spruce

Oil from 7.3% moisture content spruce

Oil from 12.8% moisture content spruce

Oil from 18.6% moisture content spruce

Figure 5-16. Optical microscopy photos of oils from different moisture spruce at 500°C reactor temperature x160

The stability of the emulsion was decided by the hydrophilicity of the organic components, so it was likely that each biomass had optimum water content for a low viscosity and stable bio-oil.

5.4 SUMMARY AND CONCLUSIONS

Feed moisture content had the following impacts on the yields of pyrolysis products and the stability of pyrolysis liquid:

- High feed moisture content gave lower char and higher gas yields,
- High feed moisture content resulted in higher oil water content and was shown to lead to oil phase separation,
- High feed moisture content increased the reaction water generated in the pyrolysis process,
- Low feed moisture gave lower liquid yield (dry feed basis),
- Very low feed moisture gave very high initial viscosity,
- Very low feed moisture gave higher viscosity index and thus lower stability,
- Moderate feed moisture content had no effect on stability when produced below 500°C, but phase separation occurred when produced above 500°C,
- Feed moisture content did not affect organic yields,
- For spruce wood, the optimum oil yields appeared at reactor temperatures of 470-490°C and higher feed moisture contents gave lower maximum yield temperatures,
- The highest liquid yield on a dry feed basis was from intermediate feed moisture contents of around 7.3 –12.8 %,
- There appeared to be an optimum amount of water in the oil, which gave the most stable and least viscous oil.

In summary, this study indicated that the likely optimum for drying biomass feedstock prior to pyrolysis was a feed moisture content between 7.3% and 12.8%. These conditions gave the best yields and stability together with a relatively low viscosity.

CHAPTER 6 . PARTIALLY OXYGENATED PYROLYSIS OF BEECH WOOD TO IMPROVE THE STABILITY OF PYROLYSIS LIQUID

> The presence of numerous and various oxygenated functions gives bio-oil-unwanted characteristics (See Chapter 3) that must be removed. Zeolite cracking of pyrolysis vapour is effective in eliminating oxygen but the loss of carbon during this process results in low liquid yields. Also, catalytic hydrotreatment using hydrogen or hydrogen donors as a means of eliminating oxygen is a very costly process. An alternative route using partially oxygenated pyrolysis was introduced and discussed in this work in order to improve the stability of bio-oil.

6.1 INTRODUCTION

The oil produced from the pyrolysis of biomass is a very complex mixture of components, consisting of organic acids, higher aldehydes, ketones, esters and water (See section 3.2). The instability of pyrolysis liquids is thought to be due to the large quantity of oxygen containing compounds present, in particular the chemically reactive carbonyl functions of aldehydes and ketones [Section 3.4,124]. The oil presents some unwanted characteristics such as high viscosity, high acidity, and chemical and physical instability (See section 3.3). Therefore, the potential for direct substitution of the biomass-derived pyrolytic oils for conventional petroleum fuels without upgrading is limited [125, 97]. Consequently, several possible ways have been considered to improve the quality of the liquid (Section 3.6). Two main methods for removal of oxygen from the bio-oil were reviewed in this work, namely hydrotreatment and catalytic vapour cracking.

Hydrotreatment aims to remove the oxygen from bio-oil through a family of deoxygenation reactions, which can be conceptually characterised as follows:

$$\underset{\text{(Bio-oil)}}{C_6H_8O_4} \quad + \quad 6H_2 \quad \rightarrow \quad \underset{\text{Hydrocarbons}}{6CH_2} \quad + \quad 4H_2O$$

This is a carbon limited system and gives a maximum stoichiometric yield of 58 wt % on liquid bio-oil or a maximum energetic yield of about 50 wt % [86].

A major disadvantage of hydrotreatment is the significant hydrogen requirement of around 700 l/kg bio-oil for full treatment [4]. Rupp suggested a range of 600-1000 l/kg bio-oil [94]. This is approximately the stoichiometric requirement, although an excess of 100-200% is required for processing to maintain a high hydrogen partial pressure. Catalytic hydrotreatment of liquid product is not an economical approach [126] because of the high hydrogen consumption, the high water content of the liquid product obtained [127], and catalyst deactivation due to the presence of a high water pressure and the strong tendency of certain compounds to form coke and block access to the catalyst [128].

Hydrotreatment requires hydrogen or a hydrogen donor under high pressure or the use of transition metal catalysts. Consequently, it is a rather expensive solution at the present time [125,129], so catalytic vapour cracking has been studied by a number of laboratories [130, 131,132,133]. This attraction of interest was due to the fact that this process is carried out prior to condensation of the pyrolysis vapours so that the addition of a supplementary step to the process is not required.

Catalytic vapour cracking makes deoxygenation possible through simultaneous dehydration and decarboxylation over acidic zeolite catalysts at atmospheric pressure [134]. Their use has been considered a potentially viable upgrading pathway by a number of researchers as the atmospheric pyrolysis process conditions result in a much lower cost than high-pressure hydro-treatment. Adjaye and Bakhshi [135] upgraded re-vaporised wood-derived oil over various catalysts, including HZSM-5, Hmordenite, and silica-alumina. These workers used the yield of hydrocarbons as well as the extent of de-oxygenation, coke formation and conversion of the non-volatile portion of the bio-oil to determine the performance of catalysts. It was found that HZSM-5 gave the best performance in terms of maximum hydrocarbon yield in the oil compared with other catalysts. The maximum hydrocarbon yield at 370 °C was 39.3 wt % of the bio-oil. Williams *et al.* [136] upgraded the vapours from the fluidised bed pyrolysis of biomass with Zeolite catalyst and found that oil yields decreased from 43.3 wt % without catalysis to 9.1 wt % at a catalyst temperature of 550°C. Another drawback of Zeolite catalytic upgrading of bio-oil is that the upgraded oils may represent a health hazard due to a marked increase in the concentrations of polycyclic aromatic hydrocarbons (PAH), which are known to be carcinogenic or mutagenic [137,138]. Furthermore, continuous catalytic pyrolysis is undesirable as coke formation is detrimental to the life of catalysts [139].

The addition of air to the reactor to give a partial gasification reaction to provide reaction heat has been used previously [6], but no work on the effects of oxygen on pyrolysis and pyrolysis products has been reported.

An adverse route, partially oxygenated pyrolysis, was introduced in this work in order to improve the stability of bio-oil. The main purpose was to oxidise the chemically reactive carbonyl groups of aldehydes and ketons into more stable chemicals by oxygen addition, because heating or in the air these carbonyls were thought to facilitate polymerisation reactions that yield an overall increase in the viscosity and decrease in the stability of the liquid. The effect of oxygen on bio-oil property and a comparison with Zeolite catalytic pyrolysis vapours was also performed in this work.

6.2 AIRFACTOR CONVERSION FROM INLET OXYGEN PERCENTAGE IN FLUIDISING NITROGEN

The airfactor, defined as the ratio of air or oxygen supplied to the gasifier or pyrolyser bed to that required for stoichiometric combustion, is the most important single operating parameter in gasification [140] and in partially oxygenated pyrolysis.

Based on beech wood elemental analysis (see section 4.4.1), the empirical formula of beech wood was determined to be $C_6H_{10}O_5$, which was referred to as the biomass formula, and hence the stoichiometric combustion reaction is as given below:

$$\begin{array}{lllll} C_6H_{10}O_5\text{ (Biomass)} & + 6\,O_2 & \rightarrow & 6\,CO_2 & +5\,H_2O \\ 162 & 192 & & 264 & 90 \\ W_{Dry\ Biomass} & W_{O_2\ for\ complete\ combustion} & & & \end{array}$$

The airfactor was calculated by Equation 6-1:

$$Airfactor = \frac{W_{O_2\ consumed}}{W_{O_2\ for\ complete\ combustion}} = \frac{W_{O_2\ consumed}}{W_{Dry\ Biomass} * \frac{192}{162}} = \frac{W_{O_2\ consumed}}{W_{Dry\ Biomass}} * \frac{162}{192}$$

Equation 6-1

Where:

$W_{Dry\ Biomass}$: Weight of feedstock used for partially oxygenated pyrolysis.

$W_{O_2\ consumed}$: Weight of Oxygen consumed in partially oxygenated pyrolysis.

$W_{O_2\ for\ complete\ combustion}$: Weight of Oxygen needed for complete combustion of total feedstock.

6.2.1 Combustion airfactor:

$$\begin{array}{lllll} C_6H_{10}O_5\text{ (Biomass)} & + 6\,O_2 \rightarrow & 6\,CO_2 & +5\,H_2O \\ 162 & 192 & 264 & 90 \end{array}$$

Totally combustion implies that 162g biomass are consumed by 192g oxygen, thus the airfactor is 1.

6.2.2 Gasification airfactor

Gasification is the thermochemical conversion of organic material to a fuel gas by partial oxidation at high temperature. (The temperature is in excess of 1000K)

$$\begin{array}{lll} C_6H_{10}O_5\text{ (Biomass)} + O_2 & \rightarrow & CO + H_2 + H_2O + CO_2 + CH_4 + \ldots\ldots \\ 162 & (25\%\text{-}30\%)*192 & \end{array}$$

thus air factor for gasification is normally 0.25 - 0.30.

6.2.3 Pyrolysis airfactor:

Pyrolysis occurs with heating in the absence of oxygen or air to produce a mixture of solid char, condensable liquids and gases. Fast pyrolysis, in particular, is a process designed to maximise the formation of condensable vapours, with a minimum of gas and char as by-products.

$$C_6H_{10}O_5 \rightarrow \text{Bio-oil (Chemicals and Water)} + \text{Char} + \text{Gases}$$

Airfactor is conventionally 0.

6.2.4 Partially oxygenated pyrolysis airfactor:

Partially oxygenated pyrolysis occurs with heating in a small amount of oxygen or air. In this work, oxygen percentages in the fluidising nitrogen ranging from 0 to 3.27-v/v % were used. This range makes airfactor lower than 0.3.

Figure 6-1 showed that air factors ranged from 0 to 0.21, which is between pyrolysis and gasification. There was a linear correlation between the air factor and the oxygen content of the fluidising nitrogen. All experiments were performed with the same feed rate, pyrolysis temperature and run time.

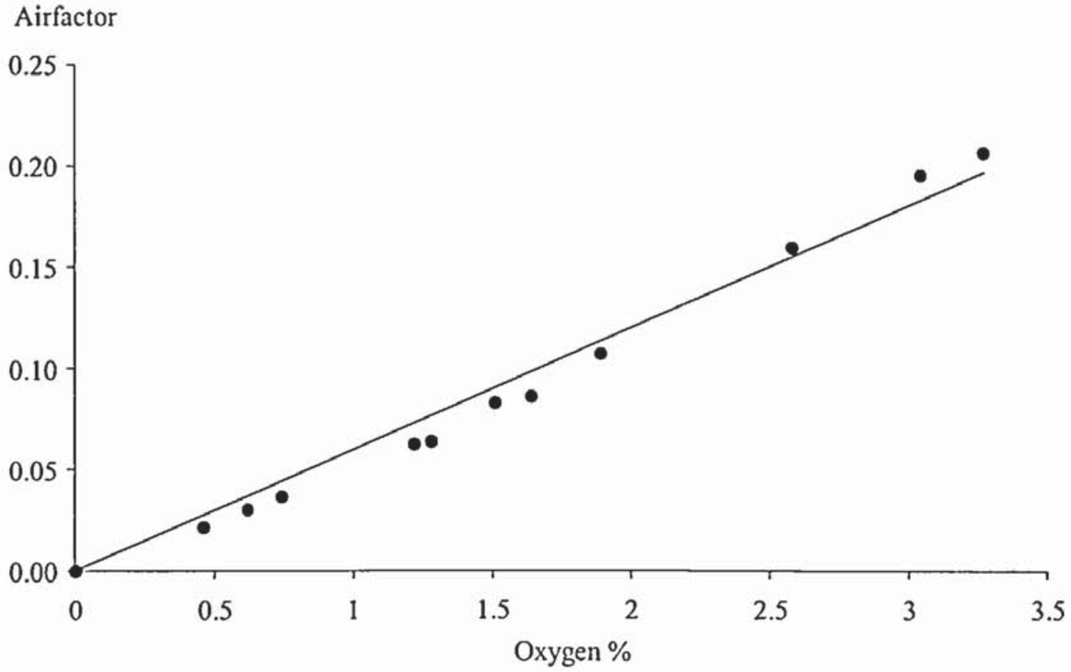


Figure 6-1. Airfactor versus percentage of oxygen in the fluidising nitrogen

6.3 PARTIALLY OXYGENATED PYROLYSIS PROCESS

It is necessary to distinguish between temperature of reaction (reactor) and furnace temperature. The latter is higher in standard pyrolysis as a temperature gradient is required to effect heat transfer to the biomass particles.

Figure 6-2 shows that the furnace temperature was about 10 to 15 °C higher than the reaction (reactor) temperature for normal pyrolysis of beech wood. This can be explained by the fact that the pyrolysis of beech wood is overall an endothermic process and therefore needs heat to be supplied during pyrolysis. Currently, commercial systems would be expected to utilise one or both of the by-products char/gas for the process heat requirement.

Figure 6-3 on the other hand shows that for partially oxygenated pyrolysis (airfactor is 0.16), the reaction (reactor) temperature was about 10 to 15 °C higher than the furnace temperature. This temperature gap was increased for higher airfactors. This result indicated that partially oxygenated pyrolysis of beech wood is an exothermic process, possibly due to the heat released in the combustion of char or organics. Therefore, it was concluded that oxygenated pyrolysis requires less heat transfer than pyrolysis without oxygen.

6.4 PRODUCT YIELD

The product yields from fast pyrolysis are a function of the biomass feed and the reactor. In this section of the work, only beech wood with moisture content of 8% on a dry feed basis was available for use as a feedstock. All runs were performed on an existing 150g/h-bench scale fluid bed reactor (See Figure 4-4). The temperature of condenser 1 in the liquid collection system was set at 0 °C by using of circulator (See section 4.2.4.1). The total hot space gas residence time was between 0.5 to 0.6 seconds (see section 4.2.3) and the pyrolysis temperature was 475 °C. In Chapter 5 the effect of pyrolysis temperature on the pyrolysis liquid was also discussed and it was found that the highest yields of liquid were between 475 °C and 500 °C. Consequently a pyrolysis temperature of 475 °C was fixed for the work reported in this chapter, which is concerned with the effect of oxygen addition on oil quality and yield.

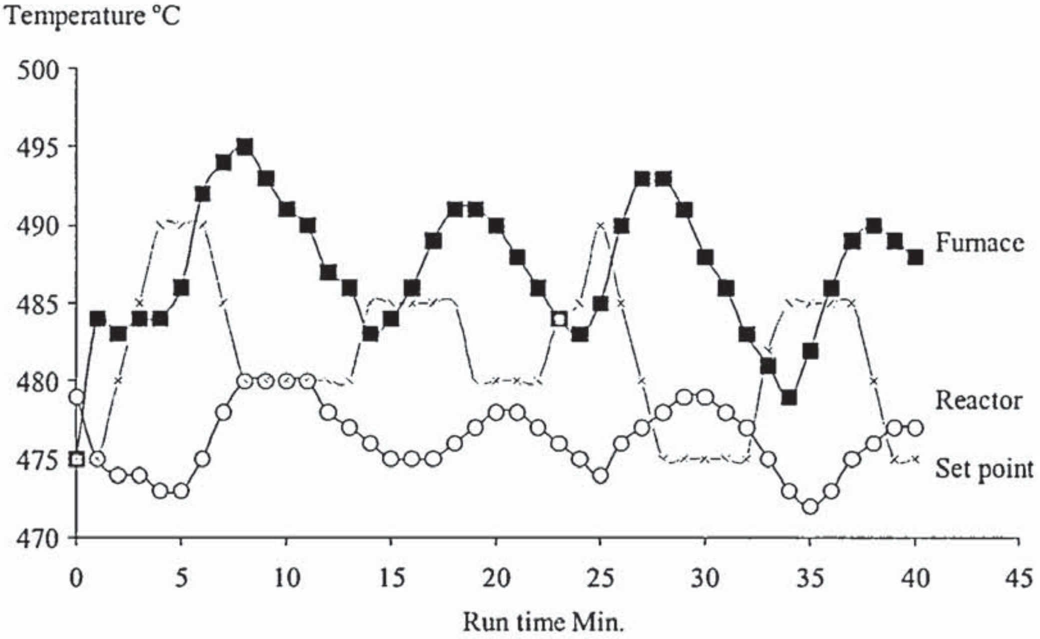


Figure 6-2. **Temperature change during pyrolysis without oxygen (Average reaction temperature 476 °C)**

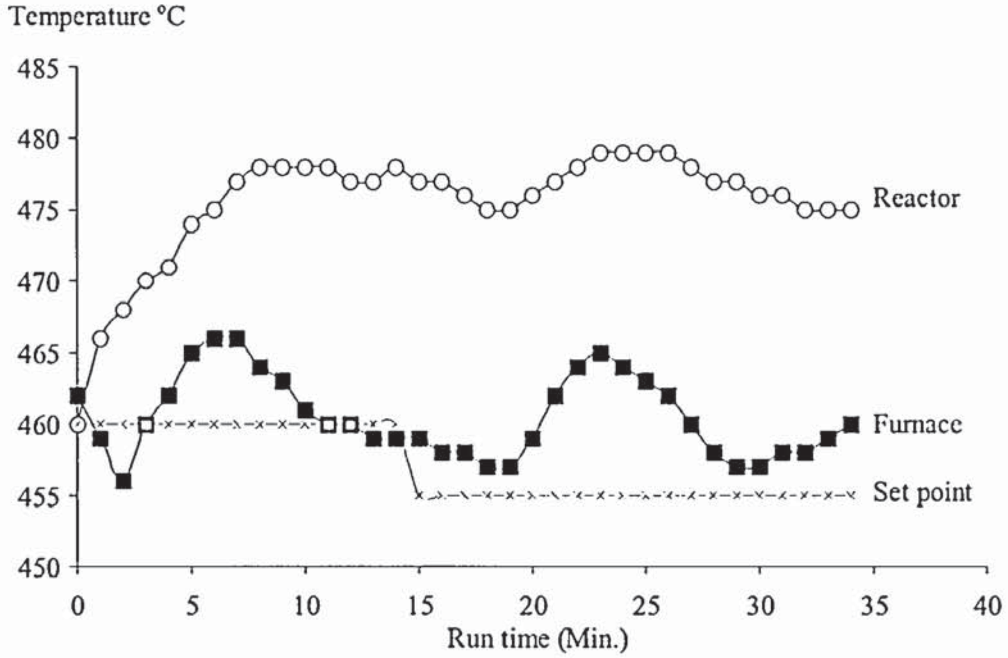


Figure 6-3. **Temperature change during pyrolysis with oxygen (Average reaction temperature 475 °C and airfactor 0.16)**

Figure 6-4 shows the variation of partially oxygenated pyrolysis product yields with airfactor. The yields of organics and oil were significantly reduced with the addition of increasing amounts of oxygen, while gas and water yields rose. Char yield was also reduced in partially oxygenated pyrolysis. It was also observed that the colour of the fluidising medium sand was grey after oxygenated pyrolysis but for normal pyrolysis without oxygen the sand was black as it was coated with char. It was assumed that this char had been combusted in partially oxygenated pyrolysis thus this is one of the reasons for very higher CO_2 content in the product gases (see figure 6-5). This revealed another advantage of using partially oxygenated pyrolysis. Char is suspected of being a major contributor to the instability of bio-oil therefore; the elimination of most small char particles by burning might be beneficial. The mass balance results (Section 4.10) also show that most of the char mass was collected in the cyclones, as the majority of the char mass is to be found in the larger char particles that would not be in the reactor long enough to experience complete combustion.

The product gases consisted largely of CO and CO_2, with lower concentrations of methane, ethane, ethylene, propane, propylene and hydrogen (See section 4.10.3.4). Figure 6-5 shows that CO_2 was the dominant gaseous product and there was a marked increase in its yield. The yield of CO experienced a slight increase for partially oxygenated pyrolysis. The oxygen that remained appeared to be directly proportional to the oxygen added for a range of airfactors.

The total gas yields increased especially for CO_2 due to combustion reaction during the process. The left oxygen percent in the product gas increased with airfactor means that not all of the oxygen added was consumed totally in the process.

The experiment results for dominant gases yields are shown in Table 6-1. It seems that there is a reaction $2CO + O_2 = 2CO_2$ equilibrium in gases products as the equilibrium constant $K = Y^2_{CO2}/(Y^2_{CO}*Y_{O2})$ was calculated using CO, CO_2 and O_2 product yield analytical results and it was found that K remained constant at a value of about 4 for oxygen percentages in the inlet gas ranging from 0.5 to 3.0%. This may be the reason that not all of the added oxygen took part in the combustion reaction during oxygenated pyrolysis.

Table 6-1. CO, CO2 and O2 concentrations in product gases

O_2% inlet	CO yields on dry feed basis	CO_2 yields on dry feed basis	O_2 outlet on dry feed basis	Actual K
0.46	3.89	9.13	1.04	5.29
0.62	4.64	10.92	1.45	3.82
0.74	4.76	12.19	1.59	4.12
1.22	4.85	14.1	2.04	4.14
1.28	5.08	15.84	2.16	4.50
2.58	5.95	28.66	4.86	4.77
3.04	6.44	33.08	5.64	4.67
3.27	6.79	35.35	6.52	4.16
Average				4.44

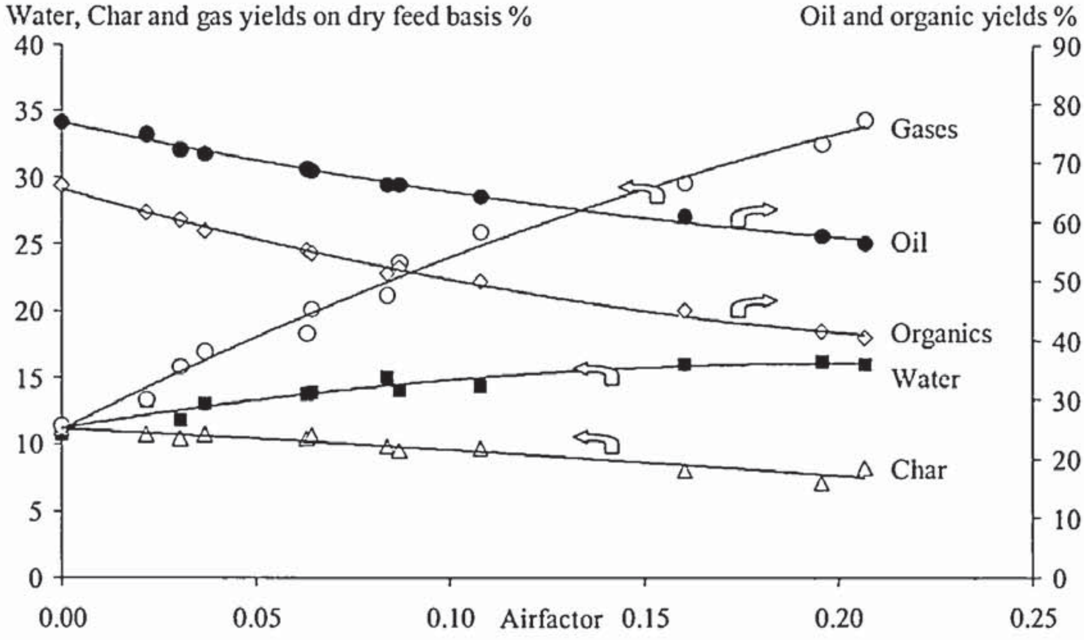


Figure 6-4. Product yields versus airfactor

The equations of product yields versus airfactor are shown as Equation 6-2 to Equation 6-6, the R-squared value of all equations are above 0.9.

Oil % = -93.829A + 75.366 **Equation 6-2**

Organic% = -116.38A + 63.349 **Equation 6-3**

Water% = $-115.71A^2 + 47.448A + 11.21$ **Equation 6-4**

Char% = -17.872A + 11.286 **Equation 6-5**

Gas% = 108.48A + 12.359 **Equation 6-6**

Where: A is airfactor.

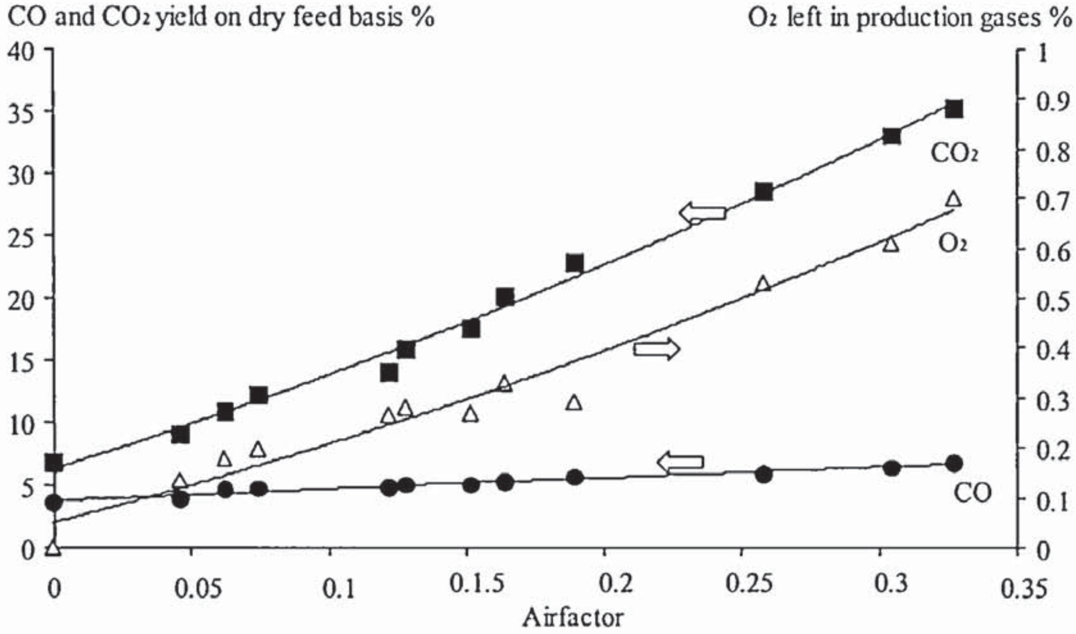


Figure 6-5. CO, CO_2 and oxygen percent in product gases versus airfactor

The equations of gases yields versus airfactor are shown as Equation 6-7 to Equation 6-9, the R-squared value of all equations are above 0.9.

CO% = 0.89A + 4.0 **Equation 6-7**

CO_2% = 138.01A + 6.7 **Equation 6-8**

O_2% = 2.9A + 0.06 **Equation 6-9**

Where: A is airfactor.

6.5 OIL VISCOSITY, WATER CONTENT AND STABILITY

The oil viscosity, water content and oil stability were measured in this work (See section 4.9.2.1, section 4.9.2.2 and section 4.9.2.3). Figure 6-6 shows the results of oil viscosity and viscosity index versus airfactor. Fresh oil viscosity decreased for greater airfactors. The oil phase separated for airfactors above 0.15. Aged oil (see section 4.9.2.3) experienced a similar but steeper drop of viscosity with greater additions of oxygen. There was, however, no further improvement in the 0.9 to 0.15 ranges of air factors; for air factors greater than 0.15 phase separation occurred. The viscosity index dropped slightly with the addition of oxygen, but experienced little further change for airfactors ranging from 0.06 to 0.15.

The solid points in Figure 6-6 are an illustration of the effect of temperature of condenser 1 on the experimental result. They are above the trend line, as the oil collection system temperature of condenser 1 was at 3 °C, which was a little different from normal setting temperature at 0 °C, which was used for all other runs.

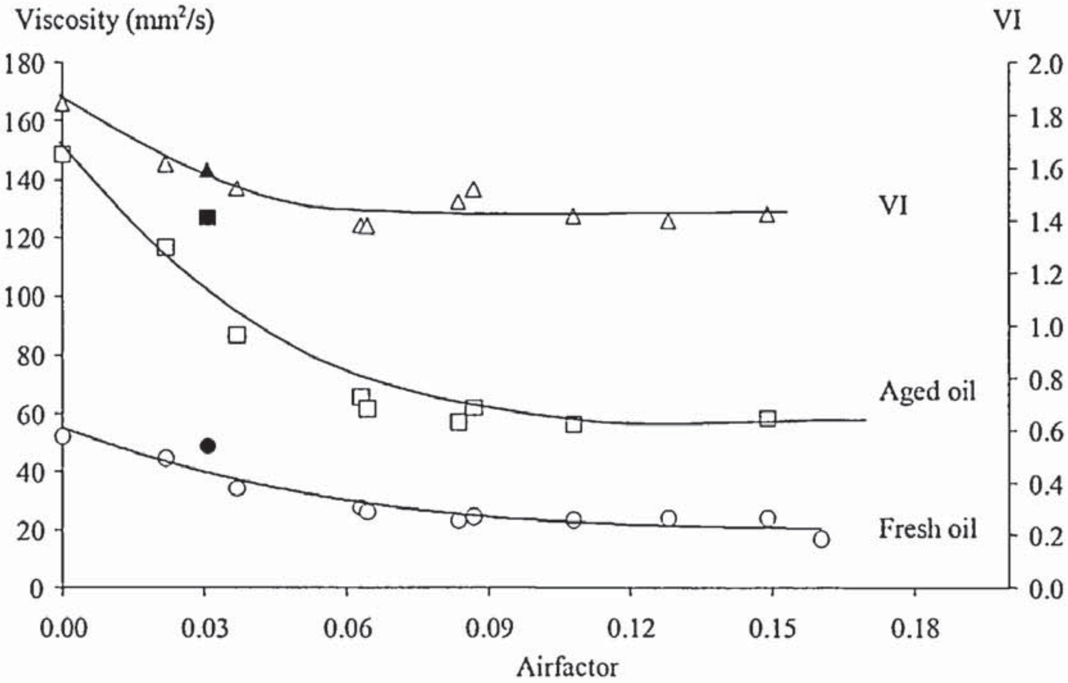


Figure 6-6. Fresh oil and aged oil viscosity and viscosity index versus airfactor

The equations of viscosity versus airfactor are shown as Equation 6-10 to Equation 6-11, the R-squared value of all equations are above 0.9.

Viscosity = $2922.6\,A^2 - 596.5\,A + 53.5$ **Equation 6-10**

Viscosity = $10771\,A^2 - 2011.4\,A + 150.2$ **Equation 6-11**

The value for the viscosity index was not affected by the temperature of condenser 1 when the latter did not change very much, here only 3°C difference, and hence VI values were close to the trend line (Also see section 4.11). This is due to the fact that the temperature of condenser 1 only affected oil water content, while there was little impact on oil stability in certain oil water content range (also see section 5.3.4). The effect of the temperature of condenser 1 on oil quality was discussed in section 4.2.4.1 and section 4.11 and was in agreement with the present result.

Figure 6-7 shows that oil water content increased for higher airfactors until a stage was reached at which phase separation occurred. This point may be referred to as the tolerable oil water content. Every feedstock has its own tolerable water content (discussed in the section 5.3.1). For Beech wood, this tolerable water content was found to be 31.5%, as illustrated by the dotted line in Figure 6-7.

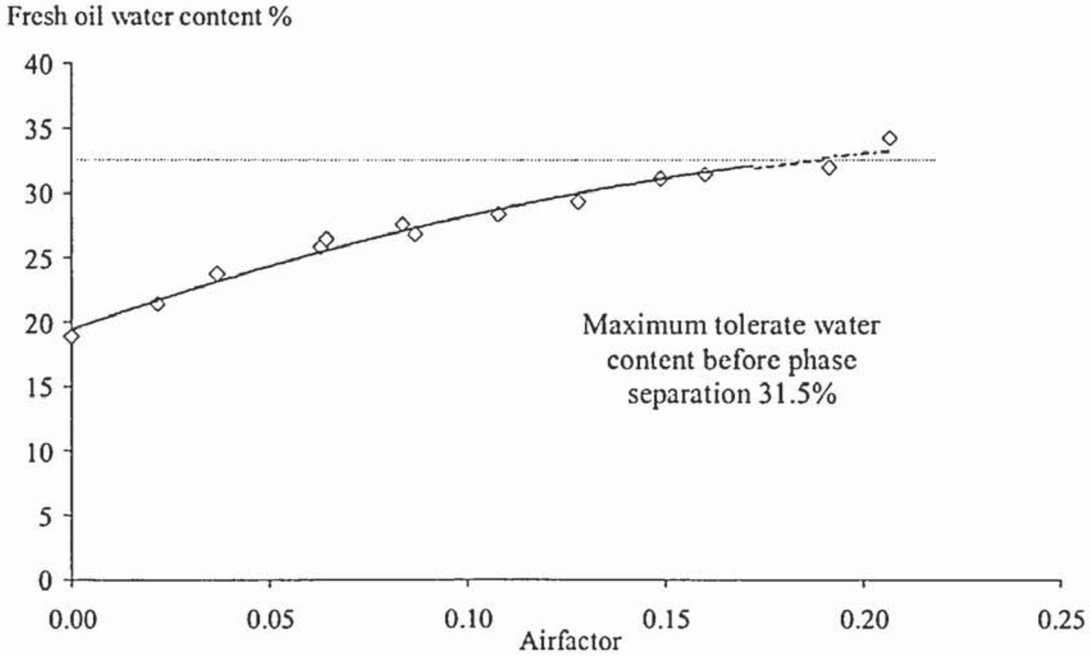


Figure 6-7. Fresh oil water content versus airfactor

6.6 CHEMICAL COMPOSITION

In this work, the aqueous fraction of the pyrolysis liquid was analysed using HPLC and GS-MS (Analysis methods see section 4.9.2.4 and 4.9.2.5). The main components of the oil are shown in Table 6-2.

Compared with the bio-oil from pyrolysis without oxygen, there were fewer aldehydes in partially oxygenated pyrolysis oils. The concentrations of acids, ketones and furans were also lower. An increase was found for sugars, while guaiacols, phenols, pyrans and syringols showed little change.

Table 6-2. GC/MS analysis results for the oil from pyrolysis with or without oxygen

	Pyrolysis beech wood without oxygen	Partially oxygenated pyrolysis of beech wood
Airfactor	0	0.11
Compound	wt.% in total oil	wt.% in total oil
Acids	7.49	6.66
Alcohols	0.07	n.q.
Aldehydes	10.42	5.64
Furans	2.38	1.79
Guaiacols	1.02	1.04
Ketones	3.94	2.85
Phenols	0.14	0.08
Pyrans	0.50	0.50
Sugars	2.02	2.73
Syringols	2.43	2.47
Others	n.q.	n.q.

The decreased concentrations of aldehydes and ketones assist in improving oil quality, as there components are among the main contributors to oil instability through their ready polymerization that increased with storage time and temperature during storage (The reason was discussed in section 3.4).

6.7 BIO-OIL PH VALUE

The organic acids cause bio-oil to be acidic, with a pH of between 2.3 to 3.0. Acids also react with other chemicals during storage, raising the viscosity of the oil. Table 6-2 shows that the oil from oxygenated pyrolysis had a lower acid concentration compared with oil from pyrolysis without oxygen, and Table 6-3 shows that oil from oxygenated pyrolysis had a higher pH value compared with oil from pyrolysis without oxygen. This showed that oil quality could be improved by the oxygenated pyrolysis of wood.

Table 6-3. pH value of bio-oil from different airfactor pyrolysis

Air factor	0	0.02	0.08	0.11
Fresh oil pH value	2.46	2.51	2.58	2.69

6.8 OIL LIGNIN CONTENT

Figure 6-8 gives the fraction of water insoluble (pyrolitic) lignin in fresh and aged oil versus airfactor (Measure methods see section 4.9.2.6). The result showed that the water insoluble lignin fraction in aged oil (80°C, 24h) (around 31%) was considerably higher than in fresh oil (19%). An increase in the airfactor led to a decrease in the fraction of pyrolytic lignin in the oil, which was slightly more pronounced in the aged oil. The underlying reason for this decrease may be summarized as follows. Pyrolytic lignin is easily polymerized to form compounds with a greater molecular weight during the oil aging process. This aging may be slowed due to decreased concentrations of unstable chemicals such as aldehydes and ketones in partially oxygenated pyrolysis. The pyrolytic lignin fraction in the fresh oil was also reduced slightly when oxygen was added, from 18.2% without oxygen to 16.9% with an airfactor of 0.11.

However, this has given rise to disagreement; guaiacols, phenols, pyrans and syringols are the main products from lignin pyrolysis. Table 6-4 shows that only phenols decreased after oxygenated pyrolysis. The total yields of lignin-derived chemicals in the liquid did not depend on whether oxygen was added. This may have been the reason that the lignin fraction in fresh oil was only affected very slightly by adding oxygen in oxygenated pyrolysis, or there were some other chemicals belonging to the lignin fraction that were not detected here.

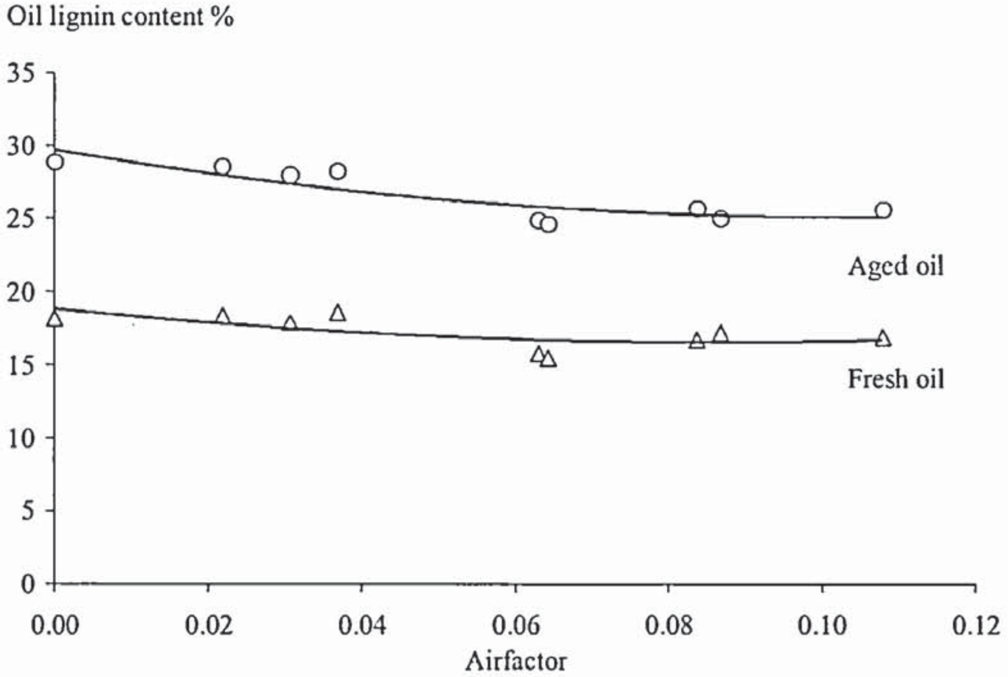


Figure 6-8. **Oil lignin content versus airfactor**

Table 6-4. **GC/MS analysis results of lignin derived chemicals from the oil**

	Pyrolysis beech without oxygen	Oxygenated pyrolysis of beech
Airfactor	0	0.11
Compound	wt.% in total oil	wt.% in total oil
Guaiacols	1.02	1.04
Phenols	0.14	0.08
Pyrans	0.50	0.50
Syringols	2.43	2.47
Total lignin derived chemicals	4.09	4.09

6.9 OIL ELEMENTAL ANALYSIS RESULTS

Elemental analysis results on a dry oil basis were calculated using the equations below. According to the result on a wet oil basis shown as Table 6-5, Table 6-6 shows the elemental analysis result of dry oil.

Total oil weight : $W_{org} + W_{wat} = W_{oil}$

Carbon equation :

$$C_{dry}\% * W_{org} + 0 = C_{wet}\% * W_{oil}$$

$$C_{dry}\% * W_{oil} * (1 - W_{wat}\%) + 0 = C_{wet}\% * W_{oil}$$

$$C_{dry}\% = \frac{C_{wet}\% * W_{oil}}{W_{oil} * (1 - W_{wat}\%)} = \frac{C_{wet}\%}{(1 - W_{wat}\%)}$$

Hdrogen equation :

$$H_{dry}\% * W_{org} + \frac{W_{2H}}{W_{H2O}} * W_{wat} = H_{wet}\% * W_{oil}$$

$$H_{dry}\% * W_{oil} * (1 - W_{wat}\%) + \frac{2}{18} * W_{oil} * W_{wat}\% = H_{wet}\% * W_{oil}$$

$$H_{dry}\% = \frac{H_{wet}\% * W_{oil} - \frac{2}{18} * W_{oil} * W_{wat}\%}{W_{oil} * (1 - W_{wat}\%)} = \frac{H_{wet}\% - \frac{2}{18} * W_{wat}\%}{(1 - W_{wat}\%)}$$

Oxygen calculated by difference :

$$O_{dry}\% = 100\% - (H_{dry}\% + C_{dry}\%)$$

Table 6-5. Elemental analysis of wet oil from pyrolysis beech with and without oxygen (Medac Ltd)

	Pyrolysis without oxygen	Partially oxygenated pyrolysis	
Run number	Run 96	Run 104	Run 108
Airfactor	0.00	0.11	0.16
Oil water content%	18.87	28.37	31.45
C (wet)%	42.79	38.07	35.77
H (wet)%	7.34	7.82	8.09
N (wet)%	<0.10	<0.10	<0.10
O (wet)%	49.87	54.12	56.15

Table 6-6. Elemental analysis on dry oil basis calculated from wet results

	Feed stock	Pyrolysis without oxygen	Partially oxygenated pyrolysis	
	Beech wood	Run 96	Run 104	Run 108
Airfactor		0.00	0.11	0.16
C (dry)%	45.55	52.74	53.14	52.17
H (dry)%	6.04	6.46	6.51	6.70
N (dry)%	<0.10	<0.10	<0.10	<0.10
O (dry)%	48.05	40.79	40.35	41.13
Heating Value (MJ/kg)*	15.4	19.8	20.1	19.9

* The heating value was calculated from the data of the elemental analysis by using Dulong's formula (see equation 6-12), which was used by many researchers [77]:

$$HHV[MJ/kg] = \left\{338.2 \times C\% + 1442.8 \times \left(H\% - \frac{O\%}{8}\right)\right\} \times 0.001 \qquad \textbf{Equation 6-12}$$

The result showed that partially oxygenated pyrolysis did not affect C, H, O and N composition in the oil but changed the oxygenated chemicals proportion. The quantity of unstable oxygenated components was decreased (Table 6-2 shows analysis results).

6.10 COMPARISON OF OXYGENATED PYROLYSIS WITH ZEOLITE CATALYTIC PYROLYSIS:

Zeolite catalytic pyrolysis has often been considered the most promising route to improve bio oil quality by many research workers (see section 6.1).

Table 6-7 show some results for Zeolite catalytic pyrolysis [141, 137] and partially oxygenated pyrolysis. Changes % was calculated by Equation 6-13.

$$Change\% = \frac{Y_{after} - Y_{before}}{Y_{before}} \times 100 \qquad \textbf{Equation 6-13}$$

Where:

Y_{after} : The product yields from catalytic pyrolysis or oxygenated pyrolysis.

Y_{before} : The product yields from pyrolysis without catalyst or without oxygen.

Table 6-7. Comparison of oxygenated pyrolysis and Zeolite catalytic pyrolysis

Oxygenated pyrolysis	Organic	Char	Water	Gases	Coke
0	66.19	11.1	10.7	11.4	0
0.08	51.28	9.81	15.0	21.1	0
Change %	-23%	-12%	40%	86%	0
Catalytic pyrolysis	Organic	Char	Water	Gases	Coke
Primary bed	43.3	17.2	14.7	14.3	0
ZSM 550 °C	6.0	17.1	19.3	37.7	11.9
Change %	-86.1%	-0.58%	31.3%	163.6%	-

Zeolite pyrolysis led to increased oil quality by lowering oxygen and increasing the carbon content of the oil. However, 80 percent of the organics were lost in the upgrading process. Furthermore, coking problems were experienced with the catalysts. Partially oxygenated pyrolysis uses an alternative way to improve oil quality by decreasing the concentration of unstable and unwanted chemicals such as aldehydes, ketones and acids.

6.11 DISCUSSION AND CONCLUSION

1. Oxygenated pyrolysis was shown to be a slightly exothermic process due to combustion reactions during the process. Consequently less heat transfer into the reactor is required. The advantage of less heat transfer also appears to be of major interest for larger reactors, where heat transfer limitations are a major problem in scale-up.
2. Organic yields decreased with greater airfactor in partially oxygenated pyrolysis due to partial combustion. The extent of yield reduction depended on how much oxygen was added in the pyrolysis process.
3. Water yields increased with increased airfactor in partially oxygenated pyrolysis due to the combustion of organics. Water is effective in lowering oil viscosity. However, too much water in the oil led to a lower heating value and oil phase separation. It was also found to be detrimental to combustion. Water enters the process via the feedstock and is also produced in reactions. Therefore, the water yield could be lowered by adjusting the airfactor and using dry feedstock.

4. The viscosity of the oil decreased in partially oxygenated pyrolysis due to increased water content, the effect of which was discussed in 5.3.5.
5. Gases yields especially CO_2 yield increased in partially oxygenated pyrolysis, this was attributed to the combustion of organics.
6. Unstable oxygenated chemicals such as aldehydes and ketones decreased in partially oxygenated pyrolysis process, this improved the oil anti-oxidant ability.
7. Partially oxygenated pyrolysis oil had a higher pH value than normal pyrolysis oil; the small reduction in total acids improved the quality of the oil by reducing oil corrosiveness.
8. Elemental analysis showed little change for carbon, hydrogen and oxygen, but heating values of oil increased compared with those of raw wood.
9. Adding oxygen reduced the lignin fraction in the oil. However, the change was not significant, presumably due to the short residence time limiting the effect on the pyrolysis of lignin.
10. Optimum Airfactor:

    Increasing the airfactor in partially oxygenated pyrolysis gave a lower oil viscosity, a lower concentration of unstable oxygenated chemicals in the oil, and generally led to more stable oil. However, this does not imply that higher airfactors are always beneficial. High airfactor pyrolysis produce more water in the oil, very high oil water content may lead to oil phase separation. Consequently there is an optimum airfactor in partially oxygenated pyrolysis, which gives the most stable oil just before oil phase separation (That means just before oil reaches its water tolerant content). Figure 6-9 shows that the optimum airfactor of partially oxygenated pyrolysis for beech wood (moisture content 8%) was approximately 0.16, that is, slightly less than the level that would lead to the oil reaching its tolerable water content which would result in phase separation.

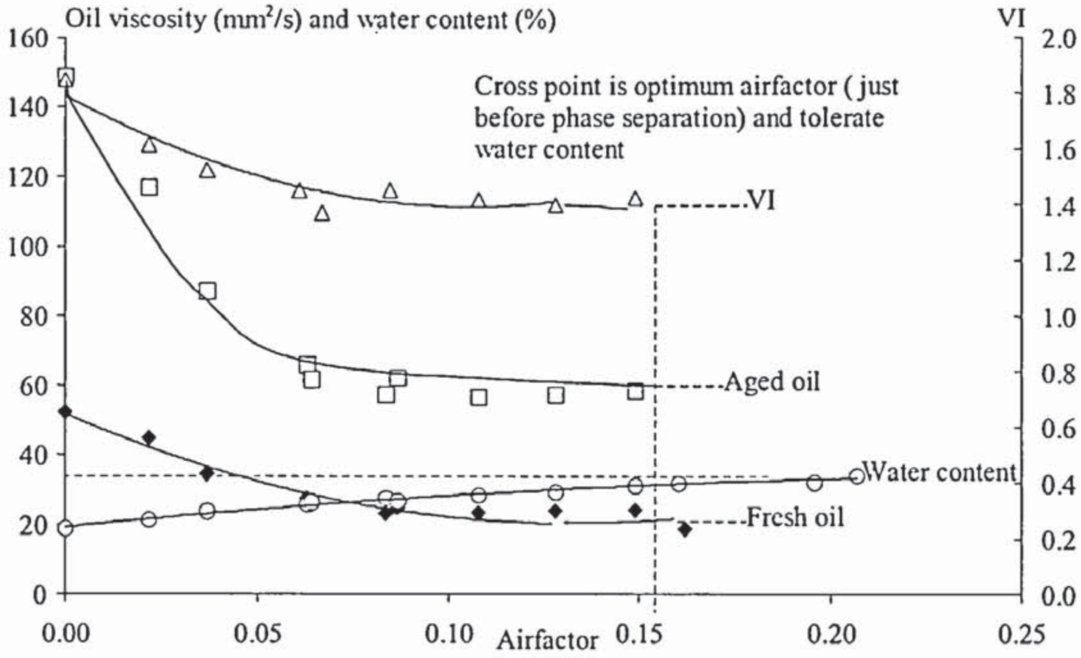


Figure 6-9. Oil stability versus airfactor

The optimum airfactor was affected mainly by oil water content. The oil produced from different feedstocks or the same feed stock with different moisture content should have different optimum airfactors. Wood with higher moisture content will give lower optimum airfactor as the water in the oil comes both from the feedstock and reaction water and high feed moisture content will result in the oil reaching its tolerable water content faster. On the other hand, bone dry wood will be slower in reaching the tolerable water content as the water in the oil comes only from reaction. Thus bone-dry feedstock will give the highest possible airfactor in partially oxygenated pyrolysis and will therefore reduce unwanted chemicals to the greatest possible extent, resulting in the most stable oil.

11. In summary, partially oxygenated pyrolysis improves bio-oil quality in the following aspects.
    - It lowers initial oil viscosity by increasing the water content of the oil through partial combustion.
    - It lowers the concentration of unstable oxygenated species in the oil by partial combustion and by encouraging reactions between them.
    - It lowers the concentration of acids species in the oil thus reduces oil corrosiveness.

- The partially oxygenated pyrolysis process requires less heat transfer to the pyrolysis reactor, which may attenuate a significant limitation to scale-up for commercial pyrolysis processes.

The possible way of improving of oil stability in partially oxygenated pyrolysis was that oxidation of unstable chemicals aldehydes and ketones lowers their amount in the oil thus improve the oil anti-oxidant ability, meanwhile increase the oil water content.

CHAPTER 7. CO-PYROLYSIS OF SPRUCE WOOD WITH METHANOL

The improvement of oil stability by adding postproduction additives has been explored by many research groups. Methanol was found to be the most effective additive, especially when it was used shortly after pyrolysis oil is produced. In the present work, the copyrolysis of spruce wood with methanol with the methanol added before condensation of the pyrolysis vapour was investigated. The results are compared with those obtained using methanol as a postproduction additive.

7.1 INTRODUCTION

One of the quality related drawbacks of bio-oil is that it has a high viscosity, which furthermore increases with storage, particularly at elevated temperature. The greatest changes in the viscosity of the pyrolysis liquid occur during the first 2-3 days after liquid production [142]. One upgrading method to prevent these viscosity increases and stabilise the liquid is the addition of chemical modifiers to the fresh pyrolysis liquid as it is produced.

Adding additives to the oil has been carried out by many groups in order to improve the oil, and in particular to improve the oil stability by lowering oil viscosity [143,144,145,146].

Bridgwater *et al.* [147, 148] added water to oil produced by Union Fenosa with initial water content of 17% in order to obtain total water contents of 20, 25 and 30%. Two main observations were reported:

- A small amount of water produced a large decrease in oil viscosity, from 1127 cp for the initial oil to 590 cp for the oil containing 20 % water.
- After 4 months storage there was no increase of viscosity for the oil containing 30 % water and a very low increase for the oil containing 25 % water.

The oil will separate into two phases when enough water is added. This method, which is easy and cheap (possibility to use bio-ethanol), nevertheless presents some inconvenience: decrease of heating value with the addition of water and increase of volume and weight for transportation and storage. In addition, it does not eliminate the chemical functions causing polymerisation.

The instability of pyrolysis liquids is thought to be due to the high quantity of oxygen containing compounds, specifically the chemically reactive carbonyl functions typical of aldehyde and ketone compounds [149]. While heating or in air these carbonyls are thought to facilitate polymerisation reactions that yield an overall increase in the viscosity and decrease in the stability of the liquid.

Chemicals such as acetone, sulphuric acid, ethyl acetate, methanol, ethanol, propanol, butanol, phenol and glycerol have also been added to the pyrolysis liquid to try to remove the sources of polymerisation [150,151]. A patent has been filed on the stabilization of pyrolysis liquid with alcohols to produce acetals [152].

Other workers have carried out similar tests [153] using water and solvents such as methanol, ethanol, butanol and octanol, the results being in complete agreement with those obtained at Aston University. The most relevant result from the work [153] was obtained with oil produced with the addition of 10% butanol: the viscosity was unchanged after 8 months storage. This phenomenon has not yet been elucidated. A possible explanation could be colloidal interaction in the mixture. In that work, it was observed that the addition of organic solvents was limited by their solubility in water.

Diebold and Czernik [104] investigated ethyl acetate, methyl isobutyl ketone and methanol, acetone, acetone and methanol, and ethanol as post-production additives to lower and stabilize the viscosity of pyrolysis oil. It was shown in that work that the rate of viscosity increase (aging) for the oil with 10wt % methanol was about one-twentieth that of oil without additives. This effect was due to physical dilution and to chemical reactions between the solvent and the oil components that prevent further chain growth. The chemical reactions that can occur between the bio-oil and methanol or ethanol are esterification and acetalization. Though not favoured thermodynamically, these reactions can progress to a large extent if appropriate conditions are applied. For example, in the presence of an acid catalyst and molecular sieves (to absorb water and to shift the reaction equilibria), bio-oil reacts readily with ethanol to form ethyl acetate, ethyl formate, and diethoxyacetal at the expense of formic acid, acetic acid and hydroxyacetaldehyde. Eventually, in addition to the decrease in viscosity and in the aging rate, other desirable changes such as reduced acidity and improved volatility, heating value, and miscibility with diesel fuels were also achieved. The simplicity, low cost, and beneficial effects of solvents, especially methanol and ethanol, on bio-oil properties, favours the addition of solvent as a practical upgrading method. It was found that methanol was the least expensive and most effective additive used, and suggested that methanol used shortly after the pyrolysis oil is produced is most effective in reducing oil viscosity [150].

The pyrolysis vapour condensation process is a complex process as discussed by Diebold and Bridgwater. Molecular beam mass spectrometry showed that there were very few molecules having a molecular weight over 200 Daltons in the initial vapour state. However, after the oil vapour had condensed, the liquid oil appeared to have much a higher average molecular weight of over 500 Daltons [5]. Also, it was suggested that polymerisation might occur among species in the pyrolysis vapour condensation process. Some reactions might not be reversible and hence the use of methanol as a postproduction additive may not be able to reduce the resulting effects.

The addition of methanol before pyrolysis vapour condensation may be more effective. Co-pyrolysis with methanol involves contacting methanol and pyrolysis vapour before the vapour condenses into oil. This work will explore the co-pyrolysis of spruce wood with methanol to determine the effects on a number of bio-oil properties.

7.2 CO-PYROLYSIS

Co-pyrolysis refers to the technique of introducing the biomass and the additives into the pyrolysis reactor simultaneously, either together or separately. In this work, the co-pyrolysis of bone-dry spruce without or with 5.1%, 7.6%, 12.5% and 15.0% methanol (99.5% of methanol purity) in wood at 500 °C has been carried out. In our liquid collection system, 85-90% of total liquid was collected by oil Pot1 at the base of the electrostatic precipitator, with the remainder being collected from Pot 2 at the base of the second condenser. Pot 2 was cooled by dry ice and acetone (-80 °C). Owing to its volatility, most of the methanol was collected by condenser 2 at temperatures as low as -80 °C. Considering that the effects of methanol were very important and that the real product oil should be the oil from both pot1 and pot 2 together, mixed oil was utilised in this work.

All oil mentioned in this work was mixed oil and the methanol percentage in wood was converted to equivalent methanol percentage in oil in order to compare the result with methanol as a post-production additive. Equivalent methanol percentage in product oil was calculated by dividing the mass of methanol used in pyrolysis of spruce wood by the mass of oil produced from pyrolysis of the same amount of spruce. Table 7-1 shows the results of the conversion of methanol percentage from feedstock basis to bio-oil basis.

Table 7-1. Conversion of methanol percentage on feedstock basis into equivalent methanol percentage on bio-oil basis.

Methanol percent in wood (%)	Spruce wood used (g)	Methanol used (g)	Oil produced (g)	Equivalent methanol percent in oil (%)
5.1	63.72	3.42	50.5	6.8
7.6	62.55	5.13	50.95	10.1
12.5	88.67	12.62	76.05	16.6
15.0	60.24	10.64	53.37	19.9

7.2.1 Product yields versus methanol percentage in co-pyrolysis of bone dry spruce with methanol

Figure 7-1 shows the resulting product yields on a dry feedstock plus methanol basis versus equivalent methanol percentage in the oil. The total oil yields remained relatively constant, the organic and gases yields increased, and the water and char yields decreased with increasing methanol content of the co-pyrolysis feed. An increase in the organic yield was expected on the basis that methanol was converted into organic product. Accordingly, the observed decrease in water and char yields were probably the result of dilution by methanol or methanol conversion products.

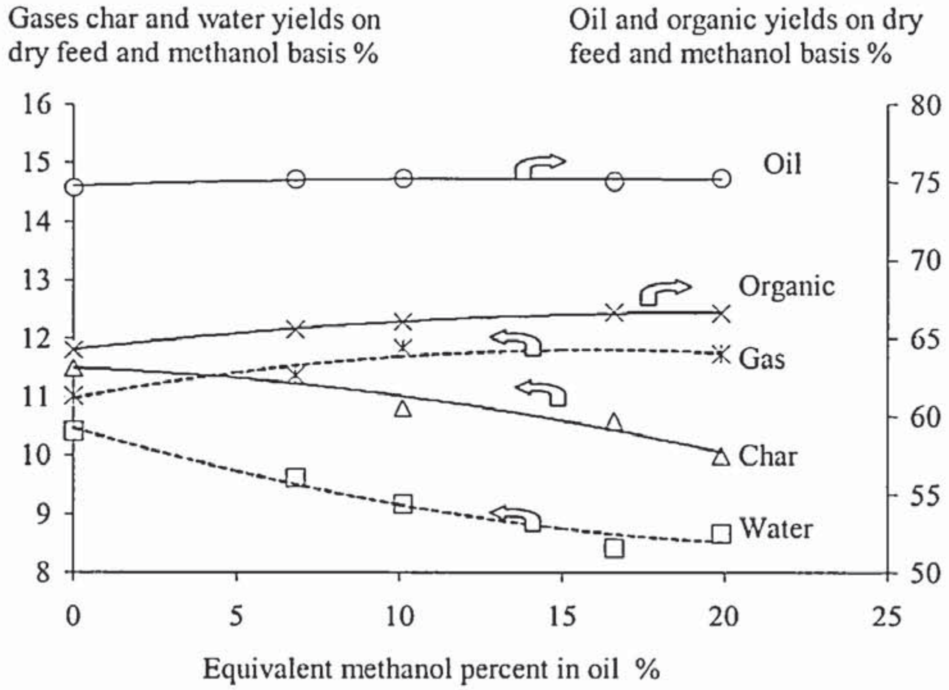


Figure 7-1 Product yields versus methanol percent

It is a reasonable assumption that char yields were not affected by methanol during co-pyrolysis process except for the dilution role on the products. Table 7-2 shows the comparison between experimentally determined char yields and the values calculated on the assumption that all methanol was transferred into products during the co-pyrolysis process.

Table 7-2. Product yields comparison between experiment result and calculation results.

Methanol percentage in feedstock	Equivalent methanol percent in oil product (%), A	Actual organic yields from co-pyrolysis (%), Oa	**Calcualtion organic yields (%), Oc**	Actual char yields from co-pyrolysis (%), Ca	**Calculation char yields (%), Cc**
0	0	64.9	**64.9**	11.49	**11.49**
5.1	6.8	65.57	**69.3**	11.37	**10.75**
7.6	10.1	66.1	**71.45**	10.81	**10.43**
12.5	16.6	66.66	**75.67**	10.59	**9.85**
15.0	19.9	66.62	**77.81**	9.99	**9.58**

Note: $Cc = 11.49\% / (1+A)$;

$Oc = 64.9\% * (1+A)$.

On the assumption that methanol alone played a dilution role and no methanol pyrolysis occurred during the co-pyrolysis process, char yields should not be affected by methanol. The calculated char yields (Cc) decreased from 11.49% to 9.58% with increasing percent methanol in the oil. This decrease in char yield was mainly due to methanol dilution. The experimentally determined char yields (Ca) decreased from 11.49% to 9.99% as the percent methanol in the feedstock increased from 0 to 15%. The experimentally determined char yields were higher than the calculated yields. This indicated that not all of the methanol was transferred into product. Part of the methanol might have been pyrolysed during the co-pyrolysis process.

The experimentally determined organic yields from the co-pyrolysis of spruce with methanol increased slightly from 64.9% to 66.2% with increasing methanol addition to the feedstock. The calculated organic yields (Oc) increased significantly with increasing methanol percent in the feedstock. Actual organic yields in the co-pyrolysis process (Oa) were less than the calculated values. This result indicated that not all of the methanol was transferred into product in the co-pyrolysis process, that is, some methanol was pyrolysed in the process.

Figure 7-2 shows that the propylene concentration in the product gases increased significantly as the methanol concentration increased. This was not the case for normal pyrolysis of spruce and hence propylene may have been a direct product of methanol co-pyrolysis.

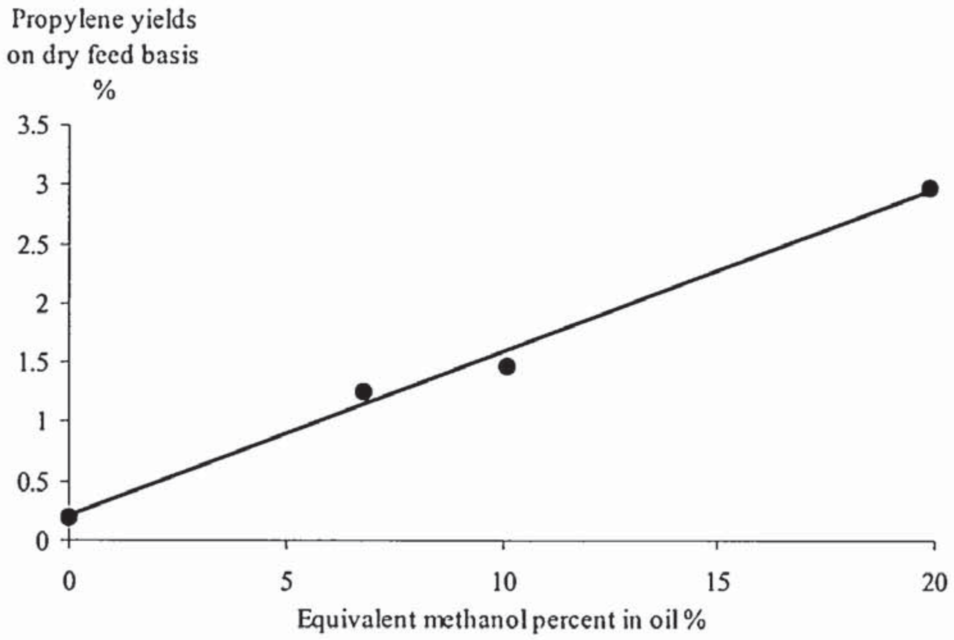


Figure 7-2. **Propylene yields versus methanol percentage**

7.2.2 Oil water content versus methanol percentage in the co-pyrolysis of bone dry spruce with methanol

Figure 7-3 shows that the water content of pot1 oil did not change with increasing methanol addition, not only for fresh oil but for aged oil also. Pot 2 oil water content decreased significantly, due mostly to the fact that the majority of the methanol (or volatiles) was collected by pot 2 in this product collection system with a resulting dilution effect. The fresh mixed oil (Mixed F) produced by mixing Pot 1 and Pot 2 oil had an increasingly lower water content due to increased dilution at larger methanol (or volatiles) concentrations. However, the mixed aged oil (Mixed A) water content did not reduce when adding methanol. A possible reason for this was that the high temperature (80 °C for 24 hours) accelerated reactions with methanol in the oil, which gave out water and masked the dilution role of methanol.

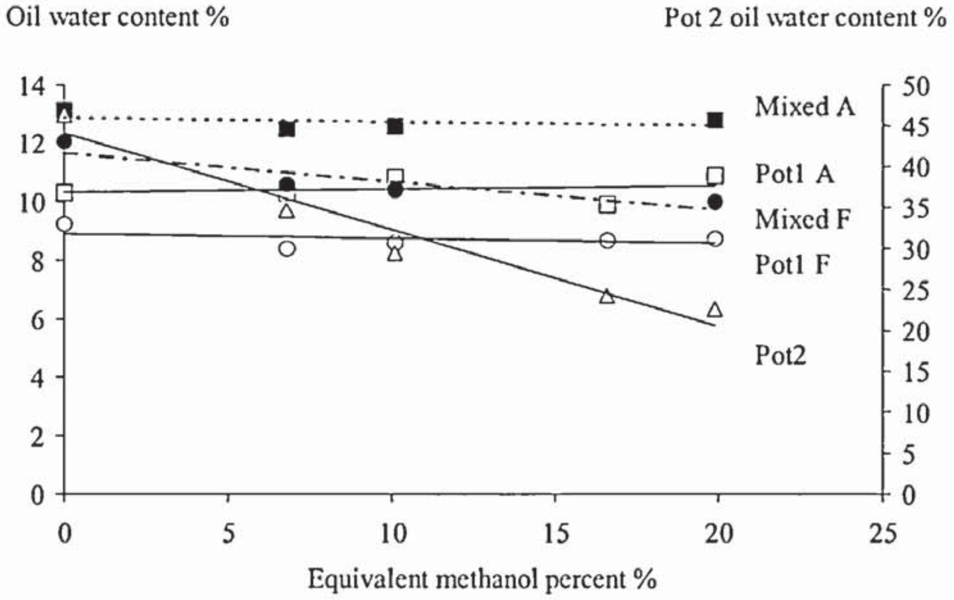


Figure 7-3. Oil water content versus methanol percentage

7.2.3 Oil viscosity versus methanol percentage in the co-pyrolysis of bone-dry spruce with methanol.

Figure 7-4 shows that there was a decrease in oil viscosity with increasing percent methanol in the co-pyrolysis process, especially for aged oil. The large decrease in viscosity for aged oil was also an indication that the oil had become more stable, this was shown as VI values increasingly decrease. A brief comparison with the oil water content results can now be made. For mixed fresh oil, methanol lowered the water content and decreased the viscosity. Under those circumstances the dilution role of methanol was dominant. For aged mixed oil, oil viscosity decreased significantly at different methanol percentages. This was attributed to the dilution role of the by-product water which produced during oil aging process.

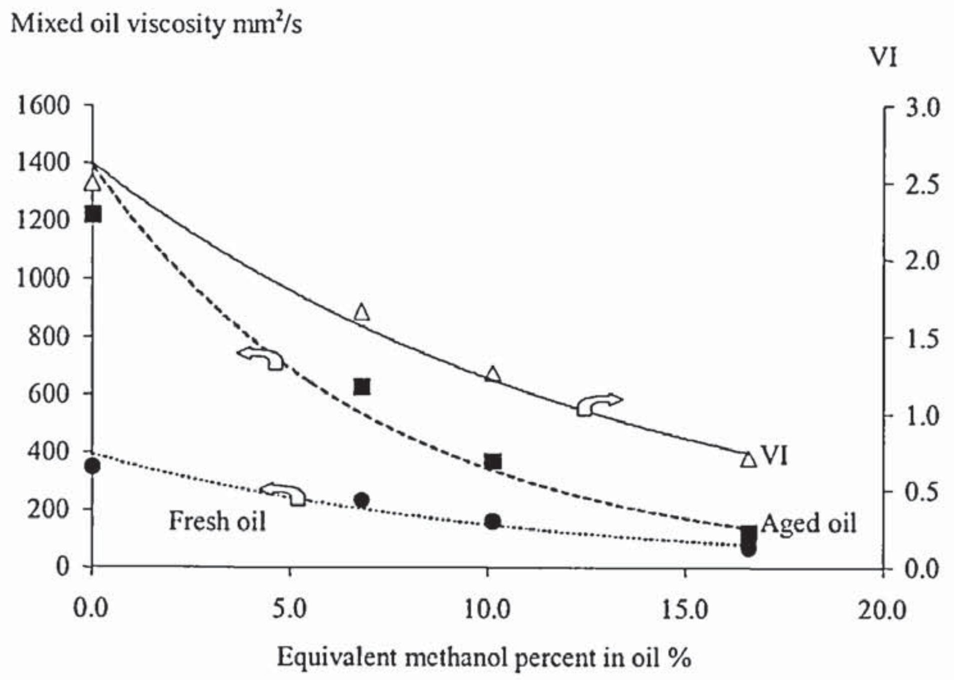


Figure 7-4. **Mixed oil viscosity and VI versus methanol percentage**

7.3 COMPARISON BETWEEN CO-PYROLYSIS WITH METHANOL AND ADDING METHANOL AS POST PRODUCTION ADDITIVE

7.3.1 Water content comparison

Figure 7-5 shows that fresh oil water content decreased slightly with larger methanol additions both for co-pyrolysis with methanol and for methanol as a post-production additive. Aged oil water content, however, did not change; a possible reason for this was the net result of two factors. The reaction product water increased during the aging process as high temperature accelerates reactions in the oil, meanwhile the water content decrease due to the dilution role of methanol. The oil water content was slightly higher with methanol as a post-production additive than for co-pyrolysis with methanol. Esterification reactions gave out water and this reaction was more effective in the former process.

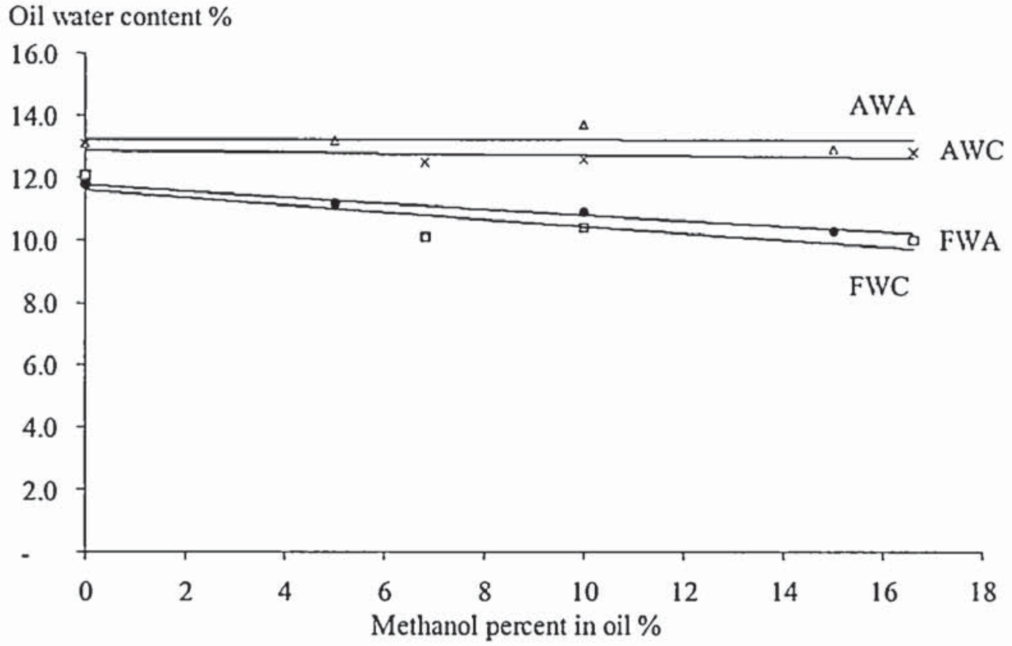


Figure 7-5. Oil water content versus methanol percentage

Note:
AWA: Aged oil water content in methanol as post-production additive process
AWC: Aged oil water content in co-pyrolysis with methanol process.
FWA: Fresh oil water content in methanol as post-production additive process
FWC: Fresh oil water content in co-pyrolysis with methanol process.

7.3.2 Oil viscosity comparison

Figure 7-6 showed that methanol addition resulted in lower oil viscosity and significantly increased oil stability both for methanol as a postproduction additive and in the co-pyrolysis process. Methanol as a post-production additive was more effective than co-pyrolysis in lowering oil viscosity, which was partly due to the fact that the oil had a slightly higher water content in the former process.

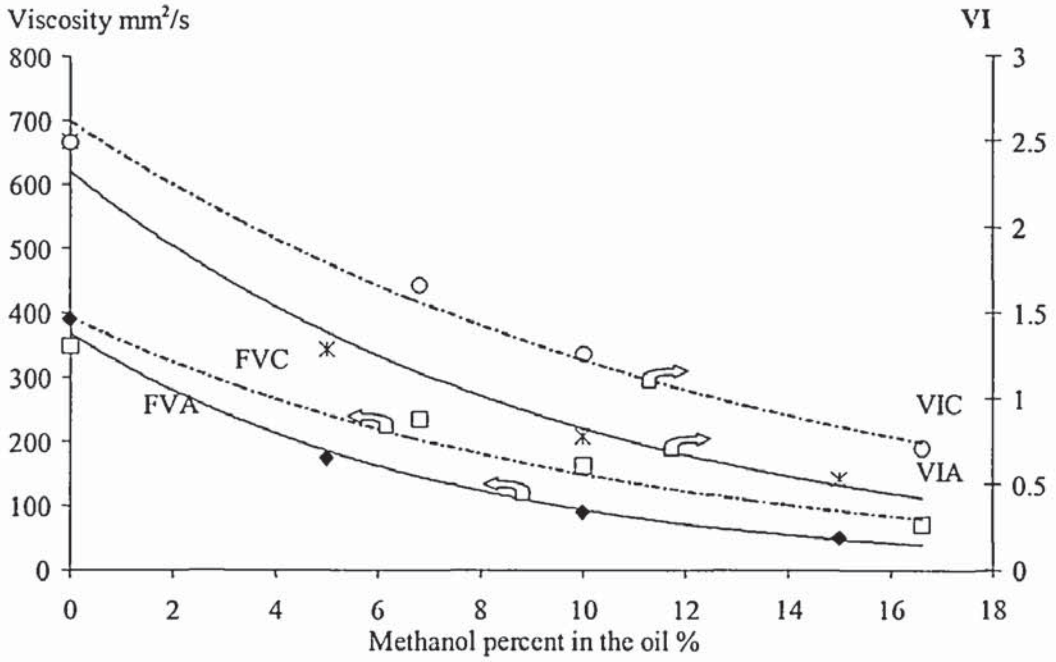


Figure 7-6. Oil viscosity and VI versus methanol percentage

Note:
VIC: VI value in copyrolysis with methanol process.
VIA: VI value in methanol as post-production additive.
FVC: Fresh oil viscosity in copyrolysis with methanol process.
FVA: Fresh oil viscosity in methanol as post-production additive.

7.3.3 Oil chemical composition comparison

Boucher stated that methanol was a good solvent for bio-oil, dissolving most of the high molecular weight components to give a diluted oil system with low viscosity [154,155]. On the other hand, Diebold and Czernik suggested that transesterification reactions could occur between methanol and a previously formed polymeric ester to form lower molecular weight products [8].

Table 7-3 shows the chemical composition of liquid from pyrolysis with and without methanol. The run numbers break down as follows: Run86, pyrolysis without methanol, R86M15, oil obtained by adding 15% methanol as postproduction additive, and Run83, co-pyrolysis with methanol, methanol percent in the feedstock 15.0% (19.9% of equivalent methanol percentage in the oil).

Table 7-3. Chemical composition of bio-oil produced from co-pyrolysis with methanol and methanol as postproduction additive.

Summary	Run86 Analysis result (A)	R86M15 Analysis result (b) (15% of methanol in oil)	Run83 Analysis result (c) (19.9% of methanol in oil)	RunM86 (2) Calculation result (B)
Compound	wt.%	wt.%	wt.%	wt.%
Acids	3.03	1.78	1.73	2.63
Alcohols	0.1	0.1	0.1	0.1
Aldehydes	12.08	9.94	9.52	10.50
Furans	1.71	1.58	1.61	1.49
Guaiacols	3.48	2.92	3.01	3.03
Ketones	3.65	2.64	2.49	3.17
Phenols	0.27	0.25	0.21	0.23
Pyrans	0.39	0.31	0.28	0.34
Sugars	3.09	2.66	2.7	2.69
Others	n.q.	n.q.	n.q.	n.q.

It was assumed that the methanol added to the oil from Run86 acted merely as a diluent. The weight percentages of the various chemicals were then calculated as B = A/1.15 when 15% methanol was added.

When adding methanol as 15% of the oil as a post-production additive, the experimental results, which have been denoted with a (b), were lower than the results given by the above calculation, which were denoted with a capital (B), especially for the chemicals, acids, aldehydes and ketones. One possible reason was that methanol reacted with acids, aldehydes and ketones when mixed together. This suggested that methanol did not merely act as a diluent, a result in disagreement with Bouche [154, 155] and in agreement with the suggestion by Diebold and Czernik [15].

For the co-pyrolysis process with 15% of methanol in the feedstock (equivalent to 19.9% of methanol in the product oil), the experimental results, which have been denoted by (c), were similar to the results for R86M15 (15% of methanol added in the oil as postproduction additive). The co-pyrolysis process consumed more methanol than consumed in the postproduction process to produce a bio-oil of similar quality because a portion of the methanol was consumed in the co-pyrolysis process.

7.4 DISCUSSION AND CONCLUSION

- Organic yields increased slightly in co-pyrolysis with methanol as part of the methanol was converted into organic oil products instead of undergoing pyrolysis.
- Char yields decreased with increasing methanol percentage in the co-pyrolysis feedstock due to dilution of the products by methanol or methanol conversion products.
- Water yields decreased with increasing methanol percentage in the co-pyrolysis feedstock due to dilution of the products by methanol or methanol conversion products.
- The total oil yields remained relatively constant as the organic yields increased and water yields decreased with increasing methanol percent in the feedstock during the co-pyrolysis process.
- Gases yields, in particular that of propylene, increased with increasing methanol percent in the feedstock, possibly as the result of methanol pyrolysis during the process.
- Oil produced from co-pyrolysis with methanol was more stable than that from normal pyrolysis due to a significant decrease in aged oil viscosity in the presence of methanol.
- Oil water content decreased in both co-pyrolysis with methanol process and when methanol was used as a post-production additive.
- Oil viscosity decreased in both co-pyrolysis with methanol and when methanol was used as a postproduction additive, but more effectively in the latter process.
- The concentration of acids, aldehydes and acetones decreased in both co-pyrolysis with methanol and when methanol was used as a postproduction additive, but the former process consumed more methanol for the same decrease.

For methanol as a postproduction additive, methanol reacted with several classes of compounds in the bio-oil including acids, aldehydes, acetones and esters. esterification reactions with acids gave water which led to lower oil viscosity. The reaction with aldehydes or ketones lowered the concentration of unstable compounds in the oil, thereby reducing the possibility polyacetal oligomer formation and resulting increased oil stability. Transesterification reactions with a previously formed polymeric ester to form lower molecular weight products gave a lower viscosity oil.

In the co-pyrolysis process, methanol was expected to play the similar role on the bio-oil product, but less methanol was transferred into bio-oil due to pyrolysis of part of the methanol during co-pyrolysis. Poor contact between the pyrolysis vapour and methanol steam did not facilitate the reactions between them before pyrolysis vapour condensation occurred. Methanol was therefore less effective in co-pyrolysis than as a bio oil additive.

CHAPTER 8 . CONCLUSIONS

A total of 120 fast pyrolysis experiments have been carried out on a 150g/h reactor in this work. Good mass balance closures have been obtained, with all experimental results accounting for greater than 95% of the mass balance. Although former workers has previously shown that this small-scale reactor produced consistently good results, the present work provided further improvement in order to gain more comparable experimental results.

Pyrolysis products have been analysed by a number of techniques. Although the equipment to carry out these analyses was already in the laboratory, experimental techniques and procedures were investigated and improved throughout the course of this work (see next chapter).

The present work included four principal sections. The effects of condenser 1 temperature on water content and on the stability of oil collected by pot 1 were discussed in section 4.11; The effect of feed moisture content on product yields and oil water content and stability were discussed in Chapter 5; The effect of partially oxygenated pyrolysis on product yields and oil water content and stability were discussed in chapter 6 and finally the effect of copyrolysis with methanol on product yields and oil water content and stability were discussed in Chapter 7. Each section of the work enabled conclusions to be drawn. In the present chapter the overall conclusions with respect to oil stability are provided.

The effects of the temperature of condenser 1 on oil stability was shown to be very important for the attainment of comparable experimental results as a small change led to a change in the pot 1 oil water content, oil viscosity and oil stability. A lower condenser 1 temperature led to lower pot 1 oil viscosity because most water and volatiles were collected at lower temperatures. Thus a lower condenser 1 temperature gave more stable pot 1 oil, but the stability of mixed oil (pot1 and pot 2) was not affected by condenser1 temperature for a 0 to 20 °C temperature change. This provided the basis for obtaining comparable experiment results by fixing the temperature of condenser 1 when using pot 1 oil as main product.

Feed moisture content affects not only the pyrolysis process, but also product yields and product characteristics. High feed moisture content gives low char and high gas yields and also gives high liquid yield. The high liquid yield was mainly due to high water yields from high feed stock moisture and high reaction water. The organic yield did not change with different feed stock moisture. High feed moisture content resulted in higher oil water content, which is beneficial in lowering oil viscosity but a very high water led to oil phase separation. A very low feed moisture content gave an unstable oil with very high viscosity. It was found that the most stable oil was produced when its water content was just below the point at which phase separation occurred.

For spruce wood, an optimum feed moisture content of 7.3 – 12.8% was found in this work. Also, a pyrolysis temperature of 475 – 500°C was found to give the highest liquid yield and the most stable and least viscous oil.

Partially oxygenated pyrolysis was shown to be a simple method of increasing oil stability as no extra step was needed in the pyrolysis process and it was an energy saving process. Char yields decreased and water yields increased with increasing airfactor in partially oxygenated pyrolysis. Organic yields decreased, especially for unstable chemicals such as aldehydes and ketones, with increasing airfactor in partially oxygenated pyrolysis. Thus partially oxygenated pyrolysis decreased the source of oil instability. An increase in the oil water content and a resulting decrease in oil viscosity occurred with increasing of airfactor in partially oxygenated pyrolysis. Furthermore partially oxygenated pyrolysis reduced the total acids in the oil, thereby improving the quality of the oil. For the partially oxygenated pyrolysis of beech wood (with moisture content 8%), the optimum airfactor of 0.15 was found to give the most stable oil.

Pyrolysis of spruce wood with methanol could improve bio-oil stability, as with the use of methanol as a postproduction additive. Unstable chemicals such as aldehydes and ketones and oxygenated chemicals such as acid decreased in the co-pyrolysis process due to reactions with methanol. The water content increased in the co-pyrolysis process, thus co-pyrolysis with methanol process gave lower oil viscosity.

Oil stability increased in co-pyrolysis with methanol, but the total results showed that co-pyrolysis with methanol were not as effective as adding methanol into bio-oil as a postproduction additive. This was due to pyrolysis of the methanol in the co-pyrolysis process.

In summary, oil stability was mainly affected by oil water content and chemical components, as the very low oil char content was not enough to play a role in this work.

Oil water content played a very important role in oil stability as the water existed in the oil in the form of an emulsion; the stability of the emulsion was one of the reasons for oil stability. The stability of the emulsion was due to the hydrophilicity of the organic components in the oil. As discussed in chapter 5, the very low water content in the oil gave very high oil viscosity and hence poor oil quality. A very high water content of the oil gave an unstable emulsion and even phase separation due to breaking of the emulsion. Lower condenser 1 temperature gave more stable oil by collecting more water and volatiles in the pot 1 oil. Moderate feed moisture content gave more stable oil by forming a stable emulsion in the oil.

The hydrophilicity of the organic component in the oil was responsible for the stability of the emulsion in the oil. However, oxygenated chemicals in the oil gave oil with lower heating value while acids made the oil corrosive. Unstable species such as aldehydes and ketones are easily oxidised even in air and polymerise with time and at elevated temperature to produce unstable oil. Partially oxygenated pyrolysis increased oil stability by oxygenation of unstable aldehydes and ketones and combustion of acids and giving out water during the process. Copyrolysis with methanol increased oil stability by increasing oil water content and decreasing the concentration of unstable species due to reaction with methanol during the process.

That is, partially oxygenated pyrolysis and co-pyrolysis with methanol both increased oil water content and decreased the concentration of unstable species in the oil, thereby resulting in an increase in oil stability.

CHAPTER 9 . EXPERIMENTAL INACCURACY AND FURTHER RECOMMENDATION

The experimental results presented in this work are believed to be the best achievable from the equipment available at Aston. However, this does not necessarily mean that they are 100 % accurate. In this work, only those runs with mass balance closure greater than 95% were used and all results were taken from the runs that proceeded without interruption.

The purpose of this chapter is to highlight the areas that might cause a potential inaccuracy if ignored and further suggestions have been given.

1. Connector tube:

For the 150-g/h rig, a transfer tube was used to connect the reactor system and collection system. The product vapours came out through the transfer tube (hot space) and into condenser 1 (collection system). It is recommended that the transfer tube be lagged in order to maintain the pyrolysis vapour temperature in the tube above 400 °C and minimise vapour condensation in the transfer tube. There was always a quantity of black residue remaining in the transfer tube after pyrolysis, despite lagging the tube.

The residue that remained on the inside of the transfer tube was assumed to be char and a small amount of pyrolytic lignin as it did not dissolve in methanol, ethanol or acetone but could be removed by soaking in alkali solution (potassium hydroxide solution). The present work involved a comparison of results obtained in the same system and hence the validity of the comparison was assumed to be unaffected by the presence of this residue. However, a poorly lagged transfer tube gave lower pyrolysis liquid yields due to secondary reactions. Partially oxygenated pyrolysis gave lower quantities of residue (less than 0.5% on a dry feed basis) compared with normal pyrolysis (approximately1.2%).

Further recommendations are as follows:

- Analysis of the residue inside the transfer tube to improve the accuracy of the determined distribution of each component.
- Partially oxygenated pyrolysis could decrease the residue on the inside of the transfer tube.
- Redesign of the equipment to decrease the length of the transfer tube and provide suitable lagging.

2. Condenser 1:

The effects of condenser 1 'temperature on bio oil was discussed in this work (Section 4.11), It was very important to keep the temperature of condenser 1 stable during the run and to use the same temperature in different runs in order to get more comparable experimental results. The main oil product came from condenser 1 so it was important to ensure that all material inside condenser 1 was drained into oil pot 1 after product collection. Condenser 1 was mounted at an angle of 60° to facilitate liquid flow to the electrostatic precipitator during the run. However, it is recommended that this angle should be changed to more than 80° and allow sufficient time (24 hours) to ensure that all material is collected in oil pot 1. A lower condenser1 temperature will result in the oil inside having a lower viscosity and allow the oil to flow more easily.

Further suggestions are as follows:

- Maintain condenser 1 at a low temperature in order to reduce pot 1 oil viscosity
- Maintain condenser 1 temperature constant by circulation through a cooler in order to ensure comparable pot 1 oils in different runs.

3. EP:

The base of the EP facilitates the trapping of oil and hence it is recommended that its configuration be changed from A to B (Figure 9-1) in order to make sure all oil flows into collection oil pot 1. Also, it is recommended that the base be redesigned into a shape that can facilitate the ready removal of all oil.

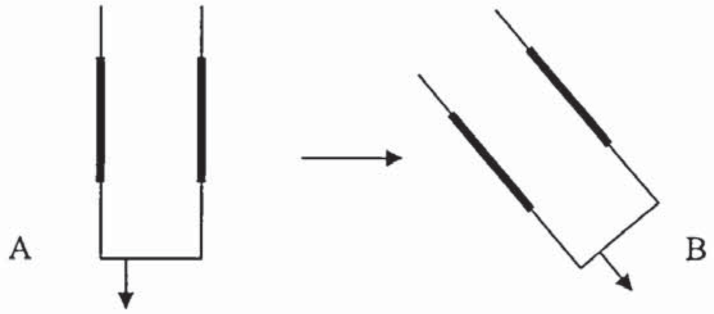


Figure 9-1. EP position

4. Oil collection

In this liquid collection system, about 90% of total liquid was collected by oil Pot1 at the base of the electrostatic precipitator. The remainder was collected from Pot 2 at the base of the second condenser, which was cooled by dry ice and acetone (-80 °C). The condenser1 temperature (10 to 20 °C) was regulated to provide for the collection of the higher molecular weight pyrolysis vapours so that the vapours collected in oil pot 2 were predominantly from the lower molecular weight fraction. Different condenser 1 temperatures facilitated the collection of different components in oil pot 1, thereby resulting in a different water content, viscosity and stability. Mixed oil pot 1 and oil pot 2 together meant that all pyrolysis vapours were collected together and was therefore unaffected by a change in condenser 1 temperature. A further redesign recommendation is that pot 1 and oil pot 2 be combined as one container in order to maintain a consistent oil product quality in different runs, not with standing a small change in the temperature of condenser 1.

5. The Karl Fischer systems:

The Karl Fischer system and method has been described previously in section 4.9.2.1 It is accurate to 0.01 %, thus it is not believed that this is a source of inaccuracy.

However it was found in the present work that some factors should be considered in order to ensure consistency in the oil water analyses between different runs.

- Calibration of the Karl Fischer apparatus should be carried out before use if not used in a laboratory with temperature and humidity control. 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%.
- It is recommended that oils be analysed at room temperature and at 24 hours after production due to oil water content changing with storage time and temperature.
- The analysis results were based on an average of three analyses, with a standard deviation of less than 0.3%.

6. The Viscosity test system:

Oil viscosity was found to change with storage time and temperature and hence it was necessary to measure the oil viscosity at the same time after production and at the same temperature in each case. The following recommendations are made to ensure more comparable experimental results.

- The water bath must be set at 25 °C ± 0.2 for all sample analysis
- The sample must be kept in the water bath for the same period of time (30 min) in order to maintain a stable temperature.
- Bubble formation in the oil should be avoided.
- The viscometer should be held vertically in the water bath.

7. Partially oxygenated pyrolysis gave more stable oil and the process was found to be energy efficient and simple. It was therefore concluded that the system was suitable for scale up. However, there remained an important unanswered question following the present work. The chemical analysis results showed that the concentration of aldehydes, ketones and acids decreased but the sugars increased on addition of oxygen. The reason for the increase in the concentration of sugar is unknown and

necessitates further work on the mechanism of the partially oxygenated pyrolysis process.

8. The pyrolysis vapour condensation process is a complex one, with possible reactions occurring between species in the pyrolysis vapour. Some reaction might not be reversed so methanol as a postproduction additive may not be fully effective on pyrolysis vapour. If methanol can be added before pyrolysis vapour condenses, the extent of polymerisation/condensation reaction may be reduced during the vapour condensation process. However, the experimental results showed that co-pyrolysis with methanol was not as effective as adding methanol into bio-oil as a postproduction additive because methanol was pyrolysed in the co-pyrolysis process. A more effective way of adding methanol might be to allow the methanol to contact the pyrolysis vapour just prior to their condensation so that methanol does not take part in pyrolysis. This work will require redesign of the pyrolysis collection system.

APPENDIX:

PREPARATION OF THE 150 G/H RIG FOR PYROLYSIS

1. First stage of preparation was to calibrate the feeder so that it fed at a rate between 100 to 150 g/hr. The feeder top flow rate and stirrer speeds have the greatest influence over the flow rate. When the flow rate had been determined, nitrogen was blown through the entrain tube to ensure there was no biomass left in it and then the feeder (with the feed) was weighed.

2. Afterwards, the reactor was set up by applying anti-seize compound (for contact between two metallic surfaces) to the swage lock joints between reactor top and body, char-pot and cyclone and cyclone top and tube and cyclone.

3. Then, 120 g of clean dry sand was weighed and added into the reactor body. A wire rod was put into the reactor top feed tube before fitting top and body together to prevent feed tube being blocked with sand.

4. All components were screwed together and tightened with a spanner. The complete reactor was weighed and placed in the furnace. Once all metallic parts of the reactor were insulated to prevent any heat losses, the furnace was warmed up. The thermocouple was attached to the reactor. The desired operating temperature was then set (set point) and some time was allowed (~45 min – 1 hour) for the reactor to reach it.

5. It was ensured that all glassware was clean and oven dried. All joints were greased with vacuum grease (for contact between glass surfaces), whilst the joint between the glass connector and the metal tube from reactor top needed 'Silver Goop' (for contact between metal and glass surfaces).

6. The cotton wool filter was packed with 25-30 g oven dry cotton wool.
7. Glassware (glass connector, Condensers 1 and 2, EP with magnet, Oil Pots 1 and 2, cotton filter with cotton) was weighed, assembled and clamped in place; ball and socket joints were held tight with metal clips.

8. When the reactor had reached the operating temperature, a small amount of fluidising gas was put through it to ensure uniform heating. At this point, the wire blocking the feed tube was kept in. Dry-ice/acetone was added in the second condenser. When the reactor was at a uniform temperature all gases were turned off, the wire was removed from feed tube and all tubes were connect to the reactor.

When all pieces of equipment had been connected in the following order, the process was as shown in Figure 0-1.

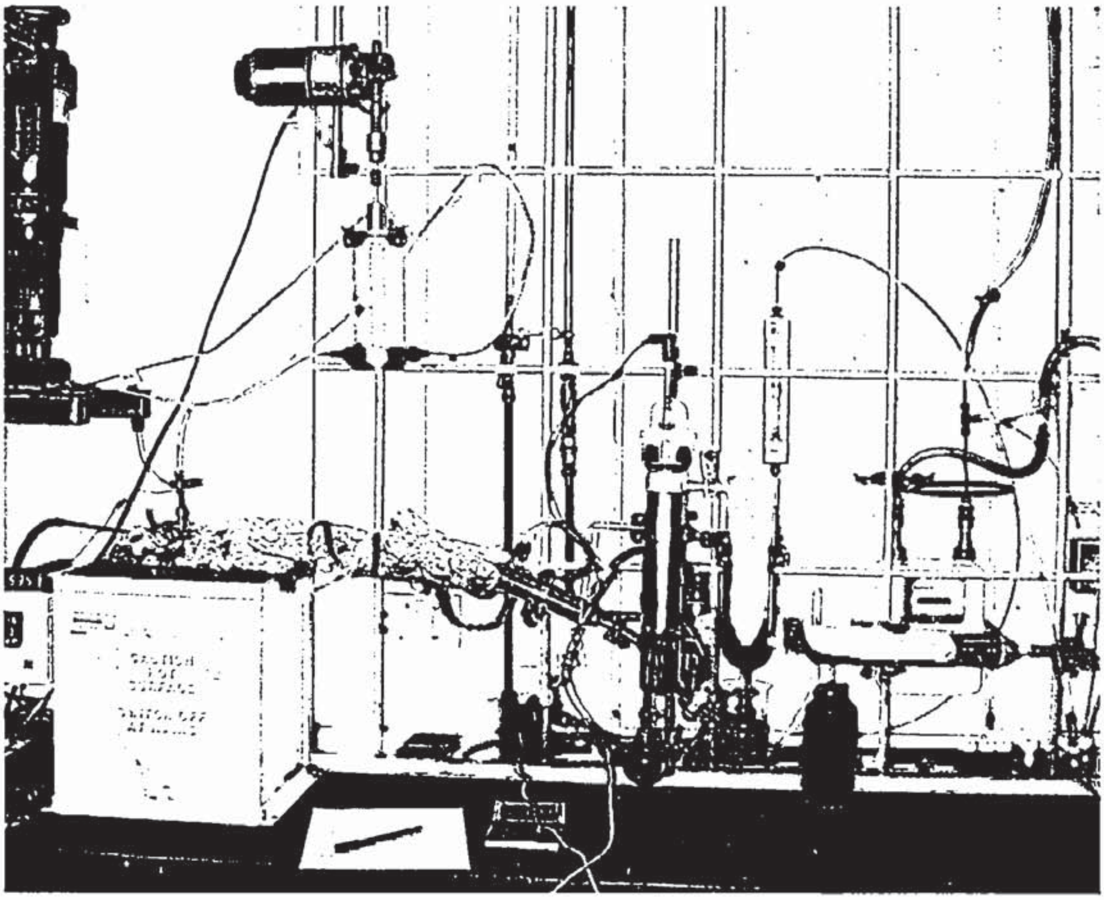


Figure 0-1. Photo of 150 g/h Rig

START UP AND OPERATION

The water supply to the first condenser was turned on, followed by the electrostatic precipitator (EP). When introducing nitrogen, the entraining gas was turned on first, followed by the fluidising gas and the feeder top gas. The on-line GC apparatus, which monitored the exit gas composition, was then started. Also, cooling air was attached at the top of the reactor. Cooling air kept the feedstock at low temperatures and therefore prevented pyrolysis from taking place at the feeding path.

When the experiment was started, biomass was feeding into the fluid bed and pyrolysis vapours were visible in the condensers. The furnace set point, furnace temperature, reactor temperature, feeder pressure drop, reactor pressure drop and gas meter readings at 1 minute intervals were noted down. During the experiment, more dry-ice was added when necessary.

In cases where during the experiment the feed tube became blocked, all gas flow was turned off; the clock was stopped and the gas meter reading was noted down. When pressures dropped to zero, the flexible tube was removed from the reactor top and so was any biomass from it. Biomass removed was weighed so that it could be accounted for in a mass balance. The reactor was then restarted as per start up, noting the gas meter reading and the time.

STANDARD SHUTDOWN PROCEDURE

The standard shutdown procedure to stop the experiment was as follows:

1) Stirrer was switched off to stop feed to reactor. Clock was stopped and gas meter reading was noted.
2) Furnace was switched off.
3) Feeder top entraining gas was turned off, followed rapidly by the fluidising gas.
4) A rod was inserted down reactor feed tube and fluidising nitrogen flow was restarted. (This prevented any sand from blocking feed tube).
5) Flow of water to condenser 1 was maintained.
6) EP was kept on until vapours had cleared, which is when it was turned off.
7) The system was left to cool down.

8) The glass ball was separated from the metal socket, since heavy lignin residue could have stuck these together.

DISASSEMBLY

When apparatus had cooled down:

- Temperature display, water and remaining nitrogen flow were turned off. Nitrogen cylinder was also switched off.
- Individual components were dismantled.
- Cooling water was switched off.
- Dry-ice/acetone was removed from the glass condenser and was allowed to dry.
- All other glassware were weighed.
- The feeder with the remaining wood was weighed. Feedstock was not weighed alone, since the small particle size meant it was difficult to handle, e.g. by sticking on the feeder walls, which could have introduced inaccuracies.

The first portion of liquid from the EP was stored at room temperature and used for physical property testing. The remaining half of this liquid was stored separately in the fridge for potential chemical analysis and KF (Karl Fischer Coulometer) moisture content analysis. The liquid from the EP and secondary (dry-ice/acetone) condenser could not be mixed since this would have led to phase separation of the liquid.

LIST OF GLOSSARY

W_{org}: The weight of organic in the oil in gram.
W_{wat}: The weight of water in the oil in gram.
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$C_{wet}\%$: Carbon percentage in wet oil.
$H_{dry}\%$: Hydrogen percentage in dry oil.
$H_{wet}\%$: Hydrogen percentage in wet oil.
$O_{dry}\%$: Oxygen percentage in dry oil.
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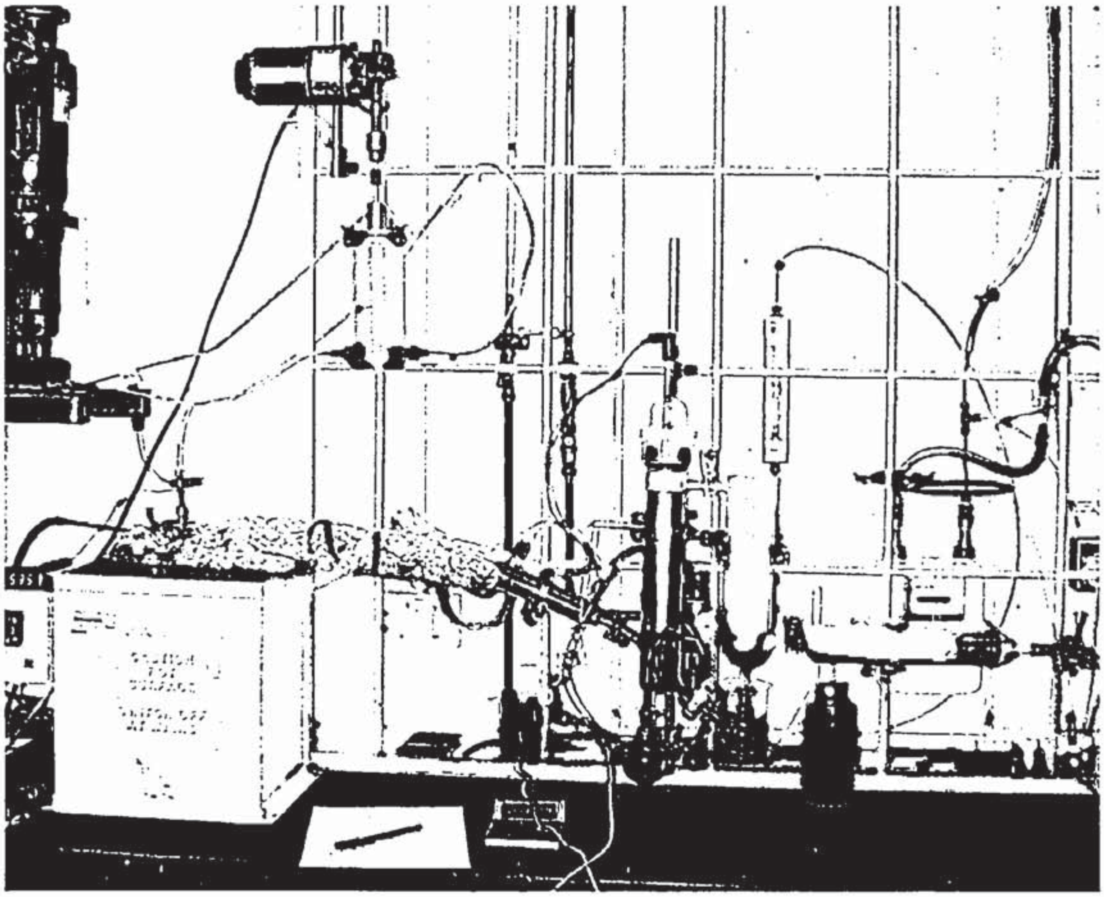

Figure 0-1. Photo of 150 g/h Rig

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$O_{dry}\%$: Oxygen percentage in dry oil.
$O_{wet}\%$: Oxygen percentage in wet oil.
HHV: High heating value.

MASS BALANCE RESULTS FOR PYROLYSIS DIFFERENT MOISTURE CONTENT SPRUCE AT DIFFERENT PYROLYSIS TEMPERATURE (TABLE 0-1 TO TABLE 0-15)

Table 0-1. Mass Balance result of bone dry spruce feed at 450 °C

Summary						
Run title	PL54B450					
Feed stock	Spruce from kielder		(Bone dry spruce)			
Average temperature	451.2	°C				
Residence time	0.54	s				
Feed rate	118.77	g/h	(Wet feed/Time)			
Input O2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	69.28	69.28	0.00	-		69.28
	Oil	Water	Char	Organics	Gases	
Output (g)	51.68	9.00	10.51	42.68	5.26	67.45
Yields in dry Basis (%)	74.60	12.99	15.17	61.61	7.59	97.36
Yields in Wet Basis (%)	74.60	12.99	15.17	61.61	7.59	97.36
Fresh Oil pot 1 water content		11%				
Oil pot 2 water content		54%				
Aged oil 1 water content		12%				
Gas From GC	Yields in dry base					
Methane	0.50%					
Carbon Dioxide	6.48%					
Ethylene	0.12%					
Ethane	0.22%					
Hydrogen	0.05%					
Propylene	0.00%					
Carbonmonoxide	0.23%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm^2/s)	491.84	2008.52	3.08			
** CO can not be detected so it made lower mass balance.						

Table 0-2. Mass Balance result of bone dry spruce feed at 475 °C

Summary						
Run title	PL69B475					
Run Number	69					
Feed stock	Spruce from kielder		(Bone dry)			
Average temperature	476.3	°C				
Residence time	0.57	s				
Feed rate	161.56	g/h	(Wet feed/Time)			
Input O2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	80.78	80.71	0.07	-		80.78
	Oil	Water	Char	Organics	Gases	Closure
Output (g)	59.64	10.08	12.42	49.56	7.52	79.58
Yields in dry Basis (%)	73.81	12.41	15.39	61.40	9.32	98.51
Yields in Wet Basis (%)	73.83	12.48	15.38	61.35	9.31	98.51
Pot1 fresh oil water content	11.0%					
Pot1 aged oil water content	11.8%					
Pot2 oil water content	50.6%					
Gas From GC	Yields in dry base					
Methane	0.51%					
Carbon Dioxide	6.23%					
Ethylene	0.10%					
Ethane	0.16%					
Hydrogen	0.04%					
Propylene	0.00%					
Carbon monoxide	2.26%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 ^{0}C (mm^2/s)	445.93	1864.75	3.18			

Table 0-3. Mass balance result of bone dry spruce feed at 500 °C

Summary						
Run title	PL53B500					
Feed stock	Spruce from kielder		(Bone dry)			
Average temperature	500.1	°C				
Residence time	0.52	s				
Feed rate	141.87	g/h	(Wet feed/Time)			
Input O2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	78.03	77.58	0.45	-		78.03
	Oil	Water	Char	Organics	Gases	Closure
Output (g)	58.59	10.03	9.39	48.51	7.86	75.78
Yields in dry Basis (%)	74.87	12.34	12.10	62.52	10.13	97.10
Yields in Wet Basis (%)	75.09	12.85	12.03	62.16	10.07	97.11
Pot1 oil water content	9.9%					
Pot1aged oil water content	10.9%					
Pot2 oil water content	55.0%					
Gas From GC	Yields in dry base					
Methane	0.57%					
Carbon Dioxide	6.39%					
Ethylene	0.14%					
Ethane	0.17%					
Hydrogen	0.06%					
Propylene	0.00%					
Carbon monoxide	2.79%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm^2/s)	693.09	2758.14	2.98			

Table 0-4. Mass Balance result of bone dry spruce feed at 525 °C

Summary						
Run title	PL56B525					
Run Number	56					
Feed stock	Spruce from kielder		(Bone dry)			
Average temperature	523.3	°C				
Residence time	0.51	s				
Feed rate	165.72	g/h	(Wet feed/Time)			
Input O_2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	82.86	82.79	0.07	-		82.86
	Oil	Water	Char	Organics	Gases	Closure
Output (g)	60.57	9.83	8.55	50.74	11.13	80.25
Yields in dry Basis (%)	73.08	11.79	10.33	61.29	13.44	96.85
Yields in Wet Basis (%)	73.10	11.86	10.32	61.24	13.43	96.85
Pot1 fresh oil water content	9.6%					
Pot1 aged oil water content	10.3%					
Pot2 oil water content	49.7%					
Gas From GC	Yields in dry base					
Methane	0.78%					
Carbon Dioxide	6.69%					
Ethylene	0.23%					
Ethane	0.19%					
Hydrogen	0.07%					
Propylene	0.00%					
Carbon monoxide	5.47%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm2/s)	734.65	3203.25	3.36			

Table 0-5. Mass Balance result of bone dry spruce feed at 550 °C

Summary						
Run title	PL70B550					
Feed stock	Spruce from kielder		(Bone dry)			
Average temperature	551.1	°C				
Residence time	0.47	s				
Feed rate	133.14	g/h	(Wet feed/Time)			
Input O2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	66.57	66.52	0.05	-		66.57
	Oil	Water	Char	Organics	Gases	Closure
Output (g)	48.28	7.33	6.98	40.88	9.94	65.14
Yields in dry Basis (%)	72.41	10.94	10.50	61.47	14.94	97.84
Yields in Wet Basis (%)	72.53	11.02	10.49	61.42	14.92	97.84
Pot1 fresh oil water content	7.7%					
Pot1 aged oil water content	9.8%					
Pot2 oil water content	47.7%					
Gas From GC	Yields in dry base					
Methane	0.81%					
Carbon Dioxide	6.35%					
Ethylene	0.23%					
Ethane	0.08%					
Hydrogen	0.09%					
Propylene	0.10%					
Carbon monoxide	6.75%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm$_2$/s)	1253.64	6178.35	3.93			

Table 0-6. Mass balance result of 7.3% moisture content spruce feed at 450 °C

Summary						
Run title	PL60B450					
Feed stock	Spruce from kielder					
feed moisture content	7.3%					
Average temperature	452.4	°C				
Residence time	0.54	s				
Feed rate	161.30	g/h	(Wet feed/Time)			
Input O_2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	67.21	62.62	4.59	-		67.21
	Oil	Water	Char	Organics	Gases	Closure
Output (g)	51.86	12.62	8.79	39.24	5.46	66.11
Yields in dry Basis (%)	75.49	12.83	14.04	62.66	8.71	98.24
Yields in Wet Basis (%)	77.16	18.78	13.08	58.38	8.12	98.36
Pot1 fresh oil water content	17.8%					
Pot1 aged oil water content	19.8%					
Pot2 oil water content	65.0%					
Gas From GC	Yields in dry base					
Methane	0.42%					
Carbon Dioxide	5.77%					
Ethylene	0.05%					
Ethane	0.05%					
Hydrogen	0.02%					
Propylene	0.00%					
Carbon monoxide	2.40%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm_2/s)	91.86	254.88	1.77			

Table 0-7. Mass balance result of 7.3% moisture content spruce feed at 475 °C

Summary						
Run title	PL61B475					
Feed stock	Spruce from kielder					
Feed moisture content	7.3%					
Average temperature	475.4	°C				
Residence time	0.52	s				
Feed rate	163.37	g/h	(Wet feed/Time)			
Input O_2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	68.07	63.42	4.65	-		68.07
	Oil	Water	Char	Organics	Gases	Closure
Output (g)	52.72	12.83	7.63	39.89	5.69	66.04
Yields in dry Basis (%)	75.80	12.91	12.03	62.89	8.97	96.80
Yields in Wet Basis (%)	77.45	18.85	11.21	58.60	8.36	97.02
Pot1 fresh oil water content	17.6%					
Pot1 aged oil water content	19.9%					
Pot2 oil water content	63.6%					
Gas From GC	Yields in dry base					
Methane	0.46%					
Carbon Dioxide	5.76%					
Ethylene	0.07%					
Ethane	0.05%					
Hydrogen	0.03%					
Propylene	0.00%					
Carbon monoxide	2.61%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm^2/s)	113.48	345.14	2.04			

Table 0-8. Mass balance result of 7.3% moisture content spruce feed at 500 °C

Summary						
Run title	PL62B500					
Feed stock	Spruce from kielder					
Feed moisture content	7.3%					
Average temperature	500.7	°C				
Residence time	0.50	s				
Feed rate	160.27	g/h	(Wet feed/Time)			
Input O_2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	66.78	62.22	4.56	-		66.78
	Oil	Water	Char	Organics	Gases	Closure
Output (g)	52.01	12.58	6.56	39.40	6.11	64.65
Yields in dry Basis (%)	76.21	12.89	10.55	63.32	9.81	96.57
Yields in Wet Basis (%)	77.88	18.83	9.83	59.00	9.14	96.81
Pot1 fresh oil water content	17.5%					
POt1 aged oil water content	19.1%					
Pot2 oil water content	60.6%					
Gas From GC	Yields in dry base					
Methane	0.63%					
Carbon Dioxide	6.13%					
Ethylene	0.13%					
Ethane	0.06%					
Hydrogen	0.05%					
Propylene	0.00%					
Carbon monoxide	2.82%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm^2/s)	112.87	347.43	2.08			

Table 0-9. Mass balance result of 7.3% moisture content spruce feed at 525 °C

Summary						
Run title	PL63B525					
Feed stock	Spruce from kielder					
Feed moisture content	7.3%					
Average temperature	527.5	°C				
Residence time	0.47	s				
Feed rate	176.98	g/h	(Wet feed/Time)			
Input O_2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	73.74	68.71	5.03	-		73.74
	Oil	Water	Char	Organics	Gases	Closure
Output (g)	54.76	13.94	6.72	40.82	9.71	71.19
Yields in dry Basis (%)	72.38	12.97	9.78	59.41	14.13	96.29
Yields in Wet Basis (%)	74.26	18.91	9.11	55.35	13.17	96.54
Pot1 fresh oil water content	17.5%					
POt1 aged oil water content	19.0%					
Pot2 oil water content	63.9%					
Gas From GC	Yields in dry base					
Methane	0.93%					
Carbon Dioxide	6.89%					
Ethylene	0.25%					
Ethane	0.09%					
Hydrogen	0.08%					
Propylene	0.00%					
Carbon monoxide	5.89%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 ^{0}C (mm^2/s)	122.78	497.53	3.05			

Table 0-10. Mass balance result of 7.3% moisture content spruce feed at 550 °C

Summary						
Run title	PL64B550					
Feed stock	Spruce from kielder					
Feed moisture content	7.3%					
Average temperature	554.4	°C				
Residence time	0.47	s				
Feed rate	147.77	g/h	(Wet feed/Time)			
Input O_2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	61.57	57.37	4.20	-		61.57
	Oil	Water	Char	Organics	Gases	Closure
Output (g)	43.75	11.46	5.29	32.29	8.77	57.81
Yields in dry Basis (%)	68.94	12.65	9.22	56.28	15.29	93.45
Yields in Wet Basis (%)	71.06	18.62	8.59	52.44	14.25	93.90
Pot1 oil water content	17.6%					
Pot2 oil water content	65.5%					
Gas From GC	Yields in dry base					
Methane	0.95%					
Carbon Dioxide	6.34%					
Ethylene	0.40%					
Ethane	0.11%					
Hydrogen	0.12%					
Propylene	0.00%					
Carbon monoxide	6.34%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 ^{0}C (mm^2/s)	158.12	625.09	2.95			

Table 0-11. Mass balance result of 12.8% moisture content spruce feed at 475 °C

Total Mass Balance						
Run title	PL71B475					
Feed stock	Spruce from kielder					
Feed moisture content	12.8%					
Average temperature	476.2	°C				
Residence time	0.52	s				
Feed rate	144.95	g/h	(Wet feed/Time)			
Input O_2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	61.12	54.19	6.93	-		61.12
	Oil	Water	Char	Organics	Gases	Closure
Output (g)	48.56	14.68	6.22	33.88	5.14	59.92
Yields in dry Basis (%)	76.82	14.30	11.48	62.52	9.49	97.79
Yields in Wet Basis (%)	79.45	24.02	10.18	55.43	8.42	98.04
Pot1 fresh oil water content	21.6%					
Pot1 aged oil water content	23.5%					
Pot2 oil water content	72.2%					
Gas From GC	Yields in dry base					
Methane	0.45%					
Carbon Dioxide	5.45%					
Ethylene	0.06%					
Ethane	0.05%					
Hydrogen	0.04%					
Propylene	0.00%					
Carbon monoxide	3.45%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm^2/s)	73.04	217.37	1.98			

Table 0-12. Mass balance result of 12.8% moisture content spruce feed at 500 °C

Summary						
Total Mass Balance						
Run title	PL72B500					
Run Number	72					
Feed stock	Spruce from kielder					
Feed moisture content	12.8%					
Average temperature	500.0	oC				
Residence time	0.49	s				
Feed rate	123.86	g/h	(Wet feed/Time)			
input O2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	wet feed	dry feed	water	oxygen		Total
Input (g)	61.93	54.90	7.03	-		61.93
	Oil	Water	Char	Organics	Gases	closure
Output (g)	48.19	14.50	6.75	33.67	6.07	60.99
Yields in dry Basis (%)	74.93	13.61	12.30	61.32	11.06	98.30
Yields in Wet Basis (%)	77.81	23.41	10.91	54.37	9.81	98.49
Pot1 fresh oil water content	23.2%					
Pot1 aged oil water content	25.3%					
Pot2 oil water content	70.0%					
Calculated water content of bio-oil		30.1%				
Gas From GC	Yields in dry base					
Methane	0.50%					
Carbon Dioxide	5.84%					
Ethylene	0.10%					
Ethane	0.06%					
Hydrogen	0.05%					
Propylene	0.00%					
Carbon monoxide	4.51%					
Propane						
N-Butane						
Oxygen left in output N2	0.00%					
Viscosity	Fresh oil	aged oil	AVI			
25 0C (mm2/s)	58.07	174.32	2.00			

Table 0-13. Mass balance result of 12.8% moisture content spruce feed at 450 °C

Summary						
Run title	PL73B450					
Feed stock	Spruce from kielder					
Feed moisture content	12.8%					
Average temperature	450.0	$^{\circ}$C				
Residence time	0.53	s				
Feed rate	116.10	g/h	(Wet feed/Time)			
Input O_2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	58.05	51.46	6.59	-		58.05
	Oil	Water	Char	Organics	Gases	Closure
Output (g)	45.91	14.39	6.81	31.52	4.66	57.38
Yields in dry Basis (%)	76.41	15.17	13.23	61.24	9.06	98.71
Yields in Wet Basis (%)	79.09	24.79	11.73	54.29	8.04	98.85
Pot1 fresh oil water content	24.2%					
Pot1 aged oil water content	25.8%					
Pot2 oil water content	73.0%					
Gas From GC	Yields in dry base					
Methane	0.42%					
Carbon Dioxide	5.41%					
Ethylene	0.04%					
Ethane	0.05%					
Hydrogen	0.03%					
Propylene	0.00%					
Carbon monoxide	3.11%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 $^{\circ}$C (mm_2/s)	38.36	104.71	1.73			

Table 0-14. Mass balance result of 12.8% moisture content spruce feed at 525 °C

Summary						
Run title	PL74B525					
Feed stock	Spruce from kielder					
Feed moisture content	12.8%					
Average temperature	525.0	°C				
Residence time	0.47	s				
Feed rate	139.78	g/h	(Wet feed/Time)			
Input O_2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	69.89	61.96	7.93	-		69.89
	Oil	Water	Char	Organics	Gases	Closure
Output (g)	54.48	16.74	6.19	37.74	8.32	68.99
Yields in dry Basis (%)	75.13	14.22	9.99	60.91	13.44	98.56
Yields in Wet Basis (%)	77.95	23.95	8.86	54.00	11.91	98.72
Pot1 fresh oil water content	25.1%					
Pot1 aged oil water content	26.2%					
Pot2 oil water content	62.9%					
Gas From GC	Yields in wet base					
Methane	0.73%					
Carbon Dioxide	6.23%					
Ethylene	0.18%					
Ethane	0.08%					
Hydrogen	0.08%					
Propylene	0.06%					
Carbon monoxide	6.08%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm^2/s)	48.88	131.17	1.68			

Table 0-15. Mass balance result of 12.8% moisture content spruce feed at 550 °C

Summary						
Run title	PL75B550					
Feed stock	Spruce from kielder					
Feed moisture content	12.8%					
Average temperature	550.0	°C				
Residence time	0.47	s				
Feed rate	174.40	g/h	(Wet feed/Time)			
Input O_2 by GC result	0.00%					
Airfactor	0.000		(Reaction oxygen/Dry feed)			
	Wet feed	Dry feed	Water	Oxygen		Total
Input (g)	87.20	77.31	9.89	-		87.20
	Oil	Water	Char	Organics	Gases	Closure
Output (g)	66.70	19.74	8.66	46.96	11.46	86.82
Yields in dry Basis (%)	73.48	12.74	11.20	60.74	14.82	99.51
Yields in Wet Basis (%)	76.49	22.64	9.93	53.85	13.14	99.56
Pot1 fresh oil water content	23.8%					
Pot1 aged oil water content	24.9%					
Pot2 oil water content	61.6%					
Gas From GC	Yields in dry base					
Methane	0.90%					
Carbon Dioxide	6.36%					
Ethylene	0.25%					
Ethane	0.09%					
Hydrogen	0.11%					
Propylene	0.12%					
Carbon monoxide	7.01%					
Propane						
N-Butane						
Oxygen left in output N_2	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm^2/s)	53.87	200.89	2.73			

MASS BALANCE RESULTS OF OXYGENATED PYROLYSIS BEECH WOOD WITH DIFFERENT AIRFACTOR AT 475 °C (TABLE 0-16 TO TABLE 0-26)

Table 0-16. Mass balance of oxygenated pyrolysis of beech wood at airfactor 0

Summary						
Run title	PL96B475					
Feed stock	Beech Wood					
Feed moisture content (dry basis)		8.09				
Average temperature	476.4	°C				
Residence time	0.58	s				
Feed rate	134.01	g/h	(Wet feed/Time)			
Input O_2 by GC result	0.00%					
Airfactor	0.00		(Reaction oxygen/Dry feed)			
Input (g)	Wet feed	Dry feed	Water	Oxygen		Total
	78.17	72.32	5.85	-		78.17
Output (g)	Oil	Water	Char	Organics	Gases	Total
	61.47	13.60	8.08	47.87	8.25	77.80
	Oil	Water	Char	Organics	Gases	Closure
Yields 0n Wet Feed Basis (%)	78.64	17.40	10.34	61.23	10.56	99.53
Yields 0n Dry Feed Basis (%)	76.91	10.72	11.17	66.19	11.41	99.49
Gas From GC	Yields on dry feed basis (%)					
Methane	0.58%					
Carbon Dioxide	6.77%					
Ethylene	0.08%					
Ethane	0.04%					
Hydrogen	0.04%					
Propylene	0.22%					
Carbon monoxide	3.68%					
Propane						
N-Butane						
Outlet oxygen in nitrogen	0.00%					
Viscosity	Fresh oil	Aged oil	VI			
25 ^{0}C (mm^2/s)	52.25	148.66	1.85			
Water content	18.87%					
	52.39%					

Table 0-17. Mass balance of oxygenated pyrolysis of beech wood at airfactor 0.03

Summary						
Run title	PL97A475					
Feed stock	Beech Wood					
Feed moisture content (dry basis)		8.09				
Average temperature	474.6	°C				
Residence time	0.58	s				
Feed rate	140.14	g/h	(Wet feed/Time)			
Input O_2 by GC result	0.62%					
Airfactor	0.0304		(Reaction oxygen/Dry feed)			
Input (g)	Wet feed	Dry feed	Water	Oxygen		Total
	81.75	75.63	6.12	2.72		84.47
Output (g)	Oil	Water	Char	Organics	Gases	Total
	62.71	15.37	8.19	47.34	12.37	83.27
	Oil	Water	Char	Organics	Gases	Closure
Yields On Wet Feed Basis (%)	74.24	18.19	9.70	56.04	14.64	98.57
Yields On Dry Feed Basis (%)	72.22	11.80	10.45	60.42	15.78	98.46
Gas From GC	Yields on dry feed basis (%)					
Methane	0.56%					
Carbon Dioxide	10.92%					
Ethylene	0.10%					
Ethane	0.04%					
Hydrogen	0.03%					
Propylene	0.05%					
Carbon monoxide	4.64%					
Propane						
N-Butane						
Outlet oxygen in nitrogen	0.18%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm^2/s)	48.99	127.05	1.59			
Water content	20.74%					
	51.27%					

Table 0-18. Mass balance of oxygenated pyrolysis of beech wood at airfactor 0.04

Summary						
Run title	PL98A475					
Feed stock	Beech Wood					
Feed moisture content (dry basis)		8.09				
Average temperature	474.8	°C				
Residence time	0.59	s				
Feed rate	141.53	g/h	(Wet feed/Time)			
Input O_2 by GC result	0.74%					
Airfactor	0.0434		(Reaction oxygen/Dry feed)			
Input (g)	Wet feed	Dry feed	Water	Oxygen		Total
	82.56	76.38	6.18	3.32		85.88
Output (g)	Oil	Water	Char	Organics	Gases	Total
	63.19	16.58	8.54	46.61	13.48	85.21
	Oil	Water	Char	Organics	Gases	Closure
Yields 0n Wet Feed Basis (%)	73.58	19.31	9.94	54.27	15.69	99.22
Yields 0n Dry Feed Basis (%)	71.53	13.05	10.72	58.48	16.91	99.16
Gas From GC	Yields on dry feed basis (%)					
Methane	0.51%					
Carbon Dioxide	12.19%					
Ethylene	0.10%					
Ethane	0.04%					
Hydrogen	0.03%					
Propylene	0.01%					
Carbon monoxide	4.76%					
Propane						
N-Butane						
Outlet oxygen in nitrogen	0.20%					
Viscosity	Fresh oil	Aged oil	AVI			
25 °C (mm^2/s)	34.48	86.96	1.52			
Water content	23.76%					
	46.66%					

Table 0-19. Mass balance of oxygenated pyrolysis of beech wood at airfactor 0.07

Summary						
Run title	PL99A475					
Feed stock	Beech Wood					
Feed moisture content (dry basis)		8.09				
Average temperature	474.9	°C				
Residence time	0.58	s				
Feed rate	147.26	g/h	(Wet feed/Time)			
Input O_2 by GC result	1.22%					
Airfactor	0.0742		(Reaction oxygen/Dry feed)			
Input (g)	Wet feed	Dry feed	Water	Oxygen		Total
	78.54	72.66	5.88	5.39		83.93
Output (g)	Oil	Water	Char	Organics	Gases	Total
	59.73	16.62	8.12	43.11	14.29	82.14
	Oil	Water	Char	Organics	Gases	Closure
Yields 0n Wet Feed Basis (%)	71.17	19.80	9.67	51.37	17.02	97.87
Yields 0n Dry Feed Basis (%)	69.00	13.76	10.40	55.24	18.31	97.71
Gas From GC	Yields on dry feed basis (%)					
Methane	0.53%					
Carbon Dioxide	14.10%					
Ethylene	0.10%					
Ethane	0.04%					
Hydrogen	0.04%					
Propylene	0.01%					
Carbon monoxide	4.85%					
Propane						
N-Butane						
Outlet oxygen in nitrogen	0.26%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm²/s)	27.68	65.93	1.38			
Water content	25.85%					
	48.00%					

Table 0-20. Mass balance of oxygenated pyrolysis of beech wood at airfactor 0.08

Summary						
Run title	PL100A475					
Feed stock	Beech Wood					
Feed moisture content (dry basis)		8.09				
Average temperature	475.4	°C				
Residence time	0.59	s				
Feed rate	145.14	g/h	(Wet feed/Time)			
Input O_2 by GC result	1.28%					
Airfactor	0.0757		(Reaction oxygen/Dry feed)			
Input (g)	Wet feed	Dry feed	Water	Oxygen		Total
	77.41	71.62	5.79	5.42		82.83
Output (g)	Oil	Water	Char	Organics	Gases	Total
	58.61	16.47	8.19	42.14	15.48	82.28
	Oil	Water	Char	Organics	Gases	Closure
Yields 0n Wet Feed Basis (%)	70.76	19.88	9.89	50.88	18.69	99.34
Yields 0n Dry Feed Basis (%)	68.56	13.86	10.63	54.70	20.10	99.29
Gas From GC	Yields on dry feed basis (%)					
Methane	0.51%					
Carbon Dioxide	15.84%					
Ethylene	0.10%					
Ethane	0.04%					
Hydrogen	0.03%					
Propylene	0.01%					
Carbon monoxide	5.08%					
Propane						
N-Butane						
Outlet oxygen in nitrogen	0.28%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm^2/s)	25.98	61.82	1.38			
Water content	26.44%					
	45.99%					

Table 0-21. Mass balance of oxygenated pyrolysis of beech wood at airfactor 0.10

Summary						
Run title	PL101A475					
Feed stock	Beech Wood					
Feed moisture content (dry basis)		8.09				
Average temperature	475.4	°C				
Residence time	0.59	s				
Feed rate	147.99	g/h	(Wet feed/Time)			
Input O_2 by GC result	1.51%					
Airfactor	0.0986		(Reaction oxygen/Dry feed)			
Input (g)	Wet feed	Dry feed	Water	Oxygen		Total
	78.93	73.02	5.91	7.20		86.13
Output (g)	Oil	Water	Char	Organics	Gases	Total
	59.12	17.98	7.87	41.14	16.98	83.97
	Oil	Water	Char	Organics	Gases	Closure
Yields 0n Wet Feed Basis (%)	68.64	20.88	9.14	47.77	19.72	97.50
Yields 0n Dry Feed Basis (%)	66.33	15.05	9.81	51.28	21.17	97.32
Gas From GC	Yields on dry feed basis (%)					
Methane	0.47%					
Carbon Dioxide	17.54%					
Ethylene	0.10%					
Ethane	0.04%					
Hydrogen	0.03%					
Propylene	0.01%					
Carbon monoxide	5.06%					
Propane						
N-Butane						
Outlet oxygen in nitrogen	0.27%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm^2/s)	23.19	57.33	1.47			
Water content	27.60%					
	53.26%					

Table 0-22. Mass balance of oxygenated pyrolysis of beech wood at airfactor 0.11

Summary						
Run title	PL102A475					
Feed stock	Beech Wood					
Feed moisture content (dry basis)		8.09				
Average temperature	476.6	oC				
Residence time	0.57	s				
Feed rate	147.45	g/h	(Wet feed/Time)			
Input O_2 by GC result	1.64%					
Airfactor	0.1022		(Reaction oxygen/Dry feed)			
Input (g)	Wet feed	Dry feed	Water	Oxygen		Total
	78.64	72.75	5.89	7.44		86.08
Output (g)	Oil	Water	Char	Organics	Gases	Total
	59.03	17.13	7.65	41.90	18.96	85.64
	Oil	Water	Char	Organics	Gases	Closure
Yields 0n Wet Feed Basis (%)	68.58	19.90	8.89	48.67	22.02	99.49
Yields 0n Dry Feed Basis (%)	66.27	14.03	9.54	52.25	23.64	99.45
Gas From GC	Yields on dry feed basis (%)					
Methane	0.47%					
Carbon Dioxide	20.18%					
Ethylene	0.10%					
Ethane	0.04%					
Hydrogen	0.04%					
Propylene	0.00%					
Carbon monoxide	5.23%					
Propane						
N-Butane						
Outlet oxygen in nitrogen	0.33%					
Viscosity	Fresh oil	Aged oil	VI			
25 ^{0}C (mm^2/s)	24.71	62.18	1.52			
Water content	26.85%					
	49.98%					

Table 0-23. Mass balance of oxygenated pyrolysis of beech wood at airfactor 0.13

Summary						
Run title	PL104A475					
Feed moisture content (dry basis)		8.09				
Feed stock	Beech Wood					
Average temperature	476.2	°C				
Residence time	0.58	s				
Feed rate	144.58	g/h	(Wet feed/Time)			
Input O_2 by GC result	1.89%					
Airfactor	0.1270		(Reaction oxygen/Dry feed)			
Input (g)	Wet feed	Dry feed	Water	Oxygen		Total
	84.34	78.03	6.31	9.91		94.25
Output (g)	Oil	Water	Char	Organics	Gases	Total
	62.86	18.93	8.52	43.93	22.81	94.19
	Oil	Water	Char	Organics	Gases	Closure
Yields 0n Wet Feed Basis (%)	66.70	20.08	9.04	46.62	24.20	99.94
Yields 0n Dry Feed Basis (%)	64.31	14.35	9.69	49.96	25.94	99.94
Gas From GC	Yields on dry feed basis (%)					
Methane	0.48%					
Carbon Dioxide	22.90%					
Ethylene	0.11%					
Ethane	0.04%					
Hydrogen	0.04%					
Propylene	0.00%					
Carbon monoxide	5.66%					
Propane						
N-Butane						
Outlet oxygen in nitrogen	0.29%					
Viscosity	Fresh oil	Aged oil	VI			
25 °C (mm^2/s)	23.39	56.57	1.42			
Water content	28.37%					
	45.70%					

Table 0-24. Mass balance of oxygenated pyrolysis of beech wood at airfactor 0.19

Summary						
Run title	PL108A475					
Feed stock	Beech Wood					
Feed moisture content (dry basis)		8.09				
Average temperature	476.2	oC				
Residence time	0.56	s				
Feed rate	128.01	g/h	(Wet feed/Time)			
Input O_2 by GC result	2.58%					
Airfactor	0.19		(Reaction oxygen/Dry feed)			
Input (g)	Wet feed	Dry feed	Water	Oxygen		Total
	74.67	69.08	5.59	13.20		87.87
Output (g)	Oil	Water	Char	Organics	Gases	Total
	55.80	18.76	6.62	37.04	24.33	86.75
	Oil	Water	Char	Organics	Gases	Closure
Yields 0n Wet Feed Basis (%)	63.50	21.35	7.53	42.15	27.69	98.72
Yields 0n Dry Feed Basis (%)	61.02	16.01	8.05	45.01	29.57	98.64
Gas From GC	Yields on dry feed basis (%)					
Methane	0.43%					
Carbon Dioxide	28.66%					
Ethylene	0.11%					
Ethane	0.03%					
Hydrogen	0.04%					
Propylene	0.00%					
Carbon monoxide	5.95%					
Propane						
N-Butane						
outlet oxygen in nitrogen	0.53%					
Viscosity	Fresh oil	Aged oil	VI			
25 ^{0}C (mm^2/s)	16.77	56.57	2.37			
Water content	31.45%					
	48.10%					

Table 0-25. Mass balance of oxygenated pyrolysis of beech wood at airfactor 0.23

Summary						
Run title	PL109A475					
Feed stock	Beech Wood					
Feed moisture content (dry basis)		8.09				
Average temperature	476.2	oC				
Residence time	0.58	s				
Feed rate	121.52	g/h	(Wet feed/Time)			
Input O_2 by GC result	3.04%					
Airfactor	0.2316		(Reaction oxygen/Dry feed)			
Input (g)	Wet feed	Dry feed	Water	Oxygen		Total
	68.86	63.71	5.15	14.75		83.61
Output (g)	Oil	Water	Char	Organics	Gases	Total
	50.43	17.83	5.56	32.60	25.53	81.52
	Oil	Water	Char	Organics	Gases	Closure
Yields On Wet Feed Basis (%)	60.31	21.32	6.65	38.99	30.53	97.50
Yields On Dry Feed Basis (%)	57.71	16.16	7.09	41.55	32.54	97.33
Gas From GC	Yields on dry feed basis (%)					
Methane	0.39%					
Carbon Dioxide	33.08%					
Ethylene	0.10%					
Ethane	0.02%					
Hydrogen	0.04%					
Propylene	0.00%					
Carbon monoxide	6.44%					
Propane						
N-Butane						
Outlet oxygen in nitrogen	0.61%					
Viscosity	Fresh oil	Aged oil	AVI			
25 ^{0}C (mm^2/s)	23.39	56.57	1.42			
Water content	32.27%					
	47.53%					

Table 0-26. Mass balance of oxygenated pyrolysis of beech wood at airfactor 0.25

Summary						
Run title	PL110A475					
Feed stock	Beech Wood					
Feed moisture content (dry basis)		8.09				
Average temperature	476.2	°C				
Residence time	0.55	s				
Feed rate	125.16	g/h	(Wet feed/Time)			
Input O_2 by GC result	3.27%					
Airfactor	0.2452		(Reaction oxygen/Dry feed)			
Input (g)	Wet feed	Dry feed	Water	Oxygen		Total
	68.84	63.69	5.15	15.61		84.45
Output (g)	Oil	Water	Char	Organics	Gases	Total
	49.92	17.85	6.55	32.07	27.22	83.69
	Oil	Water	Char	Organics	Gases	Closure
Yields 0n Wet Feed Basis (%)	59.11	21.14	7.76	37.97	32.23	99.01
Yields 0n Dry Feed Basis (%)	56.45	16.01	8.26	40.44	34.33	99.04
Gas From GC	Yields on dry feed basis (%)					
Methane	0.43%					
Carbon Dioxide	35.35%					
Ethylene	0.11%					
Ethane	0.02%					
Hydrogen	0.05%					
Propylene	0.00%					
Carbon monoxide	6.79%					
Propane						
N-Butane						
Outlet oxygen in nitrogen	0.70%					
Viscosity	Fresh oil	Aged oil	AVI			
25 ^{0}C (mm^2/s)	16.77	56.57	2.37			
Water content	34.24%					
	47.08%					

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