DTU Library

Bio-oil from Flash Pyrolysis of Agricultural Residues

Ibrahim, Norazana

Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Ibrahim, N. (2012). *Bio-oil from Flash Pyrolysis of Agricultural Residues*. Kgs.Lyngby: DTU Chemical Engineering.

Bio-oil from Flash Pyrolysis of Agricultural Residues

Norazana binti Ibrahim
Ph.D. Thesis
August 2012
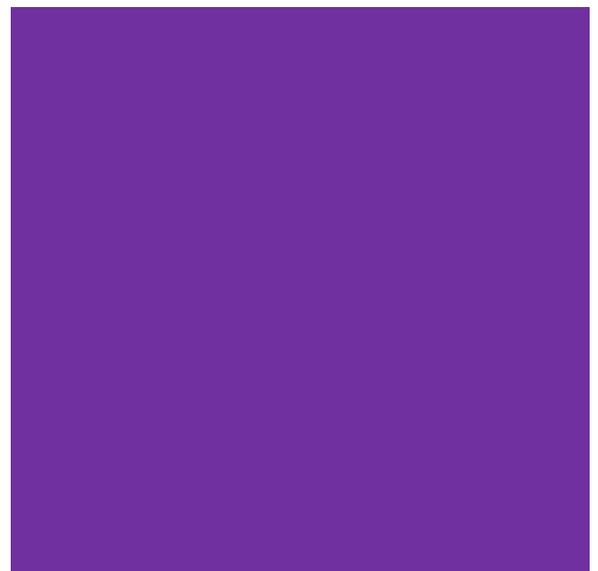
Bio-oil from Flash Pyrolysis of Agricultural Residues

Ph.D. Thesis
Norazana Binti Ibrahim

August 2012

Combustion and Harmful Emission Control Center
Department of Chemical and Biochemical Engineering
Technical University of Denmark

Preface

This dissertation was written as partial fulfillment of requirements for the degree of Doctor of Philosophy (*Ph.D.*) in Chemical Engineering at the Technical University of Denmark (*DTU*). The project has been carried out at the Combustion and Harmful Emission Control research centre (*CHEC*) at the Department of Chemical and Biochemical Engineering, from September 2007 until April 2011, under the supervision of Professor Kim Dam-Johansen and Associate Professor Peter Arendt Jensen.

This work has been financed by the Ministry of Higher Education (*MOHE*) of Malaysia and Universiti Teknologi Malaysia (*UTM*) and by the *DTU* funded Biochar Project.

My sincerest thanks to my supervisors Professor Kim Dam-Johansen and Associate Professor Peter Arendt Jensen who have provided all possible help and guidance when and where required. A special thanks to my main supervisor Professor Kim Dam-Johansen for his guidance, academic support and interest in my work. Also I am grateful to Associate Professor Peter Arendt Jensen for all the fruitful discussions besides the support provided during the development of this work.

I would also like to thank to the technical staff and other colleagues in the CHEC group for their support and contribution to a pleasant working environment.

Finally, I wish to thank to my family for their support and understanding during the writing of this thesis. I am grateful to my husband, Mohd. Kamaruddin Abd. Hamid and my lovely sons, Muhammad Afiq Zakwan and Muhammad Adam Zarif, for their unconditional support and love. Not forget to all my family members in Malaysia, thank you very much for the doa'.

NORAZANA BINTI IBRAHIM
August 2012

Abstract

This thesis describes the production of bio-oils from flash pyrolysis of agricultural residues, using a pyrolysis centrifugal reactor (PCR). By thermal degradation of agricultural residues in the PCR, a liquid oil, char and non-condensable gases are produced. The yield of each fraction is influenced by the reaction temperature and by feedstock ash composition.

It have been the objective of the present work to investigate the influence of changed operation conditions on the yield of bio-oil, char and gas; as well as to investigate the composition and storage properties of some of the produced bio-oils. Mainly the influence of feedstock type (wheat straw, rice husk and pine wood), feedstock water content and reactor temperature on the yield of char, bio-oil and gas were investigated. The storage stability of bio-oils with respect to changes in viscosity, water content and pH were investigated for straw and pine wood oil at different temperature and residence times.

Temperature plays a major role in the pyrolysis process and it determines to a high degree the fate of the final product yields and also product composition. Higher temperature favors the formation of pyrolysis gas while lower temperatures increase the yield of char. Liquid oil, however increases with temperature up to certain point and thereafter it decreases at still higher temperature due to secondary cracking of the primary products. The presence of moisture in the feed stock may also influences the pyrolysis process. The influence of reaction temperature and the moisture content on the flash pyrolysis product yield has been reported in Paper I (Chapter 2). It was observed that the presence of moisture in the wheat straw with different moisture levels of 1.5 wt. %, 6.2 wt. % and 15.0 wt. % have shown no significant effect on the pyrolysis product distribution. The fraction of bio-oil, char and gases produced from pyrolysis of straw were in the range of 40-60 wt. %, 18-50 wt. % and 5-22 wt. %, respectively, regardless of the straw moisture levels. The optimal reaction temperature for the production of bio-oil was around 525 °C to 550 °C for all straw moisture contents.

It was investigated how differences in biomass composition influence pyrolysis products yields and the composition of char and bio-oils. Details about this investigation are explained in Paper II (Chapter 3). The used pine wood had a low ash content (0.5 wt. %), the wheat straw an intermediate ash level (6.0 wt. %) and the rice husk a high ash level (13.6 wt. %). The highest alkali content, potassium (1.53 wt. %) are present in straw and the lowest potassium content level is observed in pine wood (0.04 wt. %). The feedstocks were pyrolyzed at reactor temperatures ranging from 475 to 575 $^{\circ}$C. It was observed that the formation of char and gas is affected by the biomass alkali content. Increasing biomass alkali content caused an increased feedstock conversion at low temperature, a lower maximum liquid organic yield temperature and a lower maximum liquid organics yield. In addition, the chemical

compositions of the bio-oils and the chars of the investigated feedstocks were also analyzed.

The utilization of the pyrolysis oil in static combustion equipments such as boilers and turbine have shown that the suitability of the pyrolysis oil to substitute fossil fuel. However, several limitations still arise due to the instability of the pyrolysis oil that may cause problems with transport and storage. Pyrolysis oil contains more than hundred of chemical compounds and has a wide range of volatility (different boiling points). The stability and aging of bio-oils generated by bench scale pyrolysis of wheat straw and pine wood are discussed in Paper III (Chapter 4). It was found that the bio-oil from wheat straw shows better stability compared to the bio-oil from pine wood. In addition, both bio-oils are fairly stable stored in a closed container at room temperature for up to 130 days, with no phase separation and only small changes in physical properties were observed.

The combustion behavior of pyrolysis oils derived from wheat straw and pine wood are investigated and discussed in Paper IV (Chapter 5). The investigation is done in two parts. In the first part, the technique of thermogravimetric analysis (TGA) was applied to study the thermal treatment of the pyrolysis oils under well controlled temperature in an oxidative (O_2) and non-oxidative (N_2) environment. It was found that the drying phase occurred below 200 °C, evaporation of light components and cracking of heavy fractions occurs at the temperature above 200 up to 500 °C, and finally the char combustion occurs at temperatures above 500 up to 700 °C. In the second part, the combustion of single droplets of pyrolysis oils were investigated and compared with the heavy fossil fuel oil by making experiments in a single droplet combustion chamber. The initial oil droplet diameters were in between 500 μm to 2500 μm. The experiments were performed at a temperature ranging between 1000 and 1400 °C with an initial gas velocity of 1.6 m/s and oxygen concentration of 3%. It was observed that the burning of bio-oil droplet experienced large swelling with swelling factors up to 4 times of the initial droplet diameter. However, the burning of heavy fossil fuel oil droplet showed neither swelling nor bubbling. In addition, the droplet burning lifetimes for bio-oils (droplet size of 1500 μm at a temperature of 1000 °C were found to be longer (13 s and 9 s for straw oil and wood oil, respectively) than the heavy oil (6 s) at the temperature of 1200 °C. It can be concluded that the combustion of bio-oils droplet are different from the combustion of heavy fossil fuel oil in terms of ignition, devolatilisation and char combustion. The bio-oil is difficult to ignite and has a shorter devolatilisation time and a longer char combustion time.

Resumé på Dansk

Denne PhD rapport beskriver produktionen af bio-olie via flash pyrolyse af biomasse udført på en Pyrolyse Centrifugal Reaktor (PCR). Via Pyrolysen på PCR enheden dannes bio-olie, koks og ikke kondenserbare gasser. Hovedformålet med projektet har været at undersøge indflydelsen af ændrede proces forhold på udbyttet af bio-olie, gas og koks; og at undersøge lagringsegenskaberne for producerede bio-olier. Indflydelsen af anvendt biomasse type (hvede halm, ris skaller og fyrretræ), biomasse vandindhold og pyrolyse reaktor temperatur på produkt sammensætningen er undersøgt. Lagringsstabiliteten af halm og fyrretræs bio-olie med hensyn til ændringer i viskositet, vandindhold og PH er undersøgt som funktion af tid og lagringstemperatur.

Denne PhD rapport indeholder kapitler der omhandler følgende emner: Litteratur studie om hurtig pyrolyse anvendt til produktion af pyrolyse olie (kapitel 1), Eksperimentel undersøgelse af indflydelsen af pyrolyse reaktor temperatur og biomasse vandindhold på de producerede produkter (kapitel 2), Karakterisering af flash pyrolyse produkter fra hvedehalm, risskaller og fyrretræ (kapitel 3), Undersøgelse af bio-oliers lagrings stabilitet (kapitel 4), Undersøgelse af bio-olie forbrænding (kapitel 5) samt konklusioner og anbefalinger til videre arbejde (kapitel 6).

Med anvendelse af hvedehalm udførtes en eksperimentel undersøgelse af indflydelsen af pyrolyse reaktor temperatur og biomasse vandindhold på de producerede produkter. For hvedehalm fandtes den optimale temperatur hvor der dannes mest bio-olie til 525 °C. Ved højere temperaturer forøges den dannede gas mængde og ved lavere temperaturer ses en højere mængde koks. Bio-olie vand indholdet stammer både fra vand dannet under pyrolysen samt fra biomassens fugtindhold. De udførte forsøg viste at ændret fugt indhold i den anvendte biomasse (vandindhold fra 1.5 til 15.0 wt%) ikke ændrede på udbyttet af bio-olie, koks og gas på tør basis.

Indflydelsen af biomasse type og aske indhold på pyrolyseprodukterne er undersøgt, ved at udføre PCR pyrolyseforsøg ved reaktor temperaturer på fra 475 til 575 °C med fyrretræ med lavt askeindhold (0,5 vægt%), hvedehalm med et askeindhold på 6,0 vægt% og risskaller med et højt askeindhold (13,6 vægt%). Hovedsagelig biomassernes alkali indhold påvirker pyrolyseprocessen. Den højeste alkaliindhold, kalium (1,53 vægt %) findes i hvedehalmen, og det laveste indhold af kalium niveau er observeret i fyrretræ (0,04 vægt%). Forøget biomasse alkaliindhold giver en øget omdannelse ved lav temperatur og et lavere maksimalt bio-olie udbytte.

Ved anvendelsen af bio-oli som brændsel i for eksempel dieselmotorer eller kedler, har det betydning om bio-olien ændre egenskaber ved længere tids oplagring. Pyrolyse olie indeholder et stort antal forskellige iltholdige kulbrinter som kan polymisere og give anledning til ændret viskositet, og i nogle tilfælde separation af

olien i flere faser. Stabiliteten af bio-olie fra halm og fyrretræ blev undersøgt ved lagring i lukkede beholdere op til 130 dage og ved temperature op til 80°C; og ved analyse af de lagrede oliers viskositet, vandindhold og PH. Bio-olien fra hvedehalm var mere stabil end olie fra fyrretræ. For bio-olie lagret ved 20°C i op til tre måneder observeredes kun små ændringer i olie egenskaberne.

Forbrændingen af pyrolyseolier fra hvede halm og fyrretræ er undersøgt og sammenlignet med forbrændingen af tung fyringsolie. Undersøgelsen er udført ved brug af termogravimetrisk analyse (TGA) og ved at udføre fyringsforsøg på en enkelt partikel reaktor, hvor forbrændingen kan følges via et video kamera. Ved TGA forsøgene kunne der observeres en tørrefasen under 200°C, afdampning af lette komponenter og krakning af tunge fraktioner forekommer ved temperaturer mellem 200 og 500°C, og der dannes en koks rest på cirka 25 vægt% af den våde bio-olie. Ved forbrænding af enkelte olie dråber sås en swelling på op til 4 gange den oprindelige dråbediameter. Desuden var omsætningstiden for brændende bio-olie længere (13s og 9s er for halm olie og træolie) end den tunge olie (6s) ved en temperatur på 1200 °C, en iltprocent på 3 vol% og en start dråbestørrelse på 1,5 mm.

Introduction to this Thesis

Biomass is a renewable resource with great potential as an alternative to fossil fuels for supplying energy (Garcia-bacaicoa *et al.*, 2008; Kumar *et al.*, 2009). The potential for biomass to supply much larger amounts of useful energy with reduced environmental impacts compared to fossil fuels has stimulated substantial research and development of systems for handling, processing, and converting biomass to heat, electricity, solid, liquid and gaseous fuels, and other chemicals and products. The use of biomass to substitute of fossil resources results in low sulphur dioxide emissions and almost no net atmospheric carbon emissions, and hence serves to mitigate greenhouse gas and global climate change impact (Kumar *et al.*, 2009). Besides, upgrading of biomass represents an attractive way of use of agricultural and forestry residues that could improve rural economies.

Pyrolysis and other thermochemical conversion processes offer an important opportunity for the utilization of the biomass from agricultural and forestry residues. However, the pyrolysis process is regarded as a promising process for the biomass utilization (Bridgwater and Peacocke, 2000). Pyrolysis of biomass can be described as the direct thermal decomposition of the material in the absence of oxygen to obtain an array of solid, liquid and gas products. Conventional pyrolysis consists of the slow, irreversible, thermal decomposition of the organic components in biomass. Slow pyrolysis has traditionally been used for the production of charcoal. Short residence time pyrolysis (fast, flash, rapid, ultrapyrolysis) of biomass at moderate temperatures, on the other hand, has generally been used to obtain high yield of liquid products (Yaman, 2004).

Flash pyrolysis is an irreversible thermo-chemical process in which a biomass is rapidly heated in the absence of oxygen, whereby the biomass decomposed and can be separated into distinct fractions of bio-oil, char and gas. Flash pyrolysis processes produce 40-75 wt. % of liquid bio-oil, 15-25 wt. % of solid char, and 10-20 wt. % of non-condensable gases, depending on the feedstock used. Many studies have been carried out to determine the operating parameters that influence the distribution of pyrolysis products as well its composition. Temperature, biomass initial moisture content, particle size, heating rate, and type of biomass are parameters that can affect the yield of the pyrolysis products. Therefore, it is important to study the effects of these parameters when it is wanted to optimize the pyrolysis products.

Pyrolysis of biomass is of particular interest because of the bio-oil utilized valuable product. For this reason, its storage and stability are important parameters. At present, the utilization of the pyrolysis oil especially for the power production is still under development and need further study for the standardization and the quality improvement. On the other hand, the pyrolysis oil can substitute fuel oil or diesel in many static applications including boilers, furnaces and turbines for the electricity generation. Many researchers performed combustion tests using different scale boilers, internal combustion engines and gas turbine injectors and systems (Solantausta *et al.*, 1995). They demonstrated that the pyrolysis oil could be burnt efficiently in standard or modified equipment. Nevertheless, several challenges still arise due to the unusual properties of pyrolysis oil and quality of the product.

The main objective of this work is to optimize the flash pyrolysis process in order to produce bio-oil from different agricultural residues by using a bench scale pyrolysis centrifuge reactor (PCR). The influences of pyrolysis operating conditions such as temperature, feedstock moisture content and type of biomass on the pyrolysis products yield are experimentally investigated. Detailed investigation of the bio-oils storage and stability are performed. Finally the bio-oils combustion characteristic is carried out.

This thesis is partly written as a collection of manuscripts submitted to scientific journals. An introduction to the field is given in Chapter 1. Chapter 2 presents studies on the influence of the reaction temperature and water content on wheat straw pyrolysis. Chapter 3 deals with the characterization of the flash pyrolysis products of wheat straw, rice husk and pine wood. Chapter 4 concerns about the stability and aging of the flash pyrolysis bio- oil, whereas Chapter 5 deals with the behaviour of bio-oil droplet combustion. It should be noted that each chapter can be read separately, but it is recommended to start with the Chapter 1 in order for the reader to acquire a general introduction of this field.

Chapter 1 is a literature review where the biomass constituent, biomass flash pyrolysis processes and pyrolysis products distributions, the stability of pyrolysis oils and the combustion of the pyrolysis oil are overviewed.

Chapter 2 presents the results obtained from the flash pyrolysis of wheat straw with different moisture content and the effect of reactor temperature on the pyrolysis product yield is also discussed.

Chapter 3 has been submitted to the *Journal of Biomass and Bioenergy*, and the effect of the different biomass type (wheat straw, rice husk and pine wood) on the pyrolysis products and product compositions is discussed. The discussion of the role of feedstock ash content to the pyrolysis behaviour and the composition of pyrolysis oils and biochar are also included.

Chapter 4 has also been submitted to the *Journal of Renewable Energy*. In this chapter, the storage and the stability of the pyrolysis oils are presented. The physical changes of the wood and the straw oil at elevated temperatures and time are reported based on the storing conditions. The results are compared with literature data.

Chapter 5 discusses the combustion properties of the pyrolysis oils (wood and straw oil) and for comparison, heavy fossil fuel oil is also tested. The results obtained from both thermogravimetric analysis (TGA) and the bio-oil droplet combustion reactor are reported.

Chapter 6 presents conclusions and directions for future work.

References

Bridgwater, A. V., Peacocke, G. V. C. (2000). Fast pyrolysis processes for biomass. *Renew Sustain Energy Rev*. 4:1-73.

Garcia-Bacaicoa, P., Mastral, J. F., Ceamanos, J., Berrueco, C., Serrano, S. (2008). Gasification of biomass/high density polyethylene mixtures in a downdraft gasifier. *Bioresourse Technology*. 5485-5491.

Kumar Sadhukan, A., Gupta, P., Kumar Saha, R. (2009). Modelling of pyrolysis of large wood particles. *Bioresource Technology*. 100, 3134-3139.

Solantausta, Y., Bridgwater, A. V., Beckman, D. (1995). Feasibility of power production with pyrolysis and gasification systems. *Biomass and Bioenergy*. 9, 257-269.

Yaman, S. (2004). Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Convers. Management*. 45, 65-75.

Table of Contents

CHAPTER 1

Literature Review

1.1 Introduction

Biomass is a renewable resource with great potential as an alternative to fossil fuels for supplying energy (Garcia-bacaicoa *et al*., 2008; Kumar *et al*., 2009). To convert biomass into a convenient and effective fuel, various conversion technologies (e.g., pyrolysis, gasification, torrefaction, etc.) have been used. However, the pyrolysis process is regarded as a promising process for biomass utilization (Bridgwater, 2000). The nature of the biomass can influence the quantities and composition of pyrolysis products. Biomass is made up of several different constituents (cellulose, hemicellulose and lignin), which have different thermal behaviours. More details of the biomass constituents are presented in section 1.2. In section 1.3, the pyrolysis of biomass to produce bio-oil, gas, and char are discussed. Different types of reactors used for the pyrolysis process are presented in section 1.3.1. In section 1.3.2, the pyrolysis of cellulose, hemicellulose and lignin are discussed in details.

Flash pyrolysis is an irreversible thermo-chemical process in which a biomass is rapidly heated in the absence of oxygen, whereby the biomass decomposed and can be separated into distinct fractions of bio-oil, char and gas. Flash pyrolysis processes produce 40-75 wt. % of liquid bio-oil, 15-25 wt. % of solid char, and 10-20 wt. % of non-condensable gases, depending on the feedstock used. Details of the flash pyrolysis process are presented in section 1.4. Many studies have been carried out to determine the operating parameters that influence the distribution of pyrolysis products as well its composition. Temperature, biomass initial moisture content, particle size, heating rate, and type of biomass are parameters that can affect the yield of the pyrolysis products. In section 1.4.1, effects of these parameters are discussed in details. Several works have been done in order to predict the pyrolysis reaction mechanism, which are presented in section 1.4.2. In section 1.4.3, the details of the flash pyrolysis products are presented.

Pyrolysis of biomass is of particular interest because of the bio-oil utilized valuable product. For that reason, its storage and stability have been studied by several researchers, which are presented in section 1.5. The combustibility of the pyrolysis oil in diesel engines, turbines, and furnace/boiler for electricity generation are presented in section 1.6. Besides that, the pyrolysis oil can be upgraded and used as a transport fuels, and can be processed further to produce chemicals. Details are presented in section 1.7. Finally, the chapter ends with a set of concluding remarks (section 1.8).

1.2   Biomass Constituents

Biomass is defined as an organic matter derived directly from living organisms, available on a renewable and sustainable basis, which mainly consists of carbon, hydrogen, oxygen, nitrogen and an insignificant amount of sulfur. Biomass resources can be divided into several categories such as forest products, energy crops, agricultural waste and their waste by-products, residues from various industrial activities, such as pulp and paper mills, sawmills and the organic fraction of industrial and municipal waste.

Biomass primarily consists of cellulose, hemicellulose, lignin and other compounds such as lipids, proteins, simple sugar, starches, water, hydrocarbons and ash. Cellulose is the main cell wall component in plant biomass, which forms the framework of biomass cell walls (40-50 %) composed of the cohesive, interlaced cellulosic micro-fibrils matrix which is deposited by hemicellulose and lignin (Mc Kendry, 2002). Hemicellulose constitutes 20-40 % of the woody biomass and is the least stable species among wood components, which is composed primarily of xylan and mannan. Meanwhile, lignin is the third major wall component in the cell wall serving as a cement between wood/biomass fibers, as a stiffening agent within the fibers, and as a barrier to the degradation of the cell wall. The concentration of each component in plant matter greatly depends on the type of plant tissue, stage of growth, and growing conditions. All biomass is highly oxygenated, compared to fossil fuels as coals, due to the carbon hydrate structure and the presence of large amount of oxygen. Table 1.1 shows the fraction of cellulose, hemicelluloses and lignin in softwood, hardwood and wheat straw (Mc Kendry, 2002). Hardwood contains high fraction of cellulose ranging from 45 wt. % to 50 wt. %, whereas softwood has a high amount of lignin (27-30 wt. %) and hemicellulose (25-30 wt. %). However, the fractions of those three components in the wheat straw are in between of hardwood and softwood.

Table 1.1
Fraction of cellulose, hemicelluloses and lignin (wt. % on dry basis) in softwood, hardwood and wheat straw (Mc Kendry, 2002).

Biomass	Cellulose (wt. %)	Hemicellulose (wt. %)	Lignin (wt. %)
Softwood	35-50	25-30	27-30
Hardwood	45-50	20-25	20-25
Wheat straw	33-40	20-25	15-20

1.2.1   Cellulose

Cellulose is a complex carbohydrate which is consists of unbranched chains of linked glucose units (Mc Kendry, 2002). Cellulose is found to be a major component of the plant cell walls. It is a glucose-based polysaccharide and the repeating unit of the cellulose polymer consists of two glucose anhydride units, called as cellobiose unit as seen in Figure 1.1. Cellulose has the general formula $(C_6H_{10}O_5)_n$ and there are covalent bond, hydrogen bond and Van Der Waals forces within the polymer.

Besides, cellulose is a strong substance because the straight-chain molecule hydrogen bonds, forming a pseudocrystalline structure which gives rigidity to the structure. Cellulose is odourless, insoluble in water and most organic solvents. It can be broken down chemically into its cellubiose units by treating it with concentrated acids at high temperature.

Cellulose forms long chains that are bonded to each other by a long network of hydrogen bonds. Groups of cellulose chains twist in space to make up ribbon-like micro-fibril sheets, which are the basic construction units for a variety of complex fibers. These micro-fibrils form composite tubular structures that run along a longitudinal tree axis. The crystalline cellulose structure resists thermal decomposition better than hemicelluloses (Mohan *et al*., 2006).
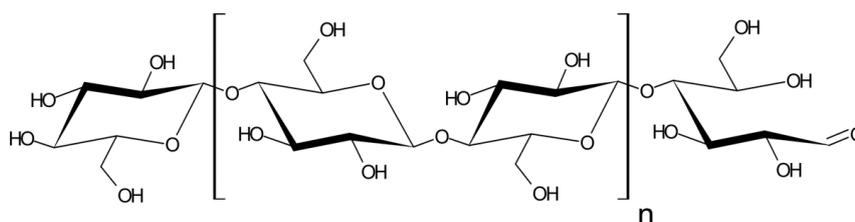
Figure 1.1 Chemical structure of cellulose (Mohan *et al*., 2006).

1.2.2   Hemicellulose

Hemicelluloses are a heterogeneous class of polymers representing, in general, 15-40 % of plant biomass and which may contain d-xylose, d-mannose, d-glucose, d-galactose, l-arabinose, d-glucuronic acid, 4-Omethyl-d-glucuronic acid (MeGlcA), d-galacturonic acid, and to a lesser extent, l-rhamnose, l-fucose, and various *O*-methylated sugars (Mohan *et al*., 2006). The chemical structures of the main components of hemicelluloses are shown in Figure 1.2. Their molecular weights are usually lower than that of cellulose and they have a weak undifferentiated structure compared to crystalline cellulose. The most abundant hemicelluloses are xylans and glucomannans. Xylans are the main hemicellulose components of secondary cell walls constituting about 20-30 % of the biomass of hardwoods and herbaceous plants. Xylans are usually available in huge amounts as by-products from forest, agriculture, agro-industries, wood and pulp and paper industries. Mannan-type hemicelluloses like glucomannans and galactoglucomannans are the major hemicellulosic components of the secondary wall of softwoods whereas in hardwoods they occur in minor amounts.
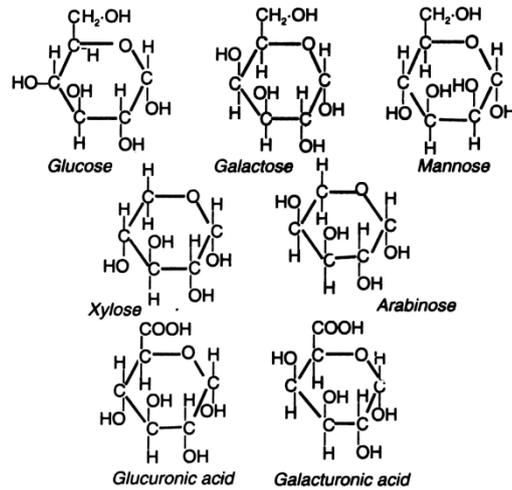
Figure 1.2 Chemical structures of the main components of hemicellulose (Mohan *et al*., 2006).

1.2.3 Lignin

As a major cell wall component, lignin provides rigidity, internal transport of water and nutrients and protection against attack by microorganisms (Mohan *et al*., 2006). Lignin is an amorphous polymer consisting of phenylpropane units, and their precurcors are three aromatic alcohols (monolignols) namely p-coumaryl, coniferyl and sinapyl alcohols. The respective aromatic constituents of these alcohols in the polymer are called p-hydroxyphenyl, guaiacyl and syringyl moieties. Wood lignins mainly contain guaiacyl and syringyl units, whereas the lignins of herbaceous plants contain all three units in significant amounts with different ratios. An example of the chemical structure of lignin is shown in Figure 1.3.
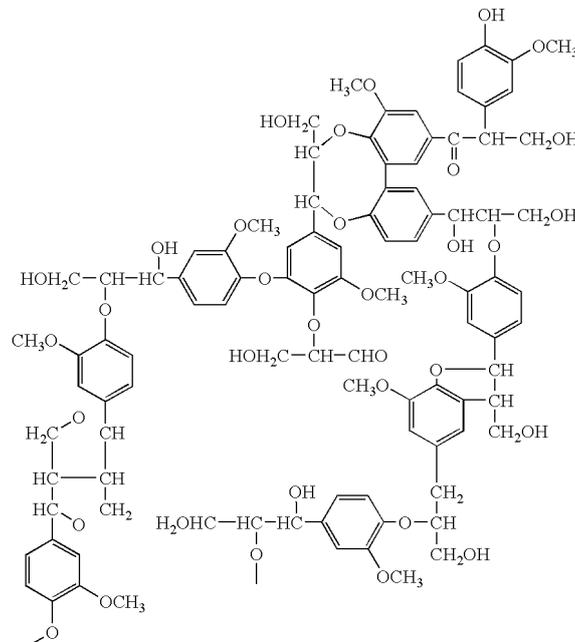
Figure 1.3 Chemical structure of lignin (Mohan *et al*., 2006).

Lignin does not exist in plant as an independent polymer but it is bonded with the other polymers, cellulose and hemicellulose forming complexes with them. Lignin is always associated with carbohydrates (in particular with hemicellulose) via covalent bonds, and this association is called lignin-carbohydrate complexes (LCC). In herbaceous plants, hydroxycynnamic acids (p-coumaric and ferulic acids) are attached to lignin and hemicelluloses via ester and ether bonds as bridges between them forming lignin/phenolics-carbohydrate complexes. Lignin and carbohydrates in wood, on the other hand, are attached to each other via benzyl ether, benzyl ester, glycosidic and acetal type bonds (Mohan *et al*., 2006).

1.2.4   Ashes

The ash composition and content varies for different biomasses and woody materials. The ash concentration in wood is often low (< 1 %) compared to the herbaceous biomass and agricultural residues which can be up to 15 % (Yaman, 2004). All the ashes contain inorganic species/alkali elements such as calcium, silica, magnesium, aluminum, iron, potassium, chlorine, phosphorus, sulfur, and titanium. The level of potassium, phosphorus and chlorine contents in agricultural residues and herbaceous biomass are higher than those of wood (Tsai, 2006). The time of harvest also may influence the concentration of ash components. For example, rainfall during harvest may decrease the chlorine and potassium content (Lede *et al*., 2007). The typical ash and some element contents in several biomasses are shown in Tables 1.2 and 1.3.

1.3   Pyrolysis of Biomass

The term 'pyrolysis', is defined as the thermal treatment of biomass, in the absence of oxygen, operating at medium temperature range usually from 400-650 °C, which results in the production of a solid (charcoal), a liquid (tar and an aqueous solution of organics) and gaseous products (Yaman, 2004). The process can be adjusted to favour the formation of charcoal, pyrolysis oil or gas. The pyrolysis method has been used for commercial production of a wide range of fuels, solvents, chemicals and other products from biomass feedstocks. Converting the solid biomass into liquid fuels, solid chars and non-condensable gases via pyrolysis have been experiencing rapid developments during the last decades (Acikgoz and Kockar, 2007; Bridgwater, 2003). Depending on the operating conditions, the pyrolysis process can be optimized based on the product demanding as summarized in Table 1.4.

Table 1.2
Ash and mineral contents in biomass (Wilen *et al*., 1996).

Types of biomass	Ash (% wt db)	Trace Components (dry basis, g/kg)		
		Na	K	Cl
Agricultural biomasses				
Wheat straw (Danish)	4.71	0.14	5.48	1.71
Barley straw (Finnish)	5.88	0.33	12.19	2.74
Rapeseed	2.86	0.17	5.77	0.97
Reed canary grass	8.85	0.15	3.48	0.64
Northern woody biomasses				
Wood chips	0.60	0.04	0.98	0.04
Forest residue chips (Finnish)	1.33	0.08	1.38	0.07
Forest residue chips (Swedish)	4.05	0.64	2.60	<0.05
Saw dust (pine)	0.08	0.02	0.48	<0.05
Spruce bark	2.34	0.09	3.00	0.28
Pine bark	1.72	0.03	2.13	0.09
European biomasses				
Sweet *Sorghum* (Italy)	4.74	0.68	4.61	3.00
Kenaf (Italy)	3.63	0.52	7.25	1.75
Mischantus (Italy)	3.31	0.26	9.70	3.27
Cane (Italy)	3.70	0.18	9.71	2.92

Table 1.3
Mineral contents in biomass (Wilen *et al*., 1996).

Types of biomass	Ash forming elements (dry basis, g/kg)							
	Ca	Si	Mg	Al	Fe	Ti	P	S
Agricultural biomasses								
Wheat straw (Danish)	52	280	11	4.3	3.8	0.25	9.9	4.4
Barley straw (Finnish)	32	290	13	<1	1.2	<0.1	11	5.7
Rapeseed	210	15	3.3	2.5	6.6	0.40	39	43
Reed canary grass	25	420	8.9	7.5	7.9	0.32	18	4.5
Northern woody biomasses								
Wood chips	240	110	31	27	15	0.34	21	6.5
Forest residue chips (Finnish)	110	180	24	25	26	3.0	14	6.5
Forest residue chips (Swedish)	85	130	11	30	14	2.1	7.7	5.4
Saw dust (pine)	299	39	71.2	10.6	12.9	0.7	22.9	7.8
Spruce bark	280	7	31	5.7	1.0	0.21	18	3.9
Pine bark	290	6	27	28	2.1	0.46	21	8.2
European biomasses								
Sweet *Sorghum* (Italy)	64	270	16	3.5	3.7	0.32	13	12
Kenaf (Italy)	220	31	36	9.4	8.5	0.49	12	23
Mischantus (Italy)	54	200	29	2.7	2.8	0.20	23	8.4
Cane (Italy)	35	230	21	5.2	3.0	0.42	26	33

Table 1.4
Pyrolysis mode and typical pyrolysis product distributions of wood pyrolysis (wt. %) (Bridgwater, 1991; 1994; 1996).

Pyrolysis Mode	Conditions	Liquid	Solid	Gases
Flash pyrolysis	Moderate temperature, short residence time particularly vapour < 1 s	75	12	13
Slow pyrolysis	Low temperature, very long residence time	30	35	35

As can be seen in Table 1.4, there are two types of pyrolysis modes: flash pyrolysis and slow pyrolysis (carbonization), which can be differentiated by the used operating temperature and vapour residence time. Flash pyrolysis of biomass is a promising route with regard to the production of solid, liquid (bio-oil or bio-crude-oil) and gaseous products to be used as possible alternative energy sources. Flash pyrolysis is used to maximize the liquid product yield using a high heating rate, a short residence time, a moderate temperatures and rapid quenching of the liquid products to terminate the secondary conversion of the products (Acikgoz and Kockar, 2007). Slow pyrolysis, on the other hand, has traditionally been used to enhance the charcoal production by using low temperature and low heating rate.

1.3.1   Type of Reactor for the Pyrolysis Process

The comparison of pyrolysis process technologies are presented in Table 1.5. Many types of reactors have been used for the pyrolysis process (Bridgewater *et al*., 1999). The most popular and widely applied is fluidized-bed reactors as it can maximize the bio-oil production easily (Bridgwater *et al*., 1999). Other reactors such as ablative reactors (vortex and rotating blade) (Diebold *et al*., 1988; 1997), rotating cone reactors and vacuum reactors, have also received much attention. Bridgwater and co-workers (Bridgwater *et al*., 1999) described the various reactors used for the flash pyrolysis process, as well as the heat transfer, advantages and disadvantages.

Fluidized bed reactor

Fluidized bed reactors are the most popular configurations for flash pyrolysis process. This is because it has the advantages of a well-understood technology that is simple in construction and operation, good temperature control and very efficient heat transfer from a heat source to the biomass particles by a mixture of convection and conduction (Bridgwater *et al*, 1999). The schematic diagram for a fluidized bed reactor is shown in Figure 1.4.

Table 1.5
The comparison of pyrolysis process technologies (Bridgwater *et al.*, 1999).

| Reactor Type	Mode of Heat Transfer	Features	Temp (°C)
Fluidized bed	90% Conduction 9% Convection 1% Radiation	• High heat transfer rates • Heat supply to fluidizing gas or to bed directly • Limited char abrasion • Very good solid mixing • Particle size limit < 2 mm in smallest dimension • Simple reactor configuration	500-800
Circulating fluid bed	80% Conduction 19% Convection 1% Radiation	• High heat transfer rates • High char abrasion from biomass and char erosion leading to high char in product • Char/solid heat carrier separation required • Solid recycle required; increased complexity of system • Maximum particle sizes up to 6 mm • Possible liquids cracking by hot solids • Possible catalytic activity from hot char • Greater reactor wear possible	450-800
Ablative	95% Conduction 4% Convection 1% Radiation	• Accepts large size feedstocks • Very high mechanical char abrasion from biomass • Compact design • Heat supply problematical • Heat transfer gas not required • Particulate transport gas not always required	500-700
Entrained flow	4% Conduction 95% Convection 1% Radiation	• Low heat transfer rates • Particle size limit < 2 mm • Limited gas/solid mixing	400-550
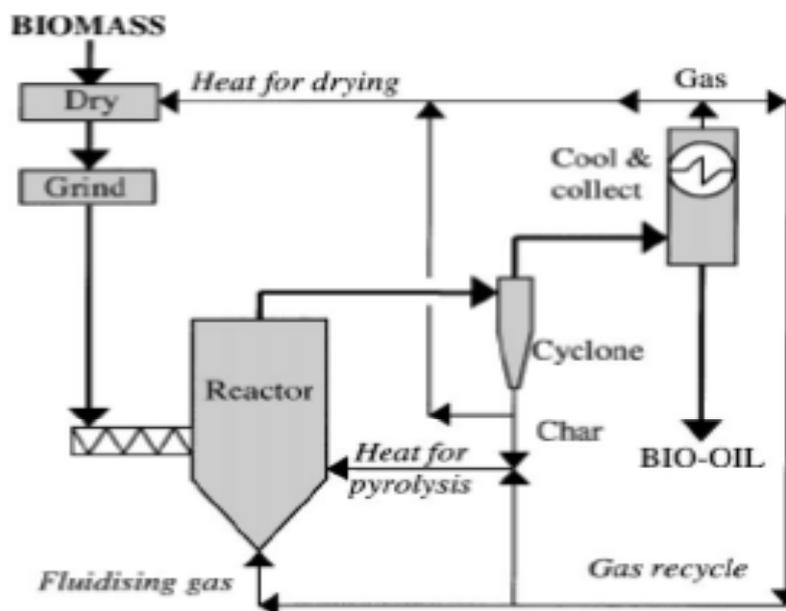
Figure 1.4 Conceptual of Fluid bed Flash pyrolysis process (Bridgwater *et al.*, 1999).

A Fluidized bed of sand arises by blowing gas through nozzles at the bottom of the reactor. The required gas flow depend on the size and mass of the fluidizing material, which is 1-2 m/s for bubbling fluidized bed and three to four times higher for circulated fluidized bed. Additionally, a minimum size above the fluidized bed which is called freeboard is required to prevent blowing out the whirl material from the reactor.

Fluidized bed pyrolysers give good and consistent performance with high liquid yields of typically 70-75 wt. % from wood on a dry-feed basis. Since the heat transfer limitation is within the particles, thus, small biomass particles size of less than 2 mm are needed to obtain good quality yields. Substantial carrier gas is needed for fluidization or transport purposes.

Ablative pyrolysis

Ablative pyrolysis is considerably different in concept from other methods of fast pyrolysis. In all the other methods, the rate of reaction is limited by the rate of heat transfer through the biomass particles, which is why small particles are required. The term 'ablation' is referred to the phenomena occurring when a solid submitted to a high external heat flux density, gives rise to solid, liquids or gases that can be rapidly and continuously eliminated (Lede, 2003). In ablative pyrolysis, heat is transferred from a hot reactor wall to 'melt' wood/biomass that is in contact with it under pressure. The pyrolysis front thus moves unidirectionally through the biomass particle. As the wood/biomass is mechanically moved away, the residual oil film both provides lubrication for successive biomass particles and also rapidly evaporates to give pyrolysis vapours for collection in the same way as other processes. The rate of

reaction is strongly influenced by pressure, the relative velocity of the wood/biomass and the heat exchange surface and the reactor surface temperature. Followings are the key features of ablative pyrolysis:

- High pressure of particle on hot reactor wall, achieved due to mechanical force or centrifugal force.
- High relative velocity between particle and reactor wall.
- Reactor wall temperature less than 600°C.

In this type of reactor, a large particle can be used as reaction rates are not limited by heat transfer through the biomass particles. This is because there is no upper limit to the size that can be processed. The process in fact is limited by the rate of heat supply to the reactor rather than the rate of heat absorption by the pyrolysing biomass, as in other reactors. Furthermore, there is no requirement for inert gas, so the processing equipment is smaller and of potentially lower cost. However, the process is surface-area-controlled so scaling is a linear function of the heat transfer area and thus does not benefit from the economies of scale of other systems such as fluid beds. In addition, the reactor is mechanically driven and is thus more complex.

An example of an ablative pyrolysis reactor is the vortex reactor which was presented by Diebold and Power (1998). The National Renewable Energy Laboratory (NREL) has developed the flash pyrolysis process using a vortex ablative pyrolyzer as shown in Figure 1.5. In this process stream, recycled gas and feed, enters the vortex reactor tangentially so that the particles are forced to the wall by large centrifugal forces. The particles slide and tumble on the reactor wall as they take a helical path through the reactor (Diebold and Power, 1988; Diebold *et al.*, 1997).
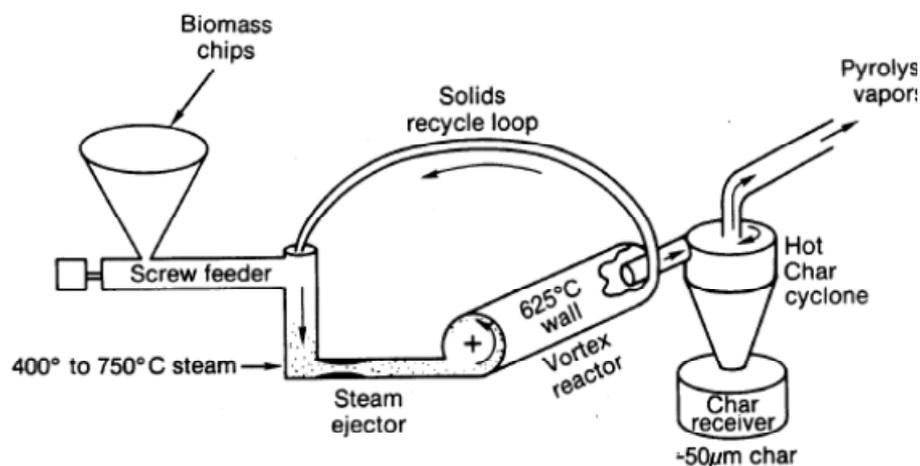

Figure 1.5 Schematic representation of the vortex reactor as presented by Diebold and Power (1988).

Shown in Figure 1.6 is another example of ablative reactor, called as pyrolysis centrifuge reactor (PCR) developed by Bech *et al.*, (2009) at CHEC (Technical

University of Denmark). In this set-up, the applied pressure of biomass on a hot wall is achieved by centrifugal forces.
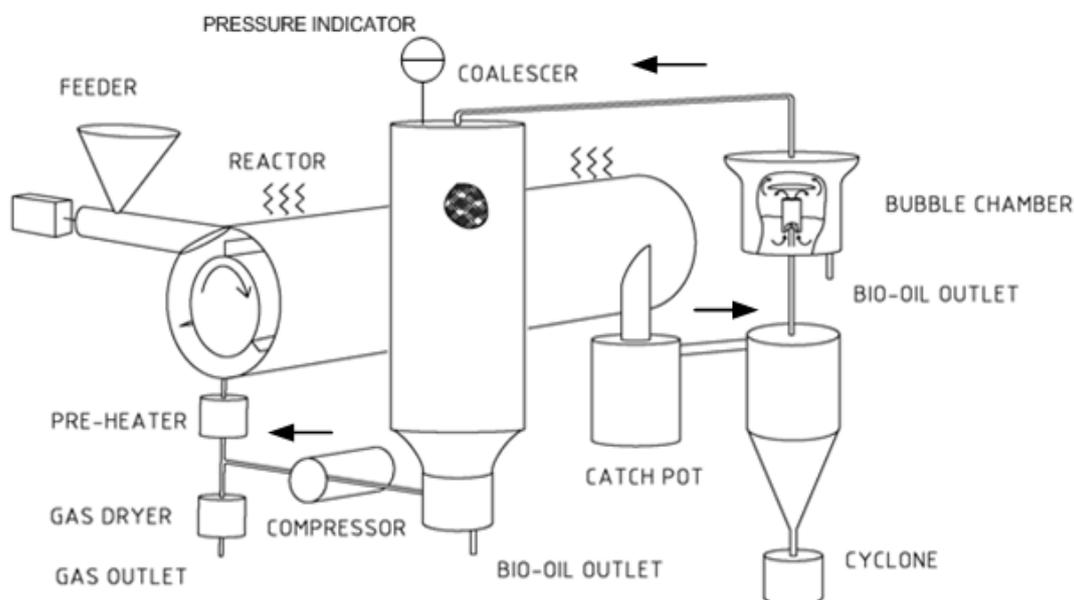

Figure 1.6 Schematic diagram of the ablative pyrolysis bench reactor system (PCR) (Bech *et al.*, 2009).

Entrained flow

Entrained flow fast pyrolysis is in principle a simple technology, but most developments have not been as successful as had been hoped, mostly because of the poor heat transfer between a hot gas and a solid particle (IEA, 2006). High relative gas velocities and high turbulence are required to obtain sufficient heat transfer. This requires large plant sizes and high gas flow rates, which results in more difficult liquid collection from the low vapour partial pressure. Liquid yields have usually been lower than bubbling fluid bed and circulating fluid bed systems.

1.3.2   Pyrolysis of Cellulose, Hemicellusose and Lignin

The mechanism of the pyrolysis involves a very complex process as it undergoes a series of reactions and it is influenced by many factors (Bridgwater *et al.*, 1999). Therefore the fundamentals studies of individual components (cellulolose, hemicellulose and lignin) that present in the biomass are crucial. The thermal degradation of each component occurs at different temperature by different pathways (Demirbas, 2001a; 2001b; Demirbas and Arin, 2002).

The basic knowledge of the role and behavior of the three principal components of biomass (cellulose, hemicelluloses and lignin) during pyrolysis is important for understanding and controlling this process. Several thermal analysis techniques have been used to obtain the experimental data. Thermogravimetric analysis (TGA) is the most common and widely used fundamental method to reveal

the pyrolysis behaviour and kinetic although it has several limitations such as low heating rate (less than 100 °C/s) and it is only applicable for small biomass samples (Yang *et al*., 2007). These conditions are insufficient to elucidate the full scale of the flash pyrolysis process but it is a simple method to investigate pyrolysis characteristic under controlled conditions. Figure 1.7 shows the TGA weight loss signal (in wt. %) and the signal derivative thermogravimetric (DTG) (in wt. %/°C) curves of the three components pyrolysis at a heating rate of 10 °C /min (Yang et al., 2007). The differential scanning calorimetry (DSC) curves for the analysis of the enthalpy of the three components pyrolysis at a heating rate of 10 °C /min (Yang *et al*., 2007) is shown in Figure 1.8.

1.3.2.1 Pyrolysis of Cellulose

Pyrolysis of cellulose produces numerous volatile products and carbonaceous residues. The decomposition of cellulose begins at temperature below 300 °C, normally at 280 up to 380 °C (Jensen *et al*., 1998; Yang *et al*., 2007; Shen *et al*., 2010). Degradation occurs through dehydration, hydrolysis, oxidation and transglycosylation. At higher temperature (300-500 °C), polymerization reaction takes place and activates the cleavage of the glycosidic linkage to produce glucose, which then dehydrated to levoglucosan (1, 6-anhydro-ß-D-glucopyranose) and oligosaccharides. At still higher temperatures, the anhydrosugar compounds undergo fission, dehydration, disproportionation and decarboxylation reactions to provide a mixture of low molecular weight gaseous and volatile products (Shafizadeh, 1982).

Cellulose from different biomass decomposes at different rates and different yield of final products. Figure 1.7 shows that the cellulose decomposes in a single well-defined narrow peak, as has been reported by (Yang *et al*., 2007). It can be seen from Figure 1.7 that the maximum weight loss rate of 2.8 wt. %/°C occurred at the temperature of 355 °C and above 400 °C, almost all the cellulose was completely pyrolyzed with a minimal amount of solid char residue left (about 6.5 wt. %). Almost the same results were also obtained by Jensen *et al*., (1998). They found that the pyrolysis of micro crystalline cellulose at a heating rate of 10 °C/min showed a maximum weight loss rate at 377 °C and it was completely pyrolyzed at 410 °C with a remaining of 4 wt. % of solid char. The peak position and width of the weight loss curve depend on the cellulose type and the conditions of the pyrolysis, especially the heating rate. Shen *et al*., (2010) observed that the peak temperature of the cellulose decomposition increased about 50 °C when the heating rate was increased from 5 to 60 °C/min.

The presence of inorganic species in the cellulose material alters the rate of decomposition and its final products. The char yield from pure cellulose is low, about 4 wt. % as reported by Jensen *et al*., (1998). When KCl was added to cellulose, a reduction of 50 °C was observed in the decomposition temperature and an increment of 4.0 to 17.5 wt. % was also observed in the char yield (Jensen *et al*., 1998).
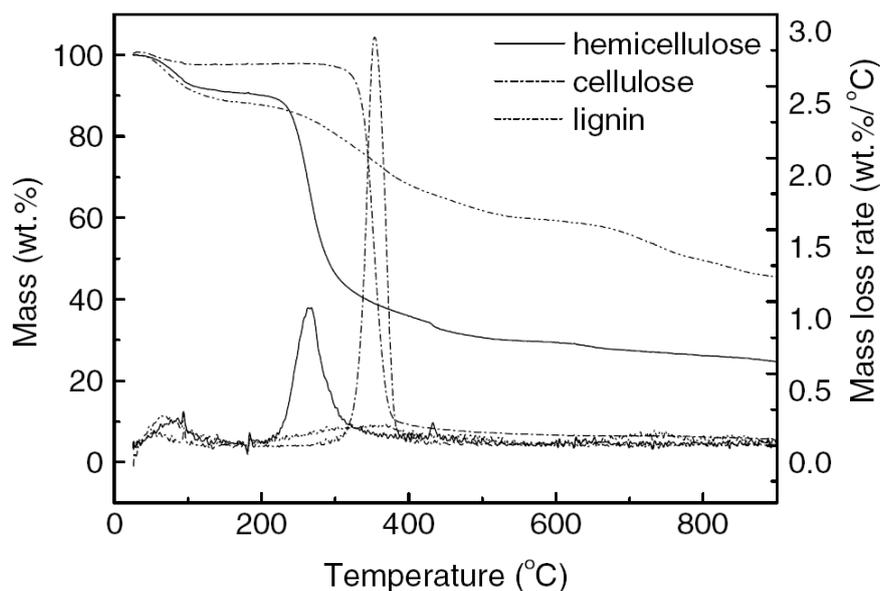
Figure 1.7 Pyrolysis of cellulose, hemicellulose and lignin in TGA at a heating rate of 10 °C/min (Yang *et al*., 2007).
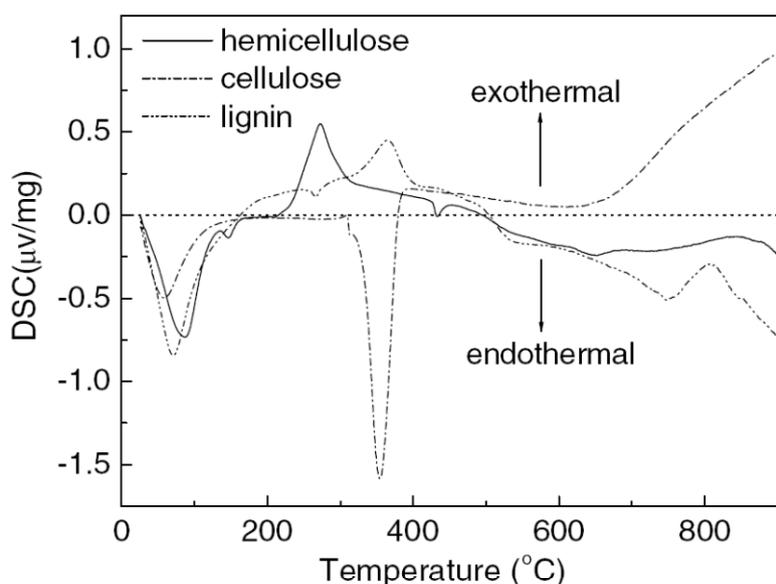
Figure 1.8 DSC curves of pyrolysis of cellulose, hemicelluloses and lignin (Yang *et al*., 2007).

As seen in Figure 1.8, when the temperature increasing to more than 200 $^{\circ}$C, the DSC profile of cellulose showed an obvious and big endothermic peak at a temperature of 355 °C, showing that the volatilization process was dominating. However, at high temperature (> 400 $^{\circ}$C) the DSC curve of cellulose showed positive values, indicating the pyrolysis reaction is exothermic. From 500 to 700 $^{\circ}$C, the DSC curve was approximately constant but beyond that it increased greatly as temperature increased further, indicating the cracking of some functional groups in the cellulose residue.

1.3.2.2 Pyrolysis of Hemicellulose

Hemicellulose, on the other hand, starts to degrade at 200 °C, which is lower than cellulose. This is because hemicellulose consists of various saccharides (xylan, mannose, glucose, galactose, etc.), which appear as a randomly, amorphous structure, rich of branches. Thus, these saccharides are very easy to remove from the main stem and degrade to volatiles at low temperatures. Besides that, hemicelluloses are thermally less stable than cellulose and evolve to more noncombustible gases and less tar. It should be noted that most of the hemicellulose do not yield significant amounts of levoglucosan.

The chemistry of the pyrolysis of hemicellulose is not very well known, but some of the overall reactions in the pyrolysis have been identified. A thermal cleavage of glycosidic groups results in glycosyl groups which partly form random condensation products and partly degrade to a variety of volatile products and char (Shafizadeh *et al.*, 1972). In many cases, xylan is used to represent a typical hemicellulose component. Compared to cellulose, the char yield from xylan is rather higher, normally in the range of 20-30 wt. % (Raveendran *et al.*, 1996). The relatively high char yield may partly be due to salts and minerals in the hemicellulose. During the extraction of xylan from biomass, the xylan may be slightly changed and some impurities may be included.

Major products from xylan decomposition are reported by Radlein *et al.*, (1991) to be 2-furaldehyde and 3-hydroxy-2-penteno-1,5-lactone. The latter is favoured over 2-furaldehyde with increasing pyrolysis temperature above 400 °C. Yang *et al.*, (2007) found that xylan started its decomposition easily with the weight loss mainly happened at 220-315 °C and the maximum mass loss rate (0.95 wt. %/°C) at 268 °C. However there is still 20 % solid residue left at 900 °C.

The DSC curve in Figure 1.8 shows that the pyrolysis of hemicellulose is an exothermic reaction from 150-500 °C with a peak found at 275 °C, showing that the charring process occurred within this temperature ranges. It can be seen that, no obvious change was observed in the DSC values at the temperature higher than 500 °C, which is consistent to its DTG curves (see Figure 1.7) where no obvious reaction (pyrolysis) happened.

1.3.2.3 Pyrolysis of Lignin

Lignin is full of aromatic rings with various branches, the activity of the chemical bonds in lignin cover an extremely wide range, which lead to the degradation of lignin occurring in a wide range of temperature and with a lower decomposition rate than cellulose and hemicellulose as shown in Figure 1.7. Pyrolysis of lignin yields phenols from cleavage of ether and carbon-carbon linkages and produces more residual char than that of cellulose and hemicellulose, typically up to 35-50 wt. % (Jensen *et al.*, 1998). The structure of lignin has been investigated using mass spectrometry to determine various lignin pyrolysis products. Dehydration reactions around 200 °C are primarily responsible for the thermal degradation of lignin (Adjaye and Bakhshi, 1995). The cleavage of a- and ß– aryl-alkyl-ether linkages occurs between 150 °C and 300 °C. Meanwhile, aliphatic side chains start splitting off from the aromatic ring at 300 °C. The degradation of lignin initially breaks relatively weak aliphatic bonds

releasing large fragments of tar. Some of these fragments are relatively reactive free radicals which can undergo a variety of secondary reactions such as cracking and repolymerization. Simultaneously, the various functional groups are decomposed to form low-molecular-weight gaseous species such as CO_2 from carboxyl, H_2O from hydroxyl, CO from carbonyl, methanol from methoxy and light hydrocarbons from aliphatics. At higher temperature (> 500 ^{o}C) the aromatic rings are rearranged and condensed, releasing hydrogen and CO in the process (Jensen *et al*., 1998).

The degradation reaction of lignin is an exothermic reaction between 150 and 500 ^{o}C, with a peak occurring at the temperature of 365 °C (see Figure 1.8). When the temperature was higher than 500 ^{o}C, the DSC values of lignin decreased to be negative. The DSC curve of lignin pyrolysis varied a lot as the temperature increases with a small endothermic peak observed near 750 ^{o}C.

1.4   Flash Pyrolysis of Biomass

Generally, flash pyrolysis is used to maximize high-grade bio-oil production from biomass. The flash pyrolysis process has been the subject of intense research since many years ago. The process is still under development and from the commercialization process point of view, the first step of the development of the flash pyrolysis process is to provide a liquid fuel that can replace fossil fuel oil in any static heating/combustion or electricity generation application such as boilers and turbines (Bridgwater, 2000). The flash pyrolysis is an irreversible thermo-chemical process in which organic material is rapidly heated in the absence of oxygen, whereby the material is decomposed and can be separated into distinct fractions of liquid, char and gas. Ash is largely retained in the char, whereas the liquid fraction is a homogeneous mixture of organics and water commonly referred as bio-oil. The flash pyrolysis process typically applies operation conditions at a high heating rate (> 200 K/s up to 10^4 K/s), moderate temperatures (400-600 °C), and a short gas residence time (< 1 s) which allow the process to produce about 50-75 wt. % of liquid bio-oil, 15-25 wt. % of solid char and 10-20 wt. % of non-condensable gases from a wood feedstock (Bridgwater, 1996). The water content of the bio-oil is usually limited to about 15-35 wt. % (Bridgwater, 1996). Besides, a small particle size of the applied biomass and an efficient char removal before rapid condensation of the vapours (bio-oil) are required in order to maximize bio-oil production and reduce cracking.

Various flash pyrolysis processes have been developed to maximize the formation of liquid oils for use as fuels or chemical feedstocks. For example, the Waterloo flash pyrolysis process has been designed by Scott and Piskorz (1982) where particle sizes of less than 1 mm as feedstock and a high heat transfer with a hot fluidized bed of sand are the main features. A vortex reactor process by using an ablative technique has been developed by (Diebold and Power, 1988). Vacuum pyrolysis also has been used as a flash pyrolysis technique by Roy et al. (1990). Bech et al. (2009) designed a centrifuge pyrolysis reactor.

Many kinds of biomass such as wheat straw (Bech *et al*., 2009; Shuangning *et al*., 2005; Zanzi *et al*., 2009), rice husk (Ji-lu, 2007; Tsai *et al*., 2007), sugarcane bagasse and rice straw (Tsai, 2006), olive waste (Zanzi *et al*., 2009), forestry wastes (Lede *et al*., 2007), animal wastes (Shinogi and Karni, 2003), municipal solid wastes

(Belidan, 2007) and woody materials (Azar *et al.* 1997; Di Blasi *et al.*, 2009; Luo *et al.*, 2004; Antal and Varhegyi, 1995), Shafizadeh, 1982; Thurner and Mann, 1981; Bilbao *et al.*, 1993; Di Blasi, 1993 have been subjected to the flash pyrolysis process.

1.4.1 Factors Influencing Biomass Pyrolysis Products

Many studies have been carried out to determine the operating parameters that influence the distribution of pyrolysis products as well its composition. Temperature, biomass initial moisture content, ash content, particle size, heating rate, and type of biomass are variables that can affect the yield of the products.

1.4.1.1 Pyrolysis Temperature

Numerous studies have investigated the effect of temperature on the final pyrolysis product yields (Smets *et al.*, 2011; Sun *et al.*, 2010; Mullen *et al.*, 2010; Sensoz and Angin, 2008; Lee *et al.*, 2005; Tsai *et al.*, 2006; Horne and Williams, 1996). Temperature is the most influential process variable because it determines the final yield of the pyrolysis products. An increase in pyrolysis temperature increases the yield of gaseous and decreases char production. The maximum yield of liquid oil is usually achieved at a temperature in the range of 450 to 600°C (Acikgoz and Kockar, 2007) and then drops with further increases in temperature. More hydrocarbons and olefins are produced in the gas at relatively high temperatures (> 650°C) (Nunn *et al.*, 1985), suggesting that thermal cracking of higher hydrocarbons takes place at high temperature. Char yields decreases gradually with temperature to an almost constant value above 650 °C when the devolatilization is almost completed.

Smets *et al.*, (2011) investigated the influence of temperature on the yield and the characteristics of the pyrolysis liquid of rapeseed cake using a semi-continuous lab-scale reactor. The flash pyrolysis were performed at four temperatures (350, 400, 450 and 550 ^{o}C) and it was observed that higher temperature results in a higher yield of pyrolysis liquid, while the yield of char deceases. This is because more components of the rapeseed cake (especially the triglycerides) are decomposed and/or volatized at higher temperature. At 550 ^{o}C, the oil fraction reaches a maximum yield of 42.1 wt. %, contains only 6.7 wt. % water and has a high calorific value of 32.8 MJ/kg, making it suitable as a biofuel candidate.

Antony Raja *et al.*, (2010) performed flash pyrolysis experiments using a fluidized bed reactor. A jatropha oil cake was pyrolysed at different pyrolysis temperatures for particles of 0.71 mm size under a fixed sweep gas velocity of 1.75 m^3/h. It was observed that the yield of pyrolysis oil increased from 42.2 % to 64.3 % when the pyrolysis temperature was increased from 350 to 500 ^{o}C. At a higher pyrolysis temperature of 550 ^{o}C, the oil yield decreased to 57.7 %. The maximum oil yield of 64.3 % was obtained at a pyrolysis temperature of 500 ^{o}C with the calorific value of 19.66 MJ/kg. The obtained oil can be used as a source of low-grade fuel directly or it can be upgraded to higher quality liquid fuel by thermo catalytic cracking or transesterification processes.

Yorgun *et al.*, (2001) conducted flash pyrolysis experiments of sunflower press oil cake in a tubular transport reactor under nitrogen atmosphere at different pyrolysis temperatures and particle size. It was found out that the yields of product

were affected significantly by the pyrolysis temperature. Generally, the yields increased to an optimum value with higher temperature and then decreased. At the lowest pyrolysis temperature (around 450 ^{o}C), decomposition was relatively slow and gas and char were the major products. As the temperature increased from 450 to 550 ^{o}C, the amount of condensable liquid product increased. The highest pyrolysis liquid yield of ca. 45 % was obtained at a final pyrolysis temperature of 550 ^{o}C with a particle size of 0.425-0.850 mm, and nitrogen flow rate of 300 cm^3 min^{-1}. At a higher pyrolysis temperature, 700 ^{o}C, the oil yield decreased to ca. 30 %. Yorgun *et al.*, (2001) concluded that secondary reactions of the liquid fraction of the volatiles and further decomposition of the char particles proceeded in the reactor with increasing pyrolysis temperature.

Tsai *et al.*, (2006) investigated the effect of the pyrolysis temperature, heating rates and holding time on the pyrolysis products by pyrolyzing rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. The maximum liquid oil yield for all investigated feed stocks was obtained at the temperature of 500 °C, with a heating rate of 200 °C/min, particle size of < 0.5 mm and holding time of 2 minutes. Acikgoz and Kockar (2007) conducted a flash pyrolysis of linseed in a tubular transport reactor with a N$_2$ flowrate of 100 cm^3 min^{-1} at atmospheric pressure. Effects of the pyrolysis temperature and particle size were studied. The optimal liquid oil yield of 68.8 wt. % was achieved at the temperature of 550 °C and a particle size of Dp > 1.8 mm.

The effect of reaction temperature on the bio-oil production was conducted by pyrolyzing of rice husk using a fluidized bed at a feed rate of 1 kg/hr (Lee *et al.*, 2005). The optimum reaction temperature range for the production of bio-oil occurred at the range of 410-510 °C. A rapid pyrolysis of agricultural residues (olive waste and wheat straw) and wood (birch) in a free-fall reactor was studied by Zanzi *et al.*, (2008), in an attempt to determine the effects of pyrolysis temperature, heating rate, and particle size on the product distribution, gas composition and char reactivity.

On the other hand, corn cobs and corn stover fast pyrolysis experiments in a bubbling fluidized bed of quartz sand at a temperature of 500 °C were performed by Mullen *et al.*, (2010) in an attempt to determine the composition of bio-oil and biochar. Approximately of 60 wt. % of bio-oil and 17-19 wt. % of biochar yields were obtained from these two corn crops.

Flash pyrolysis of waste wood in fluidized bed reactor at temperature between 400 °C to 550 °C produced a liquid oil yield of 65-68 wt. %, 16-24 wt. % of char yield and 10-15 wt. % gas yield (Horne and William, 1996). The optimum liquid oil temperature was found at 550 °C with a liquid oil yield of 68 wt. %.

In summary, higher liquid product yields and lower char yields were obtained from pyrolysis of wood as compared to the agricultural residues or herbaceous. Shown in Table 1.6 is an example of flash pyrolysis of several biomasses and their products yields, expressed in dry-ash free basis. A higher liquid and a lower char yield obtained from wood is due to its lower ash content. Additionally, the hollocelluloses (cellulose and hemicellulose) content in wood is higher and thus produces more formation of liquid oil during pyrolysis (see Table 1.1).

Table 1.6
Flash pyrolysis of several biomasses and their products yields, expressed in dry-ash free basis.

Biomass	Ash (% db)	Moisture (wt.%)	Reactor	Temperature	Liq.Organics	Char	Gas	Reaction water	References
Pine wood	0.5	7.1	Centrifuge reactor	475 – 575	21- 58	25 - 67	11 - 26*	n.a	Bech et al., 2009
Wheat straw	6.0	6.2	Centrifuge reactor	475 – 575	37 - 50	19 - 48	5 - 18	7-12	Ibrahim et al., 2010
Rice husk	13.6	11.7	Centrifuge reactor	475 – 575	25 - 52	22 - 61	6 - 13	3-10	Ibrahim et al., 2010
Pine bark	1.3	n.a	Fluidized bed reactor	400 – 800	25 - 55	18 - 34	14 - 49	n.a	Arpiainen and Lappi, 1989
Wheat straw	4.6	1.3	Fluidized bed reactor	550	48	25	18	8	Scott et al., 1999
Poplar sawdust	0.5	4.6	Fluidized bed reactor	504	66	12	11	11	Scott et al., 1999
Spruce sawdust	0.5	7.0	Fluidized bed reactor	500	67	12	8	12	Scott et al., 1999
Sunflower hulls	4.0	11.1	Fluidized bed reactor	500	46	23	20	10	Scott et al., 1999

* gas+reaction water
 n.a= not available

1.4.1.2 Feedstock Initial Moisture Content

The influence of feedstock initial moisture content was also studied by (Demirbas, 2004; Gray *et al*., 1985). Demirbas (2004) investigated the effects of initial moisture contents on the yields of oily products from slow pyrolysis of spruce wood, hazelnut shell and wheat straw. It was found that, in general, the yields of oily products (wt. %, dry feed basis) increase with increasing pyrolysis temperature from 575 to 700 °C then it decreases with increasing temperature. The yield of total oil also increases with increasing the initial moisture content of the sample. The yields of total oily products of spruce wood (moisture content: 6.5 %), hazelnut shell (moisture content: 6.0 %) and wheat straw (moisture content: 7.0 %) increase from 8.4, 6.7 and 6.2 % to 33.7, 30.8 and 27.4 %, respectively, by increasing the pyrolysis temperature from 575 to 700 °C. The moisture contents of the biomasses were varied from 41 to 70 % and it was found that the presence of water in wood influences its behaviour during pyrolysis and affects the physical properties and quality of the pyrolysis liquid.

In another study (Gray *et a*l., 1995), the presence of moisture in wood waste (Woodex) material increased the char yield by as much as 5 wt. % within the temperature range of 390 - 460 ºC. The moisture also decreased the tar yield from ash-free Woodex by as much as 10 wt. %. They proposed that the decrease in the tar yield and the increase in the char yield are probably due to the free-radical reactions between tar and moisture such as depolymerization and trapping. The formation of gases, however, was not affected by the presence of moisture.

1.4.1.3 Particle Size

The influences of biomass particle size on the pyrolysis products yields have been studied. Shen *et al*., (2009) investigated the effects of biomass particle size from 0.18 to 5.6 mm on the yield and composition of bio-oil from the pyrolysis of mallee woody biomass in a fluidized-bed reactor at 500 ºC. It was observed that the yield of bio-oil decreases as the average biomass particle size was increases from 0.3 to about 1.5 mm. Further increases in biomass particle size did not result in any further decreases in the bio-oil yield. Shen *et al*., (2009) also observed that the actual heating rates experienced by biomass, which decrease with increasing particle size, were the major factor contributing to the decreases in the yield of lignin-derived oligomers. Thus, reduces the yield of bio-oil since most of the reduction in the yield of bio-oil can be explained by the reduction in the yield of lignin-derived oligomers. On the other hand, the partial destruction of biomass cellular structure during the preparation of small biomass particles may also be responsible for the high bio-oil yield from the small biomass particles.

Şensöz *et al*., (2000) performed a pyrolysis of rapeseed in a fixed-bed reactor under static atmosphere at a final pyrolysis temperature of 500 ºC with a heating rate of 40 ºC/min. The effects of particle size on the yields of the pyrolysis products were analyzed. The particle size of rapeseed was varied in the range of 0.224 to 1.8 mm. It was observed that pyrolysis oil and char yields from rapeseed were affected by the particle size. The maximum yield of pyrolysis oil of 46 wt. % was obtained with a particle size range of 0.85 to 1.8 mm with a char yield of 20.4 wt. %. The smallest (0.224 mm) particle size produced an oil yield of 42.9 wt. % with a char yield of 22.8

wt. %. On the other hand, larger (> 1.8 mm) particle sizes produced percentage mass of oil and char products of 44.6 and 21.7 wt. %, respectively. In their study, they found that the gas yield was between 18 to19 wt. % for all the particle sizes.

As a conclusion, feed particle size is significantly affects the balance between liquid oil and char yields. Larger particle sizes tend to give more char and hence lower yield of the liquid oil is obtained (Haykiri-Acma, 2006). If liquid oil is a targeting product, then smaller biomass particle sizes are required and if char is aiming of, then larger particles are beneficial.

1.4.1.4 Heating Rate

The effects of heating rate on the pyrolysis yields have been studied. Haykiri-Acma *et al*. (2006) investigated the pyrolysis yields of rapeseed by applying TGA technique. The pyrolysis experiments were performed up to 1273 K at heating rates of 5, 10, 20, 30, 40 and 50 K/min in a nitrogen flow of 40 cc/min. Effects of heating rate on the mass losses from the rapeseed were examined using the derivative thermogravimetric analysis (DTG) profiles. It was found out that important differences on the pyrolytic behaviour of rapeseed are observed when heating rate is changed. At the lower heating rates, the maximum rates of mass losses were relatively low. When the heating rate was increased, maximum rates of mass losses also increases. These variations were interpreted by the heterogeneous structure of biomass. It was observed that heating rates affect the shape of the peaks. Increase in the heating rate shifted the main peak on the DTG profile to the lower temperatures as shown in Figure 1.9. At low heating rates, resistance to mass or heat transfer inside the biomass particles occurs, which results in a low total mass loss values and thus lower conversion of biomass to liquid or gaseous products.

Onay and Kockar (2003) conducted a slow and fast pyrolysis of rapeseed wth a particle size of 0425-0.85 mm. Slow pyrolysis was conducted using the Heinze reactor at a heating rate of 30 °C/min, whereas fast pyrolysis were performed in a well-swept fixed bed tubular reactor at a heating rate of 300 °C/min. The optimum liquid yield temperature was similar for both conditions, that occurred at 550 °C but the yields were different. At the optimum temperature, a liquid oil yield of 46.7 wt. % was obtained for slow pyrolysis, whereas 63 wt. % was achieved for fast pyrolysis.
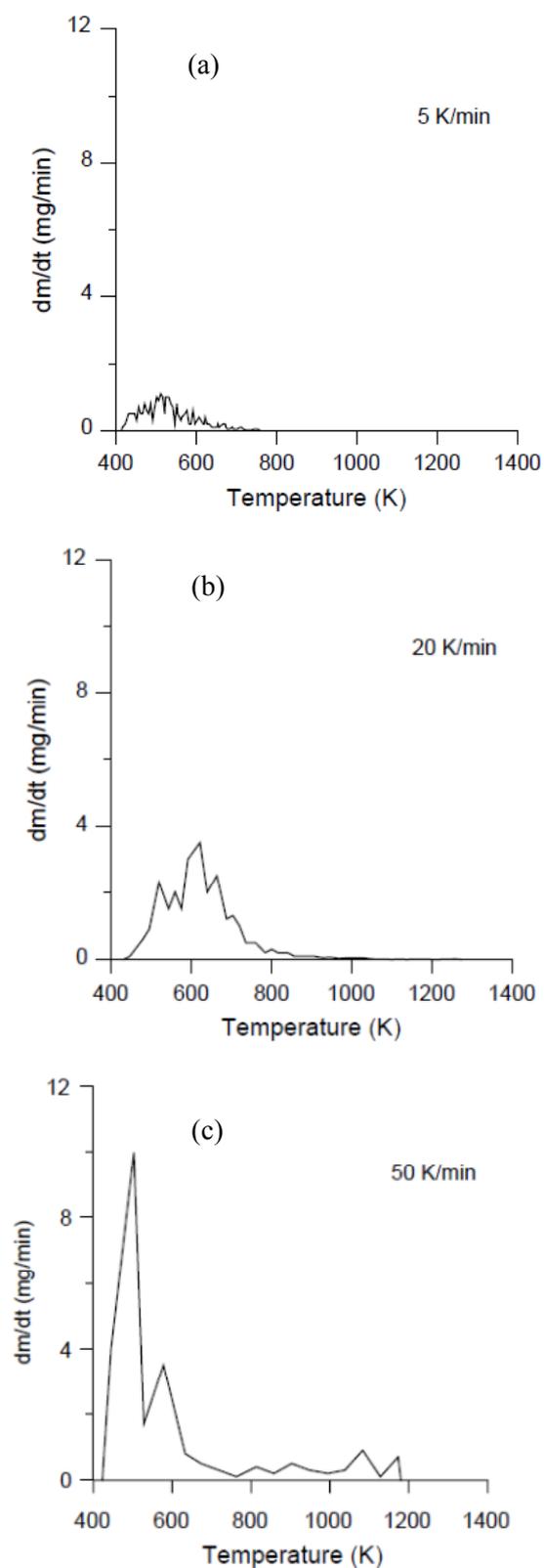
Figure 1.9 DTG curves of pyrolysis of rapeseed at different heating rates (a) at 5 K/min (b) at 20 K/min and (c) at 50 K/min (Haykiri-Acma *et al*. 2006)

1.4.1.5 Type of Biomass and Feedstock Ash content

The effects of different type of biomass on the pyrolysis products have been studied. Biomass is in general considered more reactive than coal upon pyrolysis. The wide variability of chemical and physical properties among different types of biomass, however, reflects in different reactivity. Fagbemi *et al*., (2001) evaluated the amounts of various pyrolysis products (gas, tar and charcoal) from three biomasses (wood, coconut shell and straw). A quartz tube rector was used and the temperature was varied between 400 to 900 °C. It was observed that straw appears to yield more gas that the other tested biomasses (wood and coconut shell). The low thickness of the wall of the straw wisp, compared wit the others biomasses, results in a higher heat-transfer, and hence a higher rate of pyrolysis, which is favourable to gas and tar production. The same results were also obtained for the char production. Fagbemi *et al*., (2001) also found out that at a given temperature of pyrolysis, the yield of residual solid from straw appears to be more that the other tested biomasses. The relatively high yield of char production for straw can be explained by the high ash content of this material.

Senneca (2007) analyzed the effects of different type of biomass such as pine seed shells, olive husk and wood chips on the pyrolysis products. Experiments of pyrolysis of such biomasses were conducted under inert conditions at different heating rates. It was observed that pyrolysis under inert conditions occurs in a single stage for all biomasses. DTG curves obtained from experiments of pyrolysis of wood chips showed that the DTG peak temperature increases with the heating rate from 367 ^{o}C at 5 ^{o}C/min to 460 ^{o}C at 100 ^{o}C/min. The char residue decreases with heating rate from 24 % at 5 ^{o}C/min to 14 % at 100 ^{o}C/min. For a pyrolysis of olive husk, the peak temperature increases with the heating rate from 291 ^{o}C at 5 ^{o}C/min to 346 ^{o}C at 100 ^{o}C/min. Senneca (2007) found that the char residue for a pyrolysis of olive husk is around 35 % at all heating rates. For a pyrolysis of pine seed shells, the peak temperature also increases with the heating rate from 359 ^{o}C at 5 ^{o}C/min to 432 ^{o}C at 100 ^{o}C/min. The char residue is found to be around 25 % at all heating rates. For pyrolysis of the three biomasses, Senneca (2007) also observed that pyrolysis occurs at lowest temperature in the case of olive husk (291 ^{o}C), followed by pine seed shells (359 ^{o}C) and wood chips (367 ^{o}C). The char residue is observed higher for olive husk (around 35 %), followed by pine seed shells (around 25 %) and wood chips (around 24 %). A key to the high reactivity of olive husk is that olive husk has the highest ash content of the three biomasses and in particular the highest amount of catalytically active minerals such as potassium.

In addition to the biomass principal components, i.e., cellulose, hemecellulose and lignin, minor component such as ash also plays an important role in the pyrolysis process. The presence of mineral matters either as additives or natural ash content strongly affects the pyrolysis of biomass. The influences of biomass ash content on the pyrolyis behavior and final product yield have been studied (Di Blasi *et al*., 2009; Nowakowski and Jones, 2008; Keown *et al*., 2008; Fahmi *et al*., 2007; Yang *et al*., 2006; Jensen *et al*., 1998; Azar *et al*., 1997; Pan *et al*., 1989, Stenseng, 2001). Ash in biomass consists typically of K, Na, Mg, Ca, Si and minor amount of P, S, Fe, Al and Mn. Of all the metals present in biomass, potassium has a pronounced catalytic effect on the pyrolysis reactions promoting the char and gas formation at the expense of the

tar yield with an enhancement in the activity of dehydration, demethoxylation, decarboxylation and charring reactions. The catalytical effects of mineral matters on pyrolysis behaviour and product distributions also have been investigated.

The presence of catalysts has been reported to have a significant influence on the biomass pyrolysis process by modifying the thermal behaviour. In Figure 1.10 is shown the TGA and DTG curves for the pyrolysis of wheat straw, washed wheat straw and washed wheat straw with 2 wt. % KCl added, at a heating rate of 10 K/s (Jensen *et al.*, 1998). The present of potassium lowers the biomass degradation maximum temperature and similar trend were observed by many authors (Nowakowski *et al.*, 2008; Varhegyi *et al.*, (2004), Yang *et al.*, (2006), Di Blasi *et al.*, (2009). In addition the present of mineral matters or catalysts reduces activation energy during pyrolysis of biomass. The effect of various mineral matters on the final char yields from pyrolysis of cellulose, hemicellulose and lignin in a TGA with a heating rate of 10 ^{o}C/min, was reported by Yang *et a*l., (2006) and shown in Figure 1.11.
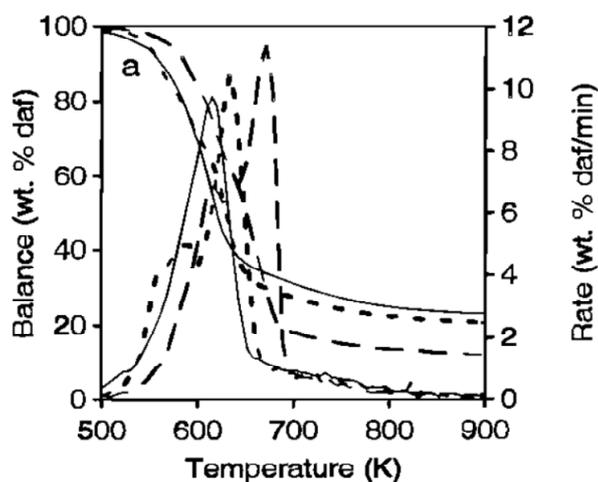

Figure 1.10 Pyrolysis of Danish wheat straw. Solid line: raw straw. Dashed line: washed straw. Dotted line: washed straw with 2 wt. % KCl added (Jensen *et al.*, 1998).
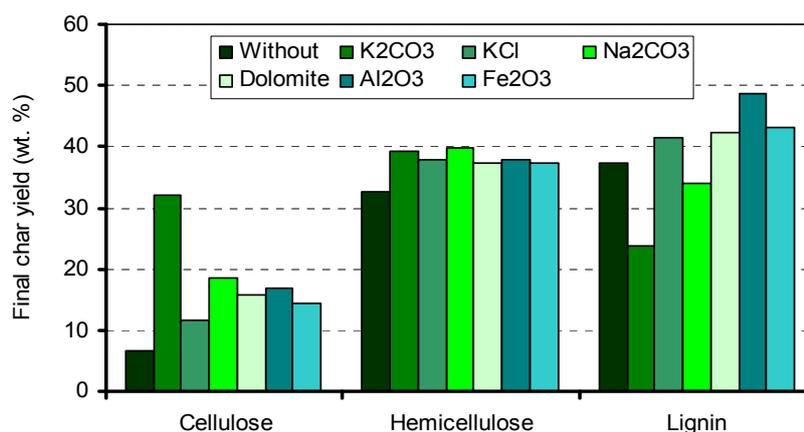

Figure 1.11 Final char yields of biomass with and without additives (Yang *et al.*, 2006).

1.4.2 Mechanism of Flash Pyrolysis Reaction

During biomass pyrolysis, several physical and chemical processes take place including biomass heating up, moisture evaporation and transportation, kinetic involving the decomposition of biomass to tar, char and light gases, heat and mass transfer, pressure build-up within the porous medium of the solid, convective and diffusive gas phase flow, variation of thermo-physical properties with temperature and composition, and change in particle size. Studies focused on the kinetics of flash pyrolysis for biomass conversion into bio-fuel are crucial for understanding both the mechanism and kinetics parameters. There have been various studies reported on the mechanism and kinetics models (Bech *et al.*, 2009; Di Blasi, 2008; Dupont *et al.*, 2009; Haseli *et al.*, 2011; Park *et al.*, 2009; Kaushal and Abedi, 2010; Radmanesh *et al.*, 2006; Ranzi *et al.*, 2008).

Detailed models available in the literature for biomass flash pyrolysis are based on coupled time-dependent conservation equations including kinetics of the biomass decomposition. A one-step global model, as the simplest model, considers decomposition of biomass into char and volatiles has been proposed, which is the most frequently applied model (Galgano and Di Blasi, 2003). Another decomposition scheme is the well-known Broido-Shafizadeh model (Shafizadeh, 1982), which assumes that the formation of an intermediate liquid compound (ILC) phase that is followed by two competing reactions; in one reaction tar is produced, and in the other one char and light gases are formed, as shown in Figure 1.12. The proposed mechanism has been used by Bech *et al.*, (2009) to model the pyrolysis process in the Pyrolysis Contrifuge Reactor (PCR). Bech *et al.*, (2009) predicted the product distribution by pyrolysis of wood and used modified parameters for straw, in order to include the catalytic effect of the ash content. The developed model describes the yields from flash pyrolysis of wood and straw in the PCR satisfactorily.
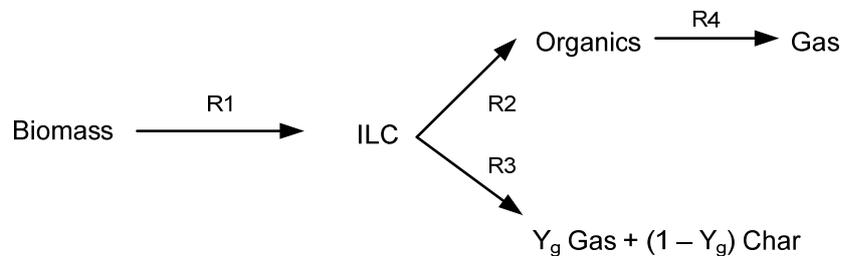

Figure 1.12 The Broido-Shafizadeh model for biomass pyrolysis (Shafizadeh, 1982).

Chan *et al.*, (1985) used a pyrolysis model of three primary reactions and one secondary reaction, the products of the secondary tar reaction are divided into light gases (carbon monoxide, ethane, ethylene) and aromatic tars. Weighting between both product groups depends on the boundary conditions. The kinetic data are determined from experiments with pine wood. Koufopanos *et al.*, (1991) took into account the nature of secondary reactions from a different viewpoint. In their model, biomass undergoes primary reactions to decompose into volatile and gases (reaction 1) and char (reaction 2). The primary pyrolysis products participate in secondary reactions to produce also volatile, gases and char of different compositions (reaction 3). This kinetic mechanism has been applied to model pyrolysis of biomass particles (Babu

and Chaurasia, 2004; Sadhukhan *et al*., 2009). In a recent comprehensive review study by Di Blasi (2008), the chemical kinetics of wood and biomass pyrolysis is critically discussed.

Dupont *et al*., (2009) performed biomass pyrolysis at high temperatures (1073 to 1273 K) and high heat fluxes (10-100 kW/m^2). The experiment results were compared to predictions of the kinetic mechanism of Ranzi *et al*., (2008) and encouraged results were obtained.

Park *et al*., (2010) studied thermal decomposition of 25.4 mm diameter dry wood spheres both experimentally and theoretically. Wood spheres were pyrolyzed in a vertical tube furnace at temperatures ranging from 683 to 879 K. Mass loss and temperatures of the sample were measured during pyrolysis. Peak temperature shows two distinct thermal events consisting of sequential endothermic and exothermic reactions. Numerical investigations of these endo/exothermic reactions using various pyrolysis kinetics models were conducted to determine the pyrolysis mechanism and the heats of the pyrolysis reactions. Based on the experimental and numerical results, a new wood pyrolysis model is proposed. The model consists of three endothermic parallel reactions producing tar, char and an intermediate solid and a subsequent exothermic decomposition of the intermediate solid to char and an exothermic decomposition of tar to char and gas. The proposed pyrolysis model shows good agreement with the experiments.

Kaushal and Abedi (2010) have developed a simple one-dimensional model to describe particle pyrolysis under continuous operation in a bubbling fluidized bed. The model is made up of number of sub-models that includes reaction kinetics, bed hydrodynamics, interphase mass transfer and mass and energy balance. The effects of operating parameters on biomass pyrolysis product yield were simulated. Results show that reaction temperature plays an important role in the yield of bio-oil. The model is robust and has a good agreement between predicted and published measuring results.

1.4.3   Flash Pyrolysis Products

Pyrolysis oil, solid char and non-condensable gases are the primary products of biomass pyrolysis. In practice, the fast pyrolysis of wood produces 50-75 wt. % of liquid oil, 15-25 wt. % of char and 10-20 wt. % of gases (Mohan et al., 2006), and the water content in bio-oil is usually in the range of 15 to 35 wt. %. However, the fraction of each product can vary, depending on the operating conditions and types of biomass used (Mohan *et al*., 2006).

1.4.3.1 Pyrolysis oil

The pyrolysis oil is a mixture of organic compounds and water. The pyrolysis oil has a dark brown to reddish colour and is a free-flowing organic liquid. It is also referred to as bio-oil, pyrolysis liquids, bio-crude oil or tar, which is composed of a very complex mixture of oxygenated hydrocarbons and consists of more than 180 compounds and they are often grouped as acids, alcohols, ketones, aldehydes, phenols, alkenes, furans, guaiacols, oxygenates and sugars (Marsman *et al*., 2007; Diebold, 2000; Diebold and Power, 1988). Therefore it greatly differs from the widely

used petroleum-based fuel oil as seen in Table 1.7, and it is less stable due to a high amount of reactive oxygen-containing compounds and low-boiling volatiles. The molecular weight of pyrolysis oil varies in the range of 100-1200 g/mol (Czernick *et al*., 1994).

The pyrolysis oil has a distinctive odor, an unpleasant smell due to the presence of low molecular weight compounds such as aldehydes and acids. Pyrolysis oils are characterized by their acidity, low energy value, high viscosity, and instability. The instability of pyrolysis oil makes the handling, storage and combustion difficult. After prolonged storage especially at higher temperatures, the oil tends to increase their molecular weight owing to chemical reactions, and hence increase the viscosity and has a tendency to separate into a thin oil phase and a thick tar phase.

Table 1.7
Typical properties of wood pyrolysis bio-oil and heavy fuel oil (Bridgwater, 1999; Zhang *et al*., 2007).

Physical Properties	Bio-oil	Heavy fuel oil
Moisture content (wt. %)	15-35	0.1
pH	1.5-3.8	-
Specific gravity	1.2	0.94
Elemental composition (wt. %)		
C	54-58	85
H	5.5-7.0	11
O	35-40	1.0
N	0-0.2	0.3
Ash	0-0.2	0.1
HHV (MJ/kg)	16-19	40
Viscosity (measured at 50 ^{o}C) (cP)	40-100	180
Solids (wt. %)	0.2-1	1

Several researchers have analysed the composition of pyrolysis oil from various biomass feedstocks using GC-MS and HPLC method (Ates *et al*., 2004; He *et al*., 2009; Perez *et al*., 2007; Mullen and Boateng, 2008; Di Blasi *et al*., 2009). Mullen and Boateng (2008) analyzed the composition of pyrolysis oils from switchgrass and alfalfa stems by GC-MS and HPLC. Most of the components identified are the phenols, furan, acids, aldehydes, ketones, sugar, oxygenates and nitrogen compounds. The concentration of each component however, were varied reflecting the different biomass feedstock used. In addition, the present of mineral matters also affect the composition of pyrolysis oil (Di Blasi *et al*., 2009). The influence of chemical state of alkali compounds (NaOH, KOH, N_2CO_3, K_2CO_3, $KC_2H_3O_2$ and NaCl) and the nature of alkali metal impregnated in fir wood on the pyrolysis process and product composition was experimentally investigated by Di Blasi *et al*., (2009) in a fixed-bed reactor at 800 K. An increment yield of phenolics and some minor carbohydrates compounds (1-hydroxy-2butanone, 2-methyl-2-cyclopentenone, 3-ethyl-2-hydroxy-2-cyclopentenone, and 3-methyl-2-cyclopentenone) was observed by the presence of sodium and potassium hydroxides. They found that NaOH is effective for the production of guaiacol, cresols, and 4-ethylguaicol (factors of increase between 2.5 and 4), whereas KOH favors the production of *cis*isoeugenol, *trans*-isoeugenol, and phenol (factors of increase of 2-6). Table 2.8 summarizes the composition of fir wood

pyrolysis oil catalyzed by several alkaline compounds and extracted fir wood, where all the ash was removed was used for comparison (Di Blasi *et al.*, 2009).

Uzun *et al.*, (2007) investigated the composition of olive-oil residue at different pyrolysis temperature (400, 500, 550 and 700 ºC) with a constant heating rate of 300 ºCmin[-1] and found that the formation of aliphatics and polars (oxygenates groups such as ketones, acids, esters, alcohols) had an optimum yield at a temperature of 500 ºC and 400 ºC, respectively. At 700 ºC, the yield of aromatics was at maximum and it is thus concluded that the secondary reactions takes place at high temperature which causes aromatization, polymerization, condensation and cracking reactions.

Table 1.8
Yields of the main compounds in pyrolysis oil of extracted wood and wood catalyzed by alkaline compounds (Di Blasi *et al.*, 2009).

	extraction	NaOH	KOH	Na_2CO_3	K_2CO_3
major carbohydrates (%)	13.51	4.89	6.29	6.87	6.24
acetic acid	3.40	1.45	2.42	2.36	2.51
hydroxyacetaldehyde	4.53	1.52	1.88	2.03	1.80
hydroxypropanone	1.52	1.76	1.89	2.36	1.76
levoglucosan	4.00	0.16	0.10	0.12	0.17
minor carbohydrates (%)	0.60	1.57	1.43	1.21	1.37
1-hydroxy-2-butanone	0.19	0.81	0.51	0.78	0.77
2-methyl-2-cyclopentanone	0.03	0.12	0.07	0.08	0.05
3-ethyl-2-hydroxy-2-cyclopentanone	0.07	0.23	0.40	0.18	0.16
3-methyl-2-cyclopentanone	0.03	0.09	0.12	0.07	0.05
acetoxyacetone	0.08	0.09	0.09	0.10	0.09
propinoic acid	0.20	0.23	0.24	0.24	0.25
furan (%)	0.67	0.85	0.90	0.68	0.89
2-acetylfuran	0.03	0.03	0.07	0.05	0.03
2-furaldehyde	0.28	0.12	0.11	0.10	0.10
2(*5H*)-furanone	0.26	0.09	0.14	0.08	0.10
2-methyl-2-furaldehyde	0.06	0.03	0.02	0.04	0.04
furfuryl alcohol	0.04	0.58	0.56	0.41	0.62
phenols (%)	2.10	4.19	3.83	2.89	2.34
4-acetonguaiacol	0.06	0.08	0.09	0.07	0.07
4-ethylguaiacol	0.15	0.06	0.41	0.32	0.18
4-methylguaiacol	0.55	0.48	0.31	0.42	0.33
eugenol	0.11	0.13	0.08	0.08	0.07
guaiacol	0.40	1.20	1.12	0.86	0.72
cis-isoeugenol	0.32	0.70	0.72	0.40	0.40
trans-isoeugenol	0.14	0.27	0.39	0.17	0.18
vanillin	0.15	0.11	0.07	0.11	0.07
4-propylguaiacol	0.06	0.15	0.13	0.08	0.07
3,4-dimethylphenol	0.01	0.00	0.02	0.01	0.01
cresols	0.08	0.29	0.22	0.15	0.10
hydroquinone	0.04	0.03	0.09	0.04	0.06
phenol	0.03	0.15	0.18	0.08	0.08

1.4.3.2 Char

The char contains most of the inorganic components and it is a carbon-rich solid residue, usually representing about 50 % of the carbon content of the biomass. Char can be used as an energy carrier or as a soil fertilizer (Gaunt and Lehmann, 2008;

Mathews, 2008) to improve soil quality and enhance plant growth. The capability of char can enhance soil fertility, prevent soil erosion, improve soil quality by raising soil pH, trapping moisture, attracting more beneficial fungi and microbes, improving cation exchange capacity, and helping the soil hold nutrient have been attracted many researchers to investigate in details the role of char in soil amendment. Studies (Lehmann, 2007) showed that the use of char in soil increases crops yields and therefore reduce the need for chemical fertilizer and at the same time it minimizes the adverse environmental effects on agrochemicals on the environment. Besides, char also is widely used in water purification, metal extraction, medicine (poison absorption), gas cleanup (SO_2, dioxins and Hg removal), and food industry (organic impurities removal).

1.4.3.3 Pyrolysis Gas

The pyrolysis gas consists mainly of carbon monoxide, carbon dioxide, hydrogen, methane and light hydrocarbons (Sanchez et al., 2009; Zheng, 2007). The pyrolysis gas is combustible and can be used to generate electricity or can be recycled in the pyrolysis process to provide heat.

1.5   Storage and Stability of Pyrolysis Oil

Pyrolysis oil is a liquid mixture of oxygenated compounds containing various chemical functional groups such as phenols, furans, ketones, alcohols, acids and aldehydes, and thus it has a wide range of boiling temperature. During storage, particularly at elevated temperature, these species tend to react to each other and forms larger compounds and thus change the chemical compositions of pyrolysis oil, particularly its viscosity. Liquid fuel viscosity is an important parameter in combustion application as it affects the atomization of spray injector, pump and pipeline sizing, combustion efficiency and emissions.

Several researchers have reported that the properties of pyrolysis oil change as a function of time and temperature under regular storage condition. The stability of pyrolysis oil from hardwood (Czernik et al., 1994; Sipila et al., 1998; Diebold et al., 1996; Oasmaa and Czernik, 1996) and softwood (Oasmaa et al., 1997; Ba et al., 2004; Fahmi et al., 2008) was studied previously. They concluded that the aging rate occur faster at high temperature. Shown in Figure 1.12 is an example of viscosity of softwood oil as a function of storage time, aged at different temperatures (Oasmaa et al, 1997). The viscosity increase rate was higher at high temperature but the changes were only small at room temperature, suggesting that polymerization proceed rapidly at high temperature.
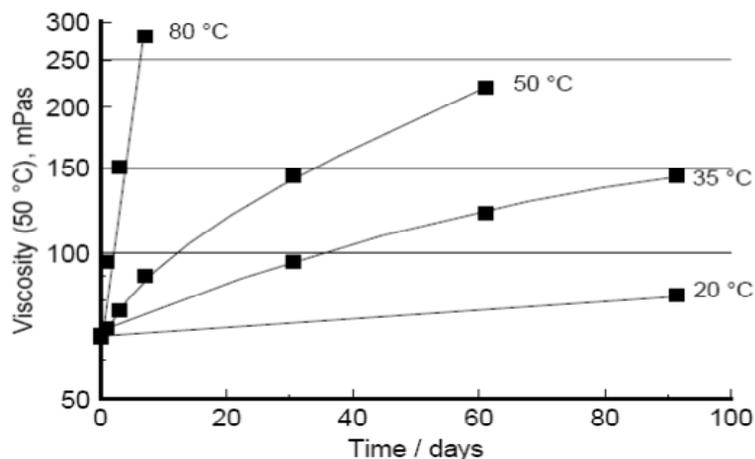
Figure 1.12 Viscosity of softwood oil as a function of storage time, aged at different temperatures (Oasmaa *et al*., 1997).

The viscosity is related to the molecular weight of the material in the pyrolysis oil as shown in Figure 1.13. During storage, particularly at high temperature, the formation of larger molecule from polymerization reaction is dominant resulting in an increase of the viscosity. FTIR analysis determined by Czernik *et al*., (1994) showed that the fraction of high molecular weight material increased while the low molecular weight material decreased during aging.
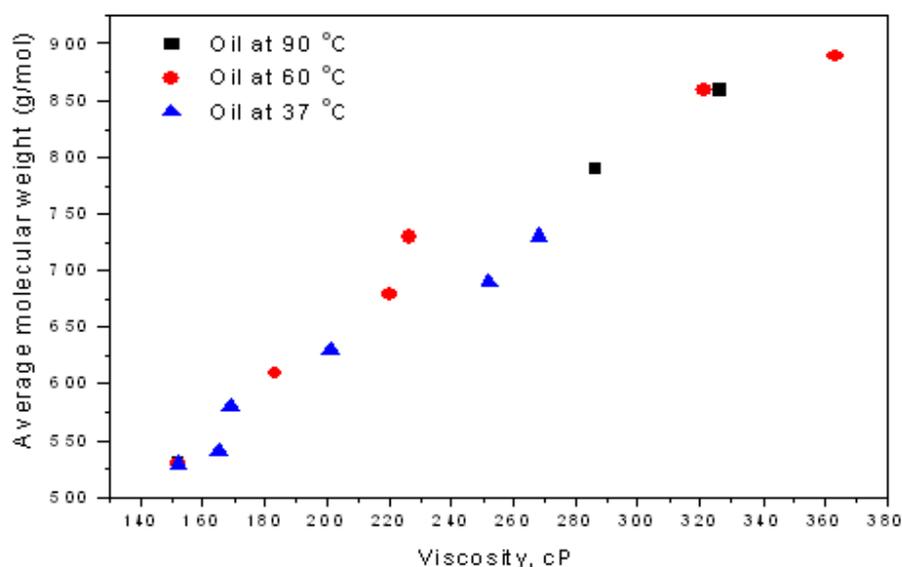

Figure 1.13 The bio-oil viscosity and average molecular weight (Czernik *et al*., 1994).

In an attempt to enhance bio-oil utilization, recent research activity has focused on the optimization of biomass conversion processes towards fuels and chemicals, by applying various catalytic systems to upgrade pyrolysis oils, through several routes. One is the upgrading of the biomass pyrolysis bio-oil by using mainly

metallic or bifunctional (hydrogenating and acidic) catalysts in hydrotreating processes, resulting in naphtha-like products as potential high-quality fuels additives (Bridgwater, 1994; Huber and Dumesic, 2006; Stoikos *et al.*, 1991; Bridgwater, 1996). The other route is the *in situ* upgrading of the biomass pyrolysis vapors in specially designed fluidized or fixed-bed or combined reactor systems, in which the vapors react directly with an acidic catalyst towards the formation of the bio-oil, gases and solid residues (char and coke) (Williams and Nugranad, 2000; Antonakou *et al.*, 2006; Thring *et al.*, 2000; Adam *et al.*, 2006; Triantafyllidis *et al.*, 2007). In addition, *in-bed* mixing of the solid biomass with the catalyst in the pyrolysis reactor has also been tested (Ates *et al.*, 2006). The *in situ* catalytic upgrading of the biomass pyrolysis vapors, usually results in additional water formation and formation of a coke-solid residue (consisting mainly of formed charcoal and coke), as well as a decrease in the yield of organic phase of the bio-oil.

1.6   The Combustibility of Pyrolysis Oil

At present the utilization of pyrolysis oil especially for power production is still under development and need further study for the standardization and quality improvement. However, pyrolysis oil can substitute fuel oil or diesel in many static applications including boilers, furnaces, engines and turbines for electricity generation. Many researchers performed combustion tests using different scale boilers (Solantausta *et al.*, 1995), internal combustion engines (Solantausta *et al.*, 1995; Solantausta *et al.*, 1994; Solantausta *et al.*, 1993) and gas turbine injectors and systems (Solantausta *et al.*, 1995; Lopez and Monfort, 2000). They demonstrated that the pyrolysis oil could be burnt efficiently in standard or modified equipment. Nevertheless, several challenges still arise due to the unusual properties of pyrolysis oil and quality of the product.

1.6.1   Combustion in Diesel Engines

Some medium and low speed diesel engines are known for their ability to run on low quality fuels. The main concerns for operating diesel engines on bio-oils are some specific properties of these liquids such as difficult ignition due to the its low heating value and high water content; acidity that may cause corrosiveness and coking problem because of the presence of thermally unstable compounds in bio-oils (Bridgwater and Peacoke, 2004).

Researchers began investigating the use of bio-oils in diesel engines since the early of 1990s. Solantausta *et al.*, (1993) conducted pioneering work in this area using a high-speed single cylinder engine with a compression ratio of 15:1. It was very difficult to get the bio-oil to auto-ignite without substantial amounts of nitrated ignition additives. In addition, carbon deposits formed at the injectors causing plugging problems. Further test was performed on larger scale medium speed engines, equipped with pilot fuel capabilities and it showed more promise (Solantausta *et al.*, 1994). While auto-ignition was not a problem; it was only difficult to maintain proper adjustment on the injectors, and excessive wear and corrosion were seen in the

injector loop. Much of this was attributed to the acidity and particulate matter in the oil.

Baglioni *et al*., (2001) conducted a series of tests on emulsions of bio-oil in diesel fuel using a 6.25 kW single-cylinder engine. They were able to operate the engine using emulsions with up to 50% of bio-oil. The main problems were deposits and erosion of the injectors. Recently, Chiaramonti *et al*., (2003) used bio-oil-diesel emulsions in four different engines and observed significant damage of the injectors and the fuel pumps, greater than that reported for pure bio-oil.

1.6.2   Combustion in Turbines

Combustion turbines are a well-established technology that offers the potential of producing power and heat at relatively high efficiencies. They are primarily fueled on petroleum distillates or natural gas but if properly designed, in conjunction with appropriate fuel specifications, they should be able to operate on any liquid fuel including bio-oil. Of critical importance in these devices is particulates and alkali metal content in the fuel. This is especially important if sulfur is also present due to alkali sulfate formation during the combustion process. Alkali sulfates will stick to and aggressively corrode the turbine blades. Fortunately, biomass is very low in sulfur but it does contain alkali (K and Na) and alkali earth (Ca and Mg) metals that are sequestered in the char during pyrolysis. A small portion of this char is typically entrained with the pyrolysis vapors and captured with the bio-oil product. Consequently one of the key issues using bio-oils in combustion turbines is the effective removal of char from the oil. The acidic nature, low heating value, and higher viscosity properties of bio-oil can be addressed by appropriate design and material selection in the turbine.

Andrews *et al*., (1997) tested a 2.5 MW turbines operating on bio-oil fuel (after starting on diesel) and ran it through its full operating range from idle to full power without any difficulties. Measured emissions on bio-oil were lower for NOx, SOx, and HC but higher for particulates. The higher particulates may have been due to higher levels of char in the bio-oil, but this property was not measured.

Strenziok *et al*., (2001), at the University of Rostock in Germany, tested a smaller commercial 75 kW turbine on bio-oils. In this demonstration the combustion chamber was modified to enable dual fuel operation with diesel and bio-oil. Under dual fuel operation they were able to achieve 73% of the full output power that would have been obtained from diesel alone. The ratio of fuel blend was 40% bio-oil and 60% diesel. When compared to straight diesel operation the CO and HC emissions were higher while the NOx was lower.

1.6.3   Combustion in Furnace/Boiler

Furnaces and boilers are common devices used for heat and power generation. They are able to operate with a great variety of fuels ranging from natural gas and petroleum distillates to saw dust and coal/water slurries. Bio-oil seems thus to be a suitable boiler fuel as long as it has consistent characteristic, provides acceptable emissions level and is economically feasible.

Most research on bio-oil combustion in boilers has been carried out in Finland (Bridgwater and Peacoke, 2004). Extensive tests have been performed by Gust, (1997) in a 2.5 MW Danstoker boiler supplied with a dual fuel burner. The boiler operated satisfactorily in a dual fuel mode at different fuel oil to bio-oil ratios. The operation on pyrolysis oil without the auxiliary fuel required only relatively minor modifications to improve combustion stability. With such modifications emissions of CO and NOx were at acceptable levels (30 ppm and 140 ppm respectively) but particulates were still high (2.5-5 in the Bacharach scale). VTT Energy (Oasmaa *et al.*, 1997) in collaboration with Oasmaa *et al.*, (2001) performed a series of tests on a wide range of bio-oils in an 8 MWt nominal capacity furnace operated at 4 MWt out put. The main findings of these tests, which were consistent with Gust´s work (Gust, 1997), can be summarized as follows:

- Some modifications of the burner and boiler sections were required to improve combustion.
- The flame from bio-oil combustion was longer than that from burning standard fuel oil.
- A support fuel was necessary during start-up and, in cases of lower quality bio-oils even during operation.
- There were clear differences in combustion behavior and emissions for different bio-oils tested; those with high viscosity and water and solids content showed significantly worse performances.
- Emissions, in general, were lower than from burning heavy fuel oil except for particulates. They strongly depended on the proper handling of bio-oil and its quality.

1.7   The Utilization of Pyrolysis Oil

Figure 1.14 summarizes the possibilities of the utilization of pyrolyis oil. A range of chemicals including food flavourings, specialties such as hydroxyacetaldehyde, resins, agri-chemicals, fertilizers, and emissions control agents can also be extracted or derived from pyrolysis oil. For power generation, at least 400 hours operation has been achieved on a 250 kWe specially modified dual fuel engine (Leech, 1997) and substantial experience has been gained on a modified 2.5 MWe industrial gas turbine.
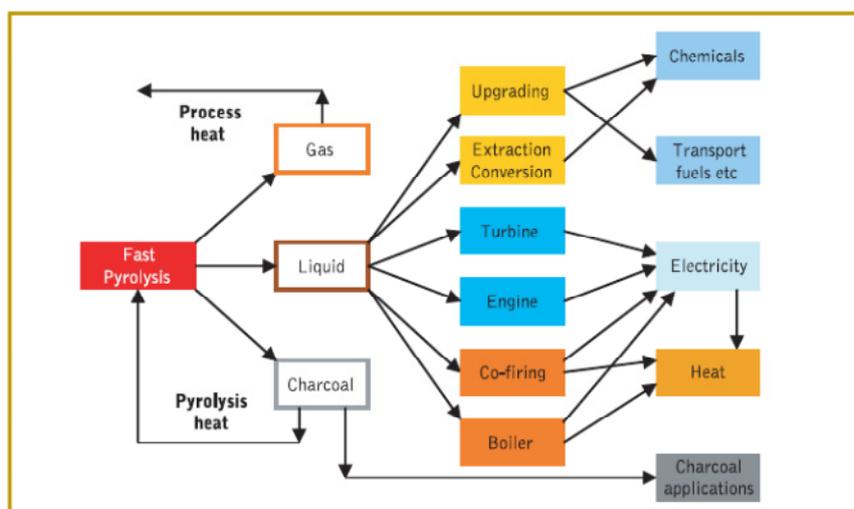
Figure 1.14 Applications for products of flash pyrolysis (IEA 2006).

1.8   Conclusion

This chapter has described some important aspects of biomass pyrolysis. Liquid oil, char and gas are the three products produced from biomass pyrolysis, which can be used for energy purposes and chemical production. Biomass typically consists of cellulose, hemicellulose and lignin. The pyrolysis of cellulose could be finished in a narrow temperature range, producing up to 98 % of volatile, depending on its source. On the other hand, the pyrolysis of lignin covered a wide temperature range, converting to 60 % of volatile at a maximum. Another main component hemicellulose produced volatile between cellulose and lignin, within a lower temperature range than cellulose and a much narrower temperature range than lignin (Jensen *et al*., 1998; Yang *et al*., 2007; Shen *et al*., 2010).

Biomass pyrolysis is a thermochemical process that highly depends on the operating conditions. Therefore knowledge of the influence of each parameter on the pyrolysis process is crucial. Reaction temperature and heating rates are the most important parameters in determining the final yield of pyrolysis products. More gas and less char and liquid oil are produced at higher temperatures. Flash pyrolysis maximizes the production of liquid oil whereas slow pyrolysis enhances the char production. Other parameters such as types of biomass and biomass ash content, biomass initial moisture content and particle sizes are also affect the pyrolysis products. The mechanism and kinetics of pyrolysis process is also described. It involves a complex mechanism; however, simplified models are widely used in the literature. Liquid bio-oil contains a broad range of oxygenated species and functional groups and can be classified as acids, alcohols, aldehydes, esters, ketones, phenols, furans, alkenes, aromatics, sugar and oxygenates. Due to the relatively high acidity, viscosity and high oxygen and water content of pyrolysis pyrolysis bio-oil, the handling, storing and combustion of bio-oil may be difficult. Therefore, study of pyrolysis bio-oil storage stability is important in order to gain a better understanding of the physical and chemical changes induced during storage.

References

Acikgoz, C., Kockar, A. M. (2007). Flash pyrolysis of Linseed (*Linum usitatissimum L.*) for production of liquid fuels. *Journal of Analytical and Applied Pyrolysis*. 78, 406-412.

Adam, J. , Antonakou, E., Lappas, A., Stőcker, M., Nilsen, M. H., Bouzga, A., Hustad, J. E., Øye, G. (2006). In-situ catalytic upgrading of biomass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials. *Microporous Mesoporous Mater*. 96, 93-101.

Adjaye, J. D., Bakhshi, N. N. (1995). Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil: Part I: Conversion over various catalysts. *Fuel Processing Technology*. 45, 161.

Andrews, R. G., Fuleki, D., Zukowski, S., Patnaik, P. C. (1997). Results of Industrial Gas Turbine Tests Using a Biomass Derived Fuel. In: R. P. Overend, E. Chornet (eds.) *Making a Business from Biomass in Energy, Environment, Chemicals, Fibers, and Materials*. New York: Elsevier Science Inc., 425-435.

Antal Jr., M. J., Varhegyi, G. (1995). Cellulose pyrolysis kinetics: The current state of knowledge. *Ind. Eng. Chem. Res*. 34, 703-717.

Arpiainen, V., Lappi, M. (1989). Products from the flash pyrolysis of peat and pine bark. *J. Anal. Appl. Pyrolysis*. 16, 355-376.

Ates, F., Putun, E., Putun, A. E. (2004). Fast pyrolysis of sesame stalks: yields and structural analysis of bio-oil. *J. Anal. Appl. Pyrolysis*. 71, 779-790.

Antonakou, E., Lappas, A., Nilsen, M. H., Bouzga, A., Stőcker, M. (2006). Evaluation of various types of Al-MCM-41 materials as catalysts in biomass pyrolysis for the production of bio-fuels and chemicals. *Fuel*. 85, 2202-2212.

Antony Raja, S., Robert Kennedy, Z., Pillai, B. C., Lindon Robert Lee, C. (2010). Flash pyrolysis of jatropha oil cake in electrically heated fluidized bed reactor. *Energy*. 35, 2819-2823.

Ba, T., Chaala, A., Garcia-Perez, M., Roy, C. (2004). Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Storage stability. *Energy & Fuel*. 18, 188-201.

Babu, B. V., Chaurasa, A. S. (2004). Heat transfer and kinetics in the pyrolysis of shrinking biomass particles. *Chemical Engineering Science*. 59, 1999-2012.

Baglioni, P., Chiaramonti, D., Bonini, M., Soldaini, I., Tondi, G. (2001). Bio-Crude-Oil/Diesel Oil Emulsification: Main Achievements of the Emulsification Process and Preliminary Results of Tests on Diesel Engine. In: Bridgwater, A.V. (ed.) *Progress in Thermochemical Biomass Conversion*, Blackwell Science, Oxford, UK, 1525-1539.

Bech, N., Larsen, M. B., Jensen P. A., Dam-Johansen, K. (2009). Modelling solid-convective flash pyrolysis of straw and wood in the pyrolysis centrifuge reactor. *Biomass and Bioenergy*. 33, 999-1011.

Belidan, M. (2007). Experimental studies on municipal solid waste and biomass pyrolysis. Ph.D. Thesis. Norwegian University of Science and Technology, Trondheim Norway.

Bilbao, R., Millera, A., Murillo, M. B. (1993). Solid weight loss in the thermal decomposition of cellulose and pine sawdust. *Ind. Eng. Chem. Res*. 32, 257-271.

Bridgwater, A. V., Kuester, J. L. (1991). *Research in Thermochemical Biomass Conversion*. Elsevier Science Publishers: London.

Bridgwater, A. V. (1994). Catalysis in thermal biomass conversion. *Applied Catalysis*. 116, 5-47.

Bridgwater, A. V. (1996). Production of high grade fuels and chemicals from catalytic pyrolysis of biomass. *Catal. Today*. 29, 285-295.

Bridgwater, A.V., Meier, D., Radlein, D. (1999). An overview of fast pyrolysis of biomass. *Organic Geochemistry*, 30, 1479-1493.

Bridgwater, A. V., Peacocke, G. V. C. (2000). Fast pyrolysis processes for biomass. *Renewable and Sustainable Energy Reviews*. 4, 1-73.

Bridgwater, A. V., Peacoke, G. V. C. (2004). Fast pyrolysis processes for biomass. *Renewable and Sustainable Energy Reviews*. 4, 1-73.

Chan, W. C. R., Kelbon, M., Krieger, B. B. (1985). Modelling and experimental verification of physical and chemical processes during pyrolysis of a large biomass particle. *Fuel*. 64, 1505-1513.

Chiaramonti, D., Bonini, M., Fratini, E., Tondi, G., Gartner, K., Bridgwater, A. V., Grimm, H. P., Soldaini, I., Webster, A,. Baglioni, P. (2003). Development of Emulsions from Bio mass Pyrolysis Liquid and Diesel and Their Use in Engines – Part 1: Emulsion Pro duction, *Biomass & Bioenergy*. 25, 85-99.

Czernik, S., Johnson, D. K., Stewart, B. (1994). Stability of wood fast paralysis oil. *Biomass & Bioenegy*. 7, 1-6.

Diebold, J. P., Power, A. (1998). Engineering aspects of the vortex pyrolysis reactor to produce primary pyrolysis oil vapors for use in resin and adhesives. *Thermochemical Biomass Conversion*. 610.

Diebold, J. P., Scahill, J. W. (1997). Improvement in the vortex reactor design. *Thermochemical Biomass Conversion*. 242-252.

Diebold, J.P., Power, A. Engineering aspects of the vortex pyrolysis reactor to produce primary pyrolysis oil vapors for use in resin and adhesives. Thermochemical Biomass Conversion (1988) 610.

Diebold, J. P. A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-Oils, NREL.1 (2000). 3-42.

Diebold, J. P., Scahill, J. W., Czernik, S., Phillips, S. D., Feik, C. J. (1996). Progress in the production of hot-gas filtered biocrude oil. In: Bridgwater, A.V., Hogan, E. (eds.). *Bio-oil production and utilization*. Proceedings of the Second EC/Canada Workshop on Thermal Biomass Processing. CPL Scientific Information Services, Ltd.: Newbury, U.K. 66-81.

Demirbas, A. (2001a). Recent advances in biomass conversion technology. *Energy Edu. Sci. Tech*. 6, 77-83.

Demirbas, A. (2001b). Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Convers. Manage*. 41, 1357-1378.

Demirbas, A., Arin, G. (2002). An overview of biomass pyrolysis. *Energy Sources*. 24, 471-482.

Demirbas, A. (2004). Effect of initial moisture content on the yields of oily products from pyrolysis of biomass. *Journal of Analytical and Applied Pyrolysis*. 71, 803-815.

Di Blasi, C., .Galgano, A., Branca, C. (2009). Effects of potassium hydroxide impregnation on wood pyrolysis. *Energy & Fuels*. 23, 1045-1054.

Di Blasi, C. (1993). Modeling and simulation of combustion processes charring and non-charring solid fuels. *Progress in Energy Combustion Science*. 19, 71-104.

Di Blasi, C. (2008). Modeling chemical and physical processes of wood and biomass pyrolysis. *Progress in Energy and Combustion Science*. 34, 47-90.

Dupont, C., Chen, L., Cances, J., Commandue, J. M., Cuoci, A., Pierucci, S., Ranzi, E. (2009). Biomass pyrolysis: kinetic modeling and experimental validation under high temperature and flash heating arte conditions. *J. Anal. Appl. Pyrolysis*. 85, 260-267.

Fahmi, R., Bridgwater, A. V., Darvell, L. I., Jones, J. M., Yates, N. (2007). The effect of alkali metals on combustion and pyrolysis of lilium and Festuca grasses, switchgrass and willow fuel. *Fuel*. 86, 1560-1569.

Fahmi, R., Bridgwater, A. V., Donnison, I., Yates, N., Jones, J. M. (2008). The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. *Fuel*. 87, 1230-1240.

Fagbemi, L., Khezami, L., Capart, R. (2001). Pyrolysis products from different biomasses: application to the thermal cracking of tar. *Applied Energy*. 69, 293-306.

Galgano, A., Di Blasi, C. (2003). Modeling wood degradation by the unreacted-core-shrinking approximation. *Ind. Eng. Chem. Res*. 42, 2101-2111.

Garcia-Bacaicoa, P., Mastral, J. F., Ceamanos, J., Berrueco, C., Serrano, S. (2008). Gasification of biomass/high density polyethylene mixtures in a downdraft gasifier. *Bioresourse Technology*. 99, 5485-5491.

Gaunt, J. L., Lehmann, L. (2008). Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production. *Environ. Sci. Techno*. 42, 4152-4158.

Girio, F. M., Fonseca, C., Carvalheiro, F., Duarte, L. C., Marque, S., Bogel-Lukasik, R. (2010). Hemicellulose for fuel ethanol: A review. *Bioresource Technology*. 101, 4775-4800.

Gray, M. R., Corcoran, W. H., Gavalas, G. R. (1985). Pyrolysis of a wood-derived material. Effects of moisture and ash content. *Ind. Eng. Chem. Process Des. Dev*. 24, 646-651.

Gust, S. (1997). Combustion Experiences of Flash Pyrolysis Fuel in Intermediate Size Boilers. In: Bridgwater, A. V., Boocock, D. G. B. (eds.). *Developments in Thermochemical Biomass Conversion*. Blackie Academic & Professional, London. 481-488.

Haseli, Y., van Oijen, J. A., de Goey, L. P. H. (2011). Modeling biomass particle pyrolysis with temperature-dependent heat of reactions. *J. Anal. Appl. Pyrolysis*. 90, 140-154.

Haykiri-Acma, H. (2006). The role of particle size in the non-isothermal pyrolysis of hazelnit shell. *J. Anal. Appl. Pyrolysis*. 75, 211-216.

Haykiri-Acma, H., Yaman, S., Kucukbayrak, S. (2006). Effect of heating rate on the pyrolysis yields of rapeseed. *Renewable Energy*. 31, 803-810.

He, R., Phillip ye, X., English, B. C., Satrio, J. A. (2009). Influence of pyrolysis conditio non switchgrass bio-oil yield and physicochemical properties. *Bioresource Technology*. 100, 5305-5311.

Horne, P. A., Williams, P. T. (1996). Influence of temperature on the products from the flash pyrolysis of biomass. *Fuel*. 75, 1051-1059.

Huber, G. W., Dumestic, J. A. (2006). An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery. *Catalysis Today*. 111, 119-132.

Ibrahim, N., Jensen, P. A., Dam-Johansen, K. (2010). Effect of biomass mineral matter on the pyrolysis product yields. In: Proc. Of the 18th European Biomass Conference and Exhibition, Lyon, 3-7 May 2010.

IEA - International Energy Agency (2006), www.ieabioenergy.com.

Jensen, A., Dam-Johansen, K., Wojtowicz, M. A., Serio, M. A. (1998). TG-FTIR study of the influence of potassium chloride on wheat straw pyrolysis. *Energy & Fuel*. 12, 929-938.

Ji-lu, Z. (2007). Bio-oil from fast pyrolysis of rice husk: Yields and related properties and improvement of the pyrolysis system. *J. Anal. Appl. Pyrolysis*. 80, 30-35.

Keown, D. M., Hayashi, J. I., Li, C. Z. (2008). Effects of volatile-char interactions on the volatilisation of alkali and alkaline earth metallic species during the pyrolysis of biomass. *Fuel*. 87, 1187-1194.

Koufopanos, C. A., Papayannanos, N., Maschio, G., Lucchesi, A. (1991). Modeling the pyrolysis of biomass particles: studies on kinetics, thermal and heat transfer effects. *The Canadian Journal of Chemical Engineering*. 69, 907-915.

Kumar Sadhukan, A., Gupta, P., Kumar Saha, R. (2009). Modelling of pyrolysis of large wood particles. *Bioresource Technology*. 100, 3134-3139.

Lede, J., Broust, F., Fatou-Toutie, N., Ferrer, M. (2007). Properties of bio-oils produced by biomass fast pyrolysis in a cyclone reactor. *Fuel*. 86, 1800-1810.

Lede, J. (2003). Comparison of contact and radiant ablative pyrolysis of biomass. *J. Anal. Appl. Pyrolysis*. 70, 601-608.

Lee, K. H., Kang, B. S., Park, Y. K., Kim, J. S. (2005). Influence of reaction temperature, pretreatment, and a char removal system on the production of bio-oil from rice straw by fast pyrolysis, using a fluidised bed. *Energy & Fuel*. 19, 2179-2184.

Leech, J. (1997). Running a dual fuel engine on pyrolysis oil, Biomass Gasification and Pyrolysis. Kaltschmitt, M. and Bridgwater, A.V. (Eds.), CPL Press, Newbury. 495-497.

Lehmann, J. A. (2007). Handful of carbon. *Nature*. 447, 143-144.

Lopez, J. G., Monfort, S. J. J. (2000). Preliminary test on combustion of wood derived fast pyrolysis oils in a gas turbine combustor. *Biomass & Bioenergy*. 19, 119-28.

Luo, Z., Wang, S., Liao, Y., Zhou, J., Gu, Y., Cen, K. (2004). Research on biomass fast pyrolysis for liquid fuel. *Biomass & Bioenergy*. 36, 455-462.

Marsman, J. H., Wildschut, J., Mahfud, F., Heeres, J. J. (2003). Identification of components in fast pyrolysis oil and upgraded products by comprehensive two-dimensional gas chromatography and flame ionisation detection. Renewable fuels and chemicals by thermal processing of biomass. *Chem. Eng. Journal*. 91, 87-102.

Mathews, J.A. (2008). Carbon-negative biofuels. *Energy Policy*. 26, 940-45.

Mc Kendry, P. (2002). Energy production from biomass (part 1): overview of biomass. *Bioresource Technology*. 83, 37-46.

Mohan, D., Charles, U. Pittman, J., Philip, H. S. (2006). Pyrolysis of wood/biomass for bio-oil: Critical Review. *Energy & Fuels*. 20, 848-889.

Mullen, C. A., Boateng, A. A., Hicks, K. B., Goldberg, N. M., Moreau, R. A. (2010). Analysis and comparison of bio-oil produced by fast pyrolysis from three barley biomass/byproduct streams. *Energy & Fuels*. 24, 699-706.

Mullen, C. A., Boateng, A. A. (2008). Chemical composition of bio-oils produced by fast pyrolysis of two energy crops. *Energy & Fuels*. 22, 2104-2109.

Nik-Azar, M., Hajaligol, M. R., Sohrabi, M., Dabir, B. (1997). Mineral matter effects in rapid pyrolysis of beech wood. *Fuel Processing Technology*. 51, 7-17.

Nowakowski, D. J, Jones, J. M. (2008). Uncatalysed and potassium-catalysed pyrolysis of the cell-wall constituents of biomass and their modell compounds. *J. Anal. Appl. Pyrolysis*. 83, 12-25.

Nunn, T. R., Howard, J. B., Longwell, J. P., Peters, W. A. (1985). Product composition and kinetics in the rapid pyrolysis of sweet gum hardwood. *Ind. Eng. Chem. Process Des. Dev*. 24, 836.

Oasmaa, A., Czernik, S. (1996). Fuel oil quality of biomass pyrolysis oil-state of the art for the end user. *Energy & Fuels*. 13, 914-921.

Oasmaa, A., Leppamaki, E., Koponen, P., Levander, J., Tapola, E. (1997). Physical characterization of biomass-based pyrolysis liquids. Application of standard fuel oil analyses; VTT Publication 306; VTT: Espoo, Finland. 46 pp + appendices (30 pp).

Oasmaa, A., Kytö, M., Sipilä, K. (2001). Pyrolysis Oil Combustion Tests in an Industrial Boiler. In: *Progress in Thermochemical Biomass Conversion* (Ed. Bridgwater, A.V.), Blackwell Science, Oxford, UK. 1468-1481

Pan, W. P., Richards, G. N. (1989). Influence of metal ions on volatile products of pyrolysis of wood. *J. Anal. Appl. Pyrolysis*. 16, 117-126.

Park, H. J., Park, Y. K., Dong, J. I., Kim, J. S., Jeon, J. K., Kim, S. S., Kim, J., Song, B., Park, J., Lee, K. J. (2009). Pyrolysis characteristic of oriental white oak: kinetic study and fast pyrolsyis in a fluidized bed with and improved reaction system. *Fuel Processing Technology*. 90, 186-195.

Park, W. C., Atreya, A., Baum, H. R. (2010). Experimental and theoretical investigation of heat and mass transfer processes during wood pyrolysis. *Combustion and Flame*. 157, 481-494.

Perez, M. G., Chaala, A., Pakdel, H., Kretschmer, D., Roy, C. (2007). Vacuum pyrolysis of softwood and hardwood biomas Comparison between product yields and bio-oil properties. *J. Anal. Appl. Pyrolysis*. 78, 104-116.

Radlein, D., Piskorz, J., Scott, D. S. (1991). Fast pyrolysis of natural polysaccharides as a potential industrial process. *J. Anal. Appl. Pyrolysis*. 19, 41-63.

Radmanesh, R., Courbariau, Y., Chaouki, X. J., Guy, C. (2006). A unified lumped approach in kinetic modeling of biomass pyrolysis. *Fuel*. 85, 1211-1220.

Ranzi, E., Cuoci, A., Faravelli, T., Frassoldati, A., Migliavacca, G., Pierucci, S., Sommariva, S. (2008). Chemical kinetics of biomass pyrolysis. *Energy & Fuels*. 22, 4292-4300.

Raveendran, K., Ganesh, A., Khilar, C. (1996). Pyrolysis characteristics of biomass and biomass components. *Fuel*. 75, 1812-1822.

Roy, C., de Caumia, B., Plante, P. (1990). Performance Study of a 30 Kg/hr Vacuum Pyrolysis Process Development Unit. In *5th European Conference on Biomass for Energy and Industry*; Grassi, G., Goose, G., dos Santos, G., Eds.; Elsevier Applied Science: London. 2595.

Sadhukan, A. K., Gupta, P., Saha, R. K. (2009). Modelling of pyrolysis of large wood particles. *Bioresource Technology*. 100, 3134-3139.

Sanchez, M. E., Lindao, E., Margaleff, D., Martinez, O., Maron, A. (2009). Pyrolysis of agricultural residues from rape and sunflowers: production and characterization of bio-fuels and biochar soil management. *J. Anal. Appl. Pyrolysis*. 85, 142-44.

Scott, D. S., Piskorz, J. (1982). The flash pyrolysis of aspen-poplar wood. *Can. J. Chem. Eng*. 60, 666-670.

Scott, D. S., Majerski, P., Piskorz, J., Radlein, D. (1999). A second look at fast pyrolysis of biomass-RTI process. *J. Anal. Appl. Pyrolysis*. 51, 23-37.

Senneca, O. (2007). Kinetics of pyrolysis, combustion and gasification of three biomass fuels. *Fuel Processing Technology*. 88, 87-97.

Sensoz, S., Angin, D., Yorgun, S. (2000). Influence of particle size on the pyrolysis of rapeseed (*Brassica napus. L.*): fuel properties of bio-oil. *Biomass & Bioenergy*. 19, 271-279.

Sensoz, S., Angin, D. (2008). Pyrolysis of safflower (Charthamus tinctorius L.) seed press cake: Part 1. The effects of pyrolysis parameters on the product yields. *Bioresource Technology*. 99, 5492-547.

Sipila, K., Kuoppala, E., Fagernae`s, L. (1998). Characterization of biomass–based flash pyrolysis oils. *Biomass & Bioenergy*. 14, 103-13.

Shafizadeh, F. (1982). Introduction to pyrolysis biomass. *Journal of Analytical and Appied Pyrolysis*. 3, 283-305.

Shafizadeh, F., McGinnis, G. D., Philpot, C. W. (1972). Thermal degradation of xylan and related model compounds. *Carbohydrate Research*. 25, 22-23.

Shen, D. K., Gu, S., Bridgwater, A. V. (2010). The thermal performance of the polysaccharides extracted from hardwood: cellulose and hemicelluloses. *Carbohydrates Polymers*. 82, 39-45.

Shen, J., Wang, X. S., Perez, M. G., Mourant, D., Rhodes, M. J., Li, C. Z. (2009). Effects of particle size on the fast pyrolysis of oil malee woody biomass. *Fuel*. 88, 1810-1817.

Shinogi, Y., Karni, Y. (2003). Pyrolysis of plant, animal and human waste: Physical and chemical characterization of the pyrolytic products. *Bioresource Technology*. 90, 241-247.

Shuangning, X., Weiming, Y., Li, B. (2005). Flash pyrolysis of agricultural residues using a plasma heated laminar entrained flow reactor. *Biomass & Bioenergy*. 29, 135-141.

Smets, K., Adriaensens, P., Reggers, G., Schreurs, S., Carleer, R., Yperman, J. (2011). Flash pyrolysis of rapeseed cake: Influence of temperature on the yield and the characteristic of the pyrolysis liquid. *J. Anal. Appl. Pyrolysis*. 90, 118-125.

Solantausta, Y., Bridgwater, A. V., Beckman, D. (1995). Feasibility of power production with pyrolysis and gasification systems. *Biomass & Bioenergy*. 9, 257-269.

Solantausta, Y., Nylund, N. O., Westerholm, M., Koljonen, T., Oasmaa, A. (1993). Wood pyrolysis liquid as fuel in a diesel power plant. *Bioresource Technology*. 46, 177-88.

Solantausta, Y., Nylund, N. O., Gust, S. (1994). Use of pyrolysis oil in a test diesel engine to study the feasibility of a diesel power plant concept. *Biomass & Bioenergy*. 7, 297-306.

Stenseng, M. (2001). Pyrolysis and combustion of biomass. PhD. Thesis. Technical University of Denmark.

Stoikos, T. (1991). In: Bridgwater, A.V. and G. Grassi, G. (eds.). Biomass Pyrolysis Liquids, Upgrading and Utilisation. Elsevier, London. 227–239.

Strenziok, R., Hansen, U., Künster, H. (2001). Combustion of Bio-oil in a Gas Turbine. In: Bridgewater, A.V. (ed.). *Progress in Thermochemical Biomass Conversion*. Oxford: Blackwell Science. 1452-1458.

Sun, S., Tian, H., Zhao, Y., Sun, R., Zhou, H. (2010). Experimental and numerical study of biomass flash pyrolysis in an entarined flow reactor. *Bioresource Technology*. 101, 3678-3684.

Thring, R. W., Katikaneni, S. P. R. and Bakhshi, N. N. (2000). The production of gasoline range hydrocarbons from Alcell® lignin using HZSM-5 catalyst. *Fuel Process. Technology*. 62, 17-30.

Thurner, F., Mann, U. (1981). Kinetic investigation of wood pyrolysis. *Ind. Eng. Chem. Proc. Des. Dev.* 20, 482-488.

Tonbul, Y. (2008). Pyrolysis of pistachio shell as a biomass. *Journal of Thermal Analysis and Calorimetry*. 91, 641-647.

Triantafyllidis, K. S., Iliopoulou, E. F., Antonakou, E. V., Lappas, A. A, Wang, H., Pinnavaia, T. J. (2007). Hydrothermally stable mesoporous aluminosilicates (MSU-S) assembled from zeolites seeds as catalysts for biomass pyrolysis. *Micropor. Mesopor. Mater*. 99, 132-139.

Tsai, W. T. (2006). Fast pyrolysis of rice straw, sugarcane baggase and coconut shell in an induction-heating reactor. *J. Anal. Appl. Pyrolysis*. 76, 230-237.

Tsai, W. T., Lee, M. K., Chang, Y. M. (2007). Fast pyrolysis of rice husk: Product yields and compositions. *Bioresource Technology*. 98, 22-28.

Twaiq, F. A,. Mohamed, R. A., Bhatia, S. (2003). Liquid hydrocarbon fuels from palm oil by catalytic cracking over aluminosilicate mesoporous catalysts with various Si/Al ratios. *Microporous Mesoporous Mater*. 64, 95-107.

Uzun, B. B., Putun, A. E., Putun, E. (2007). Composition of products obtained via fast pyrolysis of olive –oil resides: Effect of pyrolysis temperature. *J. Anal. Appl. Pyrolysis*. 79, 147-143.

Varhegyi, G., Gronli, M. G., Di blasi, C. (2004). Effects of sample origin, extraction and hot water washing on the devolatilization kinetics of chestnut wood. *Ind. Eng. Chem. Res*. 43, 2356-2367.

Volker, S., Rieckmann, T. (2002). Thermokinetic investigation of cellulose pyrolysis-impact of initial and final mass on kinetic results. *J. Anal. Appl. Pyrolysis*. 62, 165-177.

Wilen, C., Moilanen, A., Kurkela, E. (1986). Biomass feedstock analyses. VTT (Technical Research Centre in Finland) Publication, 282.

Williams, P. T., Nugranad, N. (2000). Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks. *Energy*. 25, 493-513.

Yaman, S. (2004). Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Convers. Management*. 45, 65-75.

Yang, H., Yan, R., Chen, H., Lee, D. H., Zheng, C. (2007). Characteristic of hemicellulose, cellulose and lignin pyrolysis. *Fuel*. 86, 1781-1788.

Yang, H., Yan, R., Chen, H., Lee, D. H., Liang, D. T. (2006). Influence of mineral matter on pyrolysis of palm oil waste. *Combustion & Flame*. 605-611.

Yorgun, S., Sensoz, S., Kockar, O. M. (2001). Flash pyrolysis of sunflower oil cake for production of liquid fuels. *J. Anal. Appl. Pyrolysis*. 60, 1-12.

Zanzi, R., Sjostrom, K., Bjornbom, E. (2009). Rapid pyrolysis of agricultural residues at high temperature. *Biomass & Bioenergy*. 23, 357-366.

Zhang, Q., Chang, J., Wang, T. Xu, Y. (2007). Review of biomass pyrolysis oil properties and upgrading research. *Energy Conversion and Management*. 48, 87-92.

Zheng, J. L. (2007). Bio-oil from fast pyrolysis of rice husk: yields and related properties and improvement of the pyrolysis system. *J. Anal. Appl. Pyrolysis*. 80, 30-35.

<div align="right">**CHAPTER 2**</div>

Influence of Reaction Temperature and Water Content on Wheat Straw Pyrolysis

Abstract

The aim of this study was to investigate the influence of reaction temperature and wheat straw moisture content on the pyrolysis product yields, in the temperature range of 475 - 575 °C. Samples of straw with moisture contents from 1.5 wt. % to 15.0 wt. % were fed to a bench scale Pyrolysis Centrifuge Reactor (PCR). The experimental results show that the changes in straw moisture content have no significant effect on the distribution of pyrolysis product yields. The maximum bio-oil yields approximately 60 (wt %, on dry ash free feedstock basis) was observed around 525 °C - 550 °C for all straw moisture levels. The water content in the wet straw bio-oil was the highest. The heating value of bio-oil and solid char were measured and the percentages of its energy distribution were calculated. The energy distributions of bio-oil, char and gas were 56-69 % 24-33 %, and 2-19 %, respectively.

Keywords: Flash pyrolysis; moisture content; wheat straw; bio-oil; heating value.

2.1   Introduction

The flash pyrolysis process has been subject of intense research in the last decades mainly with the objective to maximize the organics liquid yields [1, 2]. During pyrolysis, biomass is thermally decomposed without an oxidizing agent to produce a solid charcoal, liquid oil and gases. High heating rates of the biomass particles and a short gas residence time at temperature of 450-600 °C are required to obtain the highest possible liquid yield [3]. Depending on the feedstock and operating conditions, the flash pyrolysis of wood produces 50-75 wt. % of liquid bio-oil (including water), 15-25 wt. % of solid char and 10-20 wt. % of non-condensable gases [4, 5]. The process is a promising thermal conversion route of biomass to produce a nearly ash-free liquid fuel with a high volumetric energy density. The char contain most of the inorganic components and it can be used as an energy carrier or as a soil fertilizer [6, 7]. The pyrolysis gas can be used to generate electricity or to provide heat for the pyrolysis process. The pyrolysis gas consists mainly of carbon monoxide, carbon dioxide and light hydrocarbons [8, 9]. Also, the liquid oil can be directly used without any upgrading as a fuel oil in many combustion applications such as boilers. Upgrading is probably needed if the bio-oil shall be applied to smaller engines. The liquid oil is composed of a large variety of higher molecular weight

species, organic acids, aldehydes, alcohols, phenols and other oxygenates. This oil is also known as a pyrolysis liquid, bio-oil or tar and has a lower heating value of 15-20 MJ/kg , about half that of conventional fuel oil [10]. Bech and co-workers [11, 12] measured the heating value of bio-oil produced from wheat straw at a reactor temperature of 550 °C and the value was determined to approximately 15 MJ/kg (dry basis). The pyrolysis oil can undergo secondary reactions to be further broken down into gas, refractory tar and water [13, 14]. The distribution and the yield of the pyrolysis products depend on several operating parameters including biomass characteristic, feedstock particle size, temperature, heating rate, and reactor configuration, as well as the extraneous addition of catalysts [15].

Over the last two decades, extensive studies have been conducted to understand the flash pyrolysis process and to obtain the optimal conditions for producing high quality bio-oil. The effect of biomass properties has been a research area, but only little attention has been focused on the effect of feedstock moisture content on wood flash pyrolysis [16] and none wheat straw moisture influence studies has been found. The presence of water in biomass could influence the pyrolysis behaviour and affects the physical properties and quality of the bio-oil. Previous studies [16-19] indicate that moisture may change the product composition or enhance some pyrolysis reactions. Shafizadeh [17] found that the decomposition rate of wet cellulose was much faster than that of dry cellulose when subjected to the same conditions in a closed system at 200 °C. Gray and co-workers [16] found that the presence of moisture increased the char yield by as much as 5 yield wt. % (relative to dry sample). A recent study investigated the effect of wood moisture content on the flash pyrolysis oil yield [18]. They found that, as the wood moisture content increases, the char and gas yield increase and the produced water decreases but the liquid organics yield remains constant. In contrary, another researcher [19] found that the pyrolysis oil yield produced from conventional pyrolysis at a low heating rate of 5 K/s, was increased with increasing fuel moisture content and the oil obtained from dry feedstock was very viscous especially at higher temperatures. This paper reports results of a study on the effect of straw moisture content on wheat straw pyrolysis yield and the obtained product distribution.

2.2   Experimental

2.2.1   Material

The wheat straw pellets used in this study were manufactured by compressing straw and extruding it to pellets in a 'Pellet Mill'. The pellets were crushed in a roller mill and were further screened into a fraction with a particle diameter < 1.40 mm. The particles appeared to have a more or less spherical shape. An analysis of the wheat straw is shown in Table 2.1. Straw samples with moisture contents of 1.5 wt. % ('dry straw'), 6.2 wt. % ('as received straw') and 15.0 wt. % ('wet straw') were used for the experiments. Wet straw samples were prepared by sprinkling water on it to achieve a moisture content of 15.0 ± 1 wt. % and storing it for 3 to 4 days to ensure that the water had been fully distributed. Dry straw samples were prepared by drying at 105 °C for at least 24 hr.

2.2.2 Apparatus and Procedures

The flash pyrolysis experiments were conducted in a bench scale Pyrolysis Centrifuge Reactor (PCR) as depicted in Figure 2.1 [11, 12]. The set-up consists of a screw type feeder, an ablative centrifuge reactor, an electric heater, a cyclone, a condenser, a coalescer, a gas dryer and a pump. The biomass was introduced by the screw feeder into the horizontally oriented Ø 82 x 200 mm tubular reactor. Here, a three-blade rotor with a clearance of 2 mm to the reactor wall rotate at a fixed speed of 14800 rpm creating a centrifugal force at the pipe wall of approximately 1.0×10^4 g (acceleration), and thereby provides rotation of the gas and the biomass particles. The reactor wall was heated electrically by four independent heating zones located on the outer surface of the reactor tube. While undergoing reaction, the particles moved down the reactor pipe before leaving suspended in the gas through the tangential outlet. Larger char particles were removed by a change-in-flow separator whereas fines were collected by the cyclone. Vapors were condensed in a direct water cooled condenser (bubble chamber) filled with previously produced bio-oil. The temperature in the condenser was controlled to be 55 to 75 °C by means of a pipe coil cooled by tap water. Aerosols that were not retained by the condenser were collected in a coalescer filled with ROCKWOOL® (fibers). In the coalescer aerosols were removed and the bio-oil was collected in a conical flask. The gas was pumped to the preheater and heated to 400 °C before it is recirculated to the reactor in order to maintain a desired gas residence time of 0.2-0.3 s and avoid condensation of liquid products within the reactor. The amount of produced gas was measured by a temperature compensated gas meter and a sample was collected in a gas bag. Before the gas volume was measured, it was cooled to ambient temperature in order to remove water. The gas residence time in the reactor was calculated based on the experimental data obtained (from pyrolysis product yield). Details about the reactor are presented in previous work [12, 20, 21].

Table 2.1.

Analysis of wheat straw

Analysis	Wheat straw
Proximate	
Volatile matter, %db	74.7
Ash, %db	5.9
Moisture, %wt	5.9
HHV (MJ/kg, dry basis)	18.75
Ultimate (wt%, dry ash free basis)	
Carbon	49.4
Hydrogen	6.2
Nitrogen	1.11
Sulphur	0.17
Oxygen (by difference)	43.12
Ash Composition (%wt)	
Cl	14.4
Si	22.03
Al	0.51
Fe	0.27
Ca	3.9
Mg	11.02
Ti	0.02
Na	1.19
K	25.4
P	2.37
O (by difference)	18.89

db: dry basis

In this work, samples of straw with different moisture contents (1.5 wt. %, 6.2 wt. % and 15.0 wt. %) were treated to investigate the moistures effect on the pyrolysis products distribution of bio-oil, char, water and gas. To start an experiment, a 500.0 g sample of straw was placed in the feeder and the system was purged with nitrogen. The heat tracing of the reactor outlet tube was turned on and after the reactor reached the selected temperature, the rotor speed was adjusted to about 14800 rpm. The obtained straw feed rate was approximately 23 g/min. The experiment was run for 14-20 minutes and stopped just before the coalescer pressure meter reading reached a pressure of -400 mbar. The pressure was decreasing due to blocking of the condenser nozzle that has an inner diameter of 4.0 mm. Therefore the experiment was stopped to avoid a decreased gas flow in the system. After the system had cooled, liquid and char yield in addition to spend raw material was determined gravimetrically. The gas yield was calculated on the basis of the measured gas volume and a molecular weight measurement obtained immediately after the run in order to minimize the potential effect of light gasses diffusing out of the gas bag. Liquid samples were filtered through a Whatman #4 filter paper on a Buchner funnel to remove char from the bio-oil. The char left on the filter was washed thoroughly using ethanol and acetone and dried under an infrared light bulb for 10 minutes. Then the residual mass of char was

determined. The water content in the liquid products from the condenser (bubble chamber) and the conical flask below the coalescing filter was determined by refractive index measurements [21]. The liquid left in the coalescer was assumed to be similar in composition to the liquid collected in the condenser and the amount was determined by weighing the coalescer before and after the run. Overall, the yield of pyrolysis oil was determined from the condensed liquid in the condenser and coalescer. The char yield was determined from the char collected in the direct char separator, the cyclone and the char in the oil (char left on the filter). The mean values and standard deviations of the mean values for each yield of pyrolysis products were determined by making two to three experiments at each condition. All yields shown in Figures are given on a dry ash-free feedstock basis (daf). All data points presented are average values and the range indicates a 95 % confidence interval.
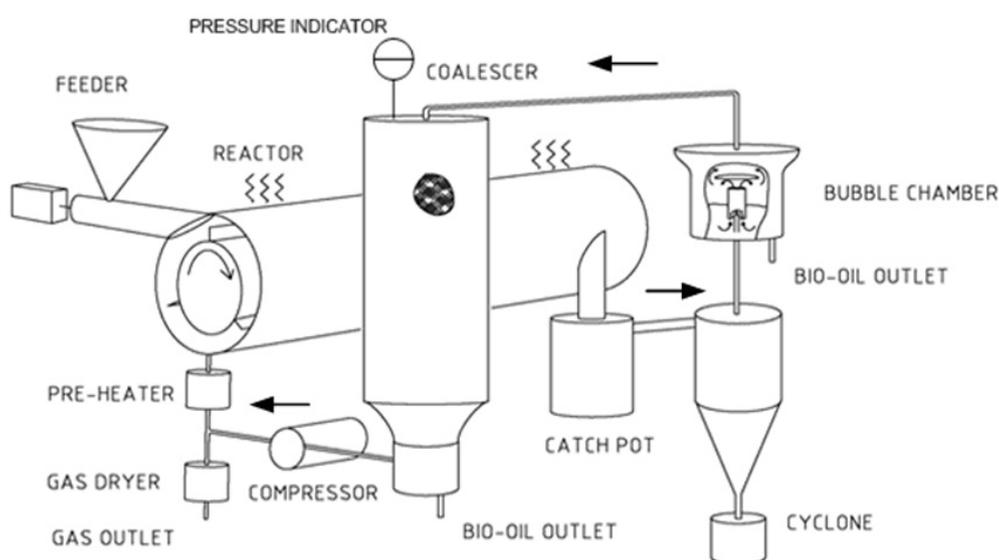
Figure 2.1. Schematic diagram of the ablative pyrolysis bench scale reactor system [11, 12].

2.2.3 Higher heating value and energy distribution in pyrolysis products

The higher heating value (HHV) of bio-oil and char was measured by a bomb calorimeter IKA C200 using the standard DIN 51900-1, whereas the heating value of the pyrolysis gas was calculated by difference [22].

$$HHV_{gas} = \frac{HHV_{biomass} - \left(HHV_{oil} \times Y_{oil}\right) - \left(HHV_{char} \times Y_{char}\right)}{Y_{gas}}$$

where HHV represents the higher heating value in J/g and Y is the yield of each pyrolysis product. The energy distribution of the pyrolysis products were calculated as:

$$\% \, Energy \, distribution = \frac{HHV_a \times Y_a}{HHV_{biomass}} \times 100$$

Where a is the pyrolysis products (bio-oil, char and gas).

2.3   Results

2.3.1   Mass Balance

Figure 2.2 shows an example of mass balance closures of the pyrolysis products distribution from as received straw at different reactor temperatures. The pyrolysis products are char, gas and bio-oil and the latter is subdivided into the liquid organics and produced water. The product yields were determined on a dry ash free (daf) basis, taking into account the ash and moisture content of the feedstock. Therefore, the water yields presented is the water generated by the pyrolysis reaction excluding the water input of the feed. The overall mass balance closures for all investigated straw moisture levels were between 89 and 103 wt. %, in the temperature range of 475-575 °C.
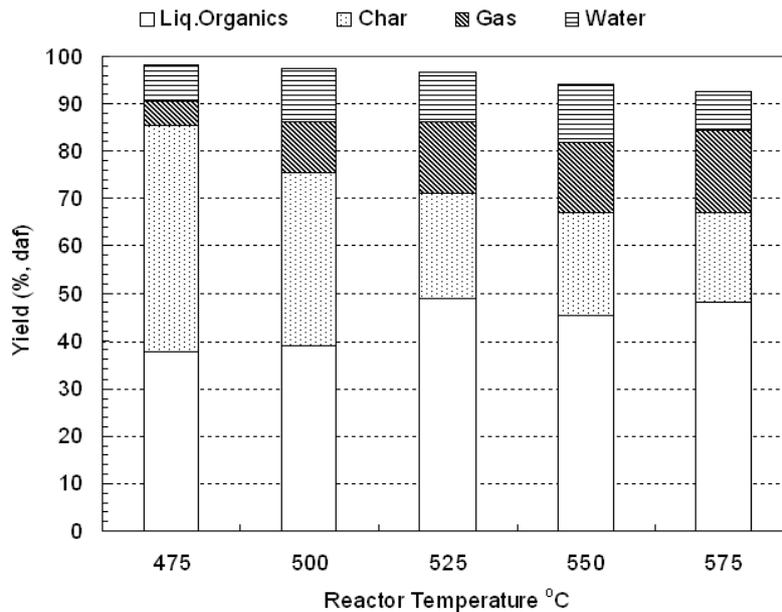
Figure 2.2 Overall mass balance closures for as received straw (6.2 wt. % water).

2.3.2   Bio-oil

Figure 2.3 presents the obtained bio-oil yields as a function of feedstock moisture contents and pyrolysis temperatures. The presented bio-oil yields are the liquid organics plus the water generated during the pyrolysis process. The bio-oil yield obtained is in the range of 40-60 wt. %, for all straws within the investigated temperatures. Maximum bio-oil yields of approximately 60 wt. % for all straw

moisture levels occurred at the temperature range from 525 °C to 550 °C. The yields of bio-oil produced from another type of wheat straw (moisture content: 5.8 wt. % and ash content: 6.8 % db) done by previous study [11] was around 50-57 wt. % within the similar temperature range. The maximum bio-oil of approximately 57 wt. % also occurred around 525 °C. The level of bio-oil yields obtained is comparable to the current results.

Further increasing of reactor temperatures, cause a lower of bio-oil yield due to conversion of tar to gases. It can be seen on Figure 2.3 that similar bio-oil yields were obtained with different straw moisture content.
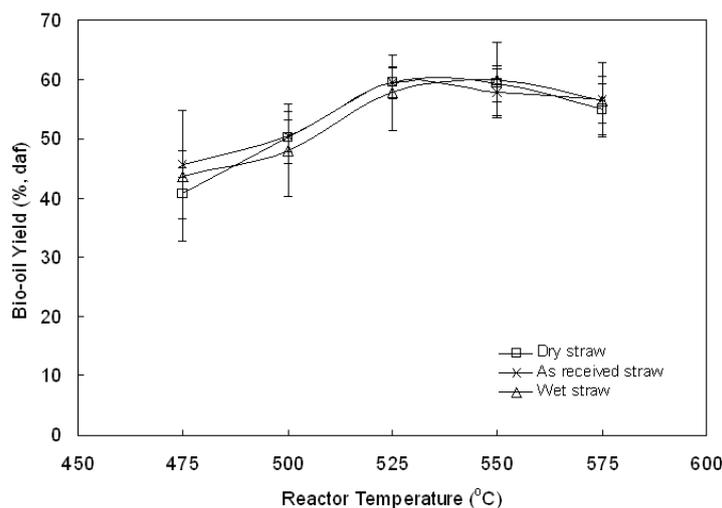
Figure 2.3. Total bio-oil yields as a function of pyrolysis temperature.

2.3.3   Water content

The water content in the bio-oil was analyzed. The water in the bio-oil originates from the original moisture in the feedstock and dehydration reactions occurring during the pyrolysis process [23]. It is reported in many studies that the water content in bio-oil varies over a wide range 15 – 35 wt. % (dry basis), depending on the feedstock and process conditions [24, 25]. However, for rice straw, the water content measured in the bio-oil is rather high, typically in between 50-60 wt. % (dry basis) [26]. In this work the analysis of water content in bio-oil seen in Figure 2.4 showed that in wet straw oil, the water content was 33-44 wt. %, 24-32 wt. % in as received straw oil and 19-22 wt. % in dry straw oil. If no water were formed during the pyrolysis process, the wet straw oil would contain 24-35 wt. % water and the dry straw straw oil would contain 10-13 wt. % water. It can be concluded that the water in bio-oil mostly originates from the original moisture in feedstock. Therefore it is an advantage to dry the biomass before pyrolysis, to less than 10 % water in order to minimize the water in the bio-oil.
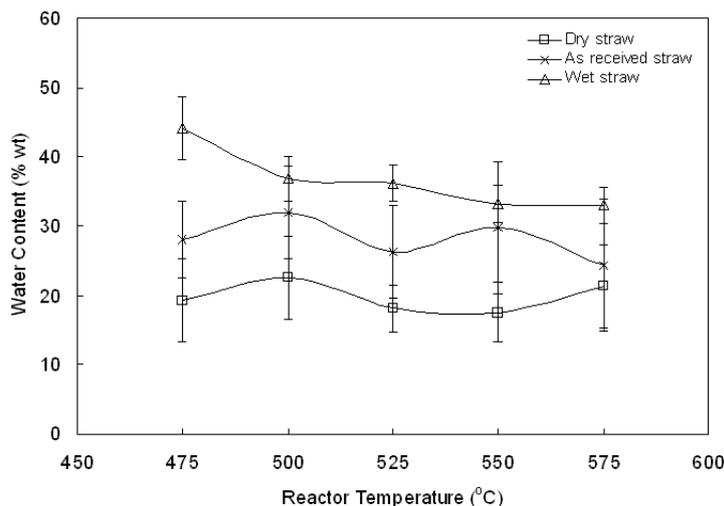
Figure 2.4. Water content in bio-oil as a function of temperature.

2.3.4   Liquid Organics Yield

Figure 2.5 shows the liquid organics produced at different straw moisture contents. In the temperature range of 475-575 °C, the liquid organics yields were similar at all straw moisture levels. The maximum liquid organic yields appear at 525 °C to 550 °C and the maximum yields were approximately 50 wt. %. At these temperatures also, approximately 40 wt. % of liquid organic yields was produced using another type of wheat straw (moisture content: 5.8 wt. %) in a PCR unit [12]. The difference is due to the different characteristics of feedstock used but the pyrolysis operating conditions remains the same. The current study shows that the effect of straw moisture on the liquid organics distribution is insignificant and the yield remains constant at each reactor temperature. These results are in line with experimental results reported by Westerhof *et al.*, [18]. In their work, they pyrolysed the pine wood with different moisture contents ranged between 0 wt. % to 20 wt. %, in a fluidized bed reactor by applying the flash pyrolysis concept and an approximately 46 wt. % of liquid organics yields (on a dry feedstock basis) was obtained for all wood moisture levels at a reactor temperature of 480 °C [18].

2.3.5   Char Yield

As seen in Figure 2.6, a decreasing char yield with temperature is observed for all straw moisture levels, with a minimum char yield of approximately 18 wt. % at 575 °C. A significant difference in char yield for the different straw moisture levels was only observed at 475 °C. The maximum char yields were observed at 475 °C; 41 wt. % (dry straw), 47 wt. % (as received straw) and 51 wt. % (wet straw). The high char yield with high straw moisture at 475 °C could be explained by a slow particle surface temperature rise because of water evaporation. The low particle heating rate cause an increased char yield.
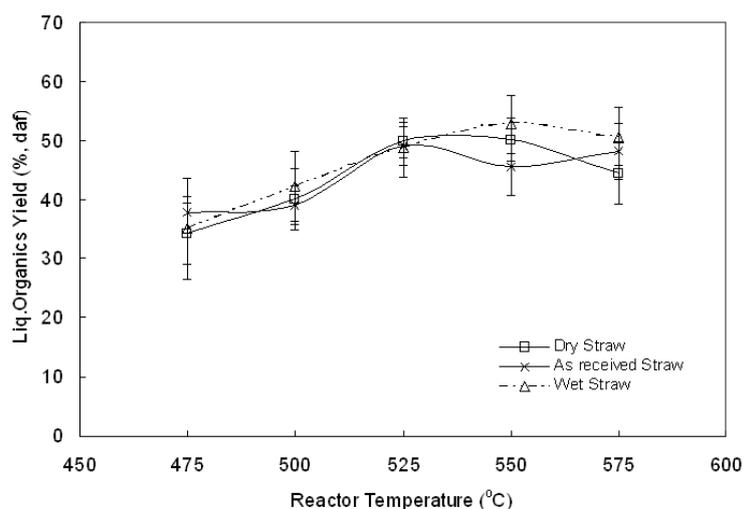
Figure 2.5. Effect of straw moisture content and reactor temperature on the liquid organics yield.

In addition, at a lower temperature, the char formation is favoured due to the dehydration reactions of cellulose is dominant [27]. At temperatures below 300 °C, depolymerization, the elimination of water (dehydration), rearrangement and formation of carboxyl and carbonyl groups, evolution of CO and CO_2, development of free radicals and condensation to char occur [23, 27]. At higher reaction temperatures a decreased char and an increased liquid organics yield is observed. This is probably due to that at high temperatures, cellulose depolymerizes rapidly producing levoglucosan, which is a tar component [23]. In addition, the time for dehydration reaction to take place is much shorter at high temperatures and high heating rates which result in more an unstable material left for depolymerization to primary volatiles and therefore lower final char yields [28].
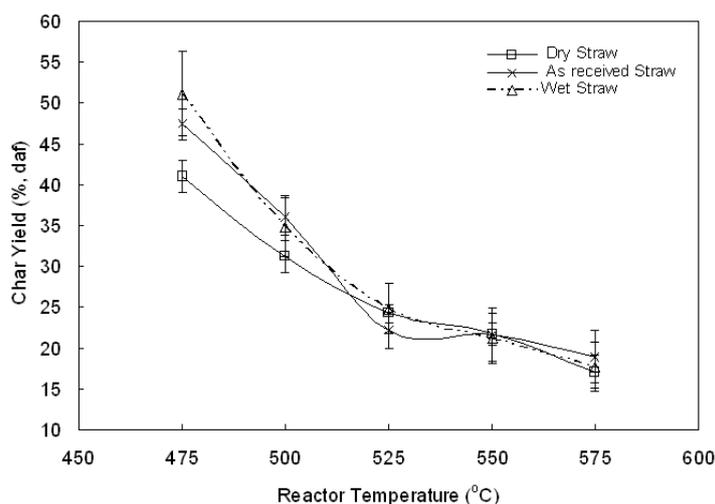
Figure 2.6. Effect of straw moisture content and reactor temperature on the char yield.

2.3.6 Pyrolysis Gas Yield

Generally the temperature has a dominant effect on the pyrolysis gas yield as seen in Figure 2.7. The gas yield increases as temperature increase for all straw moisture levels. The high gas yield at high temperatures are causes by the pyrolysis oil vapor being converted into gases through secondary cracking [29-31]. However, the straw moisture content does not influence the formation of the gases. The current results are in good agreement with previous study [16] although they used a woodex material in a batch fluid-bed reactor at a heating rate of 300 °C/min. In the present work, the gas yields obtained are in the range of 5-20 wt. % for all straw types and it can be concluded that the gas formation was not affected by the presence of fuel moisture contents.
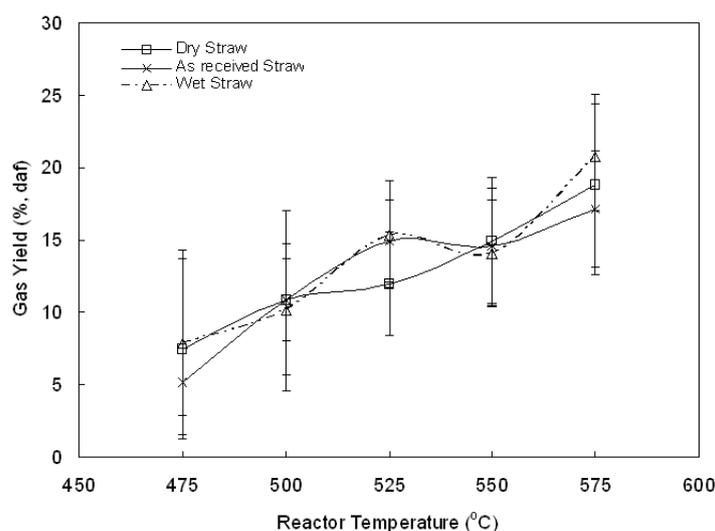
Figure 2.7. Effect of straw moisture content and reactor temperature on the pyrolysis gas yield.

2.3.7 Water Yield

The water yield discussed here is referring to the water that formed from the dehydration reactions throughout the pyrolysis process. The water produced by reaction for all straw moisture levels was measured as shown in Figure 2.8. The curves showed that the change in feedstock moisture content and reactor temperature has no significant effect on the water yield, and that a mean yield of 9 wt. % water was produced. The similar water yield of approximately 9.9 wt. % was obtained from forest-residue pyrolysis done at the VTT laboratory [32].
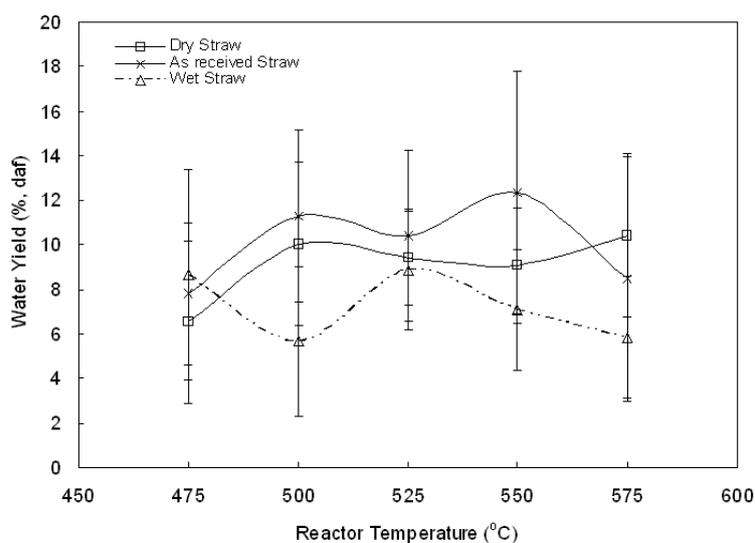
Figure 2.8. Effect of straw moisture content and reactor temperature on the produced water yield.

2.3.8 Gas Molecular Weight

Figure 2.9 shows the effect of straw moisture contents and reactor temperatures on the pyrolysis gas molecular weight. It is seen that the gas molecular weight was not significantly affected by straw moisture content or temperature. The gas molecular weight was in the range of 31-35 g/mol. Bech et al. 2007 found the pyrolysis gas molecular weight from wheat straw to be approximately 37 g/mol and not affected by reactor temperatures [12, 21]. It was slightly higher probably due to the different characteristic of the used wheat straw.
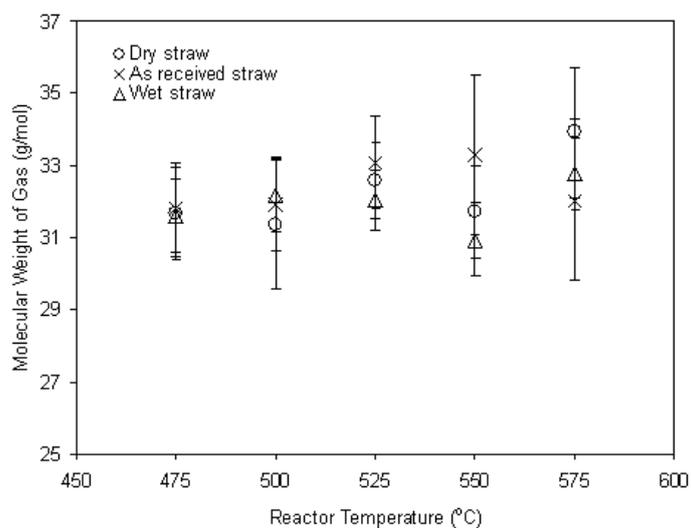
Figure 2.9. Effect of feedstock moisture content and reactor temperature on the pyrolysis gas molecular weight.

2.3.9 Gas residence time

The gas residence times in the reactor was calculated based on the performance curve of the positive displacement gas pump and the yield data obtained from the experiments. The molecular weight of tar was taken to be 350 g/mol [11, 33] and it was assumed that the straw was instantaneously pyrolyzed when subjected to the reactor entrance. It was found that the gas residence time only changed a little with varying straw moisture content as seen in Figure 2.10. In this experimental series, the hot gas residence time varied between 0.19 and 0.23 s. It can be concluded that within this range the yields of products at different moisture content of feedstock were probably not affected by the small gas residence time changes seen in Figure 2.10.
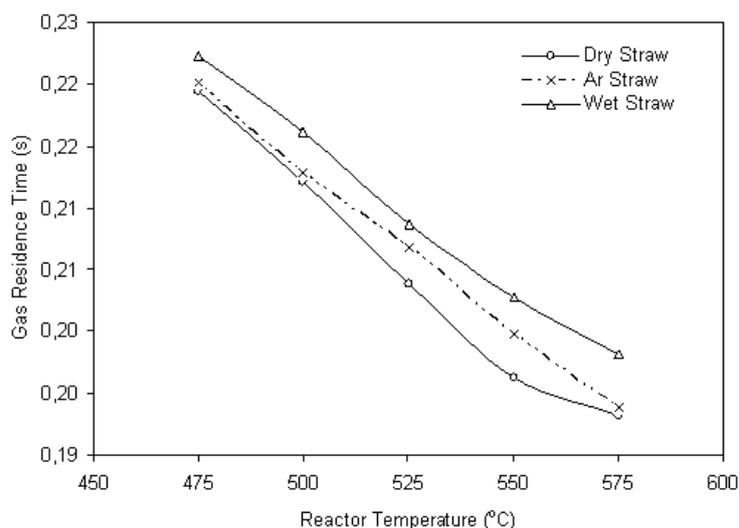
Figure 2.10. Effect of straw moisture content and reactor temperature on the gas residence times.

2.3.10 Heating values and energy distribution of the pyrolysis products

The higher heating value of bio-oil and char were determined and their energy distributions were calculated as shown in Figure 2.11. Bio-oils have a medium heating value in the range of 15-17 MJ/kg (as produced or wet basis), approximately half that of conventional fuel such as gasoline, kerosene and diesel [34]. However, the heating value of bio-oil is very close to those of methanol and ethanol [34]. Char has a higher heating value of about 19-21 MJ/kg (as produced) and it is comparable with lignite and bituminous coal [34]. The energy distribution of bio-oil, char and gas for all straw types were around 56-69 %, 24-33%, 2-19 %, respectively, as seen in Figure 2.11. At higher temperatures, the energy content of bio-oil and char reduce while the energy content in the pyrolysis gas increases. It is seen that an increased gas heating content can be obtained at high temperatures. This is important if the gas shall be used to supply energy for the pyrolysis process.
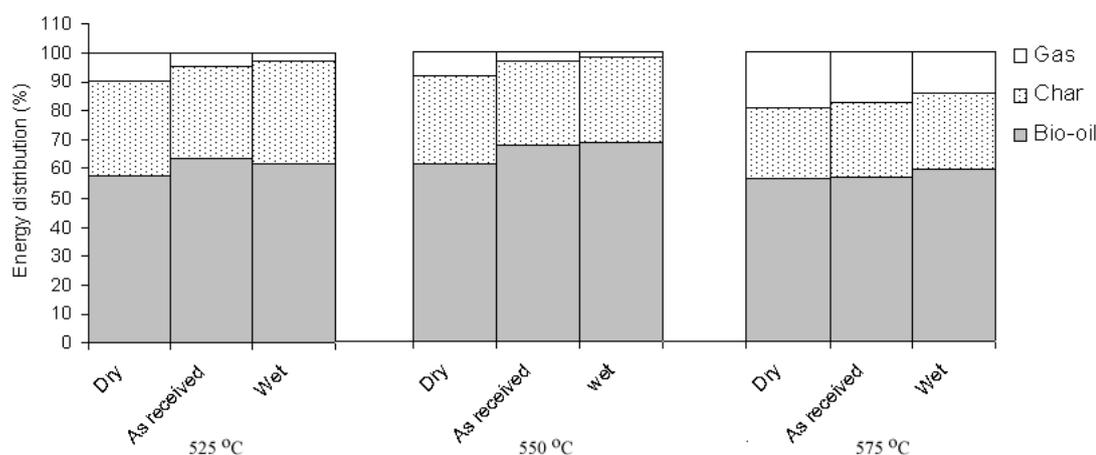
Figure 2.11. The percentage of energy distributions of pyrolysis products from different straw moisture content as a function of temperature.

2.4   Discussions and Conclusions

The influence of straw moisture content and reactor temperature on the flash pyrolysis product yield has been experimentally investigated. In the current study the fraction of bio-oil, char and gases produced from pyrolysis of straw were in the range of 40-60 wt. %, 18-50 wt. % and 5-22 wt. %, respectively, regardless of the straw moisture levels. The straw bio-oil yields obtained are slightly lower than the 50-75 wt. % that reported in the literatures for woody material [4, 5]. However the yield is reasonable due to the different feedstocks used. The optimal reaction temperature for the production of bio-oil was around 525 °C to 550 °C for all straw moisture contents. The presence of moisture in the feedstock has shown no significant effect on the pyrolysis product distribution. The liquid organics yields were similar for all straw types and the yields were almost constant at each reactor temperature. The similar observation was discovered by another study [18]. The gas and water yields were neither affected by the feedstock moisture level. The effect of straw moisture on char yield only can be observed at the lower temperature, 475 °C. At this temperature, wet straw produces the highest char yield followed by as received straw and finally dry straw. Gray *et al*., [16] and Westerhof et al. [18] also found that more moisture in the feedstock results in an increased char yield.

Apparently, the pyrolysis temperatures have a dominant effect on the pyrolysis product yield. In general, the yield of liquid organics increased with increasing pyrolysis temperature from 475 °C to 550 °C and then decreases at higher temperatures. The gas yield kept increasing with reactor temperature due to secondary cracking takes place at higher temperatures, which in turn lead to a reduction of the liquid organics yield and an increased production of light hydrocarbon gases. There were no affect on produced water yield with increasing temperatures.

Regardless of straw moisture contents, the maximum liquid organics yield occurred around 525 °C to 550 °C with the yield ranging from 45 to 53 wt. % (Figure

2.5). The yields of liquid organics were comparable for all straw moisture levels at each reactor temperatures. The yields of reaction water and pyrolysis gas also were not affected by the moisture content of the feedstock.

Overall, the change in straw moisture content has no significant effect on the distribution of pyrolysis product yields except for char.

The water content in bio-oil increases with increasing of straw moisture content. The water content in dry straw oil was 19-22 wt. %, 24-32 wt. % for as received straw oil and 33-44 wt. % for wet straw oil. It can be concluded that the water in bio-oil mostly originates from the original moisture in feedstock. The high water content in bio-oil may cause a phase separation and lowers the heating value of the oil. The presence of water in bio-oil with higher amount also limits its utilization as a fuel, especially in combustion, as it reduces the combustion rates, delay the ignition and lower the adiabatic flame temperatures during combustion. Therefore it is an advantage to use a relatively dry feedstock in order to have a better quality of the bio-oil.

Acknowledgements

References

[1] Sipila, K., Kuoppala, E., Fagernaes, L. (1998). Characterization of biomass–based flash pyrolysis oils. *Biomass & Bioenergy*. 14, 103-13.

[2] Putun, A. E. (2002). Biomass to bio-oil via fast pyrolysis of cotton straw and stalk. *Energy Sources*. 24, 275-85.

[3] Acikgoz, C., Kockar, A. M. (2007). Flash pyrolysis of Linseed (Linum usitatissimum L.) for production of liquid fuels. *Journal of Analytical and Applied Pyrolysis*. 78, 406-412.

[4] Mohan, D., Charles, U., Pittman, J., Philip, H. S. (2006). Pyrolysis of wood/biomass for bio-oil: Critical Review. *Energy & Fuels*. 20, 848-889.

[5] IEA – International Energy Agency (2006), http://www.ieabioenergy.com

[6] Gaunt, J. L., Lehmann, L. (2008). Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production. *Environ. Sci. Techno*. 42, 4152-4158.

[7] Mathews, J. A. (2008). Carbon-negative biofuels. *Energy Policy*. 26, 940-945.

[8] Sanchez, M. E., Lindao, E., Margaleff, D., Martinez, O., Maron, A. (2009). Pyrolysis of agricultural residues from rape and sunflowers: production and characterization of bio-fuels and biochar soil management. *J. Anal. Appl. Pyrolysis*. 85, 142-144.

[9] Zheng, J. L. (2007). Bio-oil from fast pyrolysis of rice husk: yields and related properties and improvement of the pyrolysis system. *J. Anal. Appl. Pyrolysis*. 80, 30-35.

[10] Bridgwater, A. V., Peacocke, G. V. C. (2000). Fast pyrolysis process for biomass. *Renewable & Sustainable Energy Reviews*. 4, 1-73.

[11] Bech, N. (2008). PhD Thesis. *In situ flash pyrolysis of straw*. Technical University of Denmark, Denmark.

[12] Bech, N., Larsen, M. B., Jensen, P. A, Dam-Johansen, K. (2009). Modelling solid-convective flash pyrolysis of straw and wood in the pyrolysis centrifuge reactor. *Biomass & Bioenergy*. 33, 999-1011.

[13] Antal, M. J. Effects of reactor severity on the gas-phase pyrolysis of cellulose- and kraft lignin-derived volatile matter, Ind Eng Prod Res Dev 1983; 22:366–75.

[14] Antal, M. J. (1985). A review of the vapor phase pyrolysis of biomass derived volatile matter. In: Overend, R. P., Milne, T. A., Mudge, L. K. (eds.). *Fundamentals of biomass thermochemical conversion*. London: Elsevier. 511-537.

[15] Bridgwater, A. V. (1994). Catalysis in thermal biomass conversion. *Applied Catalysis*. 116, 5-47.

[16] Gray, M. R., Corcoran, W. H., Gavalas, G. R. (1985). Pyrolysis of a wood – derived material. Effect of moisture and ash content. *Ind. Eng. Chem. Process Des*. 24, 646-651.

[17] Shafizadeh, F. (1968). Pyrolysis and combustion of cellulose materials. *Adv. Carbohydr. Chem*. 23, 419.

[18] Westerhof, R. J. M., Kuipers, N. J. M, Kersten, S. R. A., Van Swaaij, W. P. M. (2007). Controlling the water content of biomass fast pyrolysis oil. *Ind. Eng. Chem. Res*. 46, 9238-9247.

[19] Demirbas, A. (2004). Effect of initial moisture content on the yields of oily products from pyrolysis of biomass. *Journal of Analytical and Applied Pyrolysis*. 71, 803-815.

[20] Bech, N., Dam-Johansen, K., Jensen, P. A. (2006). Pyrolysis method and apparatus. PCT Application. WO 2006/117005.

[21] Bech, N., Jensen, P. A., Dam-Johansen, K. (2007). Ablative flash pyrolysis of straw and wood: Bench-scale results. In: Proc 15th European Biomass Conference and Exhibition, Berlin, 7-11 May 2007.

[22] Raveendran, K., Ganesh, A. (1996). Heating value of biomass and biomass pyrolysis products. *Fuel*. 75,1715-1720.

[23] Balat, M. (2008). Mechanism of thermochemical biomass conversion processes. Part 1: Reactions of pyrolysis. *Energy Sources*. 30, 620-635.

[24] Bridgwater, A. V. (2004). Biomass fast pyrolysis process for biomass. *Thermal Science*. 8, 21-49.

[25] Elliott, D. (1994). Water, alkali and char in flash pyrolysis oils. *Biomass & Bioenergy*. 7, 179-185.

[26] Park, Y. K. , Jeon, J. K. , Kim, S., Kim, J. S. (2004). Bio-oil from rice straw by pyrolysis using fluidized bed and char removal system. *Fuel Chem*. 49, 801.

[27]   Shafizadeh, F. (1982). Introduction to pyrolysis of biomass. *Journal of Analytical and Applied Pyrolysis*. 3, 283-305.

[28]   Zanzi, R. (2001). PhD Thesis. *Pyrolysis of biomass*. Royal Institute of Technology, KTH, Stockholm, Sweden.

[29]   Radlein, D. (2002). In fast pyrolysis of biomass: A Handbook, Vol.2; Bridgwater AV, editor. Newbury, UK: CPL Press. 165.

[30]   Nuun, T. R., Howard, J. B., Longwell, J. P. I., Peters, W. A. (1985). Product compositions and kinetics in the rapid pyrolysis of sweet gum hardwood. *Ind. Eng. Chem. Process Res. Dev*. 24, 836-844.

[31]   Scott, D. S., Piskorz, J., Bergougnou, M. A., Graham, R., Overend, R. P. (1988). The role of temperature in the fast pyrolysis of cellulose and wood. *Ind. Eng. Chem. Res*. 27, 8-15.

[32]   Oasmaa, A., Sipila, K., Solantausta, Y., Kuoppala, E. (2005). Quality improvement of pyrolysis liquid: effect of light volatiles on the stability of pyrolysis liquids. *Energy & Fuels*. 6, 2556-2561.

[33]   Diebold, J. P. (1985). Master Thesis. *The cracking kinetics of depolymerised biomass vapors in a continuous, tubular reactor*. Colorado School of Mines: Golden, CO.

[34]   Rose, J. W., Cooper, J. R. Technical data on fuel. In: 7th edn, British National Comitte, World energy conference, London.

CHAPTER 3

Characterization of Flash Pyrolysis Products of Wheat Straw, Rice Husk and Pine Wood

Abstract

The objective of this work is to investigate the yield of pyrolysis products and the composition of bio-oils and chars from different biomasses. Wheat straw, rice husk and pine wood, with ash contents of 6.0, 13.6 and 0.5 wt. % (db), respectively, were pyrolyzed using a pyrolysis centrifuge reactor (PCR) at reactor temperatures ranging from 475 to 575 ° C. The wheat straw contains the highest potassium content (1.53 wt. %), whereas the pine wood has the lowest potassium content (0.04 wt. %). The maximum liquid organics yield temperature was approximately 525 °C for wheat straw and approximately 550 °C for both rice husk and pine wood. At the optimum temperatures, the liquid organics yield of 49, 52 and 58 wt. % (dry-ash free) respectively were obtained for wheat straw, rice husk and pine wood. It was also found that the gas + reaction water formation yield was highest from the wheat straw. Increasing biomass alkali content caused an increased feedstock conversion at low temperature, a lower maximum liquid organic yield temperature and a lower maximum liquid organics yield. In addition, the chemical compositions of the bio-oils and the chars of the investigated feedstocks were analyzed.

Keywords: Flash pyrolysis; biomass; ash; alkali elements; bio-oil; biochar.

3.1   Introduction

At present, biomass-derived bio-oil has received much attention due to depletion of the resources of fossil fuels [1-3] coupled with the advantages of bio-oil itself, which is considered as CO_2 neutral. In addition biomass-derived bio-oil has a negligible sulphur, nitrogen and metal content, and thus provides a biomass based fuel with a low ash content [4].

By flash pyrolysis, biomass can be converted into oil with biochar and gas as by-products. The flash pyrolysis process typically applies operation conditions at a high heating rate (> 250 K/s), moderate temperatures (400-600 °C), and a short gas residence time (< 1 s) and thus allow the process to produce about 50-75 wt. % of liquid bio-oil (mixture of organics and water), 15-25 wt. % of solid char and 10-25 wt. % of non-condensable gases [5]. The water content of the bio-oil is usually limited to about 15-35 wt. % [6, 7].

Flash pyrolysis of biomass can produce three valuable products, which can be used for energy purposes and chemicals production [6]. Bio-oil can be used for heat and power production. Its volumetric energy density is approximately four to five times higher than that of the original biomass and use of the oil simplify handling, transportation and storage. The utilization of bio-oil as a fuel especially in static combustion plants such as boilers and turbines has been tested and documented elsewhere [8-15]. Biochar from flash pyrolysis has a great potential as soil amendment as it can enhance the soil quality and plant growth by retaining nutrients and increasing the soil water holding capacity. Additionally the char may apparently retain the carbon in soil for many years [16]. The pyrolysis gas can be used to generate electricity or provide heat for the pyrolysis process.

Biomass primarily consists of cellulose, hemicellulose, lignin and minor amounts of extractives and inorganic compounds. The inorganic compounds contain different elements, such as sodium, magnesium, silicium, calcium and potassium [17]. The alkali elements potassium and sodium can act as catalysts that alter the rate of biomass degradation during pyrolysis. Because of this alteration, the yield of the pyrolysis products is influenced by the ash composition. The biomass ash content varies, for example does wood usually contain < 1 wt. % whereas rice husks and straw contain up to 25 wt. % [18]. Generally biomass ash consists of K, Na, Mg, Ca, Si, Cl and a small amount of P, S, Fe, Al and Mn and these elements can be present as silicates, oxides, carbonates, sulfates, chlorides and phosphates or bound to the organic matrix.

The effect of alkali elements and other inorganic elements present in the biomass on the pyrolysis process and the products distribution has been investigated by several researchers [17-20]. Pyrolysis experiments on pure cellulose, hemicelluloses, lignin and biomass as a whole sample with added artificial alkali elements was carried out in order to get an understanding of catalytic processes. Besides, the effect of removing metals by acid washing and water washing (demineralization) also has been studied [21-24].

Of all the metals present in biomass, potassium has a pronounced catalytic effect on the pyrolysis reactions promoting the char and gas formation at the expense of the tar yield [21, 25-28]. The catalytical effect of potassium on pyrolysis product distributions has been investigated [21, 25-28]. Jensen *et al.*, [21] performed pyrolysis of Danish wheat straw and washed wheat straw using a TG-FTIR at a heating rate of 10 °C/min, and for comparison, 2 wt. % KCl was added to the washed wheat straw, in order to study the influence of potassium on the pyrolysis behaviour. The char yield decreased from 22 % (wt., daf) for the raw straw to 12 % (wt., daf) for the washed straw. Compared to the washed straw, the amount of gases produced such as CO, CO_2, H_2O, CH_4 and CH_3OH was higher for the raw straw and the estimated tar yield was lowest for the raw straw and highest for the washed straw, whereas all the pyrolysis product yields from the washed straw sample treated with KCl was in the middle of the other two cases. The observed temperature for the maximum rate of pyrolysis degradation varied. Thus, washed straw added with 2 wt. % KCl had a maximum pyrolysis rate at 633 K, which was between the levels observed by raw straw (615 K) and washed straw at 670 K. The differences observed in pyrolysis behaviour between the raw straw and the washed straw treated with KCl suggested that some of the ash forming elements such as Ca were removed when preparing the

washed straw and KCl was probably not distributed evenly to the washed straw sample with KCl addition. Similar observations about an increasing char and gas yield at the expense of the liquid oil yield together with the lowering of the temperature of the onset of thermal decomposition of biopolymers due to the presence of alkali elements during the pyrolysis of wood [20, 22, 27] and palm oil waste [23] have been reported.

Recently, an experimental study on cellulose pyrolysis [26] at a temperature of 883 K showed that the addition of 0.8 % wt. K$^+$ (potassium salt ion) to the cellulose resulted in a reduction of levoglucosan formation from 71.8 % to 14 %, an increased formation of hydroxyacetaldehyde and acetol from 6.2 % and 1.7 % to 8.7 % and 2.9 % respectively, and at the same time an increased of the reaction water yield from 15.7 % to 26 % was observed.

Hydroxyacetaldehyde is found to be the second product after levoglucosan which is the principal pyrolysis products of cellulose. Both levoglucosan and hydroxyacetaldehyde are formed by the decomposition of active cellulose in a parallel mode. It was suggested [29] that the formation of levoglucosan from pyrolysis of cellulose results from the homolytic process (non-catalytic) which is directly obtained from the depolymerisation reaction, while hydroxyacetaldehyde is formed via a heterolytic process (catalytic) [24]. It means that the presence of mineral matters in biomass promotes the formation of hydroxyacetaldehyde.

In a recent study [25], biomass cell-wall constituents such a cellulose, xylan (hemicelluloses), chlorogenic acid (nearly a similar structure to lignin polymer units) and levoglucosan were pyrolysed as model compounds using TGA and pyrolysis-gas chromatography-mass spectrometry (PY-GC-MS) in order to gain some insight on how potassium changes the pyrolysis reactions. The addition of potassium into the cellulose, lignin and levoglucosan lowered the peak maximum conversion rate temperatures, this effect, however, was not seen for the xylan. The analytical pyrolysis tests showed that the pyrolysis of cellulose produced 5 anhydrosugar derivatives and one of them was levoglucosan which was the major product, and by addition of potassium into cellulose, further decomposition of levoglucosan and other anhydrosugars to a lower molecular weight compounds such as acetic acid, propanoic acid and 1-hydroxy-2-butanone was observed. The pyrolysis of levoglucosan samples produced anhydrosugars including levoglucosan, furfural, propanol and 2(5H)–furanone as major pyrlolysis products while the pyrolysis of levoglucosan added with potassium favoured the formation of cyclopentene derivatives and further cracking of levoglusan to dianhydrosugars was seen, and phenol and dimethyl-phenol derivatives was also detected.

Fahmi and co-workers [30] investigated the influence of lignin content and inorganic species in biomass on the pyrolysis product yields using both a TGA and a laboratory scale pyrolysis reactor. The pyrolysis experiment in the laboratory reactor showed that the total liquid yield (% wt., db) was proportional to the lignin content in biomass. An increase of the total liquid and organics yield as the fuel ash decreased was also seen. They however, discovered that the pyrolysis yields were more affected by the ash content than the lignin content. On the other hand, the quality of the liquid oil was reduced as the lignin content in biomass increased because of an increased of higher molecular weight compounds.

Numerous studies on the influence of mineral matters on pyrolysis products has been performed and documented [20-30] and most of the experimental works were conducted a low heating rates using a thermogravimetric analyzer (TGA) as it is a fundamental method to reveal the pyrolysis behaviour. However, using TGA to study the influence of alkali elements on the biomass pyrolysis is insufficient to understanding the flash pyrolysis. TGA heating rate is much lower (< 50 ºC/s) than that of flash pyrolysis which is usually above 200 ºC/s and thus affected the final products, for example the char formation is favoured at a lower heating rate and at the same time it is also affected by the presence of alkali elements. Furthermore, most flash pyrolysis studies have concentrated on woody biomass and only few studies are published on non-woody material such as grass [17], sunflower stem [31], almond shells [32] and wheat straw [21, 33, 34].

The objective of this work is to investigate the influence of different biomass types on the yield of the pyrolysis products (bio-oil, biochar and gas), and on the compositions of bio-oil and biochar. Different biomasses with different alkali contents were pyrolyzed using a pyrolysis centrifuge reactor at different reactor temperatures. The reactor temperatures were optimized in order to maximize the liquid organics yield for these different feedstocks. Then, the influence of the alkali content was investigated at these optimum reactor temperatures. It is important to understand how the naturally present minerals content in different feedstock will influence the flash pyrolysis process and the products properties.

3.2   Experimental

3.2.1   Biomass

The wheat straw and pine wood were obtained in Denmark, whereas rice husk was supplied by BERNAS Company in Malaysia. All biomass feedstocks were milled and sieve to a particle size of < 1.4 mm. The proximate elemental and carbohydrate analyses of all feedstocks used for pyrolysis are shown in Table 3.1. Biomass is primarily composed of cellulose, hemicelluloses and lignin. Pine wood [37] contains a larger fraction of cellulose (42 % dry basis) and lignin (30 % dry basis) compared to wheat straw and rice husk as can been seen in Table 3.1. Rice husk contains higher amounts of ash (13.6 % dry basis) and lower content of volatile matter (68.8 % dry basis), while pine wood has a low ash level (0.5 % dry basis) and a high volatile matter content (85 % dry basis). Wheat straw has an intermediate ash content (6.0 % dry basis) and volatile matter levels (74.7 % dry basis). The rice husk ash is primarily made of silica (≈ 85 %). However, the content of carbon, hydrogen and oxygen in these three biomasses are nearly similar to each other.

3.2.2   Pyrolysis

Pyrolysis experiments were carried out in a bench scale Pyrolysis Centrifuge Reactor (PCR) as shown in Figure 3.1. The reactor design has previously been reported in detail [33-36]. The PCR facility consists of a screw type feeder, reactor, condenser, coalescer and char separator. The principle of the process is to apply tangentially

feeding of solid biomass particles into the horizontally oriented Ø 82 x 200 mm tubular reactor. The centrifugal force created by the rotation of a three blade rotor keeps the particles sliding on the heated wall while passing through the reactor. The solid particles pyrolyze while moving down the reactor pipe and leaves suspended in the gas through the tangential outlet. Larger char particles were removed by a change-in-flow separator whereas fines were collected by a cyclone. Vapors were condensed in a direct water cooled condenser (bubble chamber) filled with previously produced bio-oil. Aerosols that were not retained by the condenser were collected in a coalescer filled with rockwool (mineral fibers).

Table 3.1.
Analysis of biomass feedstocks used for pyrolysis.

Analysis			Wheat Straw	Rice Husk	Pine Wood
Proximate	Moisture	% wt.	6.2	11.7	7.1
	VM	% db.	74.7	68.8	85
	Ash	% db.	6.0	13.6	0.5
	HHV	MJ/kg db.	18.8	17.4	20.5
	HHV	MJ/kg daf.	20.0	19.7	22.1
Ultimate	C	% daf.	49.4	50.9	49.9
	H	% daf.	6.2	6.25	6.30
	S	% daf.	0.2	0.1	<0.02
	N	% daf.	1.1	0.9	<0.1
	O (by difference)	% daf.	43.1	41.8	43.7
Ash Composition	Cl	% wt.	14.4	0.9	2.4
	Si	% wt.	22.0	47.9	14
	Al	% wt.	0.5	0.1	1.7
	Fe	% wt.	0.3	0.1	1.8
	Ca	% wt.	3.9	0.8	28.0
	Mg	% wt.	11.0	0.7	5.9
	Ti	% wt.	0.02	0.0068	0.1
	Na	% wt.	1.2	0.02	0.6
	K	% wt.	25.4	3.8	7.3
	P	% wt.	2.47	1.1	1.0
	O (by difference)	% wt.	18.9	44.7	37.4
Chemical	Cellulose	% db	40	36	42[37]
	Hemicellulose	% db	23	18	25[37]
	Lignin	% db	20	24	30[37]

daf: dry-ash free, db: dry basis

The oil collected from the coalescer contained a relatively high water content and it was less viscous as compared to the oil sample collected in the bubble chamber. A fraction of the gas was pumped to the preheater and heated to 400 °C before it was recirculated to the reactor in order to maintain a desired gas residence time (0.3-0.5 s) and avoid condensation of liquid products within the reactor. The amount of produced gas was measured by a temperature compensated gas meter and a sample was collected in a gas bag.

The biomass feedstock was fed to the reactor at a flow of 20-23 g/min and with an approximately gas reactor residence time of 0.3-0.5 s, and an initial solids heating rate of approximately 250-1000 °K/s [33]. The performed measurements

made it possible to determine the yield of char, gas, water and oil of the single experiments.
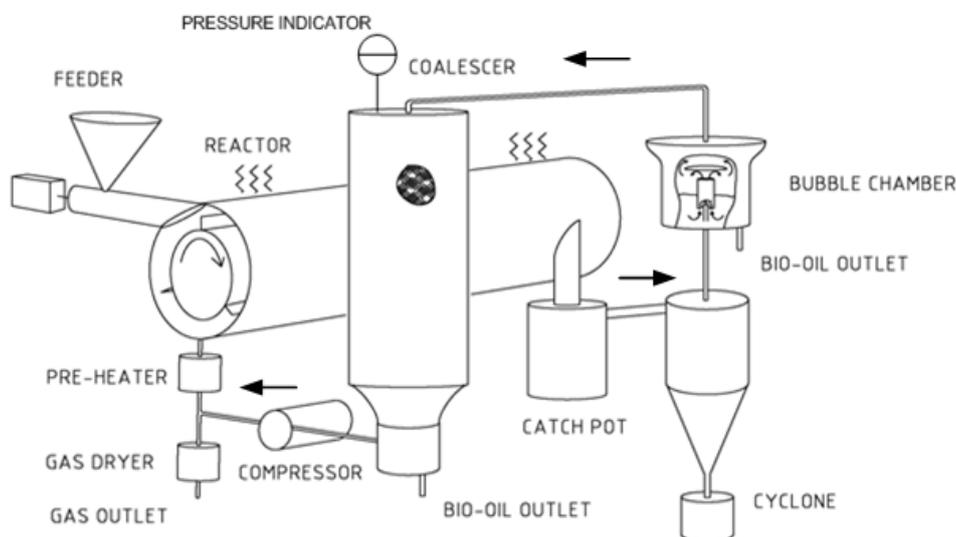
Figure 3.1. Schematic diagram of pyrolysis centrifuge reactor (PCR).

3.2.3 Product characterization

Bio-oils were analyzed as a 'whole bio-oil sample', prepared by mixing both the oil samples from the condenser and the coalescer. The chemical compositions of bio-oils were analyzed using gas chromatography-mass spectrometry (GC-MS). The samples were dissolved in THF (25 mg/mL) and analyzed by GC/MS using a Hewlett Pachard HP6890 gas chromatograph interfaced to a HP5973 Mass Selective Detector (Agilent, Denmark). 1μl samples were injected by a HP 7683 auto sampler (Agilent, Denmark) and introduced in split mode (1:20) at 250 ºC. The ion source and quadrupole rod temperature was 230 ºC and 150 ºC, respectively. The products were separated using a 0.32 mm i.d. x 30 m WCOT fused silica column coated with VF-23 ms at a thickness of 0.25 μm (Analytical, Denmark). The carrier gas was He at a flow rate of 1.2 mL/min. Separation of a wide range of products was achieved by using a temperature program from 70 ºC to 250 ºC. Full mass spectra were recorded every 0.5 s. Products were identified using NIST search engine, version 2.0 f. (Agilent, Denmark).

Only biochar collected from the cyclone were analyzed. The organic chemical composition of the biochar was determined by strong acid hydrolysis of the carbohydrates. The biochar samples were first treated with 72 % (w/w) H_2SO_4 at 30 °C for one hour and then the samples were hydrolyzed using 2.5 % (w/w) H_2SO_4 and autoclaved for one hour at a temperature of 121 °C. After that the hydrolysates were filtered and the Klason lignin content was determined as the ash free residue after hydrolysis. The composition of the carbohydrates (glucose, xylase, arabinose) found in the filtrate was analysed by a HPLC-system (Shimadzu) with a Rezex ROA column

at 63 °C using 4 mM H_2SO_4 as effluent and a flow rate of 0.6 ml/min. Detection was done by a refractive index detector (RI).

SEM-EDX (Scanning Electron Microscopy-Energy Dispersive X-ray) analyses were carried out on biochar and raw feedstocks, to examine their structure and the elements contained in the biochars.

The higher heating value (HHV) of bio-oils and biochars were measured by a bomb calorimeter IKA C200 instrument using the DIN 51900-1 standard. To make a calculated elementary analysis, the equation and method proposed by Bech and co-workers was employed [38, 39]. This method is only applicable for biomass that contains less than 2.0 wt. % Nitrogen and 1.0 wt. % Sulphur, however as seen in Table 3.1 this is the case for the investigated biomasses. The ash content in biochars was measured using an ash tracer method according to ASTM D 1102.

The water contents in bio-oil from wheat straw and pine wood were measured by using the refractive index method by using a Bellingham & Stanley Abbe 60 refractometer (estimation to within ± 0.0002) and a correlation developed by Bech and co-workers [36] as expressed by Eq. (1). The water content in rice husk bio-oil was measured using both the refractive index method and Karl Fisher titration. Using the Karl Fisher data as a reference the empirical correlation between bio-oil refractive index and water content in the rice husk oil shown in Figure 3.2 was developed. The empirical correlation is given by Eq. (2) where n_D is a refractive index number. The regression analysis predicts the intercepts 1.31 and 1.57, which is close to n_D for water (1.333) and substituted benzenes, respectively.

$$C_{water(straw,wood)} = 524(n_D)^2 - 1982(n_D) + 1804 \qquad R^2 = 0.9936 \qquad (1)$$

$$C_{water(rice\,husk)} = 695(n_D)^2 - 2385(n_D) + 2031 \qquad R^2 = 0.9970 \qquad (2)$$

By using the refractive index method, the 'whole bio-oil sample' usually gives an index reading in the range of 1.40 to 1.50 and by applying equations, the water contents can be determined.
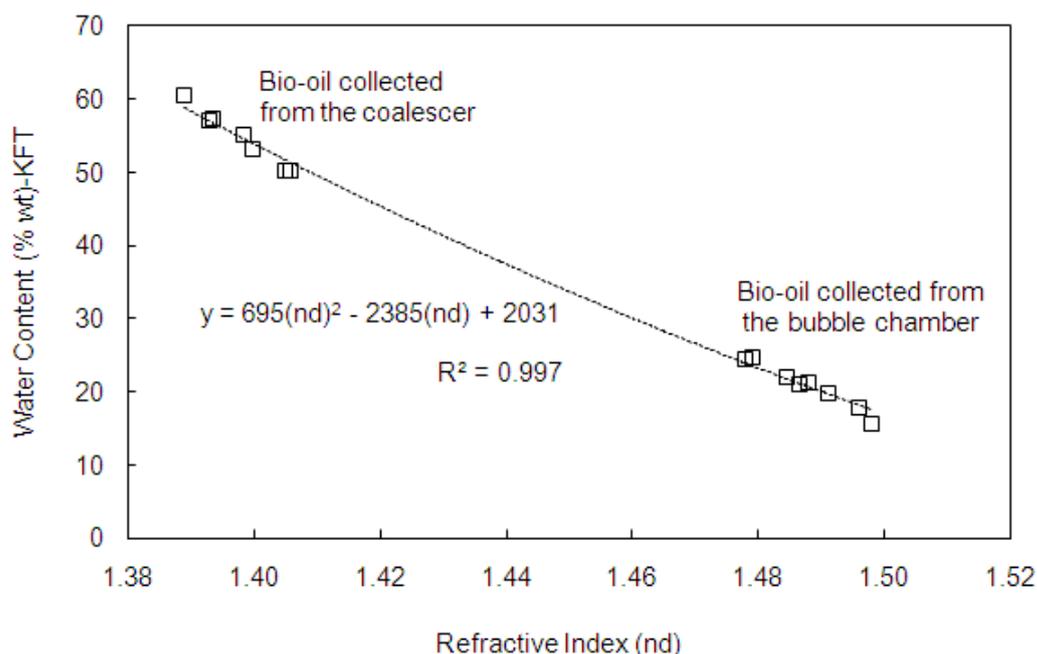
Figure 3.2. Water content determined by Karl-Fisher titration is used to make a correlation for the refractive index water content method used on rice husk bio-oil (organic/water mixture).

3.3   Results and Discussion

3.3.1   Biomass composition

Fuel analysis of all biomass feedstocks used is shown in Table 3.1. As can be seen, there are major differences between these three feedstocks, particularly the ash content. The ash content in wheat straw, rice husk and pine wood were 6.0, 13.6 and 0.50 wt. % (db) respectively. The biomass ash mainly comprises of K, Ca, Mg and Si. As shown in Figure 3.3, the wheat straw ash is dominated by K, Si and Cl, rice husk ash is characterized by a high Si content whereas pine wood ash reveals high concentrations of Ca. Especially, alkali elements are known to catalyze the pyrolysis process by changing the depolymerization mechanisms and leading to a change of pyrolysis products composition [40]. The ultimate analyses of the feed stocks are reasonably similar except that the wood sample has lower S and N contents. The volatile matter content of wood is higher than that of straw and rice husk and the higher heating value (based on the dry-ash free basis) of pine wood is the highest at 22.1 MJ/kg whereas the value for straw and rice husk respectively were 20.0 MJ/kg and 19.7 MJ/kg.
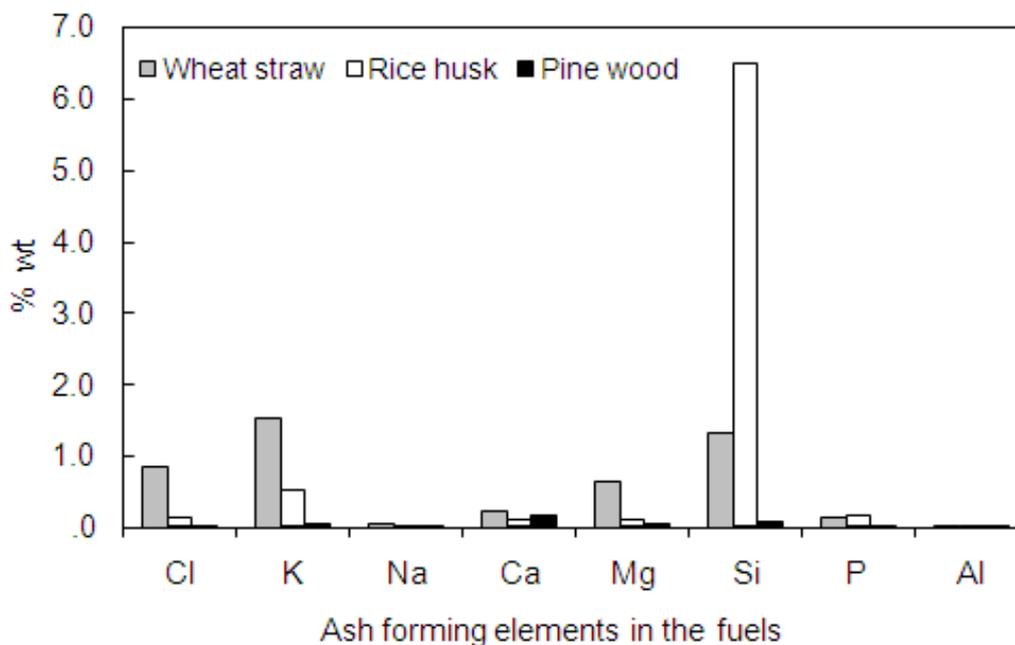
Figure 3.3. Concentration of the ash forming elements in the biomass (db, wt. %).

3.3.2   Bench scale pyrolysis results and products distribution

The behavior of biomass pyrolysis is depending on parameters such as temperature, biomass particle size, reactor configuration and types of biomass used. The latter is the main focus of this study. The yields of liquid organics, char and gas generated from wheat straw, pine wood and rice husk as a function of pyrolysis temperatures were determined with mass balances closures ranging between 92-100 % for all experiments. In Figure 3.4 an example of the mass balance data of wheat straw pyrolysis conducted at reactor temperatures from 475 to 575 °C is shown. As the reactor temperature rises, the amount of char decreases whereas the formation of gas increases. It can be seen that there is an optimum temperature to produce a maximum of bio-oil. Above the optimum temperature the amount of bio-oil decreases because a part of the tar decomposes and a larger amount of gas is formed.
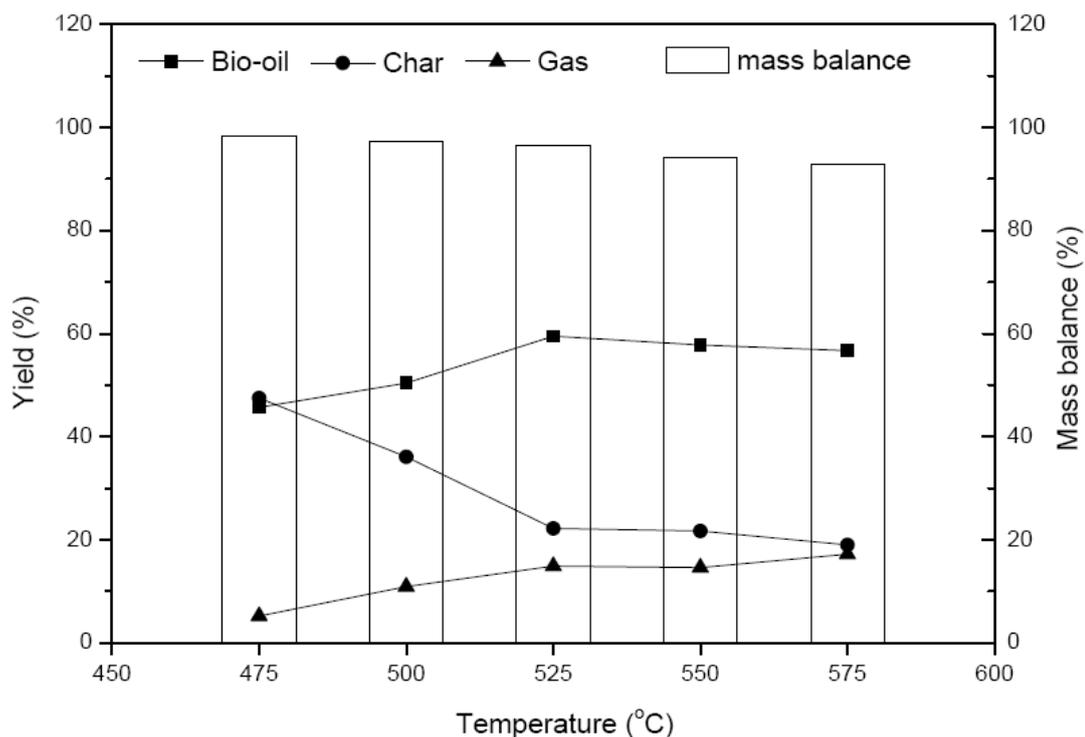
Figure 3.4. Mass balance closures for wheat straw pyrolysis (yield based on dry-ash free basis).

The element distribution in pyrolysis products is important, particularly the carbon balance. The conversion of carbon to the pyrolysis products from wheat straw is shown in Figure 3.5. In the temperature range of 475-575 °C, the bio-oil contained roughly from 38-50 % of the total feedstock carbon and approximately 40-68 % is found in biochar.

Since the pyrolysis gas was not analyzed, it is assumed that the difference of the carbon content in the bio-oil and the biochar to the carbon in the wheat straw is the carbon content in the pyrolysis gas. In Figure 3.5, it can be seen that at the optimum bio-oil yield temperature (525 °C), the oil contained 49 %, the char 45 % and the gas 6 % of the feedstock carbon. At a temperature of 475 ºC, the carbon balance in the pyrolysis gas was negative probably due a relative uncertain determination of the bio-oil carbon content.
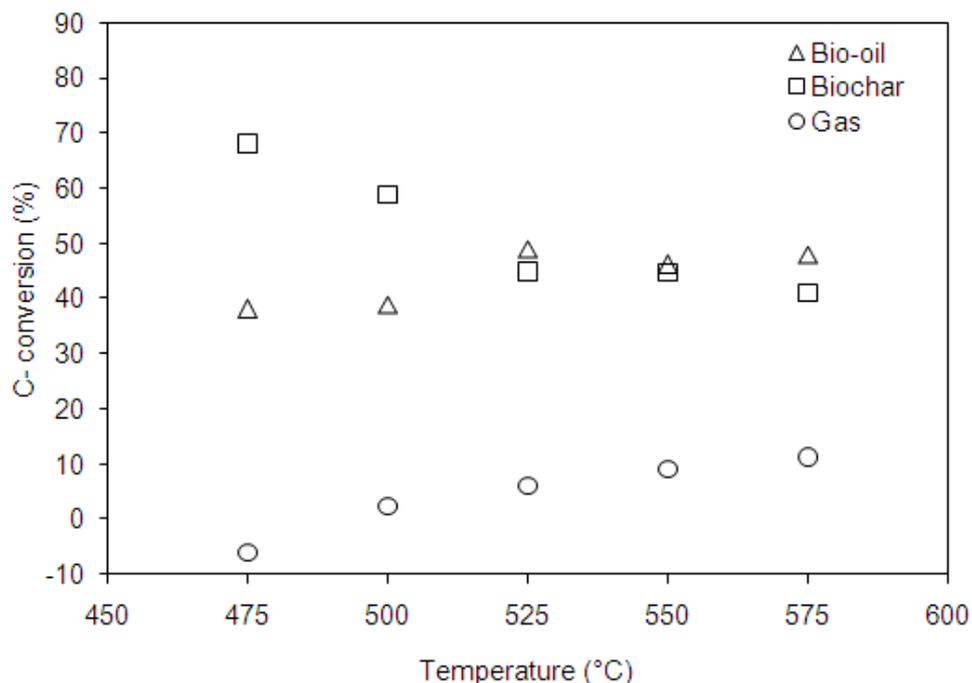
Figure 3.5. Distribution of carbon in pyrolysis products from wheat straw.

Liquid organics

The liquid organics yields of all three investigated feedstocks as a function of reactor temperature are shown in Figure 3.6. The liquid organics yield from wheat straw attained a maximum level of 49 wt. % at a reactor temperature of 525 °C. The maximum liquid organics yield from pine wood and rice husk was observed at 550 °C. The lower maximum yield temperature of straw is probably caused by the high straw potassium content that shifted the cellulose and hemicellulose decomposition to a lower temperature. A previous study [21] by TGA showed that the addition of KCl to washed straw moved the decomposition to lower temperature. Another study observed the same phenomena by adding $CaCl_2$, KCl, and $MgCl_2$ to washed sunflower stem [41].

Pine wood has the highest maximum organics yield followed by rice husk and finally wheat straw. The maximum liquid organics yields for pine wood, rice husk and wheat straw were 58, 52 and 49 wt. % (dry-ash free basis), respectively. The lower ash content in the pine wood results in a higher liquid organics yield. The lower organics yields of rice husk and straw compared to wood at temperature above 500 °C are probably caused by the alkali catalyzing a conversion of tar and feedstock to gas.

Char

Char is in this context defined as the solid product that is collected from the pyrolysis process. The char yields for all types of biomass showed a declining trend with

increasing temperatures as seen in Figure 3.7 and it reaches a minimum value at approximately 20 wt. % at temperatures of 550-575 °C.

At low temperatures, the highest char yield is obtained from rice husk and pine wood, while a lower yield is observed for wheat straw. The high rice husk char yield is apparently due to the high ash content. The lowest char yield of wheat straw is probably due to the high potassium content that catalyzes the pyrolysis conversion to take place at lower temperatures.
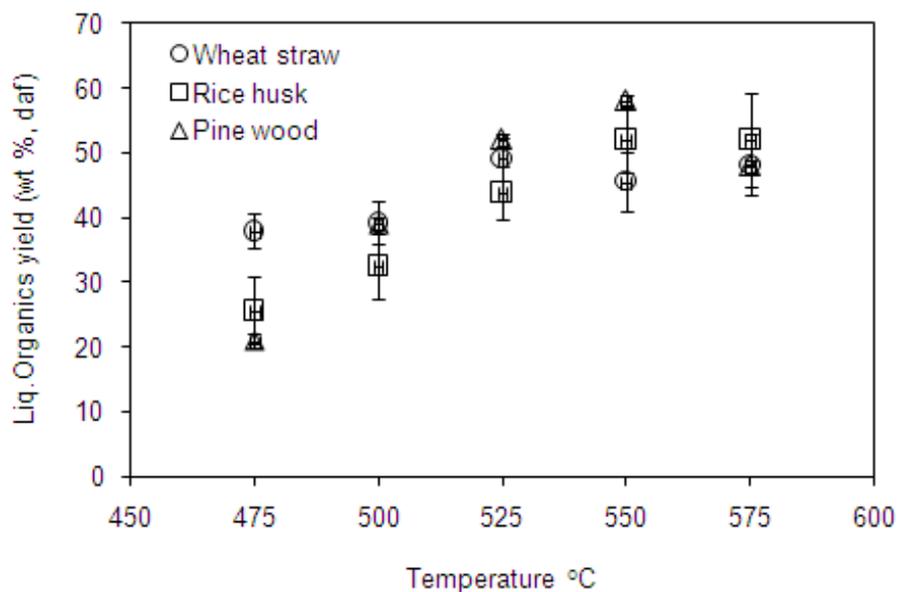

Figure 3.6. Liquid organics yield as a function of pyrolysis temperature (on dry and ash free feedstock basis) (Pine wood data from reference [33]).
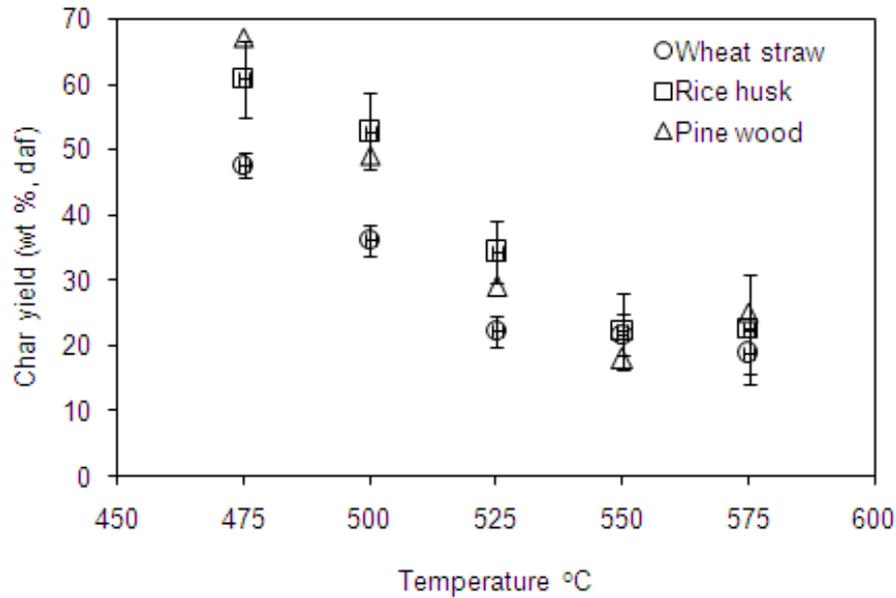
Figure 3.7. Char yield as a function of pyrolysis temperature (on dry and ash free feedstock basis) (Pine wood data from reference [33]).

Pyrolysis gas and reaction water

The yield of gas + water generated during the pyrolysis process (often called reaction water) is plotted for the comparison with the pine wood data taken from previous study [33] and shown in Figure 3.8. The yield of gas + water kept increasing with pyrolysis temperatures. The high yield at high temperatures may partly be caused by the pyrolysis oil vapor being converted into gases and water through secondary cracking of tars. It can be seen that wheat straw produced higher yield of gas + water compared to the others and this result is in good agreement with other findings [21, 42]. The higher gas + water yield for wheat straw is mainly assigned to the high potassium content in straw that catalyzes the formation of more gases.
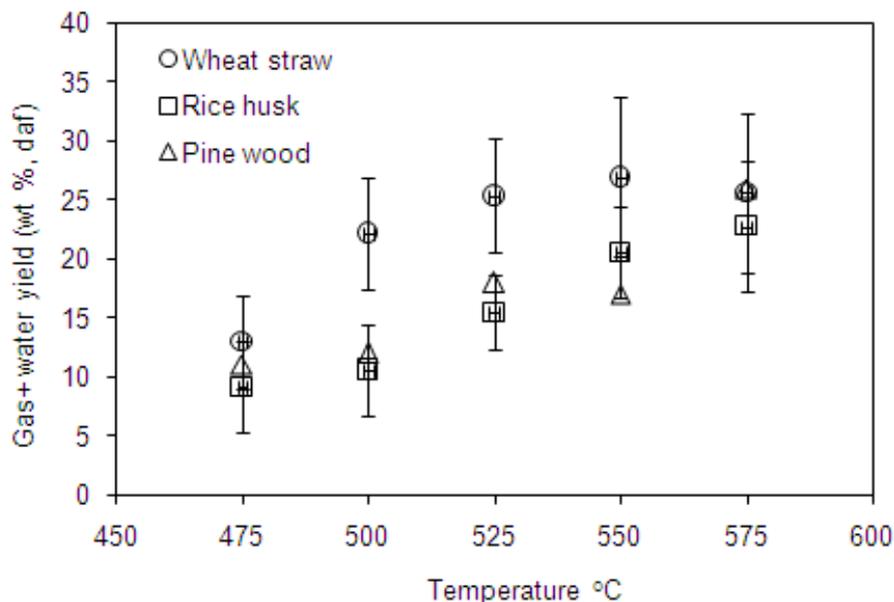
Figure 3.8. Gas + water reaction yield as a function of pyrolysis temperature (on dry and ash free feedstock basis) (Pine wood data from reference [33]).

The pyrolysis gas produced from the wheat straw and the rice husk is presented in Figure 3.9. The formation of gas was higher for the wheat straw.

In Figure 3.10 is shown the reaction water yield produced from the wheat straw and rice husk. In general, the yield of reaction water was lower for the rice husk and it is suggested that the lower concentration of potassium in rice husk ash cause less cracking of the volatiles and thus less reaction water is formed for rice husk.
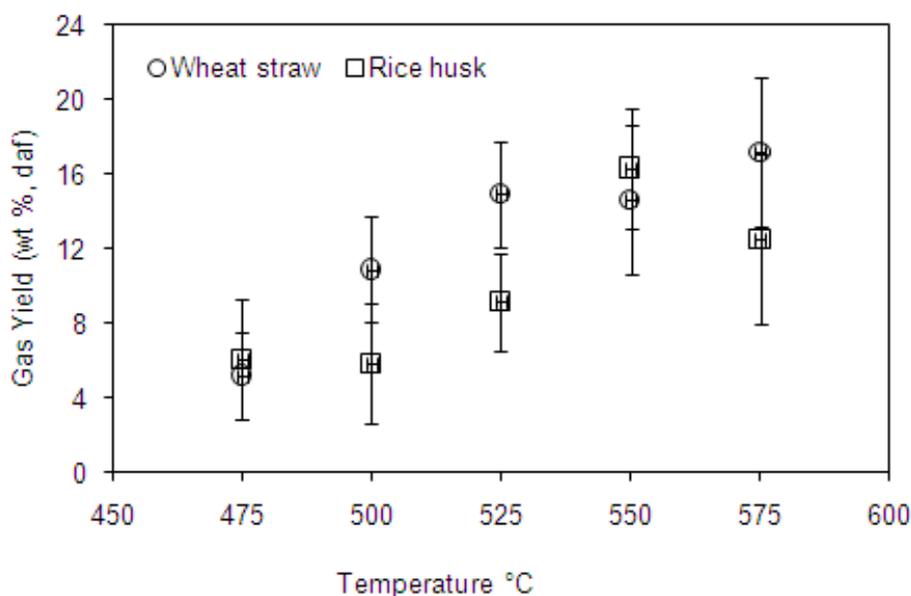
Figure 3.9. Pyrolysis gas yield as a function of pyrolysis temperature.
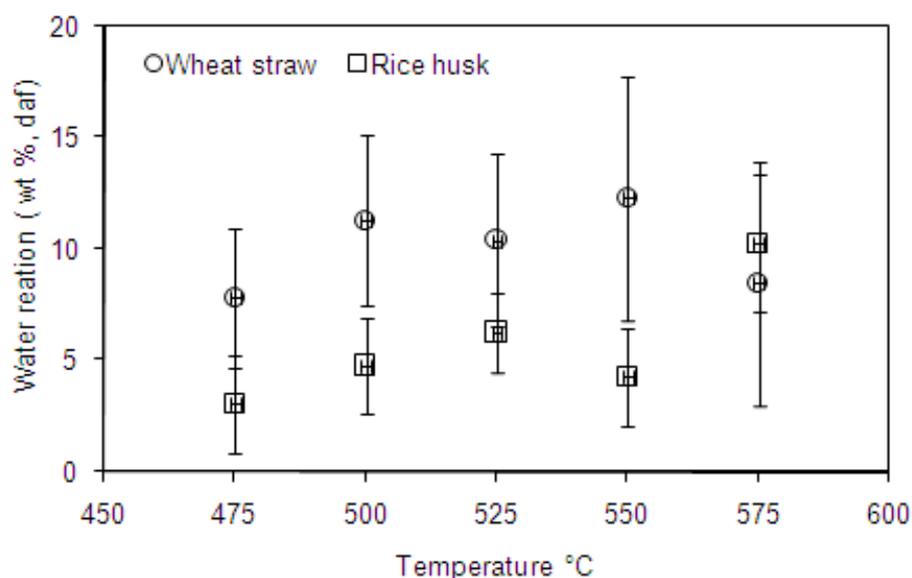
Figure 3.10. Water reaction yield as a function of pyrolysis temperature.

3.3.3   Bio-oil characterization

Bio-oils produced from wheat straw, rice husk and pine wood are dark to reddish color with a pungent odor. Table 3.2 shows some of the chemical and physical properties of bio-oils from wheat straw, rice husk and pine wood. The heating value (as produced) of all bio-oil samples was approximately 16-17 MJ/kg which is lower than those of conventional fossil fuels, mainly due to the high oxygen and water content in the bio-oils. A higher initial water content in the rice husk feedstock (see Table 3.1) resulted in a higher water content in the rice husk bio-oil. Due to this the HHV of rice husk oil is slightly lower compared to the others. However, the water contents of the bio-oils from these three feed stocks are relatively low and no phase separation was observed. Depending on the biomass used, the water content of bio-oil typically is between 15-35 wt. % [6-8]. The bio-oil water content originates from the biomass initial water and the products of dehydration reactions taking place during the pyrolysis process. The hydrogen to carbon ratio of the analyzed bio-oils is from 1.4 to 1.6 which is lower than for diesel or kerosene fuels that normally have an H/C ratio of 2.

Table 3.2.
Properties of bio-oils.

Properties	Units	Pine wood[a]	Wheat straw[b]	Rice husk[c]
Water content	wt.%	16.4	17.8	23.2
HHV (dry basis)	MJ/kg	16.7	16.4	16.1
HHV (wet basis)	MJ/kg	20.0	19.9	20.9
Energy yield	%	63.3	63.0	67.7
Elemental composition*	%db			
C		50.7	48.2	51.7
H		6.4	6.6	6.2
O		42.9	45.2	42.2
H/C**		1.6	1.6	1.4
O/C**		0.7	0.7	0.6

a: pyrolyzed at 550 °C, b: pyrolyzed at 525 °C, * based on the correlation and method proposed by Bech *et al*., 2009 [37], **: molar ratio

The individual chemical compounds present in the bio-oils from wheat straw, rice husk and pine wood were identified by GC-MS as shown in Table 3.3 and Figure 3.11. In this study, on the order of 70 compounds are detected in all bio-oil samples by GC-MS although more than hundreds of chemical compounds in bio-oil have been reported [43, 44]. Approximately 40 % of the detected compounds were assigned a chemical structure and they are listed in Table 3.3. The maximum molar weight of identified components was 200. To trace a given compound with GC-MS separation from the solvent (THF) is required; only relative few compounds, e.g. methanol, formic acid, acetone and acetone cannot be separated. On the other hand there is a cut-off for high temperature boiling compounds. In general, it can be assumed that compounds exhibiting a vapor pressure of 1 mbar at the column temperature, in this case 250 ºC, can be detected. The volatile fraction of the bio-oils defined as the amount passing the GC was estimated to approximately 10 wt. % of the bio-oil. This is lower than the approximately 20 wt. % volatile fraction detected by Girard *et al*., 2005 [45]. It may be caused by some low-molecular weight compounds as methanol, formic acid etc. escape detection as mentioned above. That 10 wt. % of the oils are detected, and the oils contain approximately 20 wt % water means that 60 wt. % of the bio-oil remains unknown, and this fraction most likely contains oligomers from lignin and carbohydrates (cellulose and hemicelluloses). In addition polymers derived from furans may add to this fraction.

It is obvious that bio-oil should be recognized as a highly oxygenated fuel, and the compounds identified may be grouped as carboxylic acids, simple oxygenates, furfural, diketones, lactones and phenols (Table 3.3). The values given in Table 3.3 are relative values based on un-corrected areas derived from the chromatograms and it is assumed that this reflect the concentrations to a reasonable extend. The chemical compounds found in the three bio-oils are almost similar with other bio-oils [45, 46]. It is a characteristic feature that the carbohydrates reveal a series of complex rearrangements before stabilizing as oxygenates [25, 46]. Lignins, by contrast, maintain significant parts of the original sub-structures and contribute in this way to the aromatics. In addition secondary products may also be formed, e.g. the acetates of hydroxylated structures (Table 3.3). Such products can be recognized as equilibrium

products in the bio-oil as they are prone to acid catalyzed hydrolysis. Hydrolysis may likewise lower the concentration of anhydro-sugars.
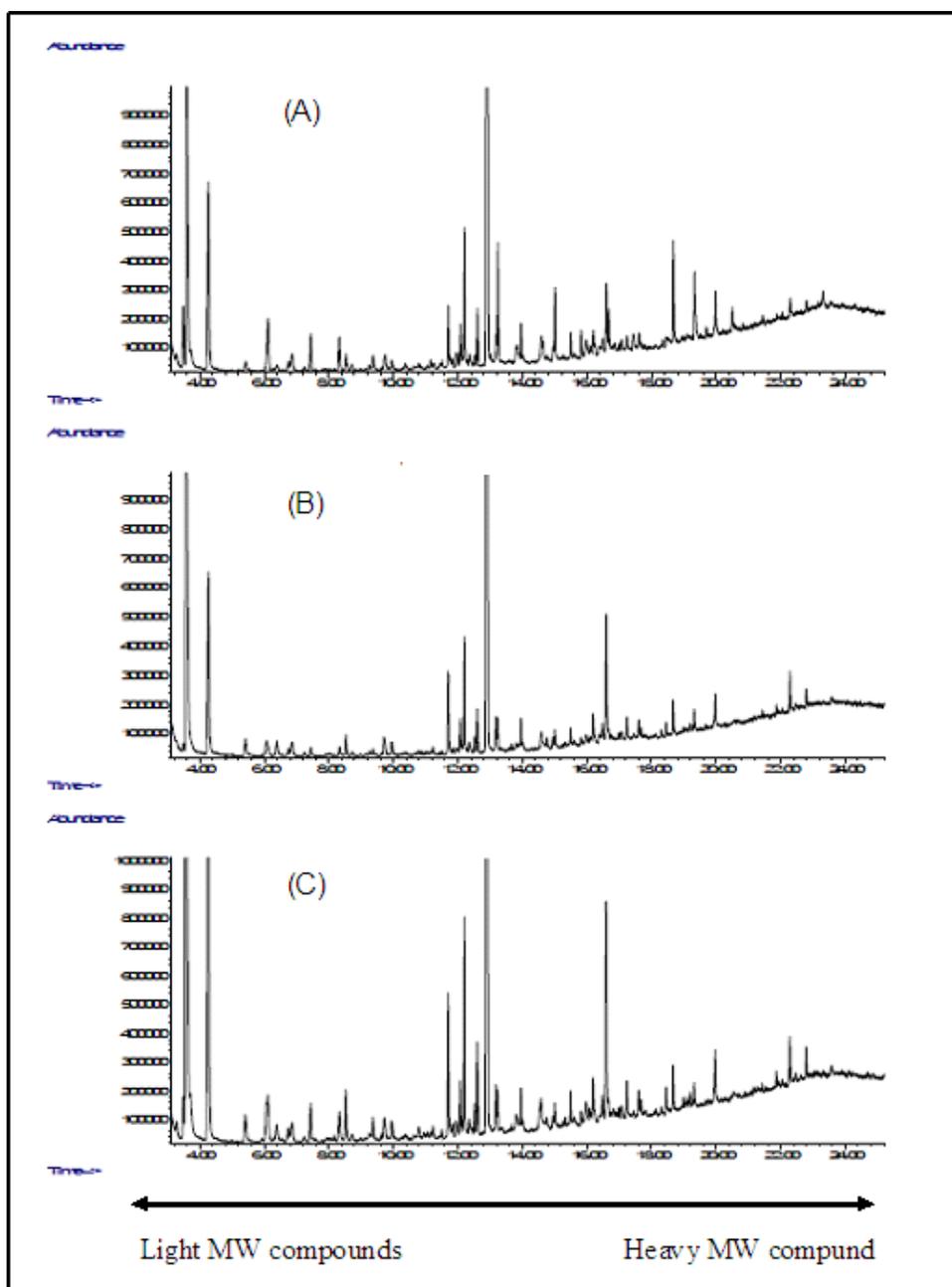

Figure 3.11. Ion chromatograms of bio-oil from (A) pine wood, (B) rice husk, and (C) wheat straw. The major signal around scan 1300 is due BHT stabilizer in the solvent (THF).

The bio-oil compositions of the three feedstocks as shown in Table 3.3 are reasonably similar. Based on the gas chromatography area percent all three oils have high concentrations of acetic acid (19.8-38.4 %) and 1-hydroxy-2-propanone (11.7-16.9 %).

The differences observed in the oil compositions are attributed to the differences in feedstock lignin and carbohydrates concentrations (see Table 3.1) or the ash content and composition (see Table 3.1 and Figure 3.3). Acetic acid is the far dominant carboxylic acid amounting while the homologues, propanoic and butyric acid are only present in moderate amounts. It should be noted that formic acid escape detection. This acid is normally present in rather high amounts [45]. Due to its acid strength formic acid contributes significantly to the corrosive properties of the bio-oil. It is difficult to explain the relative large variation of acetic acid content in terms of carbohydrate composition of the feedstocks. Thus, these concentration differences are assigned to the large variation in ash content and composition; however, it is presently not known how the ash in detail influences the bio-oil composition.

The simple oxygenates, furfurals, diketones and lactones originate from the carbohydrates. Furfural is a classical product arising from hemicelluloses. The higher concentration of furan derivatives from pine wood is reflected by a higher wood concentration of hemicelluloses (Table 3.1).

3.3.4 Biochar characterization

In Figure 3.12 the SEM images of raw biomass and its biochar produced at 550 °C are compared. Rice husk, in comparison with pine wood and wheat straw, has more dense and opaque structure due to the high content of silica. Pine wood and wheat straw have a reasonably similar structure. After pyrolysis of these feedstocks, the particle size was reduced below 100 µm.

Table 3.3.
Semiquantitative analysis of bio-oils from different feed stocks.

Compound	Wheat straw (Area %)	Rice husk (Area %)	Pine wood (Area %)
Carboxylic acids			
Acetic acid	31.4	38.4	19.8
Propanoic acid	1,4	1,1	0.7
Butanoic acid	0.1	0.3	0.3
Sum	32.9	39.8	20.8
Ketones/Aldehydes/Acetates			
Hydroxy-acetaldehyde	0.5	0.4	2.8
1-Hydroxy-2-propanone	16.9	14.0	11.7
1-Hydroxy-2-butanone	1.3	1.3	3.7
4-Hydroxy-4-methyl-2-pentanone	0.8	1.0	1.1
2-Cyclo-penten-1-one	0.4	0.3	0.4
3-Methyl-2-cyclo-penten-1-one	0.6		
1-(Acetyloxy)-2-propanone	1.5	0.9	
1.2-Ethandiol, monoacetate	0.9	1.2	0.9
Sum	22.9	19.1	20.6

| Compound	Wheat straw (Area %)	Rice husk (Area %)	Pine wood (Area %)
Furfurals			
Furfural	1.2	0.3	2.0
5-Methyl-furfural	0.1		0.1
Sum	1.3	0.3	2.1
Di-ketones			
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	0.6	0.6	0.4
3-Methyl-1,2-cyclo-pentanedione	3.5	0.1	2.0
Sum	4.1	0.7	2.4
Lactones			
γ-Butyrolactone	1.4	0.4	1.5
5-Hydroxymethyl-dihydrofuran-2-one	0.7	0.4	1.0
2(5H)-Furanone	2.1	2.0	2.4
3-Methyl-2(5H)-furanone	0.4	0.7	0.7
Sum	4.6	3.5	5.6
Phenols			
Phenol	0.5	2.0	1.1
2-Methoxy-phenol	4.6	5.3	4.6
2-methoxy-4-methyl phenol	0.7	1.6	4.2
2-methoxy-4-Ethyl-phenol	0.3	1.0	1.1
2-Methoxy-4-(2-propenyl)-phenol	0.3	0.3	1.1
2,6-Dimethoxy-phenol	4.6	6.6	2.3
1,2,3-Trimethoxy-benzene	1.0	1.0	0.6
2,6-Dimethoxy-4-(2-propenyl)-phenol	0.6	0.5	
3-Hydroxy-4-methoxy-benzaldehyde	1.0	1.7	3.8
2,6-Dimethoxy-4-(2-propenyl)-phenol	0.4		
2-propanone, 1-(4-hydroxy-3-methoxyphenyl)-	1.7	2.1	2.2
Benzaldehyde, 4-hydroxy-3,5-dimethoxy	0.3		
Ethanone-1-(4-hydroxy-3,5-dimethoxyphenyl)	1.0	1.9	0.6
Sum	16.5	24.0	21.6
Detected compounds (n) and assigned compounds (m, %)	72 (47%)	63 (43%)	70 (39%)
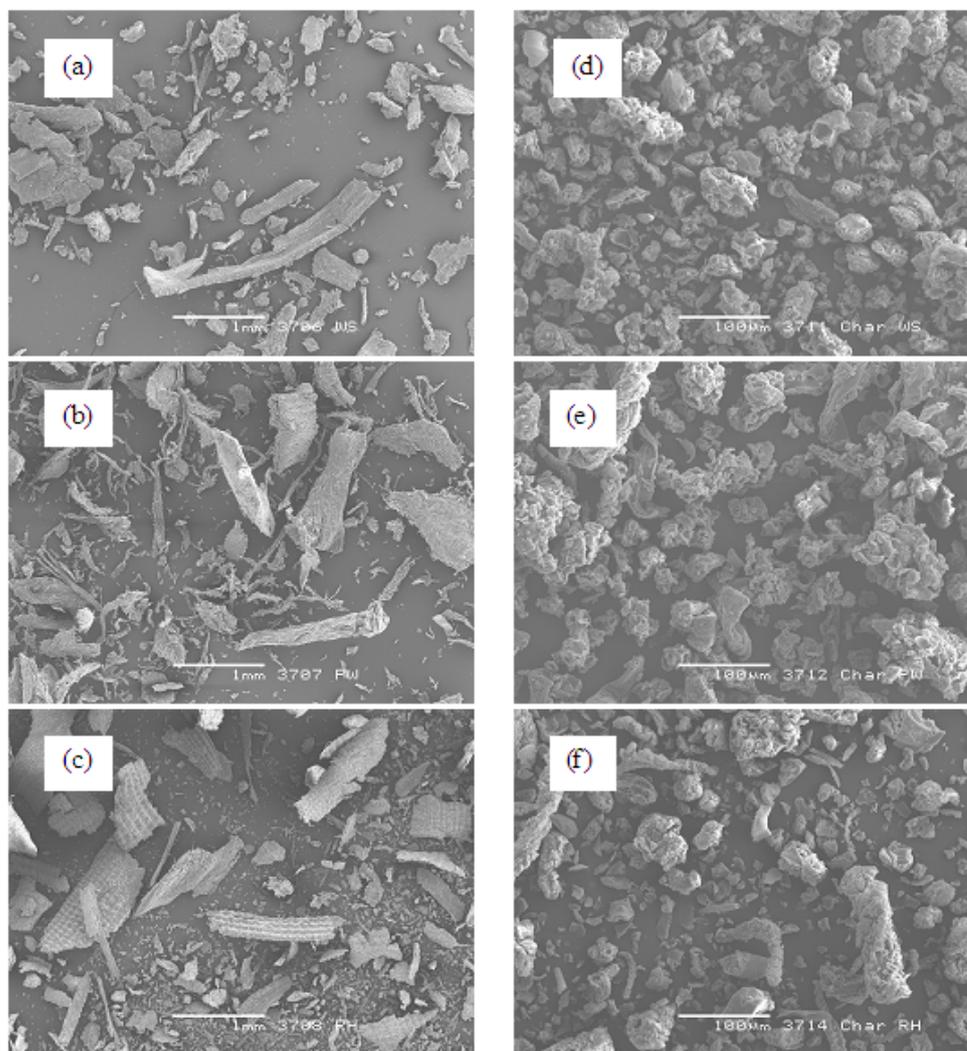
Figure 3.12. SEM images of (a) wheat straw, (b) pine wood, (c) rice husk, (d) wheat straw char, (e) pine wood char, and (f) rice husk char.

The carbohydrates residue (hemicellulose and cellulose), Klason lignin and ash in char from wheat straw and rice husk were further analyzed using the wet chemical method described in section 3.2.3 and the results are presented in Figure 3.13 as a function of pyrolysis temperatures. The carbohydrates are hydrolyzed to the corresponding monomers and assayed by liquid chromatography. Results are presented as the corresponding content of glucan (cellulose), xylan (hemicelluloses) and arabinan (hemicelluloses). As seen in Figure 3.13, the hemicelluloses char content (Arabinan and Xylan) are reduced at a reactor temperature of 575 °C, while nearly all cellulose (Glucan) is pyrolysed at 575 °C. The main organic components in the char are Klason lignin and ash. It is observed that the conversion of cellulose (Glucan) takes place at lower temperature for straw than for rice husk.
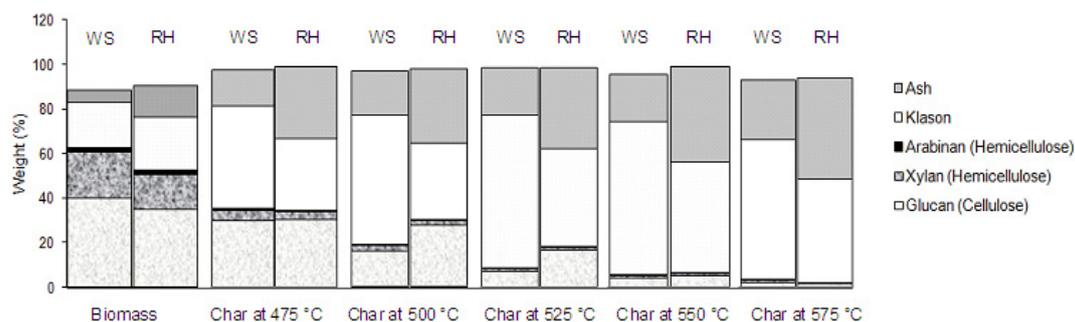
Figure 3.13. Residues in feedstock and biochar samples from wheat straw (WS) and rice husk (RH).

3.4 Conclusions

The products of wheat straw, rice husk and pine wood pyrolysis were investigated by pyrolyzation in a pyrolysis centrifuge reactor. It was an objective to investigate how differences in biomass composition influence pyrolysis products yields and the composition of char and bio-oils. The pine wood had a low ash content (0.5 wt. %), the wheat straw an intermediate ash level (6.0 wt. %) and the rice husk a high ash level (13.6 wt. %). The highest alkali content, potassium (1.53 wt. %) are present in straw and the lowest potassium content level is observed in pine wood (0.04 wt. %).

The maximum organics yield for wheat straw was obtained at 525 °C and at 550 °C for both rice husk and pine wood. At these optimum temperatures the yield of liquid organics were 49, 52 and 58 % wt. (dry-ash free basis) for wheat straw, rice husk and pine wood respectively. The optimum bio-oil yield temperature of wheat straw is slightly lower than that of pine wood and rice husk. However, the gas + water formation yield of wheat straw was higher compared to the other feedstocks and the amount kept increasing with temperature due to liquid organics decomposition. At low pyrolysis reactor temperature (475 °C) the lowest char yield was observed from straw, while at high pyrolysis temperature (575 °C) all feedstocks produced approximately 20 wt. % of char.

It is observed in this study and several other studies that the formation of char and gas is affected by the biomass alkali content. The presence of potassium in the biomass catalyzes tar conversion to form more gases and hence lowering the liquid product yield and also lowering the optimum liquid yield temperature.

The chemical compositions of bio-oils from the three feedstocks have been analyzed by GC-MS. It was estimated that approximately 10 wt. % of the bio-oil were analyzed by the GC-MS method and this fraction of the bio-oil is the most volatile. The GC-MS analysis showed that the analyzed fraction of the bio-oils is dominated by acetic acid which is 20-40 % of the volatile fraction. The amount of ketones, aldehydes, acetates, furfurals, di-ketones and lactones present in the straw oil, rice husk oil and pine wood oil are comparable.

The carbohydrate residues in biochar samples from wheat straw and rice husk were also determined. It was observed that the conversion of cellulose takes place at a lower temperature for straw than for rice husk.

Acknowledgements

References

[1]   Demirbas, A. (2000). Biomass resources for energy and chemical industry. *Energy Edu. Sci. Technol*. 5, 21-45.

[2]   Balat, M. (2005). Usage of energy sources and environmental problems. *Energy Exploration & Exploitation*. 23, 141-168.

[3]   Caputo, A. C., Palumbo, M., Pelagagge, P. M., Scacchia, F. (2005). Economics of biomass energy utilization in combustion and gasification plants: Effect of logistic variables. *Biomass & Bioenergy*. 28, 35-51.

[4]   Kozinski, J. A., Saade, R. (1998). Effect of biomass burning on the formation of soot particles and heavy hydrocarbons. An experimental study. *Fuel*. 77(4), 225-237.

[5]   Acikgoz, C., Kockar, A. M. (2007). Flash pyrolysis of Linseed (Linum usitatissimum L.) for production of liquid fuels. *Journal of Analytical and Applied Pyrolysis*. 78, 406-412.

[6]   Yaman, S. (2004). Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Convers. Management*. 45, 65-75.

[7]   Mohan, D., Charles, U., Pittman, J., Philip, H. S. (2006). Pyrolysis of wood/biomass for bio-oil: Critical Review. *Energy & Fuels*. 20, 848–889.

[8]   Bridgwater, A. V., Peacoke, G. V. C. (2004). Fast pyrolysis processes for biomass. *Renewable and Sustainable Energy Reviews*. 4, 1-73.

[9]   Oasmaa, A., Leppamaki, E., Koponen, P., Levander, J., Tapola, E. (1997). Physical characterisation of biomass-based pyrolysis liquids: Application of standard fuel oil analysis. VTT Energy, 306, 5–87.

[10]   Solantausta, Y., Bridgwater, A. V., Beckman, D. (1995). Feasibility of power production with pyrolysis and gasification systems. *Biomass & Bioenergy*. 9, 257-269.

[11]   Solantausta, Y., Nylund, N. O., Gust, S. (1994). Use of pyrolysis oil in a test diesel engine to study the feasibility of a diesel power plant concept. *Biomass & Bioenergy*. 7, 297–306.

[12]   Solantausta, Y., Nylund, N. O., Westerholm, M., Koljonen, T., Oasmaa, A. (1993). Wood pyrolysis liquid as fuel in a diesel power plant. *Biores Tech*. 46, 177-188.

[13]   Leech, J. (1997). Running a dual fuel engine on pyrolysis oil. In: Kaltschmitt M., Bridgwater, A. V., (eds.) *Biomass Gasification and Pyrolysis*, Newbury: CPL Press. 495-497.

[14]   Lopez, J. G., Monfort, S. J. J. (2000). Preliminary test on combustion of wood derived fast pyrolysis oils in a gas turbine combustor. *Biomass & Bioenergy*. 19, 119–128.

[15]   Strenziok, R., Hansen, U., Künster, H. (2001). Combustion of Bio-oil in a Gas Turbine. In: Bridgewater, A. V. (ed.). *Progress in Thermochemical Biomass Conversion*. Oxford: Blackwell Science. s2-1458.

[16]   Bruun, E. W., Hauggaard-Nielsen, H., Ibrahim, N., Egsgaard, H., Ambus, P., Jensen P. A., Dam-Johansen, K. (2011). Influence of fast pyrolysis temperature on biochar labile fraction and short-term carbon loss in a loamy soil. *Biomass & Bioenergy*. 35, 1182-1189.

[17]   Fahmi, R., Bridgwater, A. V., Darvell, L. I., Jones, J. M., Yates, N. (2007). The effect of alkali metals on combustion and pyrolysis of *Lolium* and *Festuca* grasses, switchgrass and willow. *Fuel*. 86, 1560-1569.

[18]   Raveendran, K., Ganesh, A., Khilar, K. C. (1995). Influence of mineral matter on biomass pyrolysis characteristic. *Fuel*. 74, 1812-1822.

[19]   Williams, P. T., Horne, P. A. (1994). The role of metal salts in the pyrolysis of biomass. *Renewable Energy*. 4, 1-13.

[20]   Di Blasi, C., Galgano, A. (2009). Influences of the chemical states of alkaline compounds and the nature of alkali metal on wood pyrolysis. *Ind. Eng. Chem. Res*. 48, 3359-3369.

[21]   Jensen, A., Dam-Johansen, K. (1998). TG-FTIR study of the influence of potassium chloride on wheat straw pyrolysis. *Energy & Fuel*. 12, 929-938.

[22]   Pan, W. P., Richards, G. N. (1989). Influence of meal ions on volatiles products of pyrolysis of wood. *J. Anal. Appl. Pyrolysis*. 16, 117-126.

[23]   Yang, H., Yan, R., Chen, H., Zheng, C., Lee, D. H., Liang, D. T. (2006). Influence of mineral matter on pyrolysis of palm oil waste. *Combustion and Flame*. 146, 605-611.

[24]   Richards, G. N. (1987). Glycolaldehyde from pyrolysis of cellulose. *J. Anal. Appl Pyrolysis*. 10, 251-255.

[25]   Nowakowski, D. J., Jones, J. M. (2008). Uncatalysed and potassium-catalysed pyrolysis of the cell wall constituents of biomass and their model compounds. *J. Anal. Appl. Pyrolysis*. 83, 12-25.

[26]   Wang, S., Liu, Q., Liao, Y., Luo, Z., Cen, K. (2007). A study on the mechanism research on cellulose pyrolysis under catalysis of metallic salts. *Korean J. Chem. Eng*. 24, 336-340.

[27]   Nik-Azar, M., Hajaligol, M. R., Sohrabi, M., Dabir, B. (1997). Mineral matter effects in rapid pyrolysis of beech wood. *Fuel Processing Technology*. 51, 7-17.

[28]   Di Blasi, C., Galgano, A., Branca, C. (2009). Effects of potassium hydroxide impregnation on wood pyrolysis. *Energy & Fuels*. 23, 1045-1054.

[29]   Shafizadeh, F., Fu, Y. L. (1973). Pyrolysis of cellulose. *Carbohydrate Research*. 29, 113-122.

[30]   Fahmi, R., Bridgwater, A. V., Donnison, I., Yates, N., Jones, J. M. (2008). The effect of lignin and inorganics species in biomass on pyrolysis oil yields, quality and stability. *Fuel*. 87, 1230-1240.

[31]   Varhegyi, G., Jakab, E., Till, F., Szekely, T. (1989). Thermogravimetric-mass spectrometric characterization of the thermal decomposition of sunflower stem. *Energy Fuels*. 3, 755-760.

[32]   Font, R., Marcilla, A., Verdu, E., Devesa, J. (1991). Thermogravimetric kinetic study of the pyrolysis of almond shells and almond shells impregnated with $CoCl_2$. *Journal of Anal. Appl. Pyrolysis*. 21, 249-264.

[33]   Bech, N., Larsen, M. B., Jensen, P. A., Dam-Johansen, K. (2009). Modelling solid-convective flash pyrolysis of straw and wood in the pyrolysis centrifuge reactor. *Biomass & Bioenergy*. 33, 999-1011.

[34]   Ibrahim, N., Jensen, P. A., Dam-Johansen, K. (2010). Effect of biomass mineral matter on the pyrolysis product yields. Proc 18th European Biomass Conference and Exhibition, Lyon, May 2010, 3-7.

[35]   Bech, N., Dam-Johansen, K., Jensen, P. A. (2006). Pyrolysis method and apparatus. PCT Application. WO 2006/117005.

[36]   Bech, N., Jensen, P. A., Dam-Johansen, K. (2007). Ablative flash pyrolysis of straw and wood: Bench-scale results. Proc 15th European Biomass Conference and Exhibition, Berlin, May 2007, 7-11.

[37]   Gronli, M. G., Varhegyi, G., Di Blasi, C. (2002). Thermogravimetric analysis and devolatilization kinetics of woods. *Ind. Eng. Chem. Res*. 41, 4201-4208.

[38]   Bech, N., Jensen, P. A., Dam-Johansen, K. (2009). Determining the elemental composition of fuels by bomb calorimetry and the inverse correlation of HHV with elemental composition. *Biomass & Bioenergy*. 33, 534-537.

[39]   Channiwala, S. A., Parikh, P. P. (2002). A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel*. 81, 1051-1063.

[40]   Raveendran, K., Ganesh, A., Khilar, K. C. (1995). Influence of mineral matter on biomass pyrolysis characteristic. *Fuel*. 74, 1812-1822.

[41]   Varhegyi, G., Jakab, E., Till, F., Szekely, T. (1989). Thermogravimetric-mass spectrometric characterization of the thermal decomposition of sunflower stem. *Energy Fuels*. 3, 755-760.

[42]   Fagbemi, L., Khezami, L., Capart, R. (2001). Pyrolysis products from different biomasses: Application to the thermal cracking of tar. *Applied Energy*. 69, 293-306.

[43]   Diebold, J. P. (2000). A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-Oils. NREL, 1, 1-51.

[44]   Diebold, J. P., Power, A. (1988). In: Bridgwater, A. V., Kuester, J. L. (eds.). Research in Thermochemical Biomass Conversion, London: Elsevier Appl. Sci. 609.

[45]   Girard, P., Blin, J., Bridgwater, A. V., Meier, D. (2005). An assessment of bio-oil toxicity for safe handling and transportation. Final Technical Report, 2005. http://ec.europa.eu/energy/renewables/bioenergy/doc/pyrolysis/biotoxpublishablerepo rt.pdf

[46]   Aho, A., Kumar, N., Eranen, K., Holmbom, B., Huppa, M., Salmi, T., Murzin, D. Y. (2008). Pyrolysis of softwood carbohydrates in a fluidized bed reactor. *Int. J. Mol. Sci*. 9, 1665-1675.

Stability and Aging of Flash Pyrolysis Bio-Oils

Abstract

This study evaluates the stability and aging of bio-oils generated by bench scale pyrolysis of wheat straw and pine wood. Both feedstocks were pyrolyzed at the conditions in which the productions of the liquid yields were optimal. The total liquid and char yields ranged from 49 to 58% and 18 to 22%, respectively and measured bio-oil water contents were in the range of 16 to 18%. For aging test, the samples were stored in closed glass containers at three different temperatures: at room temperature ($\approx$ 20 °C) for up to 130 days, at 50 °C for up to 14 days and at 80 °C for up to 24 hours. The bio-oils properties such as pH, water content, viscosity and heating value were measured as-produced and after aging. The results showed that the pH and heating value were not significantly affected during the aging test. On the other hand, it was found that the water content and the viscosity were significantly altered when the bio-oils were heated at 80 $^{\circ}$C, but that the variations were not critical at room temperature and after heating at 50 $^{\circ}$C. In addition, the aging rates of the bio-oil of wheat straw were slower compared to the bio-oil from pine wood. In addition, both bio-oils were fairly stable when stored at room temperature for up to 130 days due to no phase separation and small physical properties changes were observed.

Keywords: Flash pyrolysis, bio-oil, stability, aging, viscosity

4.1 Introduction

The use of bio-oils is of growing interest due to rapid consumption of petroleum oils and rising interest in environment protection [1, 2]. Bio-oils generated from the pyrolysis of biomass are considered to be a promising fuel. Pyrolysis of biomass under conditions of rapid heating and short reactor residence times produce a brown low-viscosity and single-phase pyrolysis bio-oil. The yields of fast biomass pyrolysis that are typically 50-70 % (of which 15-35 % is water), ~20 % char and the remaining 10-15 % as non-condensable gasses (such as CO_2, CO and CH_4). A wide variety of feedstock can be used to produce bio-oils, including wood, corn stover, agricultural waste, switch grass, and forest waste. The bio-oil contains a large number of organic compounds including acids, alcohols, aldehydes, esters, ketones, phenols, furans, alkenes, aromatics, sugar and oxygenates [3]. Pyrolysis bio-oils differ a great deal from petroleum-based fuels in both physical properties and chemical composition (Table 4.1). Pyrolysis bio-oils contain a higher content of water and oxygen, have a lower heating value and a lower content of carbon and hydrogen. Due to those reasons, bio-oil is a relatively low quality liquid fuel and therefore cannot be used

directly in diesel or gasoline combustion engines. However, pyrolysis bio-oil can be utilized as boiler fuel for production of heat and power.

Table 4.1
Typical properties of bio-oil and heavy fuel oil [3,4,5,6].

Physical Properties	Bio-Oil	Heavy Fuel Oil
Moisture content (wt. %)	15-35	0.1
pH	1.5-3.8	-
Specific gravity	1.2	0.94
Elemental Composition (wt. %)		
C	54-58	85
H	5.5-7.0	11
O	35-45	1.0
N	0-0.2	0.3
Ash	0-0.2	0.1
HHV, wet basis (MJ/kg)	16-19	40
Viscosity (at 50 $^{\circ}$C) (cP)	40-100	180

The objective of this study was to characterize the physical and chemical properties of the bio-oils produced from wheat straw and pine wood on a bench scale pyrolysis centrifuge reactor [7,8]. Both feedstocks were pyrolyzed at the conditions in which the productions of the liquid yields are maximized. The understanding of their physical and chemical properties is important to the control of all combustion product specifications and product storage and transportation. Most projected uses of bio-oils require that it to a reasonably degrees retain properties during storage, shipment and use. Unfortunately, some bio-oils rapidly become more viscous during storage and in some cases separation of the oil into two phases can also be observed [9-12]. For these reasons, the aging behaviors of the pyrolysis bio-oils were investigated. A more stable product should have the practical benefit of being more conducive to pumping after extended storage. The final objective of this study was to compare the physical and chemical properties, and the aging behavior of the pyrolysis bio-oils produced on the bench scale pyrolysis centrifuge reactor with oils from other pyrolysis processes.

4.2   Experimental

4.2.1   Materials

Two different feed stocks, wheat straw and pine wood were obtained from Denmark. All feed stocks were milled and sieve to a particle size of < 1.4 mm and were then converted into bio-oils in a bench scale pyrolysis centrifuge reactor. The elemental analyses and characteristics of all feed stocks are shown in Table 4.2. It is clearly seen that pine wood has a low ash content (0.5 %, db), a very low sulfur content (< 0.02 % dry-ash free), and high volatile matter (85 %, db). Wheat straw has lower moisture content as compared to the pine wood. Conversely, it has a lower heating value and higher content of ash (6.0 %, db). The C and H contents appear to be reasonably

similar for both investigated feed stocks except the N content, where wheat straw contains about 1.1 % of N and pine wood has less than 0.1 % of N. In addition, the fraction of lignin in pine wood (30 %, db) is higher as compared to the wheat straw (20 %, db) while the fractions of cellulose and hemicelluloses in wood is reasonably similar to wheat straw.

Table 4.2.
Analyses of biomass feed stocks used for pyrolysis.

Parameters	Unit	Feedstock	
		Wheat straw	Pine wood
Moisture	%. wt	6.2	7.1
Volatile Matter	%. db	74.7	85.0
Ash	%. db	6.0	0.5
C	%. daf	49.4	49.9
H	%. daf	6.2	6.3
S	%. daf	0.2	< 0.02
N	%. daf	1.1	< 0.1
O (by difference)	%. daf	43.1	43.7
Cellulose	%. db	40	42
Hemicellulose	%. db	23	25
Lignin	%. db	20	30
HHV (MJ/kg)	%. db	18.8	20.5

4.2.2 Pyrolysis Centrifuge Reactor

The bio-oils were produced from flash pyrolysis of wheat straw and pine wood in a bench scale pyrolysis centrifuge reactor [7, 8, 13, 14]. Both feedstocks were pyrolyzed at conditions providing maximum liquid yields (i.e straw pyrolyzed at a reactor temperature of 525 °C and pine wood at 550 °C). The bench scale pyrolysis centrifuge reactor is featured by a tubular reactor that has an internal diameter of 82 mm and 200 mm of the total pipe length with a three blade rotors that provides a centrifugal forces when biomass is fed. The centrifugal force created by the rotation of the three blade rotor keeps the particles sliding on the heated wall while passing through the reactor. The solid particles pyrolyze while moving down the reactor pipe and leaves suspended in the gas through the tangential outlet. Larger char particles were removed by a change-in-flow separator whereas fines were collected by a cyclone. Vapors were condensed in a direct water cooled condenser (bubble chamber) filled with previously produced bio-oil and the remaining aerosols that were not retained by the condenser were collected by a coalescer that captured a large fraction of the bio-oil produced. A fraction of the gas was pumped to a preheater and heated to 400 °C before it was recirculated to the reactor in order to maintain a desired gas residence time and to avoid condensation of liquid products within the reactor. In this experiment, the biomass feedstocks were fed to the reactor at a rate of 20-23 g/min with an approximately gas reactor residence time of 0.3-0.5 s, and an initial heating rate of approximately 250-1000 °K/s [7].

4.2.3 Determination of Physical and Chemical Properties of Bio-Oils

In order to evaluate the stability of the bio-oils, four parameters were chosen: pH, water content, viscosity and heating value. The bio-oils were stored in closed glass containers at three different temperatures: at room temperature ($\approx$ 20 °C) for up to 130 days, at 50 °C for up to 14 days and at 80 °C for up to 24 hours (samples stored at 50 °C and 80 °C were incubated in an oven). Samples were withdrawn at various time based on the designated time. The bio-oils properties were measured as-produced and after aging.

The acidity of the bio-oils was measured using a MeterLab standard pH meter PHM210 instrument. A calibration using pH 4.005 and 7.000 standard buffer solutions was carried out prior to the tests. Only room-temperature measurements were performed.

The water content of the bio-oils was analyzed by a Karl Fisher titration (KFT) method using a Metrohm 701 KF Titrino analyzer.

The viscosity of the bio-oils was measured using an Automated Microviscometer AMV 200 instrument. The viscosity was measured at 20 °C and 40 °C. The viscosity measurement temperature is usually chosen to make it possible to compare it to petroleum fuel oil specifications.

The higher heating value (HHV) of the bio-oils sample were measured by a bomb calorimeter IKA C200 instrument using the DIN 51900-1 standard. The vessel was pressurized with 30 bar of oxygen. The uncertainty of the measurements is 120 J/g. For calculated elementary analysis (C, H, O), the correlation method proposed by Bech and co-workers was employed [15, 16].

4.3 Results and Discussion

4.3.1 Stability of the Fresh Bio-Oils

The bio-oils from our process are dark-reddish viscous liquids with a pungent odor. Pyrolysis of wheat straw at the reactor temperature of 525 °C produced about 49 % of liquid organics, 22 % of solid char, 15 % of gas and 10 % of reaction water. The yield of liquid organics, char and gas (including reaction water) pyrolyzed from pine wood at 550 °C were 58 %, 18 % and 17 %, respectively. It should be noted that all the yields are expressed in dry-ash free basis (daf) and approximately 48 % (dry basis) of the feedstock carbon were contained in both bio-oils. Some key physical and chemical properties of the raw bio-oils are described in Table 4.3. As can be seen, these properties were in the range of bio-oils from other pyrolysis process but significantly different from those of petroleum derived diesels.

Table 4.3.
Physico-Chemical properties of bio-oils.

		Bio-Oils	
Parameters	Unit	Wheat Straw	Pine Wood
pH	-	3.20	3.04
Moisture	wt. %	17.8	16.4
Viscosity	cP at 40 $^{\circ}$C	27.4	47.8
HHV	(MJ/kg)	16.4	16.7

Bio-oils typically have a pH in the range of 2.0-3.8 because of the presence of organic acids, mostly acetic and formic acid [17]. The pH value of 3.04 and 3.20 are measured for the fresh pine wood and wheat straw bio-oils, respectively.

The water content in the bio-oils from a bench scale pyrolysis centrifuge reactor of wheat straw is about 17.8 wt. %, whereas 16.4 wt. % of pine wood. The water came from the original moisture in the feedstock and from dehydration reactions occurring during the pyrolysis process [17-19]. Depending on the types of biomass feedstock and operating conditions, the water content in bio-oil varies in the range of 15-35 wt. %. Usually, at these mentioned water contents, the water is miscible with the oligomeric lignin-derived components due to solubilizing effect of other polar hydrophilic compound such as low molecular weight acids, ketones, alcohols and hydroxyaldehydes, that originating from the decomposition of the carbohydrates. The presence of water has both negative and positive effects on the bio-oil properties. Obviously, it lowers its heating value, contributes to an increase in the ignition delay, and a decrease in combustion rate compared with the petroleum-based fuels. On the other hand, it improves bio-oil flow characteristics by reducing the bio-oil viscosity.

The viscosity of our fresh bio-oils samples are measured at 40 $^{\circ}$C (viscosity measurement temperature). It is found out that the viscosity of the fresh pine wood bio-oil is 47.8 cP, which is approximately double that the fresh wheat straw bio-oil (about 27.4 cP). However, these values are still low compared to the viscosity value of the heavy fuels.

The heating value of our fresh bio-oils samples are about 16.4-16.7 MJ/kg. It is similar as the heating values of bio-oils produced by other processes (16-19 MJ/kg) [9-12] but lower than that of petroleum-based fuels (40 MJ/kg).

4.3.2 Aging of the Bio-Oils

Organic species in the bio-oils samples can continue to react to form larger molecules during storage, which can contribute to the changes in the bio-oils properties. The main chemical reactions are esterification and etherification occurring between hydroxyl, carbonyl and carboxyl groups, in which water is a byproduct. Aging tests took place in covered glass containers at room temperature over a period of 130 days. The bio-oils properties such as pH, water content, viscosity and heating value were measured after aging. To further test aging characteristics, freshly generated bio-oils were aged at an accelerate rate by using elevated temperatures (50 $^{\circ}$C and 80 $^{\circ}$C) in covered glass containers between 14 days and 1 day.

pH

It was observed in this study that the pH of the bio-oils was not significantly changed during the aging tests. The range of pH values of 3.12-3.28, 3.03-3.20 and 2.96-3.20 were observed for the aged wheat straw bio-oils at room temperature, 50 ^{o}C and 80 °C, respectively, whereas, the range pH values of 2.93-3.04 (at room temperature), 2.86-3.04 (at 50 ^{o}C) and 2.78-3.04 (at 80 ^{o}C) were observed for the aged pine wood bio-oils for the same conditions.

Water Content

Figure 4.1 shows the changes of water content in the bio-oils (wheat straw and pine wood) stored at three different temperatures and aged up to 14 days. The results indicated that the water content of bio-oils increases with storing temperature as well as the length of storage period. Apparently, at higher temperature (80 °C), the water concentration of the bio-oils increases significantly after 24 hours of storage, from 17.8 wt. % to 19.3 wt. % (for wheat straw bio-oils) and from 16.4 wt. % to 17.3 wt. % (for pine wood bio-oils). The release of water suggests that some condensation or dehydration reactions occurred in the bio-oils during storage, especially when exposed to higher temperatures. However, storing the bio-oils at a room temperature and at 50 °C for up to 2 weeks showed only a little change in water content.

Viscosity

The changes of viscosity, measured at 40 °C (viscosity measurement temperature) of wheat straw and pine wood bio-oils were measured as a function of aging period at different temperatures. The results are depicted in Figure 4.2. It can be seen that the viscosity of the bio-oils increased with the aging period. The results shows that the viscosity of both bio-oils stored at room temperature and after heating at 50 ^{o}C is hardly changed with time (after 14 days). However, storing the bio-oils at 80 °C exhibits a significant increase of viscosity over 24 hours of storage; which is an increase from 27.4 to 64.3 cP (for wheat straw bio-oils) and from 47.8 to 121.6 cP (for pine wood bio-oils). The viscosity of pyrolysis oils strongly depend on their water content. Normally, the dilution with water will make the bio-oils less viscous. However, the increase in water concentration of the aged bio-oils was accompanied by an increase in its viscosity. According to Ortega et al. [20], since the bio-oils viscosity is related to the molecular weight, indicating that condensation reactions have occurred in the aged bio-oils, especially when exposed to higher temperatures.
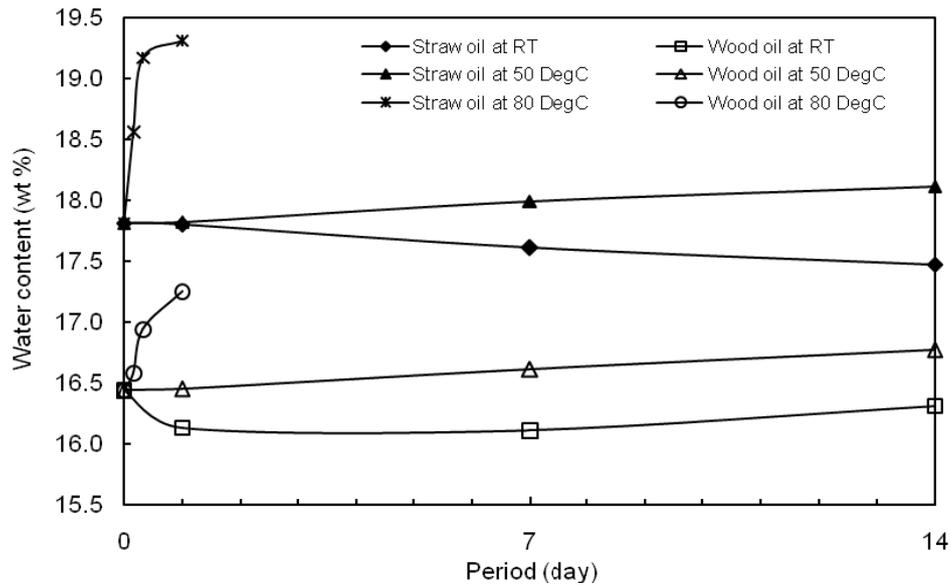
Figure 4.1. The influence of storing temperatures on the water content of two different bio-oils as a function of aging period.
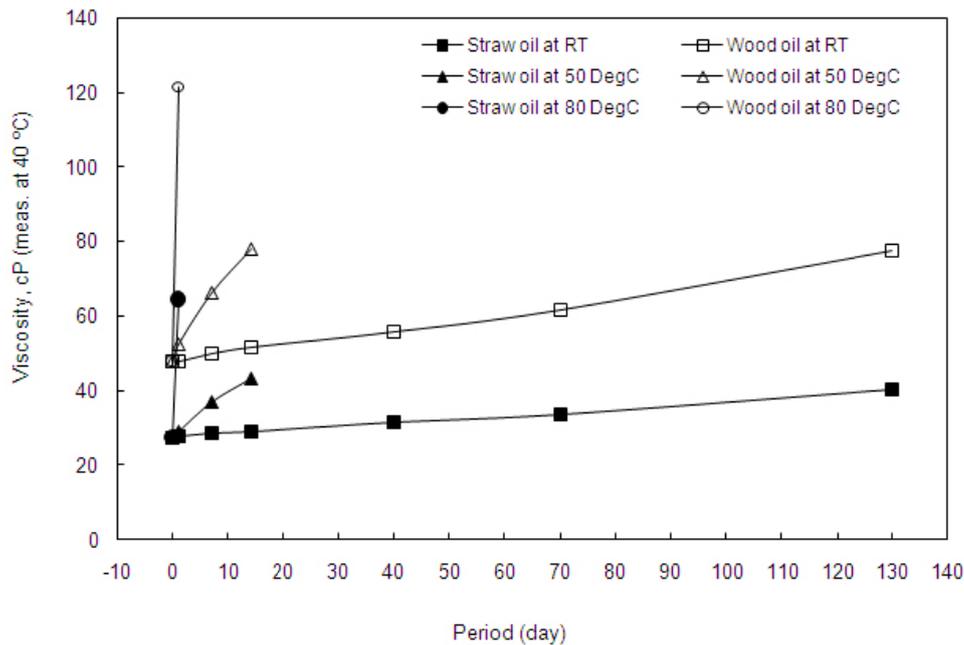

Figure 4.2. The influence of storing temperature on the viscosity (measured at 40 °C) of the closed container bio-oils as a function of aging period.

Heating Value

The higher heating value (HHV) based on wet and dry basis for closed container bio-oils from wheat straw and pine wood bio-oils stored at 80 °C and at room temperature were measured and the results are tabulated in Table 4.4. In general, the HHV values

of all samples are insignificantly affected by the storage conditions. However the HHV of wet pine wood bio-oil is observed to be slightly higher than that of wheat straw bio-oil.

Table 4.4.
The higher heating value, HHV (MJ/kg) of the closed bio-oil samples.

		Closed Container				
	Straw Bio-Oil			Wood Bio-Oil		
Time	Water content (% wt)	HHV (wet)	HHV (dry)	Water content (% wt)	HHV (wet)	HHV (dry)
(hr)			80 °C			
0	17.81	16.38	19.93	16.44	16.74	20.03
4	18.56	16.36	20.09	16.58	16.70	20.02
8	19.17	16.33	20.20	16.94	16.64	20.03
24	19.31	16.33	20.24	17.25	16.50	19.94
(day)		Room Temperature (~20 °C)				
0	17.81	16.38	19.93	16.44	16.74	20.03
7	17.61	16.33	19.82	16.11	16.61	19.80
40	18.02	16.24	19.81	16.43	16.51	19.76
130	18.69	16.18	19.90	17.40	16.58	20.08

Correlation of Viscosity Changes in Aged Bio-Oils

Attempts have been made to relate the viscosity changes of the aged bio-oils to the influence of aging period, temperature, water content and applied biomass type. The viscosity aging rate of the bio-oils was calculated by dividing the final viscosity change with the maximum storage time. The calculated aging rate for pine wood bio-oils was 0.2 cP/day at room temperature, 2.1 cP/day at 50 °C and 74 cP /day at 80 °C. For wheat straw bio-oils, the calculated viscosity rate of aging at room temperature, at 50 °C and at 80 °C, were 0.1, 1.2 and 38 cP/day, respectively. From the results, it can be seen that the aging rates of wheat straw bio-oil were slower compared to the bio-oil from pine wood.

The viscosity aging rate of the bio-oils samples as a function of temperature are shown in Figure 4.3. An empirical aging formula was obtained by linear regression and rearranged it into the Arrhenius equation (1) and (2).

Closed container wood oil:
$$Viscosity\ change\ rate\ = 8 \times 10^{12} exp\left(\frac{-9180}{T}\right)\quad \left[\frac{cP}{day}\right] \tag{1}$$

Closed container straw oil:
$$Viscosity\ change\ rate\ = 1 \times 10^{12} exp\left(\frac{-8745}{T}\right)\quad \left[\frac{cP}{day}\right] \tag{2}$$

The aging rate is expressed in cP/day and T is in K. The correlation coefficient for wood oil was 0.9721 and 0.9676 for straw oil (see Figure 4.3).
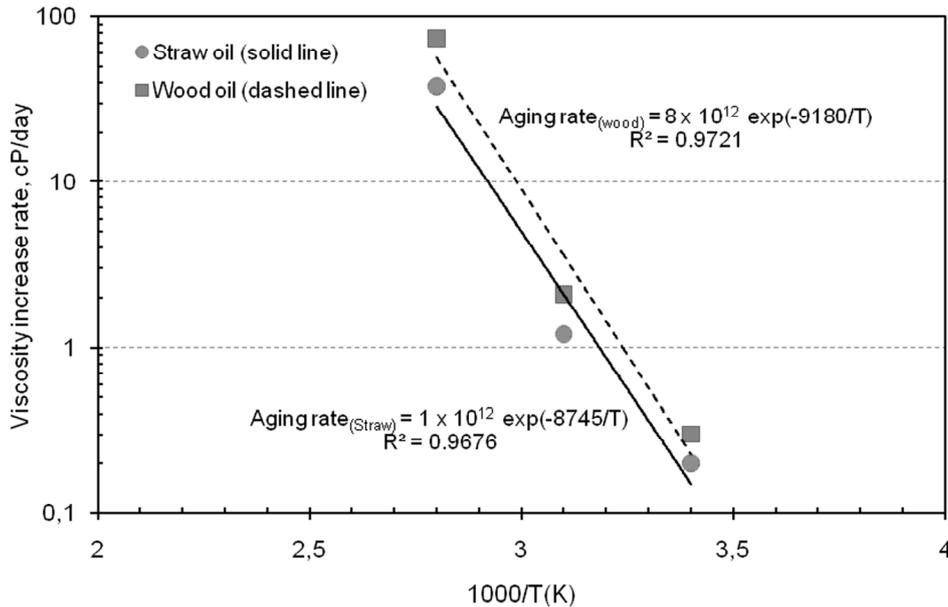

Figure 4.3. Viscosity aging rate (measured at 40 °C) of the closed container bio-oils as a function of inverse temperature.

Figure 4.4 shows the viscosity as a function of the water content in the various aged bio-oils at temperatures in the range of 50-90 °C. It is seen that changes in the water content between 16 and 20 wt. % is not a main cause of the observed viscosity changes. Further investigation was carried out by adding 2-8 wt. % of water to wheat straw bio-oils and measured the viscosity of the samples. The results are presented in Figure 4.5. It was observed that the viscosity decreased with increasing water concentration in the bio-oil. Increasing the water content from 22 to 30 wt. % decreased the viscosity from 40 to 20 cP (measured at 40 °C). However, the maximum amount of water added to the bio-oil had to be limited as phase separation was observed if adding more than 8 wt. % of water to the wheat straw bio-oil. For example, in the wheat straw bio-oil water content of 33 wt. %, a solid deposit started to form and thus showing the oil phase separation. The water addition data indicates that viscosity changes cannot simply be related to the increase in water contents during the aging study, but must be caused by formation of larger oxygenated hydrocarbons.
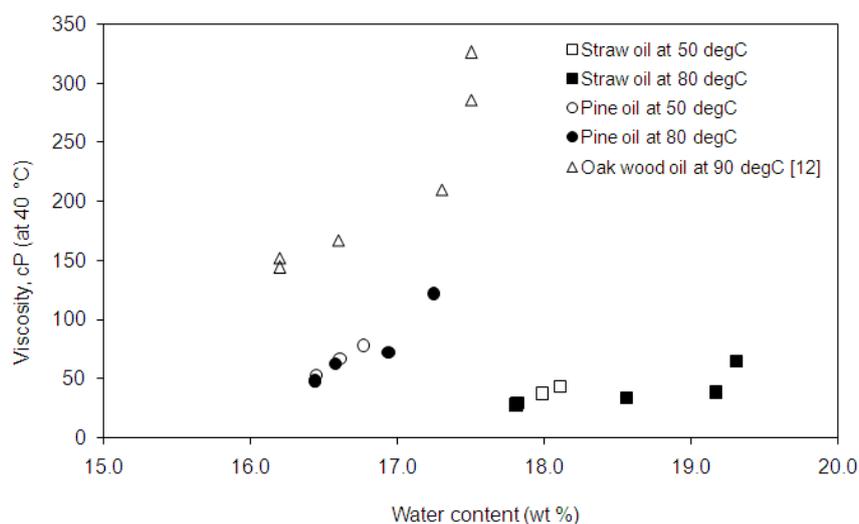
Figure 4.4. Viscosity profiles as a function of water content of the various aged bio-oils at elevated temperatures.
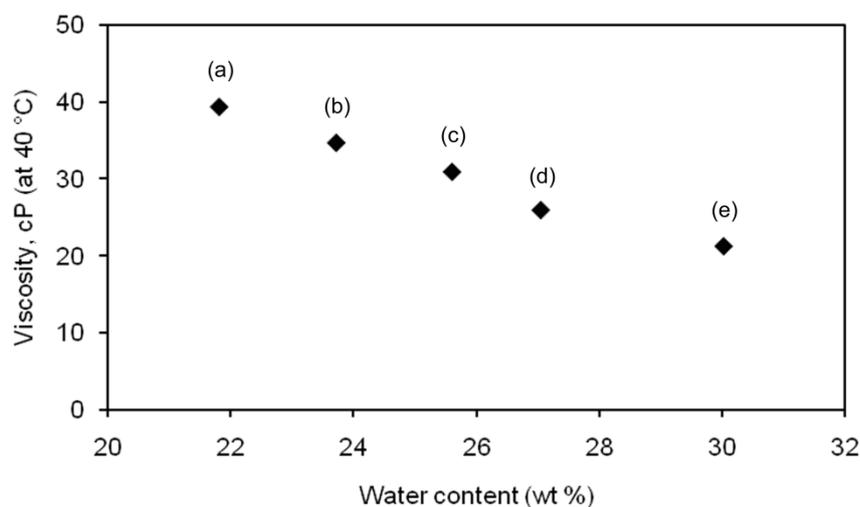
Figure 4.5. The influence of water addition to the wheat straw bio-oil, (a) original water content (b) 2 wt. % water, (c) 4 wt. % water, (d) 5 wt. % water and (d) 8 wt. % water added.

It can be seen that the small increase of the water content in bio-oil caused by storage at 50 °C and 80 °C do not explain the observed viscosity change. The viscosity increases is probably related to the changes of the bio-oil molecular weight. It is reported in other studies [12] that the molecular weight of bio-oil increased with the temperature and length of storage. After 84 days, the average molecular weight (M_w) of oak oil aged at 37 °C increased from 530 to 740 gmol^{-1} and from 530 to 900 gmol^{-1} for the oil aged at 60 °C and stored up to 9 days. A significant increased of the average molecular weight from 530 to 880 gmol^{-1} was observed for oil aged at 90 °C for 15 hours. In addition, the molecular weight distribution determined by GPC [12]

showed that the fraction of high molecular weight compounds increased while the amount of low molecular weight compound decreased during aging and thus showed that polymerization occurred during storage as indicated by the increasing of viscosity. Besides, the etherification and esterification reactions that occur between hydroxyl, carbonyl and carboxyl groups during the aging tests were also observed by conducting FTIR measurement [12].

In Figure 4.6, the viscosity measurements conducted at 20 °C and 40 °C on our aged bio-oil samples are compared. The viscosity values for all bio-oil samples measured at 20 °C are higher than that of viscosity values for the same samples measured at 40 °C. It is observed that there exists a simple linear correlation between the viscosity determination done at 20 and 40 °C. Viscosity is dependent on more than molecule size. It also depends on the kinds of attractive forces between molecules such as van der Waals forces and hydrogen bonding (usually exists in water, alcohols, acid and carbohydrates). When the temperature increases, these forces become weaker and thus melt the heavier molecules materials (for the bio-oil case - the compounds such as fatty and resins acids/alcohol and phenolic compounds), hence decrease its viscosity and this explained the lower viscosity measured at high temperature.
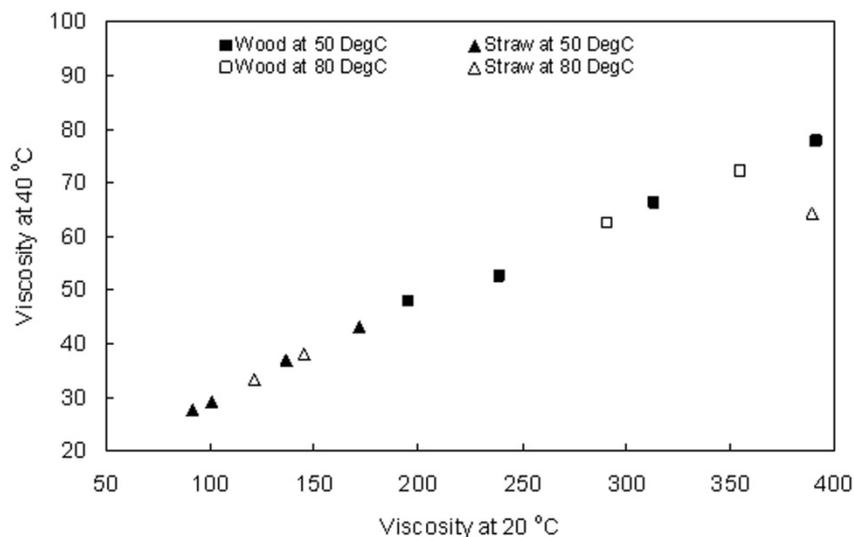
Figure 4.6. The influence of viscosity measurement temperature on the bio-oil viscosity (closed vessel).

4.3.3   Comparison with other Pyrolysis Oil Studies

It is generally observed that aging occur faster at higher temperatures whereby the oil viscosity is increased. In Table 4.5, the viscosity and water content data of fresh bio-oil of several fast pyrolysis oil studies are summarized. It can be seen that straw type biomass provides bio-oil with the lowest viscosity while soft wood and hard wood oil in most cases do have the lowest water contents.

Table 4.5
Viscosity and water contents of fresh straw, hardwood and softwood pyrolysis oils produced by different fast pyrolysis processes.

Biomass	Viscosity, cP (measured at 40 and 50 °C)	Water content (wt %)
Hardwood [12,21-24]	35-159	16-24
Softwood [22,25,26]	47-74	11-17
Straw [7,21]	13-34	18-25

In Table 4.6 the rate of changes in viscosity of pyrolysis oils of different studies are summarized. In this study the viscosity (measured at 40 °C) increase rate for bio-oils stored at room temperature was 0.1 cPday^{-1} for the wheat straw bio-oils and 0.2 cPday^{-1} for the pine wood bio-oils, and these rates is comparable with the other studies [12,23,25]. There is not observed a clear trend between the viscosity aging rates of hardwood, softwood and straw. At room temperature (20 °C) there are for closed container aging measurements observed viscosity aging rates of 0.1-0.3 cPday^{-1} and at 80 °C aging rates of 30-237 cPday^{-1}.

In all the oil viscosity studies summarized in Table 4.6 the fresh oils had water contents of 15 -19 wt. % for the wheat straw bio-oils and 13 -17 wt. % for the pine wood bio-oils and no phase separation were observed during the aging test. In another aging study [21] using an oil with an initial water content of 47 wt. %, phase separation occurred after 3 months storage at room temperature.

Table 4.6.
Viscosity aging rates of pyrolysis bio-oil (closed vessel) measured at 40 °C and 50 °C from the present and other studies.

Samples	Viscosity measurement temperature	Heating temperature/ Aging rate (cPday^{-1})				
		20 °C	35 °C	50 °C	80 °C	90 °C
Wheat straw oil	40 °C	0.1		1.2	38	
Pine wood oil	40 °C	0.2		2.1	74	
Hardwood oil	40 °C	0.3[12,26]			90[26]	300[12]
Hardwood oil	50 °C	0.1[25]	0.8[25]	2.5[25]	30.5[25]	
Softwood oil	40 °C	0.3[24]			227.3[26]	

The viscosity changes by aging can be influenced by adding water or other additives. The reduction of viscosity aging rate by adding water to bio-oil was observed by Diebold et al., [23]. The viscosity aging rate of the hardwood bio-oil stored at room temperature for 4 months was reduced when water was added to bio-oil as follows; 3.3 cPday^{-1} (20 wt. % of water content), 0.9 cPday^{-1} (25 wt. % of water content) and 0.05 cPday^{-1} (30 wt. % of water content). Besides water, methanol and ethanol are also recognized as efficient solvents to alter the viscosity of bio-oil [24].

4.4   Conclusions

Bio-oils produced from wheat straw and pine wood feed stocks in a bench scale pyrolysis centrifuge reactor were tested to measure viscosity, water content, pH and heating value at different temperature and storage time. Both feedstocks were pyrolyzed at the conditions in which the productions of the liquid yields are maximized. The measured total liquid yield, char yield and water content of the bio-oil produced from the pine wood feedstock are 58, 22, and 18 %, respectively, which are higher than the bio-oil produced from the wheat straw feedstock. The initial water content and viscosity of the fresh wheat straw and pine wood bio-oils was 17.8 wt. % and 27.4 cP (measured at 40 °C) and 16.4 wt. % and 47.8 cP (measured at 40 °C). Aging took place in closed glass containers at three different temperatures: at room temperature (~ 20 °C) for up to 130 days, at 50 °C for up to 14 days and at 80 °C for up to 24 hours and the bio-oils properties were measured as-produced and after aging. The results shows that the pH level and heating value were nearly not affected during the aging test. Aging of the bio-oils in closed containers at room temperature and 50 °C showed only slightly increased in the water contents after 14 days. However, at 80 °C, the water contents of the bio-oils increased by a factor of 1.1 after up to 24 hours of storage. The measured viscosity of fresh pine wood bio-oil is approximately 1.8 times higher than that of fresh wheat straw bio-oil. Aging of the bio-oils in closed containers at room temperature showed that the viscosity do only changed slightly with time, whereas at 50 °C, the viscosity of the bio-oils increased approximately 1.5 times after 14 days of storage. However, at 80 °C, the viscosity of the bio-oils increased drastically approximately 2.5 times after only 24 hours of storage. The viscosity increasing rates of the closed container bio-oil of wheat straw were slower compared to the bio-oil from pine wood. It is concluded that the bio-oil from wheat straw shows better stability compared to the bio-oil from pine wood. In addition, both bio-oils are fairly stable stored in a closed container at room temperature for up to 130 days, with no phase separation and only small changes in physical properties were observed.

References

[1]   Grassi, G., Bridgwater, A. V (eds.) (1990). *Biomass for energy, industry and the environment: a strategy for the future*. Commission of the European Community, Directorate General for Science Research and Development. Milan: Edizioni Esagono. P58.

[2]   Wornat, M. J., Porter, B. J., Yang, N. Y. (1994). Single droplet combustion of biomass pyrolysis oils. *Energy Fuels*. 8, 1131-1142.

[3]   Mohan, D., Pittman, C. U., Steele, P. H. (2006), Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy Fuels*. 20, 848-889.

[4]   Bahng, M. K., Mukarakate, C., Robichaud, D. J., Nimlos, M. R. (2009). Current technologies for analysis of biomass thermochemical processing: A review. *Anal. Chim. ACTA*. 651, 117-138.

[5]   Yaman, S. (2004). Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Conversion and Management. 45*, 651-671.

[6]   IEA - International Energy Agency. http://www.ieabioenergy.com (accessed in 2006).

[7]   Bech, N., Larsen, M. B., Jensen, P. A., Dam-Johansen, K. (2009). Modelling solid-convective flash pyrolysis of straw and wood in the pyrolysis centrifuge reactor. *Biomass & Bioenergy*. 33, 999-1011.

[8]   Ibrahim, N., Jensen, P.A., Dam-Johansen, K. (2010). Effect of biomass mineral matter on the pyrolysis product yields. Proceedings of the 18th European Biomass Conference and Exhibition; Lyon, France, May 3-7, 2010.

[9]   Diebold, J. P. (2000). A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-Oils. *NREL*. 1, 3-42.

[10]   Oasmaa, A., Meier, D. (2005). Norms and standards for fast pyrolysis liquids:1. Round robin test. *Journal of Analytical Applied Pyrolysis*. *73*, 323-334.

[11]   Oasmaa, A.; Kuoppala, E. Fast pyrolysis of forestry residue.3. Storage stability of liquid fuel. *Energy & Fuel* 2003, *17*, 1075-1084.

[12]   Czernik, S., Johnson, D. K., Stewart, B. (1994). Stability of wood fast paralysis oil. *Biomass & Bioenegy*. *7*, 1-6.

[13]   Bech, N., Dam-Johansen, K., Jensen, P. A. (2006). Pyrolysis method and apparatus. Application number WO 2006117005.

[14]   Bech, N., Jensen, P. A., Dam-Johansen, K. (20070. Ablative flash pyrolysis of straw and wood: Bench- scale results. Proceedings of the 15th European Biomass Conference and Exhibition, Berlin, May 7-11, 2007.

[15]   Bech, N., Jensen, P. A., Dam-Johansen, K. (2009). Determining the elemental composition of fuels by bomb calorimetry and the inverse correlation of HHV with elemental composition. *Biomass & Bioenergy*. *33*, 534-537.

[16]   Channiwala, S.A., Parikh, P. P. (2002). A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel*. 81, 1051-1063.

[17]   Elliot, D.C. (1994). Water, alkali and char in flash pyrolysis oil. *Biomass & Bioenergy*. *7*, 179-186.

[18]   Bridgwater, A. V., Peacoke, G. V. C. (2000). Fast pyrolysis processes for biomass. *Renewable and Sustainable Energy Reviews*. *4*, 1-73.

[19]   Balat, M. (2008). Mechanism of thermochemical biomass conversion processes. Part 1: Reactions of pyrolysis. *Energy Sources*. *30*, 620-635.

[20]   Ortega, J. V., Renehan, A. M., Liberatore, M. W., Herring, A. M. (2011). Physical and chemical characteristics of aging pyrolysis oils produced from hardwood and softwood feedstocks. *J.Anal. & Appl. Pyrolysis*. 91, 190-198.

[21]   Fahmi, R., Bridgwater, A. V., Donnison, I., Yates, N., Jones, J. M. (2008). The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. *Fuel*. 87, 1230-1240.

[22] Sipila, K., Kuoppala, E., Fagernaes, L. (1998). Characterization of biomass–based flash pyrolysis oils. *Biomass & Bioenergy*. 14, 103–13.

[23] Diebold, J. P., Scahill, J. W., Czernik, S., Phillips, S. D., Feik, C. J. (1996). Progress in the production of hot-gas filtered biocrude oil. In: Bio-oil production and utilization. Proceedings of the Second EC/Canada Workshop on Thermal Biomass Processing; Bridgwater, A. V.; Hogan, E., Eds. CPL Scientific Information Services, Ltd.: Newbury, U. K. 66-81.

[24] Oasmaa, A., Czernik, S. (1996). Fuel oil quality of biomass pyrolysis oil-state of the art for the end user. *Energy Fuels*. 13, 914-921.

[25] Oasmaa, A., Leppamaki, E., Koponen, P., Levander, J., Tapola, E. (1997). Physical characterization of biomass-based pyrolysis liquids. Application of standard fuel oil analyses. *VTT Publication 306.* VTT: Espoo, Finland.

[24] Diebold, J. P., Czernik, S. (1997). Additives to lower and stabilize the viscosity of pyrolysis oils during storage. *Energy and Fuel*. 11, 1081-1097.

[27] Ba, T., Chaala, A., Garcia-Perez, M., Roy, C. (2004). Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Storage stability. *Energy & Fuel. 18*, 188-201.

<div align="right">

CHAPTER 5

</div>

Oil Droplet Combustion

Abstract

The aim of this work is to investigate the combustion behavior of pyrolysis oils derived from wheat straw and pine wood. The work is done in two parts. In the first part the technique of thermogravimetric analysis (TGA) was applied to study the thermal treatment of the pyrolysis oils under well controlled temperature in an oxidative (O_2) and non-oxidative (N_2) environment. The thermogravimetry curves indicated that the combustion process of bio-oil was divided into three stages. It was found that the removal of water and evaporation of light volatiles occurs from room temperature up to 200 °C, the cracking of heavy fraction attains in temperatures of between 200-500 °C and finally the char combustion occurs at temperatures above 500 °C. The second part of this study presents an investigation on the combustion of single droplets of pyrolysis oils and heavy oil in a single droplet combustion chamber. It was observed that bio-oils droplet differ from the heavy oil in terms both of ignition, devolatilisation and char combustion. The bio-oil is more difficult to ignite and has a shorter devolatilisation time and a longer char combustion time.

Keywords: Pyrolysis bio-oil, droplet combustion, heavy oil.

5.1   Introduction

Bio-oil is produced by rapid quenching and condensation of vapors released from flash pyrolysis of biomass. It is a highly viscous liquid containing various oxygenated hydrocarbons such as acids, alcohols, aldehydes, esters, ketones, phenols, furans, alkenes, aromatics and sugar. Bio-oil also is characterized by a relatively high water and oxygen content, low heating value, typically from 16-19 MJ/kg (wet basis), and high density and acidity. The density of the liquid bio-oil is about 1200 kg/m^3, which is much higher than that of the original biomass. In addition, low sulfur and nitrogen content in the bio-oil compared to the feedstock results in a small impact on the environment when the oil is combusted.

Since the 1990's interest has developed in the use of bio-oil to substitute heavy fossil fuel oil in boilers to produce heat and electricity (Solantausta *et al*., 1993; 1994; 1995; Oasmaa *et al*., 1997; 2001; Gust, 1997; Bridgwater and Peacoke, 2004). Several researchers have performed combustion tests using different size boilers (Solantausta *et al*., 1995), internal combustion engines (Solantausta *et al*., 1995; Solantausta *et al*., 1993 and Solantausta et al, 1994) and gas turbines (Solantausta et al, 1995 and Lopez and Monfort, 2000). Experiments on bio-oil single droplets combustion have also been conducted by thermogravimetric techniques (Garcia *et al*., 2006), by fibre-suspended droplets (D'Alessio *et al*., 1998; Calabria *et al*., 2007) and in entrained flow reactors (EFR) (Shaddix and Tennison, 1998; Garcia *et al*., 2006).

Garcia and co-workers conducted thermogravimetric tests on two types of bio-oils heated from room temperature to 750 °C at a heating rate of 10 °C/min in nitrogen and in air at a flow rate of 150 mL/min. Three major stages were identified from the TG-DTG curves during the bio-oil combustion, which begins with the evaporation of light oil fractions (up to 300 °C) followed by the cracking of heavy oil fractions (above 300 °C) in the second stage. In addition, combustion of a solid residue (400-500 °C), is the final step. An almost similar thermal behavior of all tested bio-oil samples was observed in the TGA experiments. Further investigation of a single bio-oil droplet combustion was carried out in an EFR using initial droplet diameters between 58 and 62 μm at a furnace wall temperature of 700 °C and 800 °C. The EFR was operated in an inert atmosphere using Ar for evaporation studies, whereas mixtures of Ar-O_2 were used for combustion studies applying O_2 concentrations between 20 and 50 vol. %. The bio-oils were blended with 50 vol. % of Methanol in order to allow the formation of small droplets made by a Piezoelectric droplet generator (N° 36). No swelling phenomenon was observed for the bio-oil combustion in EFR experiment for droplet diameters between 58 and 62 μm. On the other hand, Liu and co-workers (Liu *et al.,* 2011) observed the occurrence of swelling of the oil sludge for droplets diameters bigger than 10 mm in a lab-scale bubbling fluidized bed reactor.

The effects of char content and simple additives of methanol and water, on the pyrolysis oil droplet combustion have also been studied by Shaddix and Tennison, (1998). The tests were performed by using an EFR with droplet diameters of 390 μm for a poplar oil mixture, and 440 μm for an Ensyn oil, at a reactor temperature of 1600 K and O_2 concentrations between 14 and 33 vol. %. They observed that microexplosions occurred earlier for the sample oil with high char content (Ensyn oil) and they suggested that the char particles facilitated nucleation of vapour bubbles leading to microexplosions at lower superheat values. Besides, the addition of water and methanol to the pyrolysis oils results in the shortest burnout time as compared to the pure pyrolysis oils.

Recently, Calabria *et al.,* (2007) investigated the combustion of bio-oil in a fibre-suspended droplets reactor using pure bio-oil from forest residue, provided by VTT and also an emulsion (30 wt. % of bio-oil + 70 wt. % of diesel oil) diesel oil was used for comparison. The size of droplets was varied between 400 μm and 1200 μm and the combustion history was recorded by high speed digital shadowgraphy. They found that both pyrolysis oil and emulsion droplets experienced swelling during combustion. The behavior of emulsions is intermediate with respect to the pure pyrolysis oil and the commercial diesel oil.

The objective of this paper is to report the experimental study on combustion of single droplets of pyrolysis oils derived from wheat straw and pine wood. The combustion of the heavy fossil fuel oil is also discussed for comparison. In the first part of this study the technique of thermogravimetric analysis (TGA) was applied to study the thermal treatment of the pyrolysis oils under well controlled temperature in an oxidative (O_2) and non-oxidative (N_2) environment. The second part of this study presents an investigation on the combustion of single droplets of pyrolysis oils in a single droplet combustion chamber and for a comparison also heavy fuel oil was used. In this study, the suspended droplet technique has been preferred because of its advantages that the droplet is stationary and easily observed. The imaging was

performed by means of fast video recording. The behavior of such droplet is investigated starting from the moment when the droplet is placed into the tube reactor (stationary), evaporates and burns until the carbon burns out completely. The combustion stages in a single droplet combustion reactor are evaluated by measuring the time of completing of each stage; the ignition, devolatilisation and char combustion stages.

5.2   Experimental

5.2.1   Bio-oil Production

Two types of bio-oils generated from flash pyrolysis of pine wood and wheat straw were used. Both biomass feedstocks were pyrolyzed under their optimum temperatures whereas other conditions were kept constant. Wheat straw was pyrolyzed at a reactor temperature of 525 °C with an oil yield of 49 wt. % (on dry-ash free basis), whereas pine wood pyrolyzed at 550 °C with a 58 wt. % (on dry-ash free basis) of liquid organic yield. Also heavy fuel oil # 77 supplied by A/S Dansk Shell were used. Table 5.1 summarizes the physical and chemical properties of the wheat straw bio-oil, pine wood bio-oil and heavy fuel oil # 77. Biomass-derived bio-oil has different characteristic compared to the heavy fuel oil. Biomass-derived bio-oil is characterized by higher content of water and oxygen as compared to the heavy fuel oil. Thus, the heating value of bio-oil is lower than that of the heavy oil. Heavy fuel oil contains higher amount of carbon which is about 1.7 times higher than that of biomass-derived bio-oil. In addition, the ash presents in the heavy oil less than 0.03 wt. % which is much lower as compared to the biomass- derived bio-oil.

Table 5.1
Bio-oils and heavy fuel oil physico-chemical properties.

Properties	Units	Pine wood oil	Wheat straw oil	Heavy oil
Water content	wt. %	16.4	17.8	< 0.1
pH		3.04	3.20	-
Ash	wt. %	1.2	1.6	< 0.03
Density (20 °C)	g/cm^{-3}	1.2307	1.1999	0.9882
Dynamic viscosity	cP			
At 20 °C		195.8	91.4	-
At 40 °C		47.8	27.4	-
At 80 °C		-	-	67.2
Heating value (wet basis)	MJ/kg	16.7	16.4	40.9
Elemental analysis	%, db			
C		50.7	50.2	85.0[*]
H		6.4	6.2	11.0[*]
O		42.9	43.6	1.0[*]

* from literatures (Caputo *et al*., 2005; Acikgoz *et al*., 2007; Yaman, 2004)

5.2.2   Simultaneous Thermal Analysis (STA)

The thermal behaviors of pine wood oil and wheat straw oil was carried out using a NETZSCH STA 449F1 thermogravimetric analyzer (TGA) coupled with differential scanning calorimetry (DSC). The TGA-DSC facilitated the acquisition of weight loss and heat flow data as a function of temperature or time. The experimental work was conducted at a heating rate of 10 °C min^{-1}, and the samples were heated from room temperature up to 700 °C in a 10 % of oxygen and nitrogen gas flow of 150 mL/min.

5.2.3   Single Droplet Combustion Facility

The combustion properties of the bio-oil were studied on the CHEC single droplet combustion facility. The set up consists of a Bunsen burner in an airtight box, a ceramic tube reactor and a gas control panel. The airtight box is used to hold the burner and the burner head is located just above the box lid, as shown in Figure 5.1. The ceramic tube is placed on the top of the burner and the tube has 4 holes which are used for oil sample insertion, and to view the combustion progress using a video camera. Propane is used to supply the heat. The flow in the reactor is controlled by a gas panel using five rotometers (see Figure 5.2). A schematic diagram with dimensions of the burner and the ceramic tube reactor is shown in Figure 5.3.

The purpose of this set-up is to evaluate the basic combustion properties of the pyrolyis bio-oils. In order to operate this set-up, the bio-oils sample was placed on a sample holder made of a thin platinum wire by using syringe, and the sample holder then inserts the oil droplet into the centre of the ceramic tube placed inside the furnace. The initial oil droplet diameters were in between 500 μm to 2500 μm. The experiments were performed at a temperature ranging between 1000 and 1400 °C with an initial gas velocity of 1.6 m/s and oxygen concentration of 3%. The experiments were repeated four to five times at the single operation conditions.

Figure 5.1. Single droplet combustion set-up.
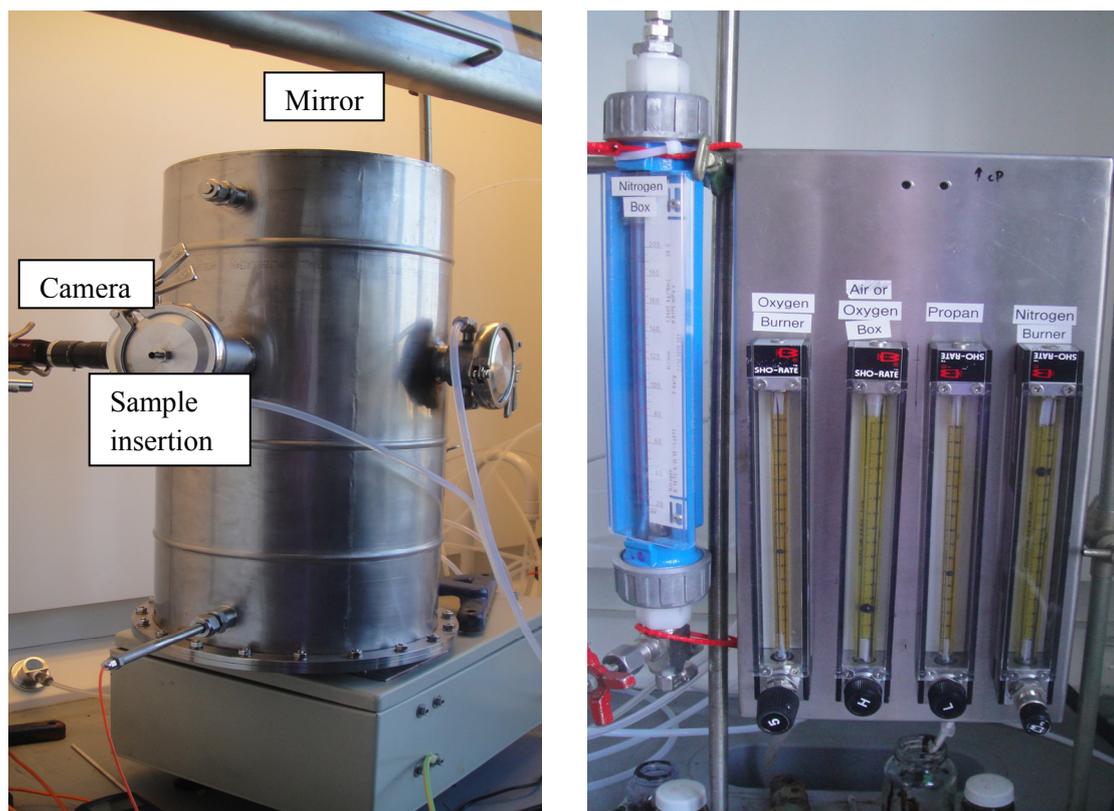
Figure 5.2. Single droplet combustion set-up.
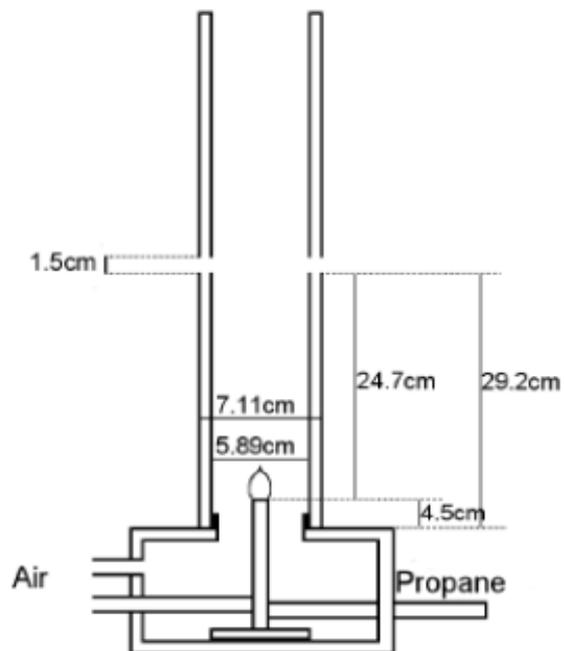
Figure 5.3. The dimension of ceramic tube reactor and burner position inside the jacket.

5.3   Results and Discussion

5.3.1   Thermogravimetric studies

Thermogravietric analysis is an analysis technique that is widely used to evaluate the thermal behavior of fuels in terms of evaporation and combustion characteristic. Figure 5.4 and 5.5 show the TG weight loss signal and DTG curves for the bio-oils from pine wood and wheat straw, heated at a heating rate of 10 ^{o}C/min under nitrogen (pyrolysis) and 10 % of oxygen (combustion) environment. A TGA curves display weight losses as a function of temperature in controlled atmosphere, whereby DTG curve emphasizes the zone of reaction where various reaction steps are taking place over the entire temperature range.

Figure 5.4 shows the TG curve of weight change of bio-oil samples as a function of temperature. Almost similar thermal behaviors are obtained for both bio-oil samples as seen in Figures 5.4(a) and Figure 5.4(b). In general, three different regions can be distinguished from a TG curve and shown by the dotted vertical lines. The first phase (temperature below 200 ^{o}C) corresponds to the removal of water and light volatiles, where the weight loss of approximately 40 % was observed for both tested bio-oils. This behavior indicates that these bio-oils are characterized by a higher content of light fractions that is easily vaporized at temperature lower than 200 ^{o}C. In addition, the GC-MS analysis of wheat straw and pine wood bio-oils done in previous work (Chapter 3) confirms that these bio-oils are dominated by acetic acid which is 20 - 40 % of the volatile oil fraction.

The second phase, occurring at temperature between 200 to 500 ^{o}C, the drop in weight of the samples is due to release of light components by cracking processes of heavy hydrocarbons (carboxylic acids, furfural, hydroxyacetaldehyde, methoxy and dimethoxyphenols compounds) (De Wild *et al*., 2008). At this stage, weights of the bio-oils are reduced to below 40 %. Finally, at the temperature above 500 ^{o}C the combustion of char residue occurred in the presence of oxygen (Phase III).

The DTG curve (Figure 5.5) confirms this, showing two maximum distinct peaks. The first maximum temperature peak rate of bio-oil from straw and wood occurred at almost similar temperature of 162 ^{o}C and the second maximum peak rate of straw bio-oil and wood bio-oil attained at the temperature of 495 ^{o}C and 470 ^{o}C respectively. The first peak represents the evolution of water and volatilization of light hydrocarbons from the bio-oil, whereas the second peak corresponds to the combustion of the residue. The combustion profile (in oxygen) diverges initially from the evaporation profile (in nitrogen) at about 400 ^{o}C.

At a final temperature of 700 °C, the solid residue left in the presence of oxygen was about 1.7 wt. % and 1.3 wt. % for the straw oil and the wood oil, respectively. On the other hand, the solid residues remaining after 700 °C in nitrogen gas were higher (i.e. 27 wt. % for the straw oil and 25 wt. % for the wood oil). Another observation is that the remaining solid residue for straw oil is higher as compared to the wood oil indicating that the straw oil contains a higher amount of ash. The events taking place during the thermal degradation of the bio-oil samples in both oxidative (O_2) and non-oxidative (N_2) environment and the corresponding temperatures and weight losses are summarized in Table 5.2.
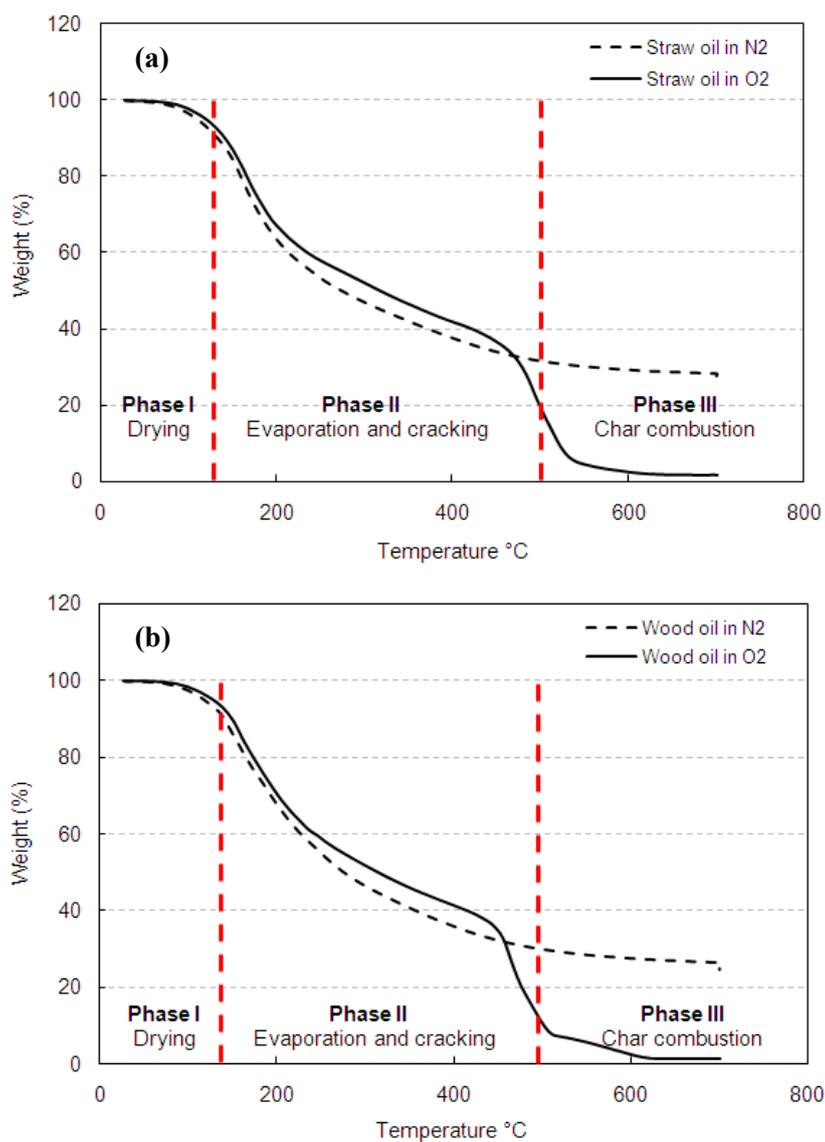
Figure 5.4. TGA curves of the pyrolysis oils (a) Straw oil and (b) Wood oil, respectively in N_2 and O_2 environment.
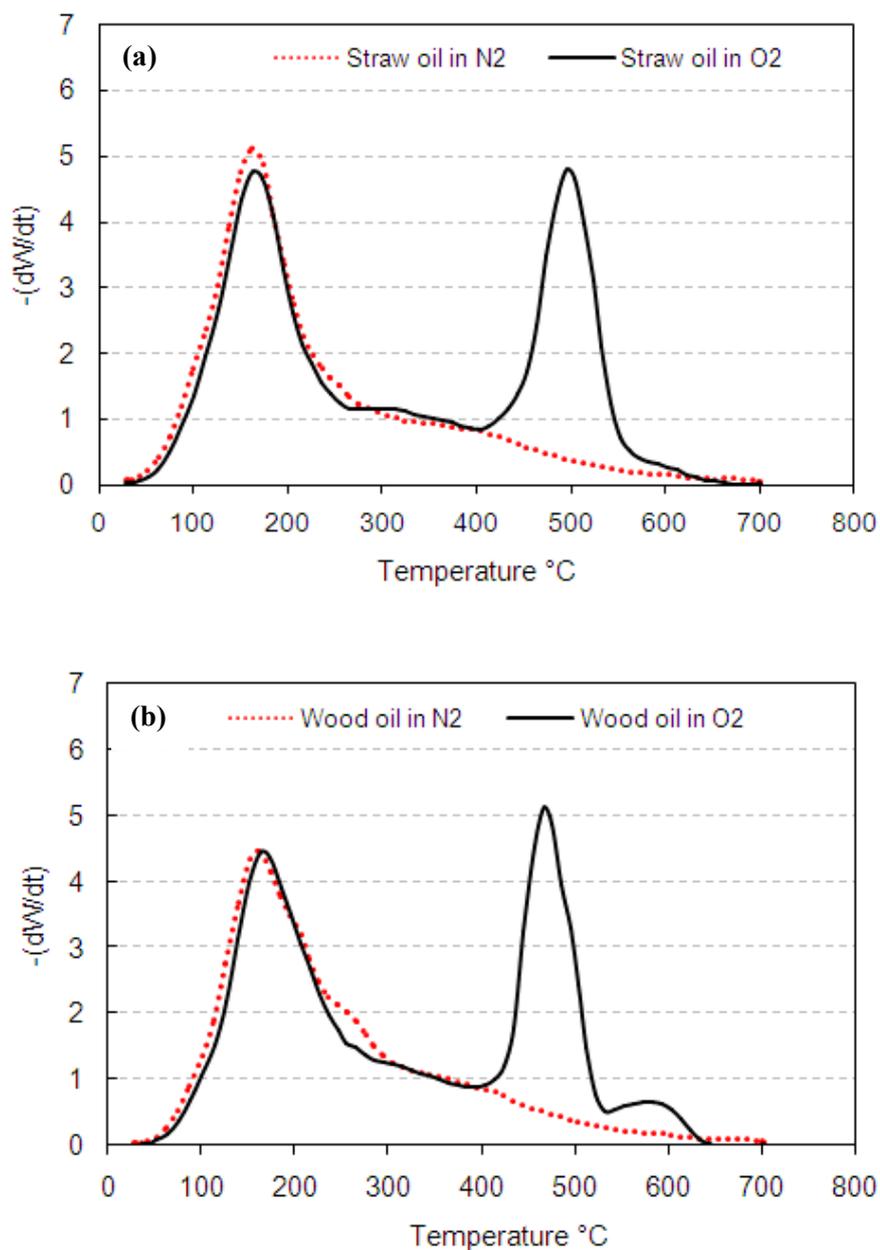
Figure 5.5. DTG curves of the pyrolysis oils (a) Straw oil and (b) Wood oil, respectively in N_2 and O_2 environment.

Table 5.2 Characteristic temperatures, mass fraction and weight loss of bio-oil samples in TGA.

Sample	First Maximum peak rate and weight loss (in N_2)	Ignition in an oxidation environment	Second Maximum peak rate and weight loss (in O_2)	Residual fraction at 700 °C (in O_2)	Residual fraction at 700 °C (in N_2)
Straw oil	162 °C; 21.5 wt. %	400 °C	495 °C; 77.9 wt. %	1.7 wt. %	27 wt. %
Wood oil	162 °C; 18.6 wt. %	400 °C	470 °C; 74.6 wt. %	1.3 wt. %	25 wt. %

5.3.2 General Single droplet combustion characteristic

In this study, the evolution of combustion of bio-oil droplets was recorded by a digital video camera. The initial bio-oil droplet diameter is assumed to be spherical. It is observed that the bio-oil droplet undergoes three main stages when it is exposed to the hot flowing gas stream which are heating and ignition, devolatilisation and char combustion, respectively. The combustion of the bio-oil droplets begins with an enveloping blue. The flame then turns to a yellow tail and finally disappears. After the flame extinction, the remaining char particle oxidizes and forms ash residues.

It should be noted that in this study, the heating and ignition time is defined as the time from the insertion of the bio-oil sample into the tube reactor until the first blue flame is visible. The devolatilization time is defined as the time from the first blue flame is seen until the last flame disappears. The char combustion time is the time from the last flame disappears until the droplet diameter diminished and the char stops glowing, and forms an ash residue.

Figures 5.6 (a-h) show a sequence of video images from the combustion of wheat straw bio-oil droplet size of 1500 μm at a temperature of 1000 °C. An initial gas velocity of 1.6 m/s and 3% of oxygen concentration were maintained in the furnace system. The first stage, which is heating up to ignition (Figure 5.6 (a-b), followed by the evaporation and the combustion of volatiles (Figures 5.5 (b-e)). During the evaporation and gas combustion, it is observed that the bio-oil droplets were surrounded by yellow flame, showing the flame of the vapors/hydrocarbons from the droplet. Finally, as all volatiles are released, the conversion of the char starts (Figures 5.6 (f-g)) and the ash is then formed (Figure 5.6 (h)).

For comparison, the droplet combustions history of heavy fuel oil is recorded and shown in Figures 5.7 (a-h). The experimental conditions were similar as for the wheat straw bio-oil. Compared to the heavy fuel oil droplet, the ignition time of the wheat straw bio-oil is longer. The heating and ignition time for the wheat straw bio-oil is about 343 ms which is longer than the heavy fuel oil, 183 ms (see Figure 5.6 (b) and Figure 5.7 (b)). The longer ignition time of the straw oil is probably caused by the higher water and oxygen content of the straw bio-oil (Solantausta *et al*., 1993; Shihadeh and Hochgreb, 2000).

Figures 5.6 (b-e) and Figures 5.7 (b-e) also show the devolatilisation process for both the wheat straw bio-oil and the heavy fuel oil. The devolatilisation is defined to start when ignition were seen. During the devolatilisation stage, it is observed that as the time increases, the wheat straw bio-oil started to show bubbling and disruption, and swelling to about twice of its original diameter (Figures 5.6 (b-e)). However, this phenomenon does not occur to the heavy fossil oil droplets (Figures 5.7 (b-e)).
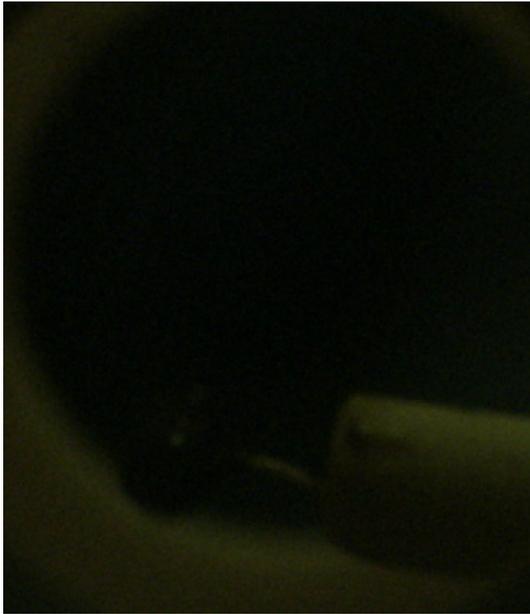
(a) Start-up at 0.0 s.
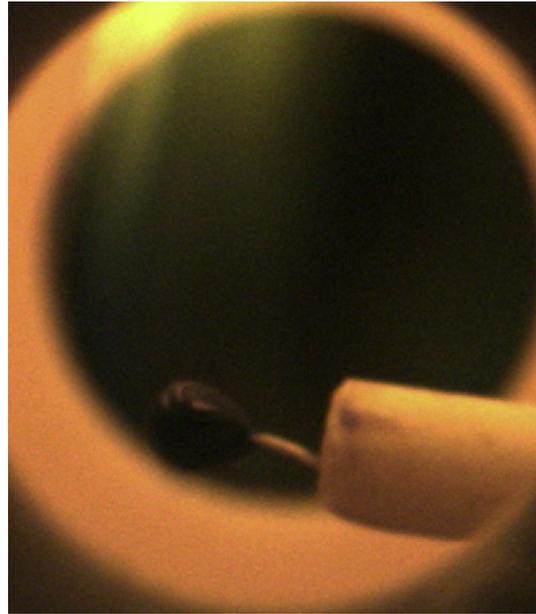
(b) Ignition seen and devolatilisation begins at 343 ms.
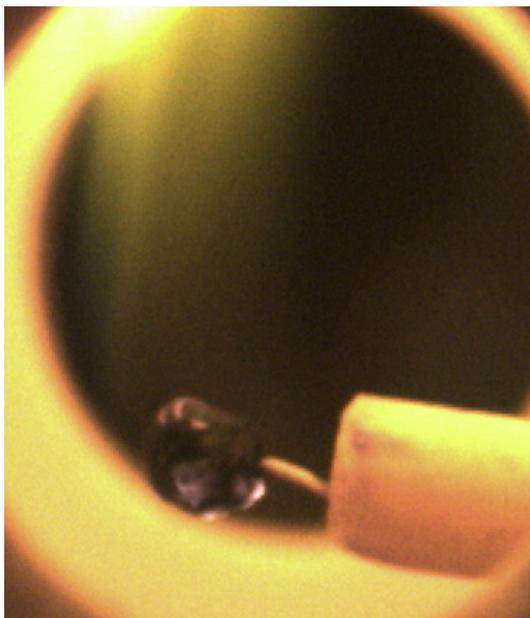
(c) Devolatilitation in progress at 434 ms.
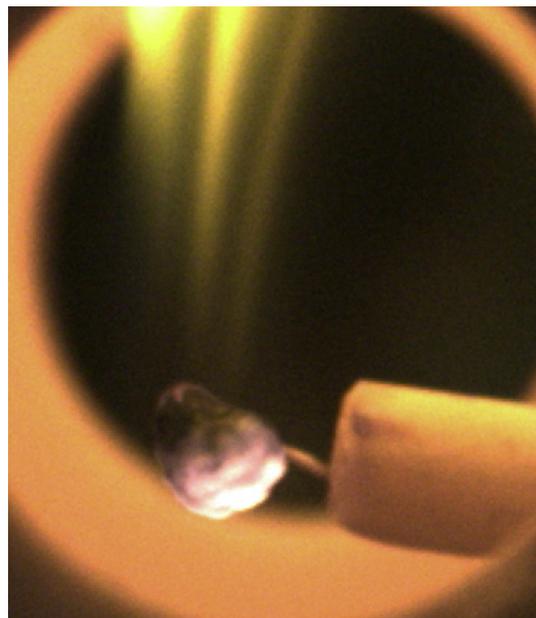
(d) Devolatilitation in progress at 571 ms.
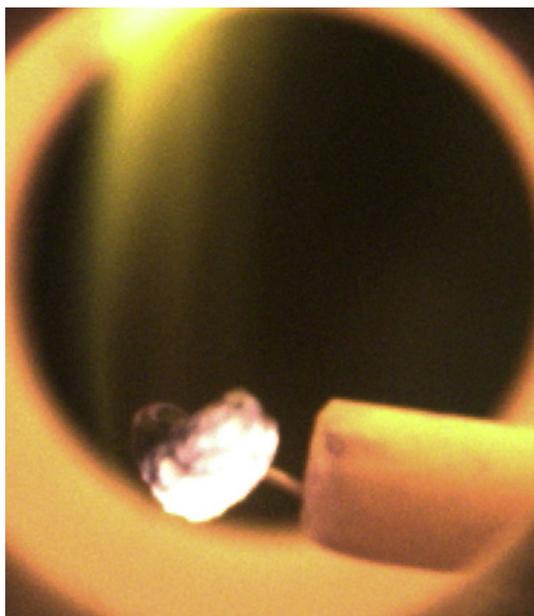
(e) Devolatilisation in progress at 707 ms.
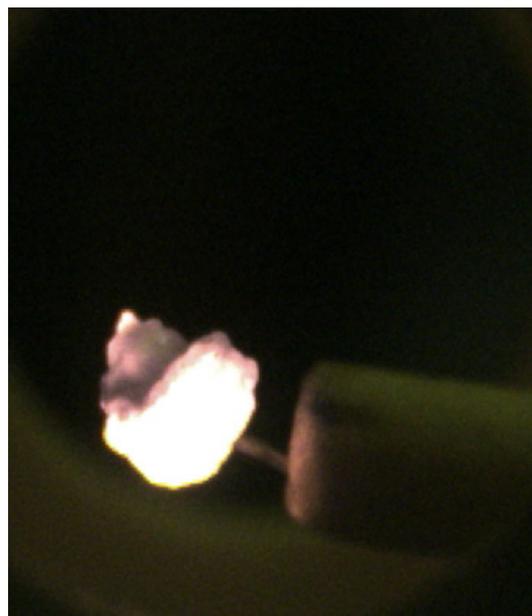
(f) Devolatilisation completed and Char oxidation starts at 2605 ms.
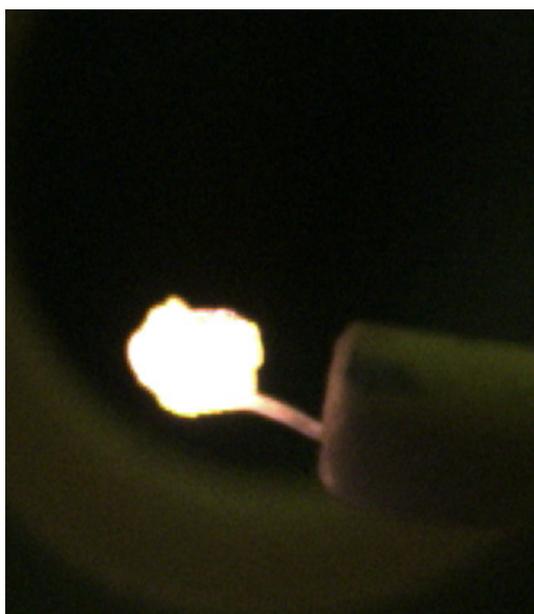
(g) Char oxidation in progress at 14058 ms.
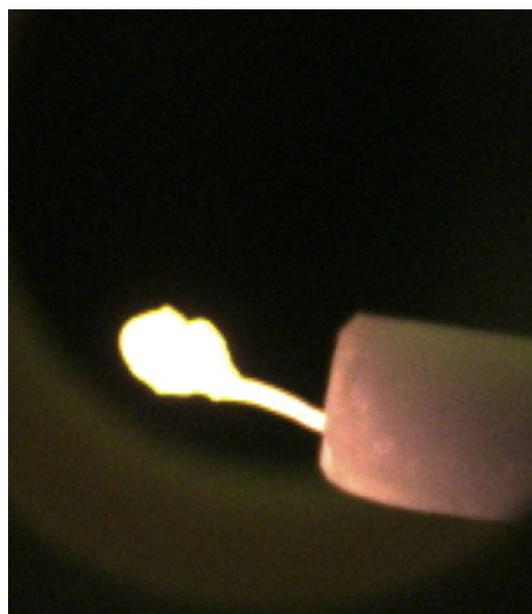
(h) End of Char oxidation with the formation of ash residue at 29121 ms.

Figure 5.6. Sequence images of combustion of the wheat straw bio-oil droplet. (Experimental conditions - Initial droplet size: 1500 μm; Reactor temperature: 1000 °C; O_2 concentration: 3% and Gas velocity: 1.6 m/s).

The bubbling and swelling event could be due to the internal evaporation of lighter species such as water vapor, alcohols, and acids. The depletion of these lighter species enriches the droplets in heavier compounds, which occurs especially on the droplet surface as internally lighter species are trapped. As a result, the vaporization of the light compounds inside the droplets generates pockets of vapors that swell the droplets. This process finally produces larger particles, which are usually 2-3 times of the original diameter and have large internal cavities and thin walls. Pine wood bio-oil droplet combustion tess reported by D'Alessio *et al.*, (1998) using smaller droplet (600 µm) and a furnace temperature of 1200 °C show a growing of the droplets up to 1.5-2 times of the initial diameter. This swelling phenomenon has also been observed by the other researcher (Calabria *et al.*, 2007). However this phenomenon is not experienced during the devolatilisation stage of heavy fossil fuel oil droplets (see Figures 5.7 (c-e)). The diameter of the heavy oil droplet remains constant until the char combustion takes place. The same observation is also reported by D'Alessio *et al.*, (1998).

Figure 5.6 (f) and Figure 5.7 (f) show the char combustion that takes place after the devolatilisation stage for the wheat straw and the heavy oil droplet, respectively. It can be seen that the flame is disappeared, showing that the devolatilisation is completed and char is started to oxidize. The char combustion of the wheat straw oil droplet begins earlier at around 2.6 s, whereas the heavy oil droplet char combustion started later at 3.5 s.

(a) Start-up at 0.0 s.
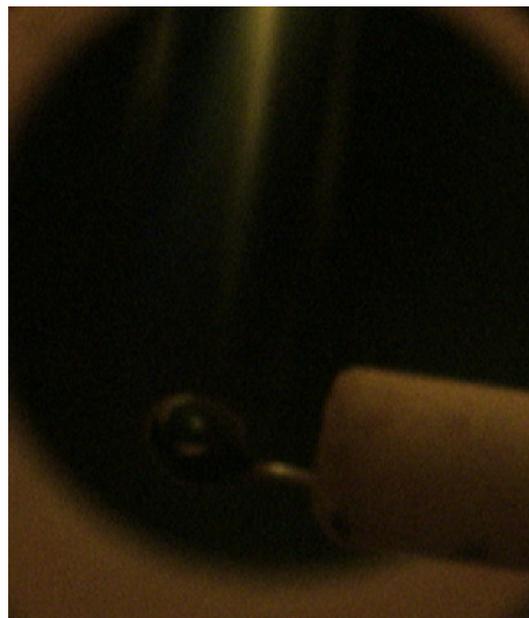
(b) Ignition seen and devolatilisation begins at 183 ms.
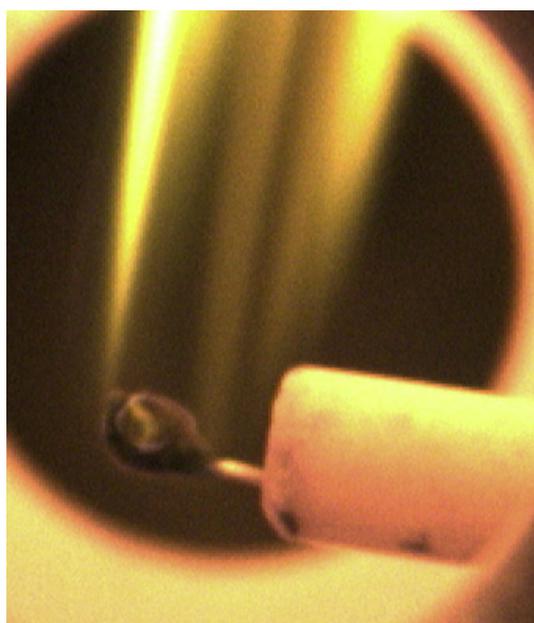
(c) Devolatilisation in progress at 1692 ms.
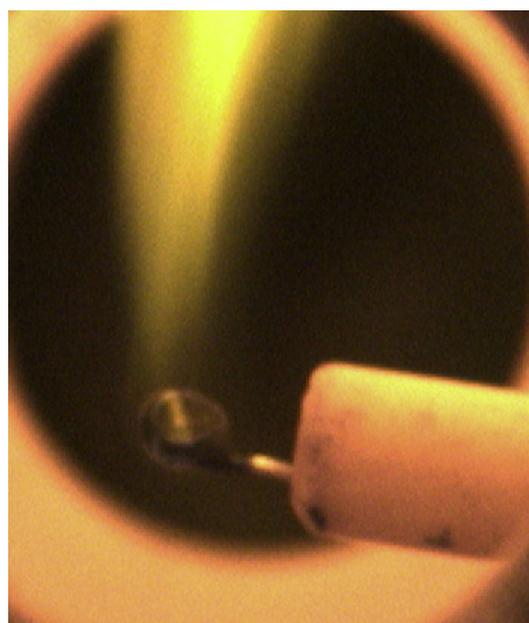
(d) Devolatilisation in progress at 1966 ms.
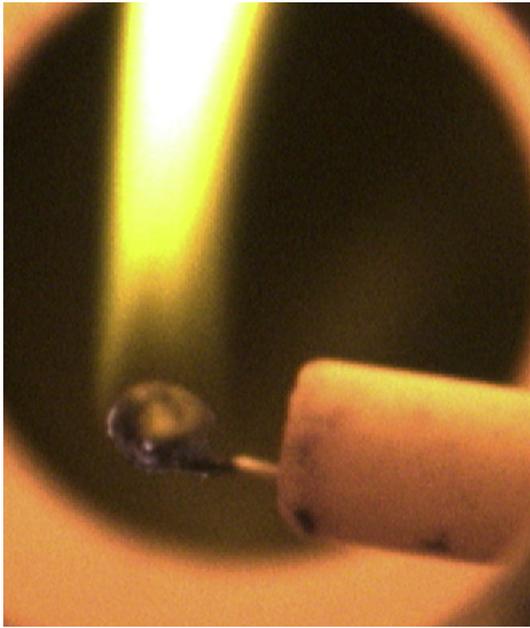
(e) Devolatilisation in progress at 2126 ms.
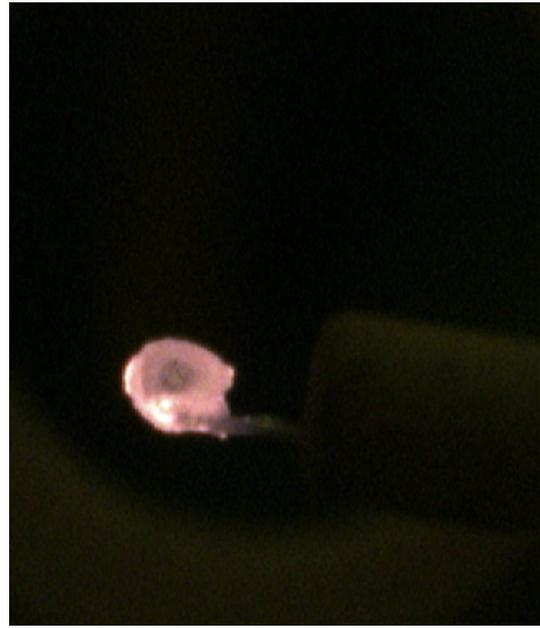
(f) Devolatilisation completed and char oxidation starts at 3520 ms.
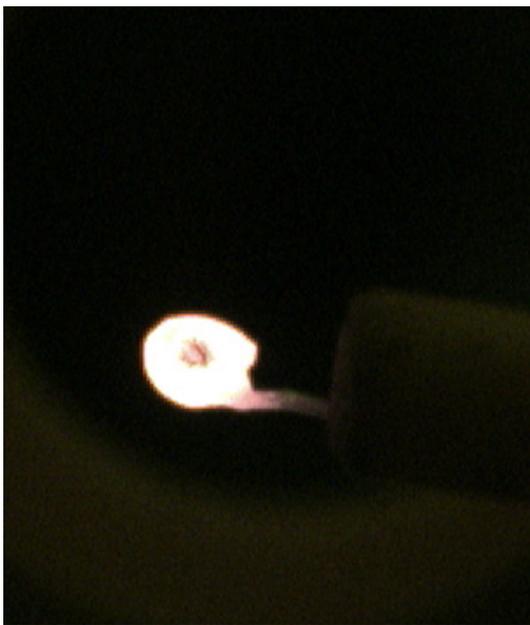
(g) Char oxidation in progress at 7840 ms.
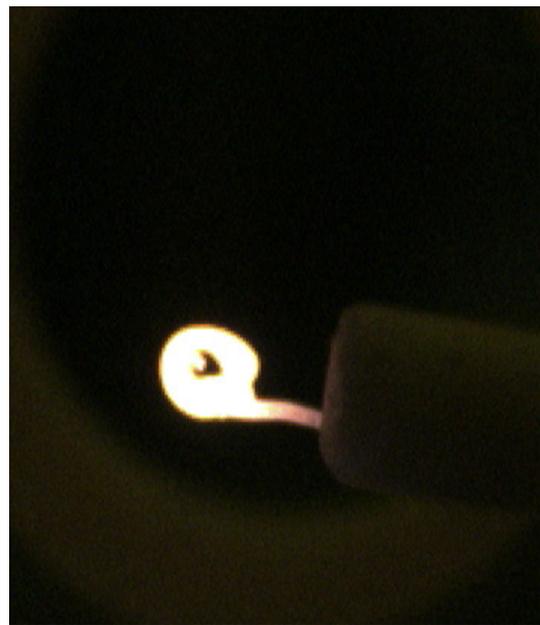
(h) End of char oxidation with the formation of ash residue at 13395 ms

Figure 5.7. Sequence images of combustion of the heavy fossil fuel oil droplet. (Experimental conditions - Initial droplet size: 1500 µm; Reactor temperature: 1000 °C; O_2 concentration: 3% and Gas velocity: 1.6 m/s).

Figure 5.8 shows a plot of $(D/D_i)^2$ for the wheat straw oil and the pine wood oil as a function of time. As the pyrolysis gas burning progresses, the droplet swelling became more intensive during the 0.5-3 s periods of combustion and after that the size of droplet started to decrease back to the original size and then decreased again after char oxidation took placed as shown in Figure 5.8. The measured swelling factor $S = D^2/D_i^2$ is up to 1.5-4.0 times of the initial diameter. On the contrary, the combustion of heavy fuel oil droplet shows no swelling and the droplet diameter remains the same until the burning is completed.
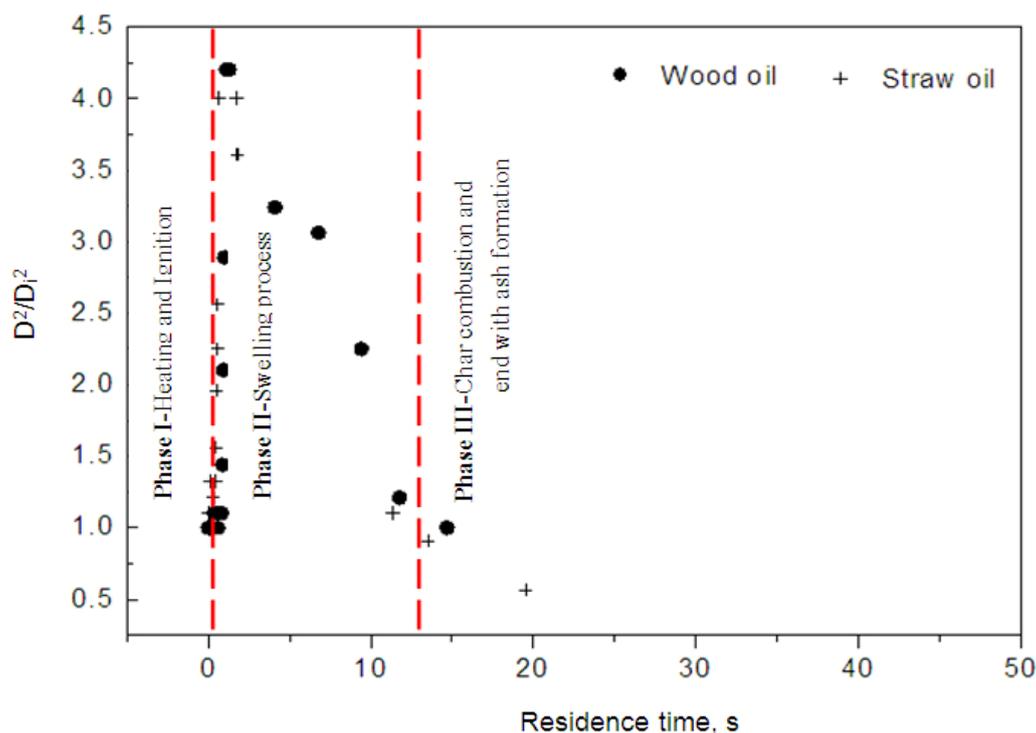

Figure 5.8. A plot of $(D/D_i)^2$ for the wheat straw oil and pine wood oil as a function of time (second). Initial droplet diameter is 1500 µm at a reactor temperature of 1000 °C, 3% of O_2 and gas velocity of 1.6 m/s.

5.3.3   The evaluation of ignition, devolatilization and char combustion time

Figures 5.9 (a-d) show the droplet combustion stages as a function of reactor temperatures. The droplet combustion is divided into three main stages, which are ignition, devolatilization and char combustion. The time for each stage was measured (in second) based on the recorded video timing.

The droplet combustion profiles can be distinguished clearly at a lower temperature of 1000 °C. At a reactor temperature of 1000 °C, the ignition time for the straw oil and pine wood oil is longer than that of heavy fuel oil, which is in the range

of 300-450 ms as shown in the Figure 5.9 (a), and it only took about 183 ms for the heavy fuel oil to ignite. As temperature increases, the ignition time for both straw oil and wood oil is reduced to an almost similar time which is approximately 200 ms. Due to the set-up limitation, the ignition time for the heavy oil can not be measured because it ignited earlier before entering the reactor central tube. It occurred very fast and this also happened sometimes to the bio-oil, particularly at higher temperatures. Therefore, the ignition times of the bio-oils could not be determined at 1400 °C. Overall, the ignition time decreases with the increasing of the reactor temprature because of more heat were supplied to the droplet.

Devolatilisation time is found to be influenced by the reactor temperature, fuel type and droplet diameter. Compared to the wheat straw oil, the devolatilisation time for pine wood oil is shorter. At 1000 °C, the devolatilisation period for the wheat straw is approximately 1800 ms and 750 ms for the wood oil sample. At a higher reactor temperature (1200 °C), the devolatilisation period of the wheat straw oil and the pine wood oil is 1670 ms and 320 ms, respectively. However, the devolatilisation time for the heavy oil was longer compared to the biomass-derived bio-oil (Figure 5.9 (b)). Biomas-derived bio-oils had a shorter devoltilization time due to the swelling phenomenon. Previous study (Liu *et al*., 2011) reported that the existence of swelling reduces the devolatilisation time.

In addition, the char combustion time for of the biomass-derived bio-oil takes longer time as compared to the heavy fossil oil char combustion phase. Besides, the total burning time (average) of a droplet of 1.5 mm for all the investigated fuels is presented in Figure 5.9 (d). It is seen that the droplet lifetime for heavy fuel oil is much shorter than the biomass-derived bio-oils for all temperature ranges. At 1000 °C, the droplet burning lifetimes for the straw oil, wood oil and heavy oil are approximately 26 s, 14 s and 13 s, respectively. The droplet burning lifetimes of 13 s, 9 s and 6 s were observed for the straw oil, the wood oil and the heavy oil, respectively at a temperature of 1200 °C. At higher temperature (1400 °C), the droplet burning lifetimes for the heavy fuel oil is reduced to 3 s, whereby almost similar time were seen for the both bio-oils to complete their burning process.
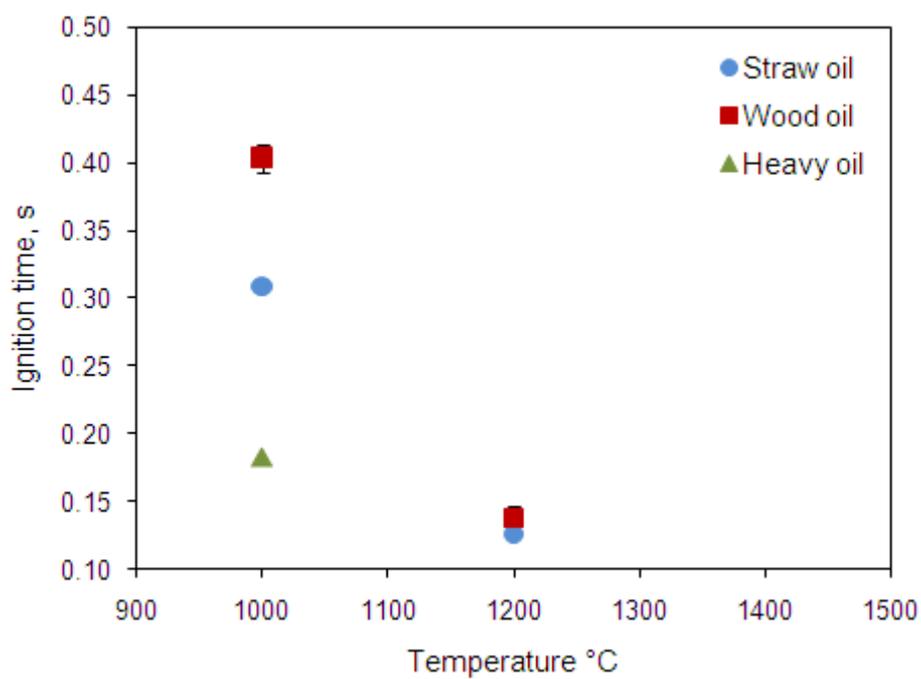
(a) Heating and ignition time
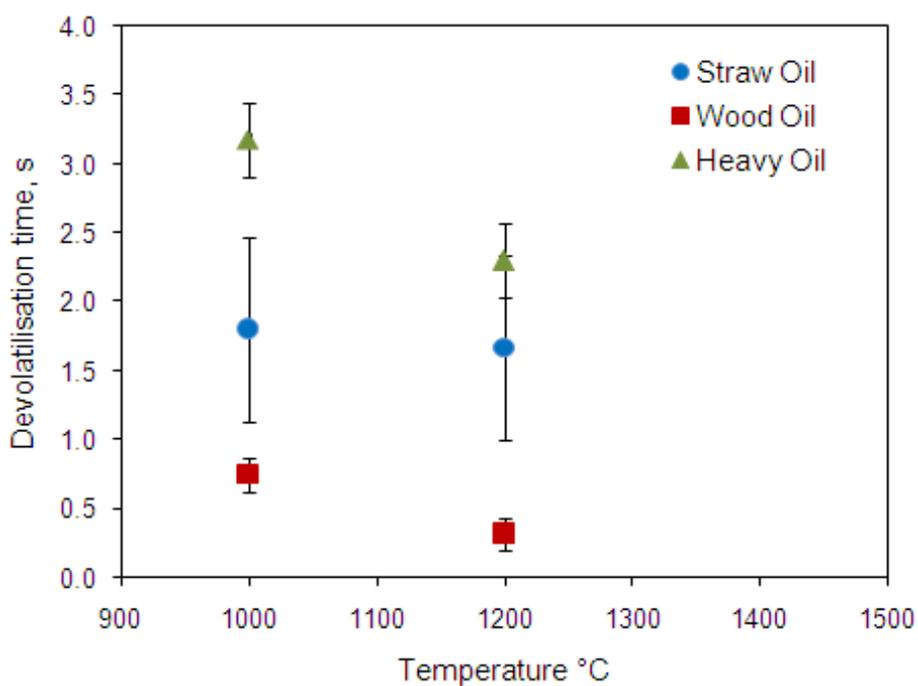
(b) Devolatilisation time
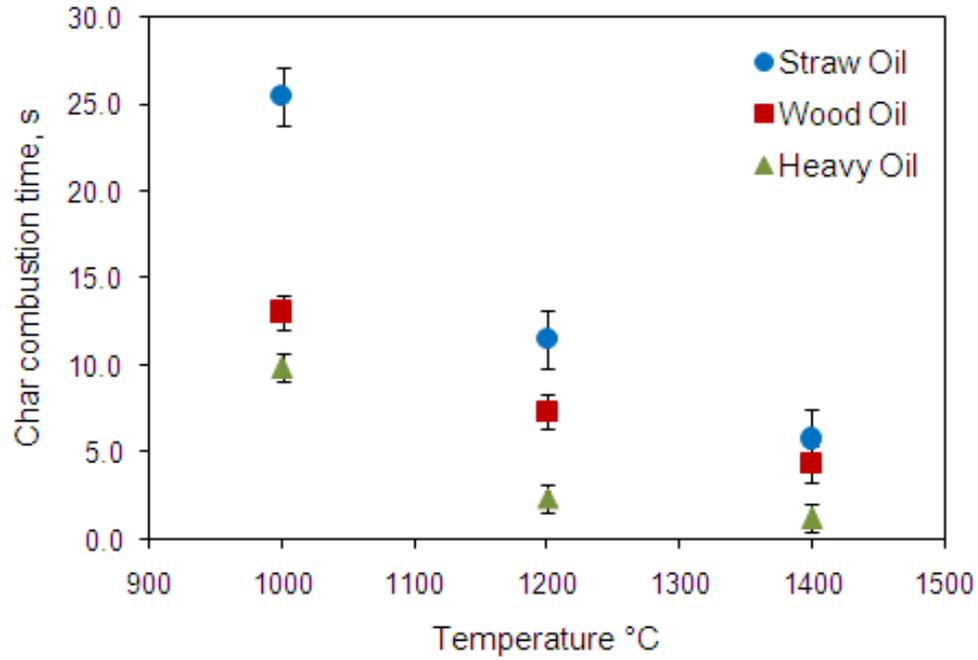
(c) Char combustion time
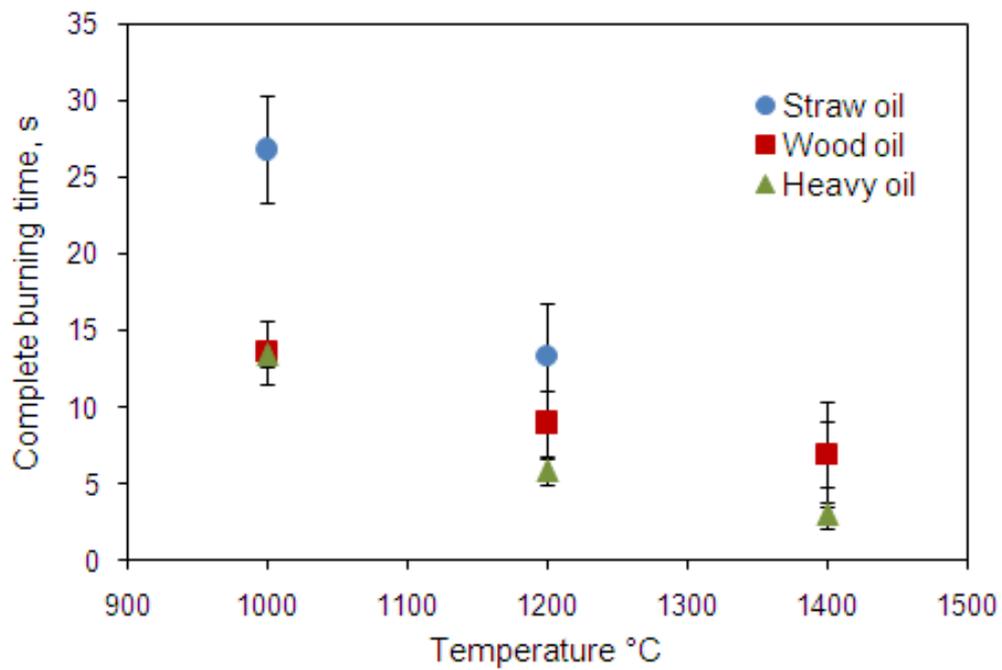
(d) Droplet lifetime.

Figure 5.9. Combustion of single droplet oils (a) Ignition time (b) Devolatilisation time (c) Char combustion time (d) Droplet completely burned out , respectively, in seconds with a droplet diameter of 1.5 mm, V = 1.6 m/s and O_2= 3 %.

5.4   Conclusion

The objective of this study is to investigate the combustion behavior of pyrolysis oils derived from wheat straw and pine wood. The work is done in two parts. The first part of this study applied the technique of thermogravimetric analysis (TGA) to study the thermal treatment of the pyrolysis oils under well controlled temperature in an oxidative (O_2) and non-oxidative (N_2) environment. Drying, evaporation of light components and cracking of heavy fractions and char combustion processes were identified through TGA-DTG curves for the tested bio-oils sample. It can be seen that the removal of water and evaporation of light hydrocarbons occurred below 200 °C, release of light components by cracking of heavy hydrocarbons in the bio-oil occurs at the temperature above 200 up to 500 °C, and finally the char combustion occurs at temperatures above 500 up to 700 °C.

The seecond part of this study investigated the combustion of single droplets of pyrolysis oils in a single droplet combustion chamber and compared with the combustion of heavy fossil fuel oil. The droplet combustion history was recorded and the time taken for each stage was measured. It was observed that the burning of bio-oil droplet experienced large swelling with swelling factors, $S=(D/Di)^2$, up to 4 times of the initial droplet diameter. The growing of the bio-oil droplet diameter during the devolatilisation stage is due to the swelling of the droplet as shown in Figure 5.6 (b-e). This phenomenon is more pronounced as temperature increases. However, the burning of heavy fuel oil droplet showed no swelling. The droplet combustion test with a diameter of 1500 μm shows that heavy fuel oil had longer devolatilisation time and shorter char combustion time as compared to the biomass-derived bio-oils. The shorter devolatilisation time of the biomass-derived bio-oil is due to a higher content of light components in the bio-oils, which is easily vaporized at a lower temperature. The TGA-DTG curves confirms this, showing one major peak at a temperature below 200 °C, with an almost 40% of initial mass of bio-oils were lost.

In addition, the shorter combustion time of the heavy fuel oil is due to the lower char content. In addition, the bio-oil droplet combustion lifetime decreases with increasing of the reactor temperature. At 1000 °C, the droplet burning lifetimes for the straw oil, wood oil and heavy oil are approximately 26 s, 14 s and 13 s, respectively. The droplet burning lifetimes of 13 s, 9 s and 6 s were observed for the straw oil, the wood oil and the heavy oil, respectively at temperature of 1200 °C. At higher temperature (1400 °C), the droplet burning lifetimes for the heavy fuel oil is reduced to 3 s, and almost similar times were seen for both bio-oils, which were 7 s. In summary, biomass-derived bio-oil is difficult to ignite, has a shorter devolatilisation time and a longer char combustion time.

References

Acikgoz, C., Kockar, A. M. (2007). Flash pyrolysis of Linseed (Linum usitatissimum L.) for production of liquid fuels. *Journal of Analytical and Applied Pyrolysis*. 78, 406-412.

Bridgwater, A. V., Peacoke, G. V. C. (2004). Fast pyrolysis processes for biomass. *Renewable and Sustainable Energy Reviews*. 4, 1-73.

Calabria, R., Chiariello, F., Massoli, P. (2007). Combustion fundamentals of pyrolysis oil based fuels. *Experimental Thermal and Fluid Science*. 31, 413-420.

Caputo, A. C., Palumbo, M., Pelagagge, P. M., Scacchia, F. (2005). Economics of biomass energy utilization in combustion and gasification plants: Effect of logistic variables. *Biomass & Bioenergy*. 28, 35-51.

De Wild, P. J., Den Uil, H., Reith, H., Kiel, J. H. A., Heeres, H. J. (2008). Biomass valorisation by staged degasification. A new pyrolysis-based conversion option to produce value-added chemicals from lignocellulosic biomass. *J. Anal. Appl. Pyrol*. 85, 124-133.

D'Alessio, J., Lazzaro, M., Massoli, P., Moccia, V. (1998). Thermo-optical investigation of burning biomass pyrolysis oil droplets. Twenty-seventh Symposium (International) on Combustion/The Combustion Institute. 1915-1922.

Garcia-Perez, M., Lappas, P., Hughes, P., Dell, L., Chaala, A., Kretschmer, D., Roy, C. (2006). Evaporation and combustion characteristics of biomass vacuum pyrolysis oils. *IFRF Combustiion Journal*. 200601, 1-27.

Gust, S. (1997). Combustion Experiences of Flash Pyrolysis Fuel in Intermediate Size Boilers. In: *Developments in Thermochemical Biomass Conversion* (Eds. A. V. Bridgwater, D. G. B. Boocock). Blackie Academic & Professional, London. 481-488.

Hallet, W. L. H., Clark, N. A. (2005). A model for the evaporation of biomass oil droplets. *Fuel*. 85, 532-544.

Liu, J., Jiang, X., Han, X. (2011). Devolatilization of oil sludge in a lab-scale bubbling fluidized bed. *Journal of Hazardous Materials*. 185, 1205-1213.

Lopez, J. G., Monfort, S. J. J. (2000). Preliminary test on combustion of wood derived fast pyrolysis oils in a gas turbine combustor. *Biomass & Bioenergy*. 19, 119-128.

Oasmaa, A., Leppamaki, E., Koponen, P., Levander, J., Tapola, E. (2007). Physical characterization of biomass-based pyrolysis liquids. Application of standard fuel oil analyses; VTT Publication 306. VTT: Espoo, Finland. 46 pp + appendices (30 pp).

Oasmaa, A., Kytö, M., Sipilä, K. (2001). Pyrolysis Oil Combustion Tests in an Industrial Boiler. In: *Progress in Thermochemical Biomass Conversion* (Ed. Bridgwater, A.V.), Blackwell Science, Oxford, UK, 1468-1481.

Shaddix, C. R., Tennison, P. J. (1998). Effects of char content and simple additives on biomass pyrolysis oil droplet combustion. Twenty-seventh Symposium (International) on Combustion/The Combustion Institute. 1907-1914.

Solantausta, Y., Nylund, N. O., Westerholm, M., Koljonen, T., Oasmaa, A. (1993). Wood pyrolysis liquid as fuel in a diesel power plant. *Bioresource Technology*. 46, 177-188.

Solantausta, Y., Nylund, N. O., Gust, S. (1994). Use of pyrolysis oil in a test diesel engine to study the feasibility of a diesel power plant concept. *Biomass & Bioenergy*. 7, 297-306.

Solantausta, Y., Bridgwater, A. V., Beckman, D. (1995). Feasibility of power production with pyrolysis and gasification systems. *Biomass & Bioenergy*. 9, 257-269.

Shihadeh, A., Hochgreb, S. (2000). Diesel Engine combustion of biomass pyrolysis oils. *Energy Fuels*. 14(2), 260-274.

Wornat, M. J., Porter, B. G., Yang, N. Y. C. (1994). Single droplet combustion of biomass pyrolysis oils. *Energy Fuels*. 8, 1131-1142.

Yaman, S. (2004). Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Convers Management*. 45, 65-75.

CHAPTER 6

Conclusions and Further Work

6.1   Conclusions

In this work, the optimization of the flash pyrolysis process in order to produce a bio-oil from different agricultural residues has been performed by using a bench scale pyrolysis centrifuge reactor (PCR). The influences of pyrolysis operating conditions such as temperature, feedstock moisture content and type of biomass on the pyrolysis products yield have been investigated. In addition, detailed investigation of the bio-oils storage and stability properties has been performed. Finally the bio-oils combustion behaviors have also been analyzed.

The main achievements obtained from this work are summarized as follows:

1. The influence of the straw moisture content and the reactor temperature on the flash pyrolysis product yield has been experimentally investigated. It was found that the presence of different moisture levels (from 1.5 – 15.0 wt. %) in the feedstock has shown no significant effect on the pyrolysis product distribution. The liquid organics yields were similar for all straw moisture levels and the yields were almost constant at each reactor temperature. It can be concluded that the water content of the bio-oil mostly originates from the original moisture in the feedstock. The high water content in bio-oil may cause a phase separation and lower the heating value of the oil. The presence of higher amount of water in bio-oils also limits its utilization as a fuel, as it reduces the combustion rates, delay the ignition and lower the adiabatic flame temperatures during combustion. Therefore it is an advantage to use a relatively dry feedstock in order to have a better quality of the bio-oil.

2. The products from wheat straw, rice husk and pine wood pyrolysis have been investigated to determine how differences in the biomass composition influence pyrolysis products yields and the composition of char and bio-oils. It was observed that the formation of char and gas is affected by the biomass alkali content. The presence of potassium in the biomass catalyzes tar conversion to form more gases and hence lowers the liquid product yield and also lowers the optimum liquid yield temperature. The chemical compositions of bio-oils from three feedstocks (wheat straw, rice husk and pine wood) have been analyzed using GC-MS. It was estimated that approximately 10 wt. % of the bio-oils most volatile fraction were analyzed by GC-MS. The results show that the analyzed fractions for all the biomasses are dominated by acetic acid which is 20 - 40 % of the volatile oil fraction.

3. The influences of storage time and temperature on pH, viscosity, heating value and water content of flash pyrolysis oil have been investigated (aging test). The bio-oil samples were stored in closed glass containers at three different temperatures: at room temperature ($\approx$ 20 °C) for up to 130 days, at 50 °C for up to 14 days and at 80 °C for up to 24 hours. It was generally observed that aging occurs faster and oil viscosity increases at higher temperatures. It was found that the pH and heating value were not affected during the aging tests whereas the water content and viscosity were significantly altered at elevated temperatures. Bio-oils viscosity increases from 27.4 to 64.3 cP (for wheat straw) and from 47.8 to 121.6 cP (for pine wood) at 80 °C over 24 hours of storage. It was also found that the aging rates of the bio-oil of wheat straw were slower compared to the bio-oil from pine wood. The viscosity increase rates for pine wood bio-oils were 0.2 cP/day (at room temperature), 2.1 cP/day (at 50 °C) and 74 cP /day (at 80 °C) respectively. For wheat straw bio-oils, the viscosity increase rates of 0.1, 1.2 and 38 cP/day were observed when stored at room temperature, at 50 °C and at 80 °C respectively. In addition, both bio-oils were fairly stable when stored at room temperature for up to 130 days.

4. The combustion behavior of bio-oils derived from wheat straw and pine wood have been studied. The study has been done in two parts. The first part of the study investigated the thermal treatment of the pyrolysis oils under well controlled temperature in an oxidative (O_2) and non-oxidative (N_2) environment using thermogravimetric analysis (TGA). The result from TGA-DTG curves show that the removal of water and evaporation of light components occurs from room temperature up to 200 °C, with an approximately 40% of the mass of bio-oils were lost at 200 °C. The devolatilisation and cracking of heavy hydrocarbons attains in the temperatures of 200-500 °C, in which the weight of the bio-oil samples is reduced to below 40% and finally the char combustion occurs at temperatures above 500 °C. The second part of the study investigated the combustion of single droplets of pyrolysis oils and compared with the combustion of heavy fossil fuel oil by making experiments in a single droplet combustion chamber. It was observed that the burning of bio-oil droplet experienced large swelling with swelling factors up to 4 times of the initial droplet diameter whereas, the burning of heavy fossil fuel oil droplet showed no swelling. In addition, the devolatilisation times of bio-oils were much shorter as compared to the heavy fossil oil due to a higher content of light components in the bio-oils, which are easily evaporated at low temperatures. The TGA-DTG curves confirms this, showing one major peak at a temperature below 200 °C, which corresponds to the removal of water and evaporation of light components in the bio-oils. However, the shorter combustion time for heavy fuel oil as compared to the bio-oils is observed and the lower formation of char in heavy oil explains the reason. Besides, the droplet burning lifetimes for bio-oils were found to be longer (13 s and 9 s for straw oil and wood oil, respectively) than the heavy fossil fuel oil (6 s) at the temperature of 1200 °C. It can be concluded that the behaviors of bio-oils droplet combustion are different from the heavy fossil

fuel oil in terms of ignition, devolatilisation and char combustion. The bio-oils are difficult to ignite and have a shorter devolatilisation time and a longer char combustion time.

6.2 Further Work

The optimization of the flash pyrolysis process in order to produce bio-oils from different agricultural residues has been performed successfully in this work by using a bench scale pyrolysis centrifuge reactor (PCR). Several parameters that influence the pyrolysis products yield have been experimentally investigated. The suitability of bio-oils to replace fossil fuel in boilers and diesel engines application have also been discussed. However, there are still a number of opportunities for further developments and improvements. Several suggestions for future work are given in terms of:

1. Scientific Analysis Challenges:

    a. To investigate the effect of heating rates on the products distribution and also products composition.

    b. To confirm the content and composition of pyrolysis gas by measuring it using GC-MS in order to get a better understand on how this product change with respect to temperature, type of feed stock, moisture content and biomass particle size.

    c. To investigate the suitability of pyrolysis oil as a liquid fuel substitution by performing the combustion test using appropriate equipment where all the necessary parameters such as emission, soot formation and deposit formations are measured.

2. Pyrolysis Centrifuge Reactor Operational Improvements:

    Several hurdles existing during operating of the PCR unit which results in lower bio-oil yield and difficulties for conducting a long run. The hurdles recognized as set up's limitations must be improved to get a longer run as well as an increase of the bio oil yield. The limitations are listed below:

    a. *Reactor preparation efforts very laborious*

        It requires one to carry (lift) substrate feedstock and feed it into the reactor feed reservoir manually. Conveyor belt is not installed for automatic feeding. Therefore, it can be handy for continuous operation or for automation of the reactor system (i.e as less human intervene as possible)

    b. *Accumulation of solid particles in the condensation nozzle impeded longer operation at lower operating temperature.*

During the course of the reaction, bio-oil is produced via condensation process. The produced bio-oil also consists of fine char (i.e. solid particles). Due to low temperature in the center of the condensation nozzle, bio-oil produced will further condensed into solid form. Thus, clogging the nozzle – the nozzle is easily clogged due to its small inner diameter of 4 mm. Consequently, this increases system pressure and after sometime blocks the incoming vapor.

c. *Gas pump blockage.*

The flow rate of recycle gas is very high (typically 45 NL/min) (based on the high mass of light fraction liquid oil collected after coalescer) and this causes a poor condensation of aerosol and some of the aerosols enter the gas pump and condensed there.

d. *Uninstalled hot-gas filtration.*

The set up do not contain a of hot-gas filtration before the condensation and therefore a high proportion of char remains in the bio-oil.

e. *Reactor configuration.*

The reactor contain a three vertical blade rotor (as shown in red arrows in Figure 6.1) that are responsible for the pressing of biomass onto the hot reactor wall surface. The capability of this vertical blade to press the biomass particle against the hot surface is limited, and blades that directly press the biomass against the wall may work better.

Figure 6.1. Image of inner wheel of pyrolysis centrifuge reactor

List of Publications

Scientific Journals

1. E. W. Bruun, H. Hauggaard-Nielsen, N. Ibrahim, H. Egsgaard, P. Ambus, P. A. Jensen and K. Dam-Johansen. Influence of fast pyrolysis temperature on biochar labile fraction and short-term carbon loss in a loamy soil. *Biomass and Bioenergy*, 35 (2011) 1182-1189.

2. N. Ibrahim, P. A. Jensen, K. Dam-Johansen and H. Egsgaard. Characterization of flash pyrolysis products of wheat straw, rice husk and pine wood. Submitted to the *Journal of Biomass & Bioenergy*.

3. N. Ibrahim, P. A. Jensen and K. Dam-Johansen. Stability and Aging of flash pyrolysis Bio-oils. Submitted to the *Journal of Renewable Energy*.

International Conference

1. N. Ibrahim, P. A. Jensen and K. Dam-Johansen, Effect of biomass mineral matter on the pyrolysis product yields. Proceedings of the 18th European Biomass Conference and Exhibition, Lyon, 3-7 May 2010.

2. N. Ibrahim, P. A. Jensen and K. Dam-Johansen, Influence of reaction water content on wheat straw pyrolysis. International Conference on Energy and Environment, Lucerne, Switzerland, 15-16 October 2012.

Appendix A

Operating Manual of Pyrolysis Centrifuge Reactor (PCR)

Flash Pyrolysis Experiment

The flash pyrolysis experiments were conducted in a bench scale Pyrolysis Centrifuge Reactor (PCR) as depicted in Figure A1. The set-up consists of a screw type feeder, an ablative centrifuge reactor, an electric heater, a cyclone, a condenser, a coalescer, a gas dryer and a pump. The biomass was introduced by the screw feeder into the horizontally oriented Ø 82 x 200 mm tubular reactor. Here, a three-blade rotor with a clearance of 2 mm to the reactor wall rotate at a fixed speed of 14800 rpm creating a centrifugal force at the pipe wall of approximately 1.0×10^4 g (acceleration), and thereby provides rotation of the gas and the biomass particles.

The reactor wall was heated electrically by four independent heating zones located on the outer surface of the reactor tube. While undergoing reaction, the particles moved down the reactor pipe before leaving suspended in the gas through the tangential outlet. Larger char particles were removed by a change-in-flow separator whereas fines were collected by the cyclone. Vapors were condensed in a direct water cooled condenser (bubble chamber) filled with previously produced bio-oil. The temperature in the condenser was controlled to be 55 to 75 °C by means of a pipe coil cooled by tap water. Aerosols that were not retained by the condenser were collected in a coalescer filled with ROCKWOOL® (fibers).

In the coalescer aerosols were removed and the bio-oil was collected in a conical flask. The gas was pumped to the preheater and heated to 400 °C before it is recirculated to the reactor in order to maintain a desired gas residence time of 0.2-0.3 s and avoid condensation of liquid products within the reactor. The amount of produced gas was measured by a temperature compensated gas meter and a sample was collected in a gas bag. Before the gas volume was measured, it was cooled to ambient temperature in order to remove water. The gas residence time in the reactor was calculated based on the experimental data obtained (from pyrolysis product yield).

Figure A1 A schematic diagram of bench scale Pyrolysis Centrifuge Reactor

Followings are the steps/procedures for operating Pyrolysis Centrifuge System (refer Figures A1 and A2).

1. Assemble bubble chamber and ensure the nozzle is centered.
2. Ensure vacuum pump can be turn freely and check for the noise. After that turn the vacuum pump on.
3. Place 500 gm of biomass sample into the feeder.
4. Bolt lid shut and open bleed valve placing the hose in a beaker of water.
5. Weight flasks for the char collection and open flow valves (under table) before mounting flasks with gaskets.
6. Weight coalescer and place with the connecting hose, conical flask and pressure gauge.
7. Closed hose from water condenser with hose clamp.
8. Check leak rate below 5/150 by adjusting small flow meter until no bubbles are observed.
9. Purge the system using Nitrogen (N_2) at flow rate of 30/150 at 5 bars and observe the activity in beaker.
10. Turn on the tracing up to 80% only.
11. Turn on the oil circulation, check the pump rotation and adjust the flow.
12. Fill the beaker with approximately 230 ml of bio-oil (b-chamber), then weight it and after that measure the refractive index of bio-oil.
13. Weight the beaker containing a towel.
14. When tracing has reached set point (SP), disconnect the hose between coalescer and vacuum adjustment valve.
15. Closed the bleed valve and tighten the hose clamp up.
16. Check up the oil temperature to 100°C and then start the motor at 30 Hz.

17. Adjust the reactor and preheat temperatures to set point (SP) temperature.
18. When reactor SP is reached, disconnect the hose clamp and connect the hose to gas meter system.
19. After that, connect thoroughly the hose between conical flask and vacuum adjustment valve.
20. Then start vacuum pump on SP and adjust from zero flow carefully. Monitor the reactor pressure.
21. Start temperature logging.
22. Turn on the cooling water until flow is not audible.
23. Turn on cooling air to oil sump a 100%.
24. Turn off N_2 flow meter and check leak rate by observing bubble flask.
25. Then, place the liquid oil (in step 12) in the bubble chamber.
26. Adjust the rotor speed to SP and note the gas meter reading.
27. After that, turn on the agitation and feeder. Note the time.
28. Start gas collection to large gas bag after approximately 5 minutes.
29. Half-way through the run, make a note of all readings.
30. Stop gas collection one minute prior to feeder stop.
31. Turn off tracing.
32. Reduce the reactor temperature and gas preheater SP to 15°C.
33. Turn off the preheater and reduce rotor speed to 30 Hz.
34. Note gas meter reading.
35. Crank up flow meter shortly in order to clean auger exit and turn off.
36. Stop logging and put on gloves.
37. Drain bubble chamber liquid into beaker with syringe.
38. Turn on small flow meter to 30/150 and disconnect hose from gas meter
39. Turn off vacuum pump, close vacuum valve and clamp the hose.
40. Drain the remaining bubble chamber liquid into beaker, weight and measure refractive index.
41. Turn off cooling water and air. Disconnect hose between bubble chamber and coalescer.
42. Empty round flask below water condenser to conical flask, measure refractive index and weight it.
43. Disconnect coalescer and weight it.
44. Dissemble bubble chamber.
45. Lightly wipe off bubble chamber stand and spilled liquid with towel in beaker and weight it.
46. Filter bubble liquid and wash char with ethanol and acetone (solvent). Then dry char and weight it.
47. Inject 20 ml of ethanol into vacuum adjustment valve and close it.
48. Measure the molecular weight of gas in gas bag.
49. When reactor temperature is below 180°C, turn off motor and note operating hours.
50. Turn off flow meter.
51. When reactor temperature is below 120°C, turn off oil circulation.
52. Determine char mass in flasks and collect it individually. Clean down pipes with drill and leave valves open.
53. Determine residual feedstock.

54. Clean vacuum pump with ethanol and drain liquid from round flask below condenser.
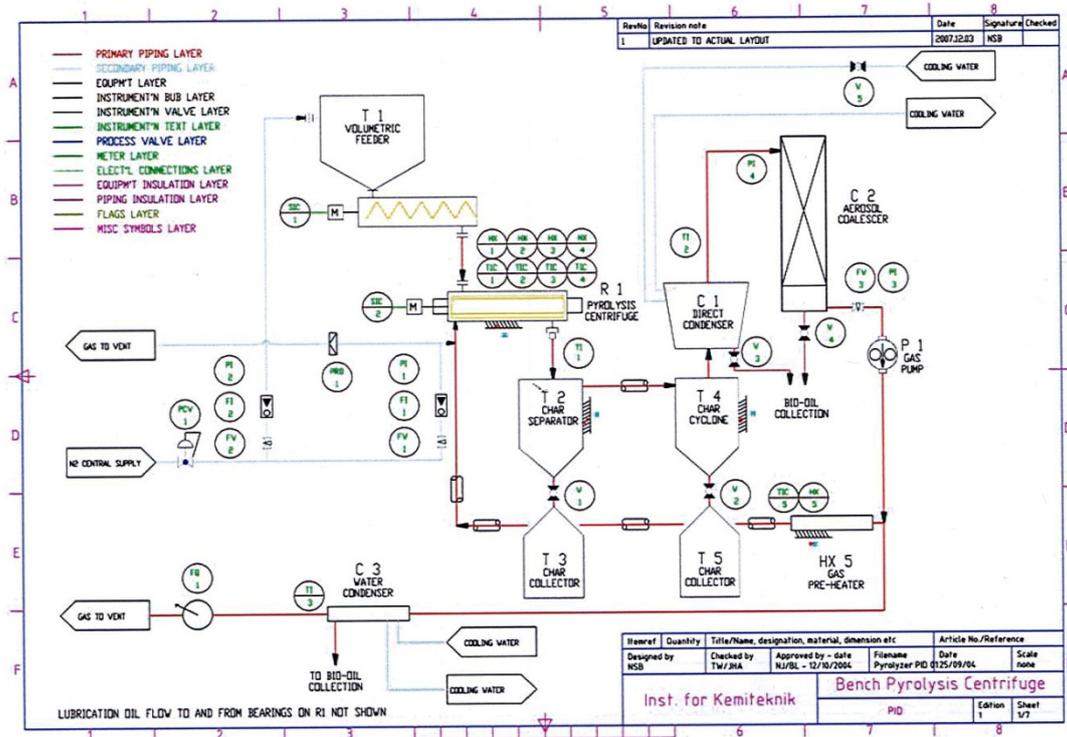
Figure A2   A process and instrumentation diagram (P&ID) of bench scale Pyrolysis Centrifuge Reactor (Bech, 2008)

Reference:

Bech, N. (2008). *In situ flash pyrolysis of straw*. PhD Thesis, Technical University of Denmark. ISBN: 978-87-91435-68-4