REFINING FAST PYROLYSIS OF BIOMASS

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PROEFSCHRIFT

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aan mijn familie, vader en Ilse

Contents

Samenvatting

Pyrolyse-olie die geproduceerd wordt uit biomassa is een veelbelovend vernieuwend alternatief voor fossiele brandstoffen. Deze pyrolyse-olie heeft transport-, opslag- en gebruiksvoordelen ten opzichte van de inhomogene biomassa waaruit zij gemaakt is.

In vergelijking met ruwe olie heeft pyrolyse-olie een andere samenstelling en andere eigenschappen. Hierdoor is direct gebruik problematisch in eindtoepassingen en conversieprocessen, die ontwikkeld zijn voor fossiele brandstoffen. Verbetering van de oliekwaliteit is nodig om de ontwikkeling van pyrolyse-olie toepassingen en de implementatie van de pyrolysetechnologie te versnellen.

Ondanks het grote aantal pyrolysestudies is het begrip van de chemische reacties en fysische processen die zich in de biomassadeeltjes en in de reactor afspelen nog beperkt. Hetzelfde geldt voor de kennis betreffende óf en hoe de olieopbrengst en oliekwaliteit gestuurd kunnen worden door middel van de procescondities. Dit proefschrift richt zich juist op deze gebieden.

Een 1 kg/uur pyrolyse-opstelling is ontwikkeld, waarbij veel aandacht is besteed aan het verkrijgen van een goede massabalans en reproduceerbaarheid van de verkregen data. Deze pyrolyse-opstelling bestaat onder meer uit een wervelbedreactor en twee tegenstroom sproeicondensors, waarin de geproduceerde pyrolysedampen worden gecondenseerd en aërosolen afgevangen worden. Er zijn experimenten uitgevoerd met verschillende soorten biomassa (dennenhout, beukenhout en stro) met verschillende eigenschappen (deeltjesgrootte, deeltjesstructuur, as- en watergehalte). De ontworpen pyrolyse-opstelling maakt het mogelijk de reactortemperatuur, kool- en asgehalte in de reactor, verblijftijd van biomassa en de geproduceerde dampen en de condensor temperatuur over een breed gebied te variëren. De verkregen producten, te weten pyrolyse-olie, gas en kool, zijn voor elk van de experimenten geanalyseerd en gekarakteriseerd. Hierbij is gebruik gemaakt van een nieuw analyseschema, waarbij de olie is opgedeeld in fracties op basis van kookpunt en functionele groepen.

Er is gekeken in welke mate de olieproductie en oliekwaliteit verbeterd kan worden voor transport, opslag en olietoepassingen. Dit is gedaan door pyrolyse-oliefracties te produceren met behulp van getrapte pyrolyse en/of stapsgewijze condensatie.

In getrapte pyrolyse-experimenten wordt de biomassa eerst behandeld op lagere temperatuur (260-360^{o}C), gevolgd door een tweede pyrolysestap op hoge temperatuur (in dit werk: 530^{o}C). Het selectief en met hoge opbrengst concentreren van bepaalde componenten en groepen met behulp van getrapte pyrolyse is slechts in beperkte mate mogelijk gebleken. Wel is het mogelijk om door middel van getrapte pyrolyse meer zicht te krijgen op het gedrag van bepaalde componenten en componentgroepen, zoals suikers, furanen en water tijdens pyrolyse.

Voor het pyrolyseproces op het niveau van een enkel deeltje kunnen de volgende conclusies worden getrokken: i) reacties die beneden de 300^{o}C plaatsvinden hebben geen invloed op de uiteindelijke productverdeling wanneer de temperatuur daarna wordt verhoogd naar 530^{o}C en ii) zelfs voor de allerkleinste deeltjes (0.25-1 mm) treedt er een massatransportlimitering op, die de uitkomst van het pyrolyseproces beïnvloedt. De waargenomen effecten bij variërende deeltjesgrootte, deeltjesstructuur en getrapte pyrolyse kunnen verklaard worden. Deze verklaring bestaat uit een mechanisme waarin een gedeelte van de biomassa, zijnde in vaste of vloeibare fase, direct of na het ondergaan van een aantal opeenvolgende reactiestappen polymeriseert tot kool of het deeltje verlaat via verdamping, sublimatie of door meesleuring.

Bij een reactortemperatuur van 500^{o}C met de kleinste houtdeeltjes (250 micrometer) werd een maximale olieopbrengst van 74 gewichtsprocent en minimale koolopbrengst van 8 gewichtsprocenten verkregen De aanwezigheid van mineralen en hun katalytische effect op dampen en aërosolen resulteert in veel lagere olie-opbrengsten. In tegenstelling tot wat vaak wordt verondersteld, is gebleken dat de verblijftijd van dampen niet zo kritisch is voor temperaturen onder de 500^{o}C, wanneer er mineraalarme kool aanwezig is.

Getrapte condensatie waarbij de eerste condensor op een hogere temperatuur (60-115^{o}C) dan die van de tweede condensor (20^{o}C) wordt bedreven, is een veelbelovende methode om componenten (groepen) te concentreren en daarmee de kwaliteit van de olie te sturen. Componenten met een hoog kookpunt, zoals suikers en niet in water oplosbare oligomeren, worden dan in de eerste condensor afgevangen, terwijl de lichtere componenten in de tweede condensor worden afgevangen .Olie-eigenschappen zoals viscositeit, elementsamenstelling, fasestabiliteit, watergehalte en de zuurgraad kunnen zo gestuurd worden.

Door het testen van een relatief zware olie en een lichtere olie in een kleinschalige vergassingsopstelling en in een hydrodeoxygenatie proces is een eerste stap gemaakt om een relatie te leggen tussen de geschiktheid van de oliën in beoogde toepassingen en zij die geproduceerd zijn onder verschillende pyrolyse condities.

Summary

Pyrolysis oil produced from biomass is a promising renewable alternative to crude oil. Such pyrolysis oil has transportation, storage, and processing benefits, none of which are offered by the bulky, inhomogeneous solid biomass from which it originates.

However, pyrolysis oil has both a different composition to and different properties from crude oil. This makes its direct use in those applications and conversion processes originally developed for fossil feeds problematic. Improvement of the pyrolysis oil's quality is essential to accelerate the development and implementation of pyrolysis technology and its commercial exploitation.

Despite the many studies on pyrolysis, the understanding of the chemical reactions and physical processes occurring in a pyrolysis reactor and in a biomass particle undergoing fast pyrolysis remains limited. The same holds for the knowledge on ways of optimizing the operating conditions and modus operandi, so as to improve both the pyrolysis oil's quality and yield. This thesis provide clarification in these two areas.

A 1 kg/h bench-scale pyrolysis plant was developed to facilitate experiments having good mass balances closures and good reproducibility of the data. The plant included a fluid bed reactor and a series of two counter-current spray condensers to collect the vapors and aerosols. Experiments were performed on a variety of biomass types, such as pine wood, beech wood and straw, with a variety of characteristics in terms of particles size, micro-structure, ash and water content. Using the developed pyrolysis plant, it was possible to vary reactor conditions such as temperature, the char/ash hold-up, the biomass and hot vapor residence times and the condenser temperature over a wide range. The char, gas and pyrolysis oil products obtained from the experiments were analyzed and characterized. To help analyze the oils, a new analysis scheme was developed in which the compounds were classified according to their boiling point and functionality.

Step-wise pyrolysis and fractional condensation was studied in this thesis, and the findings used to help increase the production of the whole pyrolysis oil and to increase the production and concentration of single compounds or groups of compounds in the pyrolysis oil. Such increases would make the oil increasingly suitable for transportation, storage and practical applications.

Next, step-wise pyrolysis experiments were performed in which the biomass was first pre-converted at a low temperature (260-360^{o}C), followed by a final

conversion step at a high temperature (530°C). It was found that increasing the yields and concentration of targeted compounds and groups of compounds was only possible to a minor extent. However, step-wise pyrolysis is a useful approach for the study of the pyrolysis behavior of compounds and compound groups such as water, sugars and furans.

When considering the processes at the particle level, the two most important conclusions are: (i) reactions running below 300°C in the heating trajectory do not affect the final product distribution of fast pyrolysis at 450 – 550°C; and (ii) even for the smallest particles studied (0.25 – 1 mm), mass transfer significantly affects the pyrolysis process. The effects of particle size, microstructure and step-wise pyrolysis can be explained in terms of a mechanism in which a part of the depolymerized biomass — being in the liquid or solid state — (i) polymerizes directly or after a sequence of reactions to char; (ii) leaves the particle via evaporation, sublimation or entrainment.

At a reactor temperature of 500°C together with particles of 250 µm, a maximum oil yield of 74 wt% and minimum char yield of 8 wt% were obtained. It was found that the vapor and aerosol interaction with minerals plays an important role in lowering the oil yield. Residence times of the vapors at temperatures below 500°C, even when in contact with the char (but excluding the effect of minerals), was found to be far less critical than has been assumed by many researchers.

Fractional condensation, achieved by operating the first condenser at a higher temperature (60- 115°C) than the second one (20°C), was found to be a promising approach to concentrating compounds (classes) and, therefore, to controlling the ultimate quality of pyrolysis oils. High boiling point compounds — such as sugars and lignin-derived oligomers — were collected in the first condenser while the lights were collected in the second condenser. The key properties of the oil — such as viscosity, elemental composition, stability, water content and acid number — could be accurately controlled.

Light and heavy (in the sense of having more large molecules) oils were tested using lab-scale gasification and hydro-deoxygenation equipment. In this way a first attempt was successfully made to relate pyrolysis oils produced at varied pyrolysis process conditions to their applicability and performance in targeted applications.

Chapter 1

Introduction

1.1 General introduction

The transformation of biomass into fuels and chemicals becomes increasingly important to mitigate global warming and diversify energy resources. The world energy consumption is about 515 EJ/year[1], mostly provided by fossil sources (80%)[2] and will grow in the coming years[1]. This can for a large part be ascribed to the projected growing population with 40% in 2050 and the increasing energy consumption in upcoming economies like China and India[3]. Fossil fuels are now the common used source for energy production, but they are not renewable nor CO_2 neutral. It is almost universally accepted that the release of CO_2 into the atmosphere coming from these fossil fuels is at least partly responsible for the climate change[4].

Next to the concerns about global warming and finite fossil fuel reserves, the security of supply and its associated politics are an important factor determining the energy scenarios[4]. Since a large amount of the fossil fuels is coming from political less stable countries, the security of fossil fuel supply is not always straight forward. This stimulates countries to develop local alternative energy programs from unconventional sources. The supply of renewable energy is one of the main challenges that mankind will face over the coming decades. Climate change, demographic developments coupled with increasing wealth, political issues and ending fossil fuel reserves drive governments to stimulate the usage of renewable resources like wind, hydro, solar and biomass for the energy supply. The current usage of biomass accounts for 13% of the total energy used, but almost all this energy is used in developing countries for heating and cooking[1]. If carefully managed, biomass-derived energy could provide[2]:

- a larger contribution than 13 wt% to the global primary energy supply;
- environmental benefits, by significant reductions in greenhouse gas emissions;
- improvements in energy security and trade balances, by substituting imported fossil fuels with domestic biomass;
- job opportunities in rural communities (economic and social development).

Biomass represents stored solar energy and is therefore the only renewable energy resource that consists of actual matter (predominantly C,H,O,N)[5]. Biomass is the sole resource available for fast introduction of renewable fuels and chemicals into the market. To illustrate this, the energy scenario of Shell predicts an increase of 2.5-3 times the current biomass usage in 2050[3].

1.2 Biomass

Biomass is produced by photo-synthesis using solar energy. In this process plants take carbon dioxide and water from their environment and use sunlight to convert them into sugars, lignin etc.[6]. Biofuels can in principal be produced from any source of biomass like wood and wood waste, agricultural residues, forestry residues and waste from the food industry. Because of the concerns about the competition with food production for first generation biofuels based on sugar, starch and vegetable oils, the interest for biofuels is now shifted towards the second generation biofuels from lignocellulosic biomass[7].

Wood is mainly used in this thesis. Wood has a well-known composition and has a low ash content, making it an ideal feed for pyrolysis research. In addition, the majority of the pyrolysis research is focussed on wood, making the comparison of experimental results more straightforward. Commercially interesting second generation biomass feedstocks are for example straw, bagasse and rice husk. Wood can generally be classified in two groups namely hardwood and softwood[5]. The softwoods are also known as coniferous woods like pine and spruces, whereas hardwoods include for example beech, oak and maple[5]. Lignocellulose, the major component of woody biomass, consists mainly out of three types of polymers namely cellulose, hemicellulose and lignin. The weight fractions of cellulose, hemicellulose and lignin varies for the different biomass species[8].

1.2.1 Cellulose

Cellulose is one of the main constituents in wood. Depending on the wood type, the content of cellulose can be up to 50 wt%[8]. Cellulose is a linear polymer consisting of 5000-10000 glucose units[9]. The chemical structure of cellulose is shown in Figure 1.1. The principle functional group of cellulose is the hydroxyl group. The cellulose structure in wood has well-ordered crystalline regions that are separated by amorphous regions[10,11].

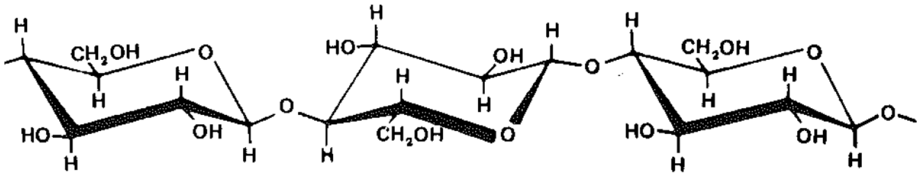

Figure 1.1: *Cellulose* [9]

1.2.2 Hemicellulose

Hemicellulose usually accounts for 25-35 wt% in dry wood. Hemicellulose is a branched polymer, which is built up from different C_5 and C_6 monomers[11]. The average number of monomers is around 150, indicating a lower degree of polymerization for hemicellulose than for cellulose. Figure 1.2 shows the monomers found in hemicellulose[11,12].

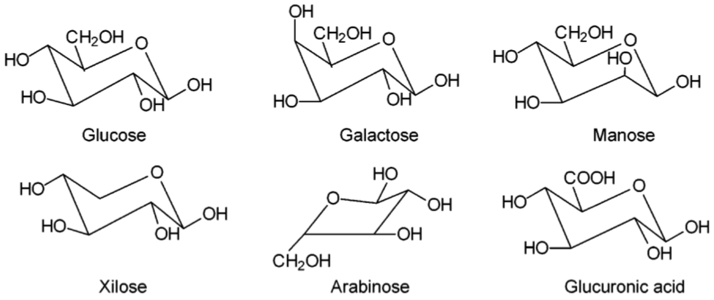

Figure 1.2: *Monomers of hemicellulose*[12].

1.2.3 Lignin

Dry wood consists usually for 16-33 wt% out of lignin. Lignin is extremely resistant to chemical and enzymatic degradation. Lignin molecules are larger than cellulose (with a molecular mass in excess of 10,000) and have a three-dimensional structure. Lignin is an amorphous polymer based on phenyl propane units[13], shown in Figure 1.3.

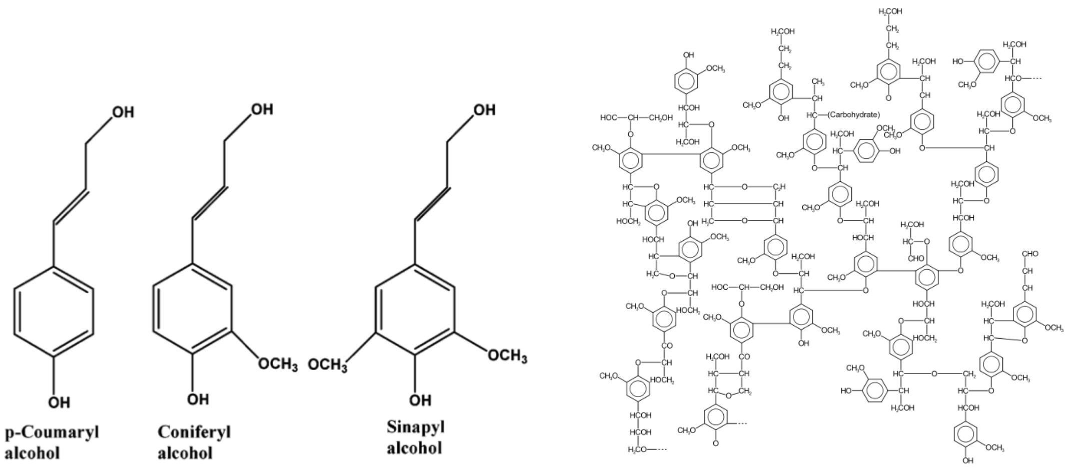

Figure 1.3: *Left, monomers of lignin*[5] *Right, example of a possible lignin structure*[9]

1.2.4 Other compounds

In addition to cellulose, hemi-cellulose and lignin, biomass contains other compounds (in lesser amounts) e.g. organic extractives and inorganic minerals[11]. Extractives (e.g. carboxylic acids, fats) are compounds that can be removed from wood by solvents such as ether. The concentration of the inorganic species can vary between the 0.5 (wood) up to 20 wt% (rice straw). The major inorganic compounds present in the biomass are K, Na, P, Mg, Si, Cl and Ca.

1.3 Thermo-chemical conversion of biomass

Wood and other biomass can be used in variety of ways to provide energy. Carbonization of biomass is a process that is operated in the absence of oxygen at temperatures between 500 and 800^{o}C while applying slow heating. It is used to make charcoal and is already a very old process. The charcoal can be used for heat production[14]. Biomass can be also directly combusted to provide heat or power[15]. Large scale biomass combustors are currently available and co-firing of biomass in coal combustion is increasingly practiced[15].

Figure 1.4 shows an overview of the many thermo-chemical conversion routes and processes to fuels and chemicals. The processes and routes depicted in this figure are only briefly discussed here; for more detailed information the reader is referred to Kersten et al.[16].

Gasification of biomass at temperatures in the rage of 800-900°C and low oxygen supply can be used to provide fuel gas (H_2, CO, CO_2, CH_4)[17] heat generation or production of electricity by an engine or turbine[17]. When pure oxygen is used instead of air at T >1250°C, the syngas (CO/H_2) thus obtained can be used to produce for instance methanol or transportation fuels by the Fischer-Tropsch process[18].

By heating of wood at relatively low temperature of 200-300°C in the absence of oxygen torrefied wood is produced[19]. Torrefied wood has an higher energy density per unit mass and better grindability compared to virgin wood[19], which makes it easier to feed and to process.

Liquefaction of biomass, which is operated at temperatures in the range of 150-420°C, yields as main product a multicomponent liquid that can be further processed in e.g. gasifiers and, via upgrading, in refinery units[20]. Hydrothermal liquefaction and super critical gasification can be used for wet biomass feedstocks[21]. These processes are used to make a liquid product or gas, respectively. The liquid from hydrothermal liquefaction can be used for heat and power production and is an intermediate for the production of transportation fuel[21].

We will not discuss here the different processes for biomass fractionation, but we will focus on the main subject of this present work: pyrolysis.

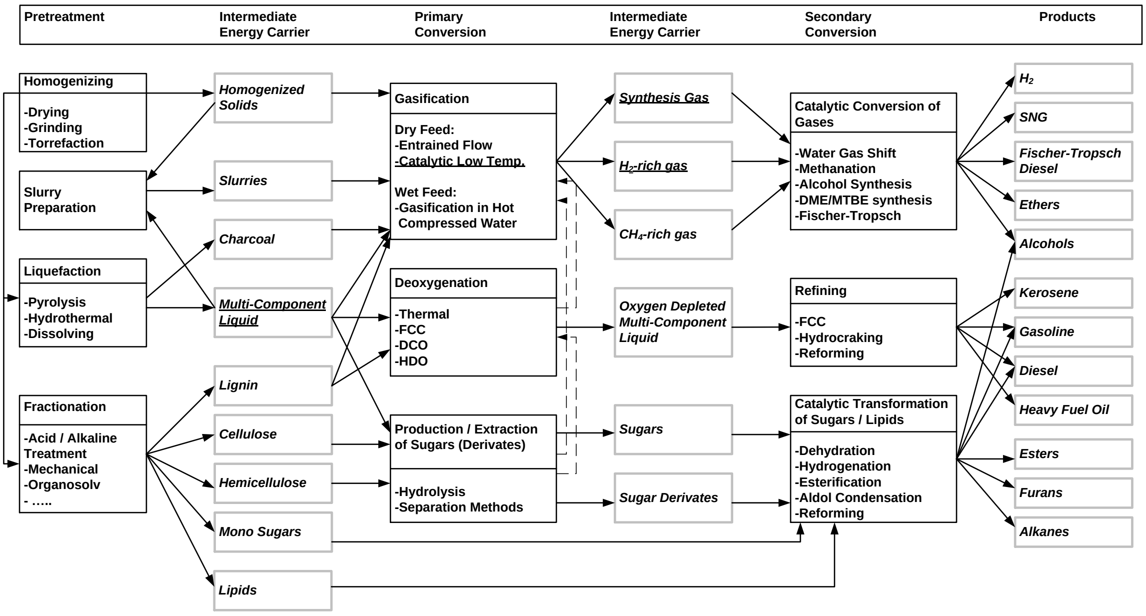

Figure 1.4: *Routes for thermo-chemical conversion of biomass to fuels and chemicals. (adapted from Kersten [16]).*

1.4 Pyrolysis

Pyrolysis of biomass is a thermo-chemical conversion method in which biomass is rapidly heated in the absence of oxygen. Pyrolysis of biomass results in different amounts of char, gas and pyrolysis oil[22], depending on the feedstock and process conditions [22,15].

Converting biomass into a liquid called pyrolysis oil as main product has the potential to overcome the problem of biomass variability and transportation and storage of the bulky and low density solid biomass (pyrolysis oil has a higher volumetric energy density than biomass). Moreover, pyrolysis oil is also generally easier to process in comparison with the original solid biomass[5,23]. Some important features of the pyrolysis process that reportedly can be tuned to maximize the pyrolysis oil yield are[24]:

- grinding the biomass to sufficiently small particles to allow for fast enough heating-up;
- drying of the biomass to a moisture content typically less than 10 wt%;
- reaction temperatures between 400-550^{o}C for most types of biomass;
- short hot vapor residence times, typically less than 2 s are required to minimize the secondary reactions of the vapors;
- rapid removal of product char to minimize cracking of vapors;
- rapid condensing of the pyrolysis vapors.

The by-products from the fast pyrolysis processes are non-condensable gasses and a solid residue called char. Char is commonly separated from the vapor / non-condensable gas stream by cyclones. Char can be used to provide the process heat or be sold as a separate product. It also has the potential to be used as fertilizer[25]. The char contains almost all the ash originally present in the wood. The non-condensable gasses can directly be used to generate heat within the process or to generate heat/electricity using engines or turbines[23].

With regard to optimize the pyrolysis oil production, a number of different approaches have been studied to achieve fast heating of the biomass and rapid removal and quenching of the products. This has resulted in various reactor concepts. Examples are the fluidized - and circulated fluidized bed reactors, ablative and cyclone-type reactors, rotating cone and screw (auger) reactors[26,27]. At the time of writing one large commercial plant is operated by Ensyn for the production of food flavor[28]. A few demonstration projects are ongoing: BTG (5 ton/hr)[29], KIT (0.5 ton/hr)[30] and VTT (0.3 ton/hr)[31]. An extensive review of all reactor types used in pyrolysis can be found elsewhere[20].

1.4.1 Physical – Chemical composition of pyrolysis oil.

Pyrolysis oil is typically a dark brown, sometimes almost black, liquid and has a smoky odor. Pyrolysis oil contains waxy materials and heavy oligomers in a matrix of other cellulose/hemicellulose derived compounds and water[32]. Typical properties of fast pyrolysis oil from biomass are summarized in Table 1.1.

Table 1.1: *Fast pyrolysis oil properties[33].*

Properties		**Typical values**
Water content (wt%)		15-30
pH		2.0-3.8
Elemental composition (wt%)	C	48.0-63.5
	H	5.2-7.2
	N	0.07-0.39
	O	32-46
HHV (MJ/kg)		15-24.3
Viscosity (cp, at 20^oC)		50-672
Solids (wt%)		0.17-1.14
Ash (wt%)		0.03-0.3
Density (kg/dm^3)		1.21-1.24

Due to its high polarity (oxygen content), pyrolysis oil is not miscible with hydrocarbons. The oxygen content also lowers the heating value of the oil compared to fossil fuels.

Water in pyrolysis oil originates from the dehydration reactions during pyrolysis and the initial water content of the biomass[34]. Hence, the water content can vary from 15 to 35 wt%. Water lowers the viscosity of pyrolysis oils which is beneficial for further applications.

Phase separation into an aqueous phase and a heavy organic phase, can occur at a water concentration higher than approximately 32 wt%[34]. This value should be considered as “indicative” as it also depends on e.g. the amount of water insoluble compounds in the oil. These insoluble heavy compounds are typically present in the range of 15-30 wt% in the pyrolysis oil and contain less oxygen (15-30%) compared to the total oil[34,35]. The molecular weight of the compounds in pyrolysis oil can vary over a wide range, from values as low as 18 gram/mole for water to values as high as around 2000 gram/mole for oligomer compounds[34]. The molecular mass is an important parameter because it is strongly related to the volatility and viscosity of the pyrolysis oil. Because of the heavy and also reactive compounds in pyrolysis oil, it is not possible to distill the oil without leaving a residue of typically 35-50 wt%[36]. Furthermore, the pyrolysis oils are rather acidic in nature (pH = 2-3), as they contain a considerable amount of carboxylic acids[35,37].

The pyrolysis oil is not a mixture of compounds at thermodynamic equilibrium nor a stable product at room temperature. The viscosity tends to increase during storage, especially at higher temperatures, due to reactions of certain reactive compounds forming larger molecules. This phenomenon is often referred to as ageing[34].

The many different compounds in pyrolysis oil have their origin from simultaneous degradation of cellulose, hemicellulose and lignin during pyrolysis. The pyrolysis oil is generally collected as one liquid (hence, using a single condenser), resulting in a very complex mixture of many different oxygenated compounds with different functional groups, see Table 1.2. This makes identification and quantification of compounds in pyrolysis oil a very difficult task. Pyrolysis oil composition has been studied by various researchers, see e.g. the work by Garcia-Perez[35], Oasmaa and Meier[37].

Table 1.2: *Fast pyrolysis oil composition*[38]

Major components	**Typical values (wt%)**
Water	27
Ether soluble organics (aldehydes, ketones and lignin monomers)	21
Volatile acids (mainly acetic)	5
Ether insoluble organics (anhydrosugars, anhydro-oligomers, hydroxyl acids C>10)	28
Lignin derivates, polymerization products and solids	15
Extractives (n-hexane soluble organics)	4

It can be concluded that the composition and related properties of pyrolysis oil differs completely from conventional fuels. Its unconventional composition and properties, as compared to the current fossil fuels, still hinder the applicability of pyrolysis oil. As a result there is currently a large R&D effort on pyrolysis oil improvement[38,39] and modification of applications to match the properties of pyrolysis oils better[40]. The commonly considered applications for fast pyrolysis oil are depicted in Figure 1.5.

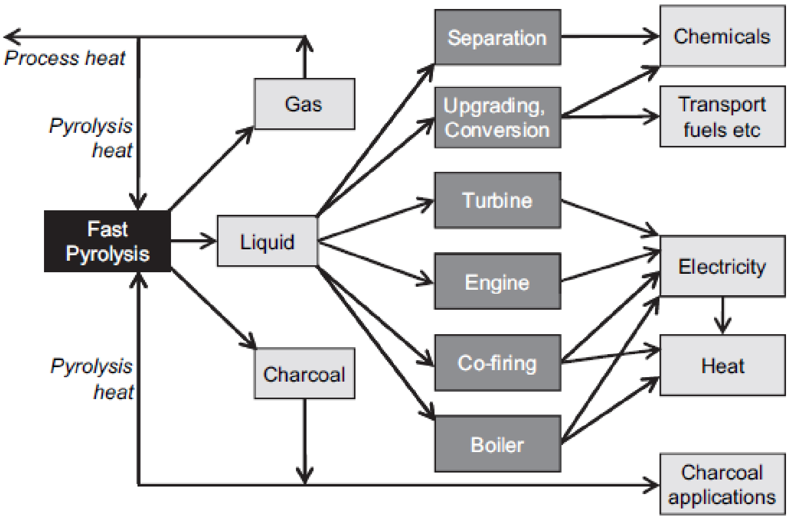

Figure 1.5: *Applications and upgrading technologies for fast pyrolysis oil (adapted from Bridgwater [24])*

1.5 Outline of the thesis

While literature on the pyrolysis of biomass is rapidly expanding, the integration of fundamental work into process concepts and pilot plant studies remains scarce. Reported experimental results obtained from bench scale pilot plants reveal that there are many operational problems resulting in poor mass balance closure. From the variety of reactors used for pyrolysis, the fluid bed principle was selected in the present investigation, because of the easy and accurate temperature control, high heating rates, variable biomass residence time and convenient overall operation characteristics.

The first part of the work is concerned with the design, construction, and operation of a 1 kg/hour pyrolysis plant based on a fluid bed pyrolysis reactor. The pyrolysis plant was designed to allow stable operation under a wide range of process conditions. The mass balance closure should be high and good reproducibility of the experiments must always be guaranteed.

Special attention was given to the condenser system. Normally the condensers used are operating far from equilibrium and compounds with high and low boiling points and aerosols are non-selectively collected throughout the condenser system.

The condenser train used in this study was designed to allow for well controlled fractional condensation of the pyrolysis vapors/aerosols over a wide range of operating conditions and with different condenser configurations. This allowed to study the potential of fractional condensation in the pyrolysis process to avoid (partly) downstream separation of the produced liquids. With this pilot plant, complemented with a few additional experimental set-ups the pyrolysis process itself was studied in the light of the desired properties of the oil related to its application.

The process was studied as a function of temperature, biomass particle size and structure, temperature programming in stepwise pyrolysis and by varying the condensation temperature of the pyrolysis vapors. Homogeneous and heterogeneous reactions of the vapors inside the particles, inside the fluid bed and in the hot zones of the freeboard, cyclones and transport lines of the pyrolysis plants were studied in the pilot plant and with specially constructed additional mini plants. The results of all experiments are reported in the different chapters as follows:

Chapter 2. In chapter 2, the effect of pyrolysis temperature on the pyrolysis oil composition and properties was studied over a wide temperature range (260-580°C). Special attention is given to the temperature range of 360 to 400oC, which is not often studied. Pyrolysis oils produced were tested in applications to demonstrate the importance of application testing in order to assess the pyrolysis oil quality.

Chapter 3. In this chapter step-wise pyrolysis of biomass is studied. In step-wise pyrolysis, biomass is first pre-converted at a lower temperature (260-360°C), after which the solid residue of the first step is re-processed at a higher temperature (530°C in our case). In both steps the gaseous and condensable products are collected. It is investigated whether it is possible to concentrate single compounds or groups of compounds in the oils (liquids) collected during the different steps. The results of the step-wise pyrolysis experiments are also used to gain insight in the pyrolysis mechanism, in particular with respect to importance of reactions taking place at lower temperatures in the heating trajectory of the biomass particles to the final pyrolysis temperature for the final product distribution.

Chapter 4. In this chapter, the effects of heterogeneous and homogeneous reactions of vapors and aerosols are studied. The process parameters varied are the vapor phase temperature, vapor phase residence time and the concentrations of char and minerals inside the biomass and reactor environment. The study aims at providing more unequivocal insight on the influence of these parameters on the oil yield and composition.

Chapter 5. In this chapter, the effects of particle geometry and micro-structure on the pyrolysis products are studied. The influence of the micro-structure is studied by comparing pyrolysis results of natural wood, solid cylinders with milled wood particles and artificial wood cylinders (steel cylinders filled with milled wood particles to the same density). Attention is given to both the pyrolysis oil yield as well as the pyrolysis oil composition.

Chapter 6. This chapter deals with the role of water in the pyrolysis process and the control of the water content in the pyrolysis oil product. Water is one of the most abundant compound in pyrolysis oil. Too high concentrations of water in the oil can easily lead to phase separation. Furthermore, water influences the higher heating value (HHV) and also the viscosity of the oil. Controlling the amount of water by pre-drying the biomass or downstream fractional condensation in the pyrolysis process in a series of condensers, each operated at a different temperature and sweep-gas load, is investigated.

Chapter 7. The effect of condensation temperature of the vapors on the pyrolysis oil composition has been studied for two different pyrolysis (reactor) temperatures. A novel analysis scheme is proposed to analyze the composition of the pyrolysis oils. The composition of the oils obtained are discussed in relation to the target applications.

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Chapter 2

Effect of Temperature in Fluidized Bed Fast Pyrolysis of Biomass: Oil Quality Assessment in Test Units

Abstract

Pine wood was pyrolyzed in a 1 kg/h fluidized bed fast pyrolysis reactor that allows a residence time of pine wood particles up to 25 min. The reactor temperature was varied between 330 and 580^{o}C to study the effect on product yields and oil composition. Apart from the physical-chemical analysis, a pyrolysis oil quality assessment has been performed by using two applications. The pyrolysis oils were tested in a laboratory scale atomizer and in a hydrodeoxygenation unit for upgrading/stabilizing of the pyrolysis oil. The pyrolysis oil yield increases from 330 to 450^{o}C, is nearly constant between 450 and 530^{o}C, and decreases again at a pyrolysis temperature of 580^{o}C. At temperatures of 360 and 580^{o}C, total pyrolysis oil yields of, respectively, 58 and 56 dry wt% can still be obtained. The produced amount of water is already significant at a reactor temperature of 360^{o}C and becomes constant at a temperature of 400^{o}C. At a temperature of 580^{o}C, the water production starts to decrease slightly. Initially the number average molecular weight of the pyrolysis oil increases at increasing temperatures, which is ascribed to the observed increase in concentration of water insoluble compound in the pyrolysis oil. At a temperature of 580^{o}C, the number average molecular weight, viscosity, and the amount of produced water insoluble compounds decreases. The oil obtained at a pyrolysis temperature of 360^{o}C produced less char, 2 versus 5 wt%, compared to the oil obtained at a pyrolysis temperature of 530^{o}C in our atomizer/gasifier. About 100% of the carbon goes to the gas phase compared to 84% for the oil obtained at a pyrolysis temperature of 530^{o}C. Therefore, the 360^{o}C oil has a better quality for this unit under the applied conditions (850^{o}C and droplet sizes of 50 μm) Testing the three pyrolysis oils (pyrolysis temperatures of 330, 530, and 580^{o}C) in the hydrodeoxygenation unit showed that pyrolysis oil with a lower viscosity resulted in deoxygenated oil of lower viscosity. The oxygen content of the three oils was almost the same, but the yield of the deoxygenated oils obtained at a pyrolysis temperature of 330^{o}C was significantly lower. Together with chemical and physical analyzes of the pyrolysis oils, feeding the pyrolysis oil into test units relevant for applications, direct information on the effect

of varied pyrolysis process parameters on the quality and applicability of the pyrolysis oil is obtained.

2.1 Introduction

Fast pyrolysis is a promising technology to produce a storable and transportable liquid (called pyrolysis oil) from inhomogeneous and bulky solid biomass. Since the 1970s, the research on fast pyrolysis of biomass has been focused on the following: maximizing the pyrolysis oil yield, reaction pathways and kinetics, and reactor and process development. During the last 5-10 years, the number of publications on the chemical composition and physical properties of pyrolysis oil has increased significantly[1-4]. Physical characterization (e.g. viscosity, density) and basic chemical analysis methods (e.g. water content, elemental composition, pH, and solid content) are nowadays well-established[5,6]. More detailed chemical analysis at the level of individual components or groups of components is still cumbersome, mainly because of the reactivity of the multicomponent mixture and the presence of oligomers.

The issue of pyrolysis oil quality has been raised, and it is recognized that the operating conditions for optimal pyrolysis oil quality do not necessarily coincide with those for maximum yield. Obviously, the required pyrolysis oil quality will depend on the application targeted[7-12]. High temperature entrained flow gasification for synthesis gas production will set different demands to the pyrolysis oil than upgrading to liquid transportation fuels via deoxygenation and (co)refining. The quality of pyrolysis oil is discussed for use in boilers, engines, and turbines,[7,8] but it is not clear what the relation between varied pyrolysis process parameters and the performance in the application is.

The pyrolysis process can be operated at different process conditions to (directly) control the pyrolysis oil quality in order to meet specific end-users requirements. The relation between the physical properties and the chemical composition of the produced pyrolysis oil under varied process conditions, and the performance (quality) of the pyrolysis oil in an application is not (always) straightforward to predict. Therefore, we propose to use in addition tests of pyrolysis oil, useful for applications (e.g., combustion, gasification, hydrotreating), as analysis tools for pyrolysis oil quality assessment. These tests will yield direct information on the following:

1. Overall performance of the pyrolysis oil in its applications, for instance, identification of operation problems such as char/soot formation during

gasification, fouling problems by ashes in combustion, and polymerization during deoxygenation.

2. Products (yields) of the applications, which are typically easier to analyze than the compounds in the original pyrolysis oil (e.g., gas and char from gasification and less reactive oil from hydrotreating versus pyrolysis oil).

On the basis of this information, relations can be derived between the physical and chemical properties (quality indicators) of the pyrolysis oil obtained at varied pyrolysis process conditions and its performance in the application. It is to be preferred to establish relations between easy to measure quality indicators and the performance of pyrolysis oil in its applications (e.g., the relation between viscosity and water content of the pyrolysis oil and coke formation in atomization/gasification). These quality indicators can be very useful (fast) screening tests, but only testing the oil in the final application can provide information on its quality.

In the literature, there seems to be consensus that the maximum oil yield is obtained in the temperature range between 400 and 550^{o}C. However, several studies indicated that still significant amounts of oil can be obtained at temperatures outside this range, especially in the range between 350 and 450^{o}C and 550 and 600^{o}C[9-12]. Oil produced at these temperatures can therefore be interesting when a higher quality, for a certain application, can be obtained compared to the oils obtained at temperatures of maximum yield.

Two excellent papers were published by Garcia-Perez[11,12]. In these, the effect of temperature on the product yields and physical-chemical properties was studied. Despite the somewhat lower mass balance closures in that study (86-96 wt%), these authors were able to show that for conditions favoring a maximum oil yield also the largest amounts of small lignin derived oligomers are obtained, which is unfavorable for their targeted application of fuel. Difficulties in analyzing the pyrolysis oil at the level of compounds and groups of compounds were recognized and clearly pointed out in that study.

In this chapter, we have studied fast pyrolysis of pine wood in a 1 kg/h laboratory scale bubbling fluidized bed (BFB) reactor at high mass balance closure. There are many operating parameters within the fast pyrolysis process that influence the product yields and composition like variation in vapor residence time,[13] particle size,[9] and condenser temperature[14,15]. In this work, we varied the temperature of the BFB pyrolysis reactor in the range of 330-580^{o}C. All other parameters were kept at a (nearly) constant value. The produced oils are subjected to physical and chemical analysis and are tested for two promising applications, by using our laboratory scale atomizer for the assessment of its quality for the pyrolysis oil gasification/combustion and the oils are tested in our hydrotreating unit for upgrading/stabilizing of the pyrolysis oil. From this, conclusions will be drawn on the quality of the pyrolysis oil produced at the distinctly different fluidized bed reactor temperatures in relation to the pyrolysis oil properties by conventional analysis and as applied in two different practical applications.

2.2 Experimental Section

2.2.1 Materials.

In the fast pyrolysis experiments, silica sand with an average particle diameter of 250 µm and a particle density of 2600 kg/m^3 (bulk density 1600 kg/m^3) was used as fluidized bed material. Pine wood with a number average particle size of 1 mm (max. 2 mm) was purchased from Rettenmaier & Sohne GmbH, Germany. Details on the composition can be found in Table 2.1.

The pine wood particle density was 570 kg/m^3, and the moisture content was 9-10 wt%, on "as received" basis (ar). Ruthenium on carbon (5% Ru/C, Sigma Aldrich) catalyst was used in the deoxygenation tests.

Table 2.1: *Composition of pine wood*[14].

Bio-chemical composition (wt%, dry)	Cellulose	35
	Hemicellulose	29
	Lignin	28
Ultimate analysis (wt%, daf)	C	46.58
	H	6.34
	O (by difference)	46.98
	N	0.04
	S	0.06
Alkali metals (mg/kg, dry)	K	34
	Mg	134
	Ca	768
	Total ash	2600

2.2.2 Experimental Setup.

Fast Pyrolysis. A continuous fast pyrolysis bench scale plant with an intake of 1 kg/h biomass (ar) has been operated. This plant is schematically shown in Figure 2.1.

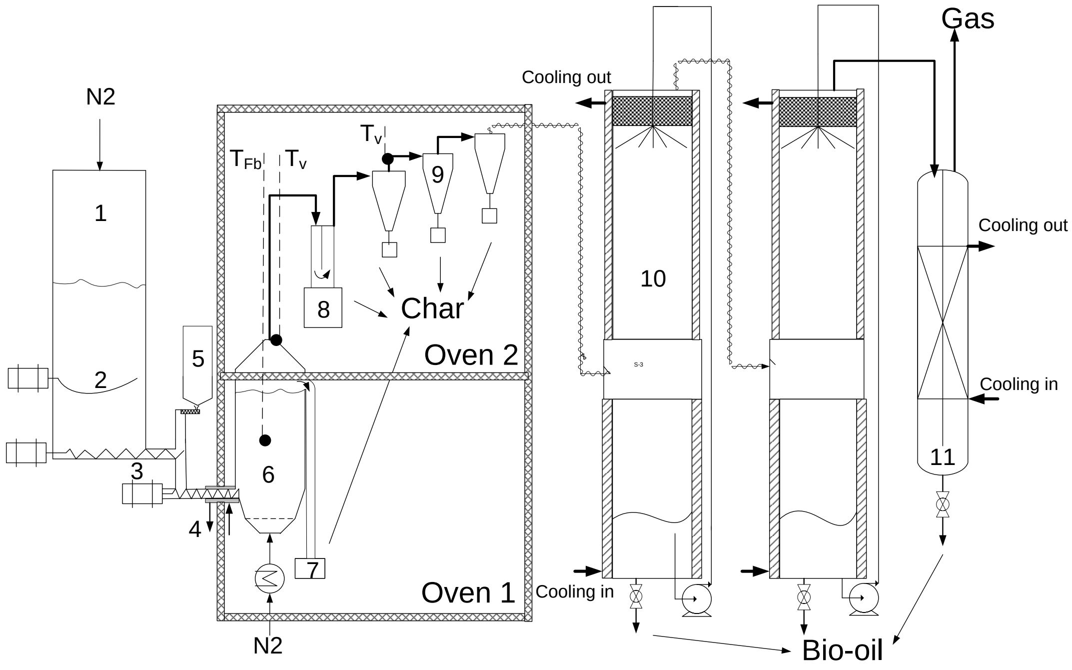

Figure 2.1: *Schematic drawing of the pyrolysis plant; 1) Biomass storage hopper, 2) Mechanical stirrer, 3) Feeding system, 4) Cooling jacket, 5) Sand storage/feeding system, 6) Fluidized bed reactor, 7) Overflow, 8) Knock-out vessel, 9) Cyclones, 10) Counter current spray condensers with cooling jackets, 11) Intensive cooler.*

The biomass was stored in a hopper with a capacity of 4 kg. Three feeding screws were installed. The first screw of this biomass feeding system was used to transport the biomass at controlled flow out of the biomass hopper and to mix this biomass with sand. Sand was stored in a second hopper and was fed with a calibrated feeding screw. The third screw transported the biomass/sand mixture into the fluidized bed reactor.

The reactor bed and the vapor phase (freeboard and char separation section) were thermostatted in two separately controlled ovens. Silica sand was used as fluidization medium and nitrogen as fluidization gas. A solids overflow tube kept the bed level constant. Sand and char particles removed via this tube were collected in a vessel. By adjusting the sand flow rate, the biomass hold-up in the reactor could be controlled.

The gas/vapor residence time inside the reactor bed was kept constant, by adjusting the fluidization gas flow rate, for all fluidized bed reactor temperatures studied. During variation of the fluidized bed reactor temperature, the vapor phase temperature (freeboard and char separation section) was kept constant at 400°C during all experiments.

For an overview of the main operating conditions, see Table 2.2. The temperature profile of the reactor was measured by eight thermocouples. The temperature gradient over the reactor was maximum 10°C. The temperature at the center of the reactor bed (T_{FB}) was used as reference for the fluidized bed reactor temperature. The temperature of the vapor phase (T_v=400°C) was measured in the freeboard outlet and cyclones (see Figure 2.1).

The vapor/gas stream leaving the reactor contained entrained sand fines and char. In a knockout vessel, all of the entrained sand and most of the char particles were removed and collected. Three cyclones, equipped with collection vessels, removed almost all residual char particles.

The condensable vapors in the vapor/gas stream were condensed in two jacketed countercurrent spray columns in series. The temperatures and pressures were measured at the gas/vapor outlet of the condenser and were monitored continuously during an experiment. The outgoing vapor/gas flow of the first condenser was led through the second condenser (identical design to the first one) both operated at 20°C and finally to an intensive cooler kept at 0°C to collect any remaining condensables in order to complete the mass balance. The volumetric flow rate of the gas leaving the intensive cooler was measured with a dry gas flow meter. For a more detailed description of the experimental bench scale plant and the mass balance the reader is referred to chapter 6.

Table 2.2: *Operating conditions.*

Experimental run time	120	min
Biomass feed rate	1.0	kg/hr
$M_{\text{sand, initial}}$	2.10	kg
Bed height	0.25	m
Bed diameter	0.10	m
U	0.14	m/s
U/U_{mf}	3.50	-
$t_{\text{fluidized bed}}$	0.80	s
$t_{\text{vapour phase, cyclones}}$	0.45-0.55	s
$t_{\text{biomass particle}}$	20-25	min
T_{FB}	330-580	^{o}C
T_V	400-540	^{o}C

2.2.3 Quality Assessment by Application Testing (1): Atomizer/Gasifier.

Pyrolysis oil has been atomized in an empty stainless steel tube (length 40 cm, diameter 4 cm). The pyrolysis oil flow rate was approximately 1.7 mL/min. The atomization temperature was around 850°C. Pyrolysis oil enters the reactor through a spray nozzle which produces very fine oil droplets of 50-100 μm. These small droplets vaporize and crack to gases (H_2, CO, CO_2, CH_4, and C_2-C_3). Apart from gases, also the formed char and condensable vapor products can be measured with this setup. Details on the setup used, mass balances, procedures, and reproducibility of experiments can be found in chapter 6.

2.2.4 Quality Assessment by Application Testing (2): Hydrodeoxygenation.

Hydrodeoxygenation experiments were performed on three pyrolysis oils, which were produced at pyrolysis reactor bed temperatures of 330, 450, and 530°C. Experiments were performed in a stirred 0.5 L autoclave. The pressure inside the autoclave was kept constant at 192 bar by resupply of hydrogen, as it is consumed by hydrodeoxygenation reactions. The reactor temperature was 300°C and 5 wt% Ru/C was used as catalyst for all three experiments because this catalyst is found to be very active in hydrodeoxygenation of pyrolysis oil.[17] At the end of each experiment, gas samples were taken and analyzed by a gas chromatograph (GC: H_2, CO, CO_2, CH_4, and C_2-C_3). The obtained product oil can consist of two or three liquid phases. The water phase was removed from the two/three phase oil. After filtering of the heavier bottom-phase oil, to remove the catalyst, the bottom-phase oil and, when present, the top-phase (“light”) oil were both separately collected as the deoxygenated oil product. All three phases were analyzed for their elemental composition, density, viscosity, and water content.

2.2.5 Analysis of the Pyrolysis Oil.

The water content of the pyrolysis oil was determined by Karl Fisher titrations (titrant: Hydranal composite 5, Metrohm 787 KFTitrino). The viscosity (Brookfield DV-E viscometer) was measured as the dynamic viscosity (cP). The molecular weight distribution of oil was measured with a gel permeation chromatograph (GPC, Agilent Technologies, 1200 series RID detector, eluent: 1 mL/min). The solvent used was tetrahydrofuran (THF; 10 mg pyrolysis oil / mL THF). The columns were the following: 3 PLgel3 μm MIXED-E placed in series. The GPC is calibrated with polystyrene standard (MW=162-30.000). An estimation of the amount of water insoluble compounds was made by using the method described below. Pyrolysis oil

(10 mL) was supplied dropwise to 500 mL of cold water (0°C) during stirring at high speed. Most of the water insoluble phase precipitates, as small solid particles to the bottom of the vessel. A filter is used to separate the two phases. After water washing of the insoluble phase for 2 h under slow speed stirring, the last soluble compounds are washed out. The suspension is filtered again and dried to evaporate the remaining water. The residual product is referred to as the water insoluble phase. The elemental composition of the pyrolysis oil was analyzed (Fisons Instruments 1108 CHNS-O). The non-condensable gases were analyzed by a GC (Micro GC Varian CP 4900). The molar fraction of the produced non-condensable gases is corrected for the amount of inert nitrogen (fluidization gas) in the gas stream. Analyses (viscosity, mole weight distribution, water insolubles, and elemental composition) were performed on the pyrolysis oil obtained from the first condenser. This oil accounts for approximately 90 wt% of the total pyrolysis oil produced.

2.3 Results

2.3.1 Mass Balance Closure and Reproducibility.

The mass balance closure of the experiments performed was always above 94 and below 101 wt%. To check the reproducibility, two sets of two experiments under identical conditions were performed in the fluidized bed fast pyrolysis pilot plant. Yields are always reported on dry biomass basis (kg product/kg dry biomass). The results of this test are summarized in Table 2.3. Of these sets of tests at reactor temperatures of 450 and 480°C, the average yields on a dry basis are the following: char 17 and 15 wt%, pyrolysis oil (produced water + organics) 57 and 58 wt%, and gas 20 and 23 wt%, respectively. These yields are well within the range of fluidized bed fast pyrolysis of wood reported in the literature.[20]

Table 2.3: *Reproducibility*

Reactor Temperature (ºC)	Organics (kg/kg dry biomass)	Water produced (kg/kg dry biomass)	Gas (kg/kg dry biomass)	Char (kg/kg dry biomass)
450 (1)	0.45	0.11	0.20	0.16
450 (2)	0.45	0.12	0.20	0.17
480 (1)	0.47	0.11	0.23	0.15
480 (2)	0.45	0.13	0.23	0.15

As can be seen, the reproducibility of the two sets of fast pyrolysis experiments is very good. The results are considered sufficiently close to allow trend detection on basis of single experiments per set of conditions.

2.3.2 Effect of Fluid Bed Reactor Temperature on Pyrolysis Products Yield.

Fast pyrolysis oil is formed by a fast heat-up and by simultaneous fragmentation and depolymerization of the cellulose, hemicellulose, and lignin present in the biomass feedstock. The produced oil is a very complex mixture of hundreds of compounds with molecular weights varying between 18 and 3000 g/mol. The total yield of the pyrolysis oil is influenced by the type of biomass, reactor configuration, and process conditions.[22,23] One of the most important parameters affecting the pyrolysis oil yield is the reactor temperature[24]. In this work, we studied the effect of fast pyrolysis temperature on the yields of fast pyrolysis products and the properties of the pyrolysis oil over a relatively large temperature range. The residence time of the biomass can be controlled by manipulation of the biomass and sand feeding rate and the use of a reactor overflow. This is crucial to ensure complete biomass conversion since higher required conversion times are expected for operating at lower reactor temperatures[10] the residence time of the biomass in the reactor is set around 20-25 min to allow full conversion over the whole temperature range. The yields of products obtained from fast pyrolysis of pine wood between 330 and 580°C are presented in Figures 2.2 and 2.3.

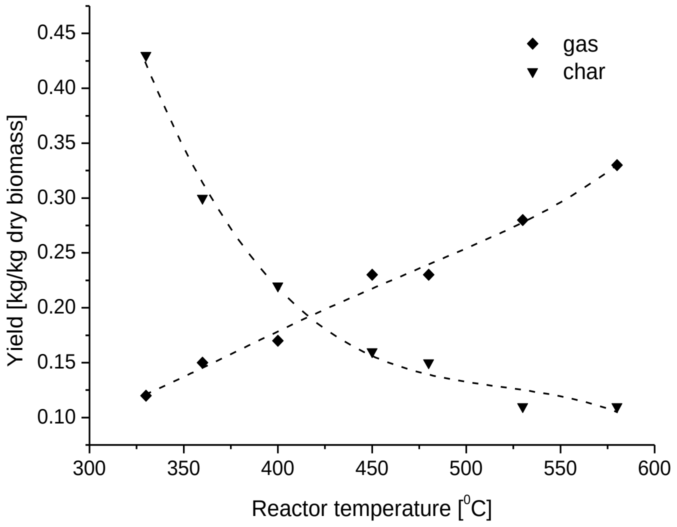

Figure 2.2: *Yields of gases and char versus the fluidized bed reactor temperature.*

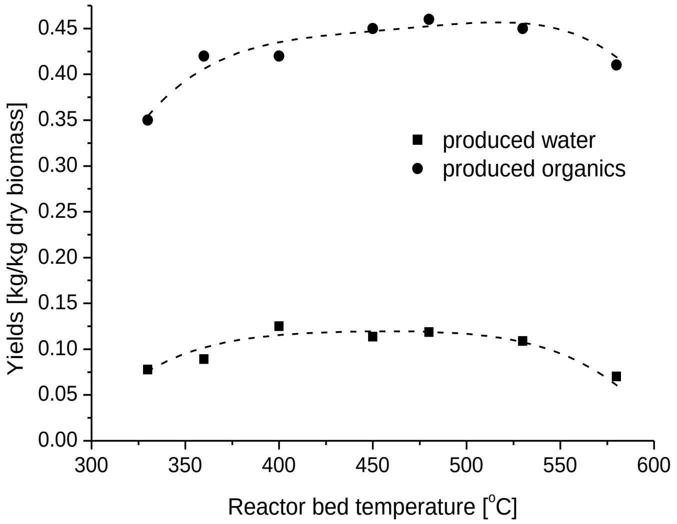

Figure 2.3: *Yields of produced organic compounds and produced water versus the fluidized bed reactor temperature.*

The yield of gases increases with increasing fluidized bed reactor temperature while the char yield decreases at higher temperature; see Figure 2.2. The steep decrease in char yield from 330 to 450°C is most likely due to increasing conversion of the original lignin fraction of the pine wood biomass. From 500°C onward, the char yield seems to reach a more or less constant level.

The continuously increasing gas yield can be explained by increasing conversion of biomass until around 450°C. At higher temperatures, also the (secondary) cracking of vapors to gases becomes more significant. Table 2.4 shows the dry gas composition (molar fraction) at varied reactor temperatures. The concentration of carbon dioxide is very high in the early stage of pyrolysis, due to the relatively low conversion temperature of mainly hemicellulose, for which it is known that carbon dioxide is one of the main gaseous degradation products[18,19] .

Table 2.4: *Dry gas composition (mol/mol) at varied fluidized bed reactor temperatures*

	Temperature [°C]					
Gasses	330	400	450	480	530	580
CO	0.0	0.50	0.54	0.50	0.54	0.58
CO_2	1.0	0.44	0.37	0.29	0.22	0.16
CH_4	0.0	0.05	0.08	0.10	0.13	0.13
H_2	0.0	0.00	0.00	0.08	0.07	0.09
C_2H_4	0.0	0.01	0.01	0.02	0.02	0.03
C_2H_6	0.0	0.00	0.00	0.01	0.01	0.01

Degradation of lignin enhances the production of hydrogen, carbon monoxide, methane, and ethane gases at somewhat higher pyrolysis temperatures[20]. At the higher pyrolysis temperatures studied also vapor cracking, water gas shift, and reforming reactions can have an effect on the gas composition observed[20].

For the pyrolysis oil yield from the condensable vapors, a small plateau of nearly constant organic yield between 450 and 530°C is observed (see Figure 2.3), in line with earlier literature findings[5,6,13]. At lower temperatures and relatively long particle residence time (min), the yield of organics decreases, but still, an acceptable yield of organic compounds (42 wt%) can be obtained between 360 and 450°C. the yield of produced organic compounds at 330°C was 35 wt%. At temperatures higher than 530°C, the organic vapors start to crack partly into non-condensable gases. Again, between 530 and 580°C, a reasonably high organic yield (around 41 wt%) can still be obtained. Both of these oils can possibly be interesting if the oil quality for a certain application is improved.

The water production showed a maximum and a nearly constant yield at temperatures between 400 and 530°C, which is in agreement with findings of others[9,11,25,26]. Noteworthy is the finding that a considerable amount of water is already produced at temperatures around 350°C. This can be explained by the early stage pyrolysis of hemicelluloses (25-35 wt% of the wood) and celluloses (40-50 wt% of the wood) and release of bounded water from the cell wall[21]. Hemicelluloses predominantly decompose, under slow pyrolysis conditions, at temperatures in the range of 200-315°C,[18,20] and celluloses decompose between 240 and 350°C[20]. One of the major decomposition products of hemicelluloses is water[18,19]. The main products of cellulose pyrolysis is levoglucosan[20] but also a significant amount of water. Generally it can be stated that water comes from the dehydratation of carbohydrates[11]. Lignin degrades over the whole temperature range from 280 to 500°C with a maximum decomposition rate between 350 and 450°C. The main products from lignin are phenols and large oligomers but also some additional water is produced[20].

The water contents of the oils obtained at different reactor temperatures are shown in Table 2.5. Despite the theoretical advantage of reducing water production at lower temperatures as indicated by Figure 2.3, the obtained oils have nearly the same water content in the range of 330-530°C. Because all initial water of the biomass feedstock is collected in the pyrolysis oil product, an increased impact of initial feedstock moisture on the produced oils can be expected when the yield of organics of the oil decreases and, as a result, the total oil yield decreases.

As a result, lowering the pyrolysis temperature below 400°C solely to reduce the water content is not recommended. Remarkably, a minimum water content of the oil produced was found for the oil produced at 580°C. See Table 2.5.

Table 2.5: *Water content of the pyrolysis oil*

Reactor temperature (^{o}C)	330	360	400	450	480	530	580
Water content of the pyrolysis oil (wt%)	31	31	33	31	33	31	25

Water is the most abundant compound in pyrolysis oil. As the water content is important for various reasons like phase stability (see Figure 2.4A), energy density (Figure 2.4B), and viscosity (Figure 2.4C) somewhat more attention was paid to the water content.

Phase separation behavior was studied by adding an increasing amount of water dropwise to the pyrolysis oil at 20°C. The mixtures were shaken for 1 min and left for 7 days to see whether or not the oil was phase-separated. Phase separation was observed for pyrolysis oils with a minimum water content of 32 wt% of the pyrolysis oil. Most likely, the point of phase separation also depends on the amount of insoluble compounds and polar compounds present in the mixture. From the onset of phase splitting, the amount of water trapped in the heavy organic phase is approximately constant.

Water has been added in equal proportions to a single phase pyrolysis oil to study the effect of water content on the high heating value (HHV) and viscosity at constant composition of the organic fraction of the pyrolysis oil. After addition of water, the oils were analyzed for their viscosity and elemental composition in order to calculate the heating value of the oils. It is obvious that both the viscosity and HHV of the single phase pyrolysis oil increase with lower water content. These results, in line with literature findings,[6] indicate the sensitivity of the viscosity towards the water content and provide a frame of reference for comparison with results (see further on) for especially the pyrolysis oil viscosity produced at other fluid bed temperatures.

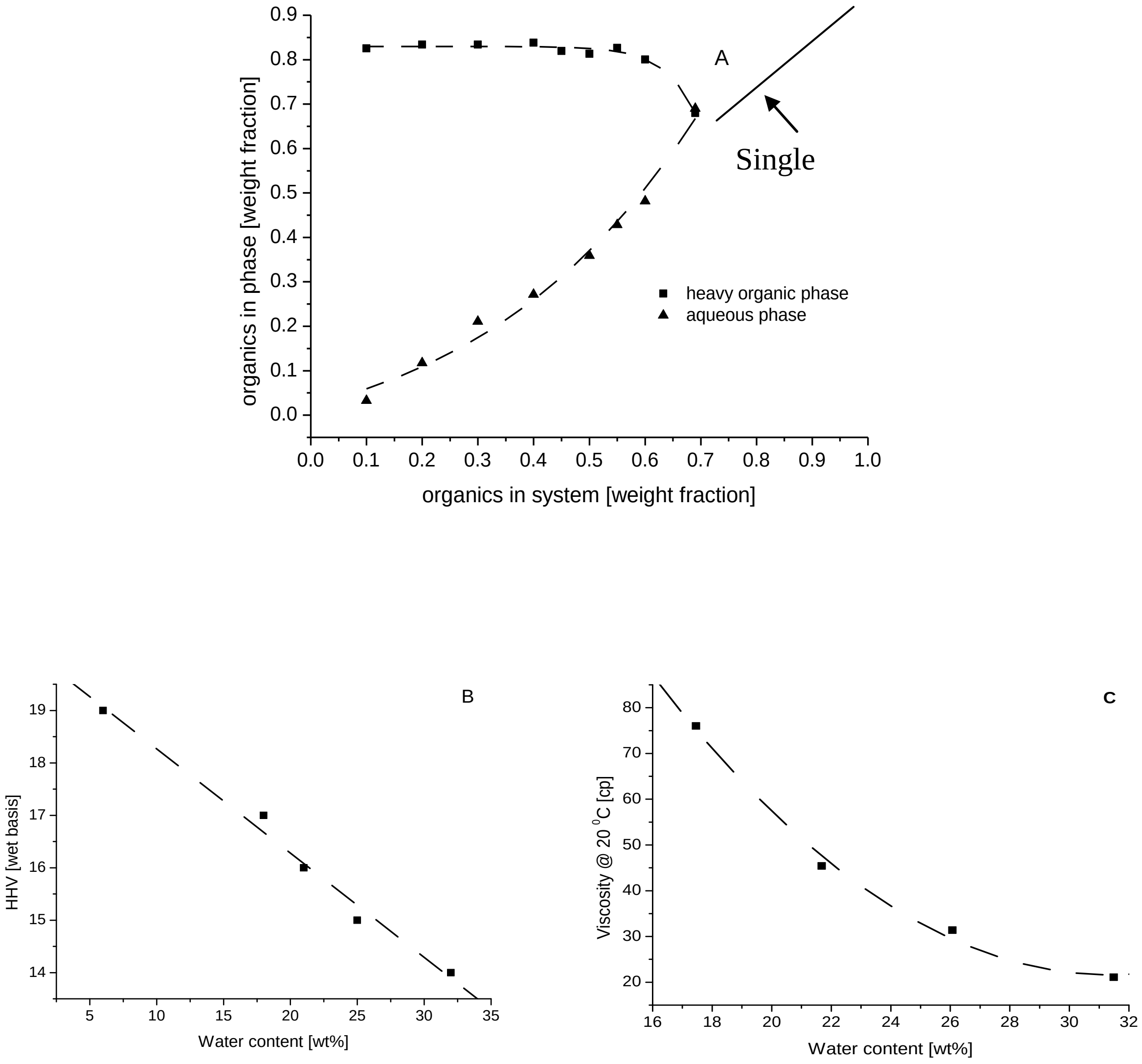

Figure 2.4: *A) Phase diagram of fast pyrolysis oil, B) HHV of fast pyrolysis oil as function of the water content, C) Viscosity of pyrolysis oil as function of the water content.*

2.3.3 Effect of Fluid Bed Reactor Temperature on Pyrolysis Oil Composition.

Figure 2.5 shows a small decrease in the H/C and O/C ratio of the organic part of the pyrolysis oil, when compared with the original pine wood feedstock, already at fast pyrolysis temperatures of 400°C (H/C) and 350°C (O/C), respectively. This can be explained by the already significant water production at these temperatures, and as a result, hydrogen and oxygen are removed. From 400°C, the H/C and O/C ratios stay nearly constant.

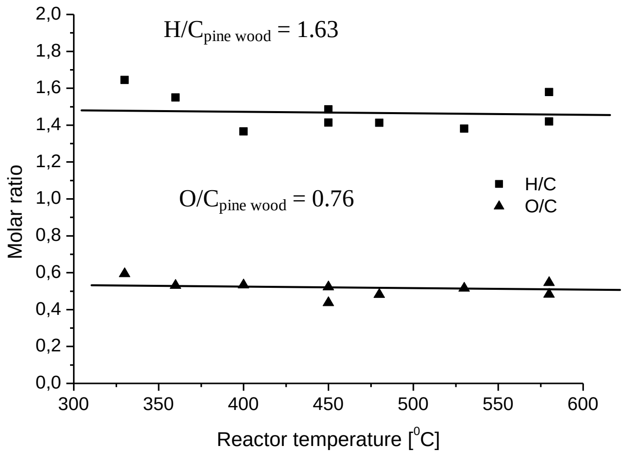

Figure 2.5: *H/C and O/C molar ratio of the pyrolysis oil. The molar ratios of pine wood and pyrolysis oil are on dry basis.*

Figure 2.6 and 2.7 shows a clear indication of an increasing amount of larger molecules formed with increasing fast pyrolysis temperatures from 360 to 530°C. At even higher temperatures (580°C), the amount of large molecules apparently starts to decrease. Although the trend of the (apparent) molecular size distribution with increasing T_{FB} seems clear, one must in general be cautious when interpreting GPC results like those of Figure 2.6 into absolute numbers for the (number average) molecular weight of the compounds present in the pyrolysis oil[4].

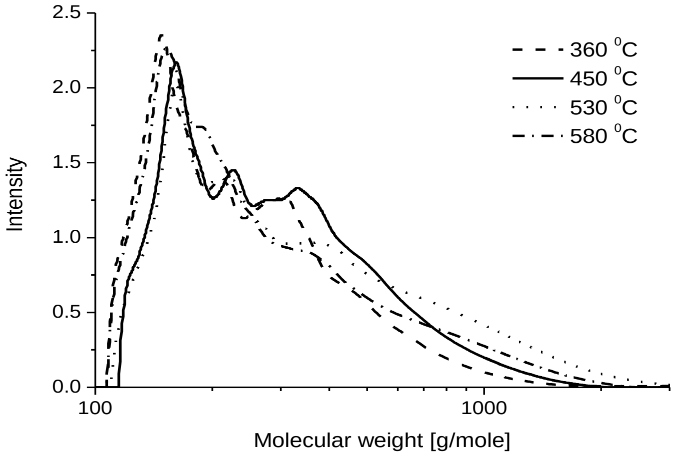

Figure 2.6: *Molar weight distribution of fast pyrolysis oil from pine wood obtained at fluidized bed reactor temperatures of 360, 450, 530 and 580^{o}C respectively.*

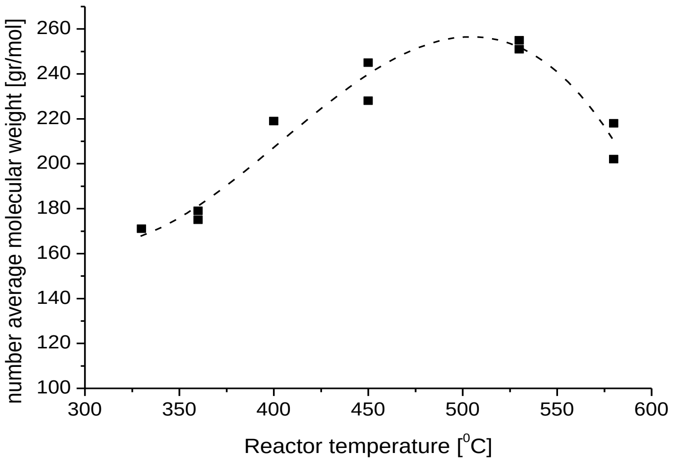

Figure 2.7: *The number average molecular weight of the pyrolysis oil as function of the fluidized bed reactor temperature.*

Strong support for the appearing result of larger molecules in the oil at increasing temperatures between 360 and 530°C and smaller molecules at a temperature of 580°C is provided by the viscosity measurements for these oils; see Figure 2.8. Note the similarity between Figures 2.7 and 2.8, and realize that the viscosity effects observed are not due to different water contents (see Table 2.5). Moreover, the oil produced at 580°C exhibits a relatively low viscosity despite having significantly lower water content than the oil produced at 530°C.

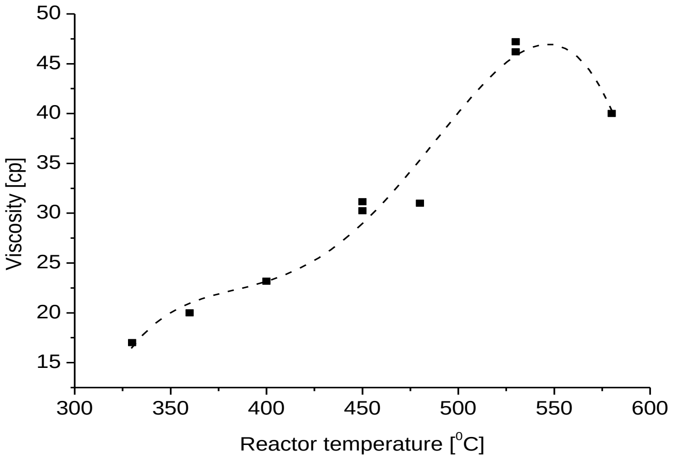

Figure 2.8: *The viscosity of pyrolysis oil as function of the fluidized bed reactor temperatures.*

The increasing molecule size with increasing reactor temperature up to 480°C is most likely due to increased lignin conversion into condensable vapors and hence into pyrolysis oil compounds. Lignin derived oligomers are known to have a high molecular weight. See Figure 2.9. The increase in water insoluble compounds, see Figure 2.10 and 2.11, is a good indication for the increasing lignin conversion until 480°C since the insoluble compounds consist mainly of lignin derived oligomers[27,28]. The trend observed is supported by the decrease in char yield (Figure 2.2).

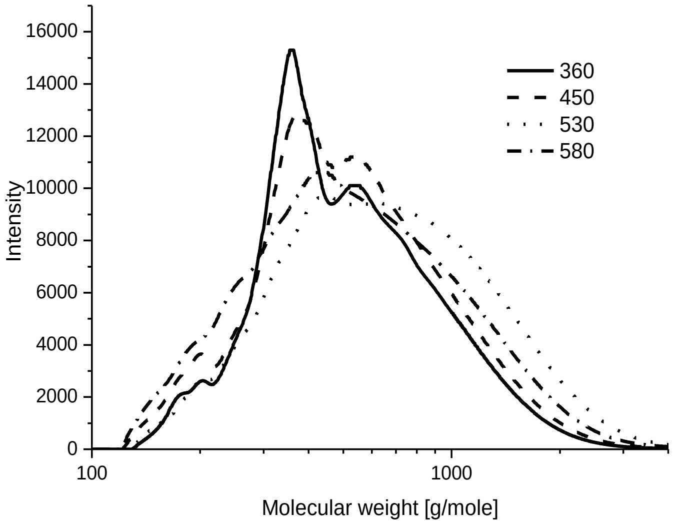

Figure 2.9: *Molar weight distribution of the water insoluble fraction of fast pyrolysis oil obtained at varied fast pyrolysis reactor temperatures.*

From 480 to 530°C, the organics production stays nearly constant as well as the amount of water insolubles but the molecular weight of the oil and the viscosity increases in this range. Most likely polymerization of the vapors to form larger molecules occurs[29] and is dominant above vapor cracking reactions to form smaller molecules. Nevertheless, the gas yield increases continuously, indicating that also significant cracking of vapors occurs.

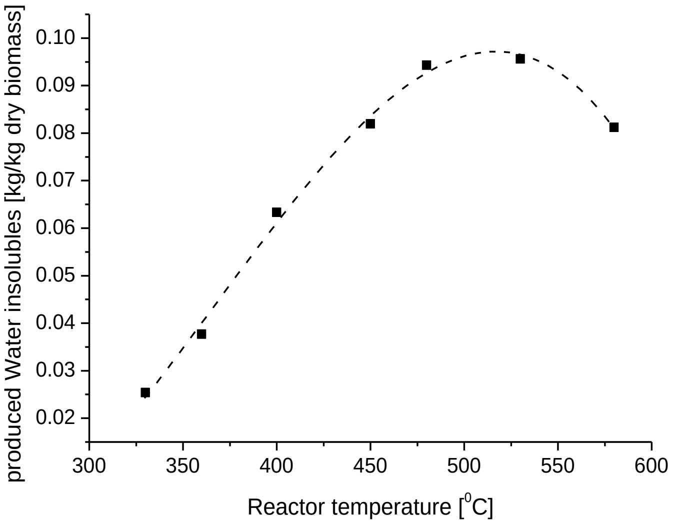

Figure 2.10: *Produced water insoluble compounds at varied fluidized bed reactor temperatures.*

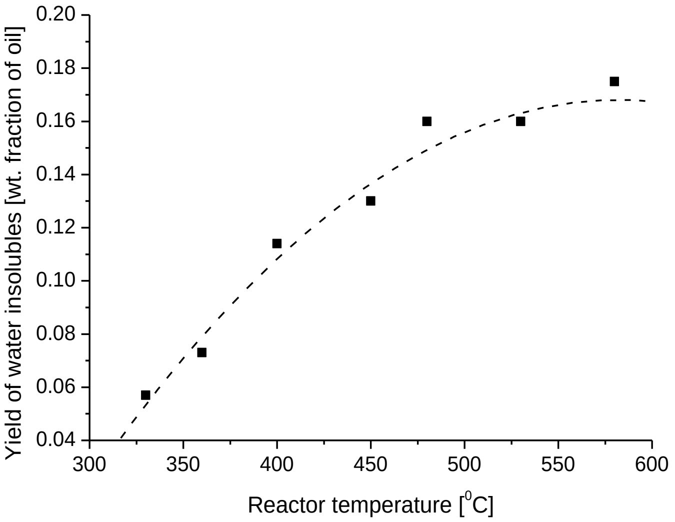

Figure 2.11: *Concentration of water insoluble compounds in the pyrolysis oil obtained at varied fluidized bed reactor temperatures.*

At 580°C, the (overall) molecular size and viscosity of the pyrolysis oil decreases (see Figures 2.6, 2.7 and 2.8) most likely due to vapor phase cracking of the condensable vapors, since the amount of char residue left in the reactor is nearly constant[30,31]. The vapor phase cracking is supported by the data presented in Figure 2.10, showing the water insoluble compound yield decrease when going from 530 to 580°C. It can be concluded that for the whole pyrolysis oil produced at these temperature (580°C) the enhanced vapor cracking is dominant above increased polymerization reactions. The amount of produced insoluble compounds decreases at a temperature of 580°C, but the viscosity decrease is not confirmed by a decreasing amount of insoluble compounds in the analyzed pyrolysis oil (see Figure 2.11). Presumably, next to the water insolubles (see Figure 2.9) also other molecules than the water insolubles in the oil (the remaining 80% of the oil) are decreasing the number average molecular weight and viscosity.

2.3.4 Effect of Fluid Bed Reactor Temperature on Pyrolysis Oil Quality: Atomization Tests.

Atomization experiments at temperatures around 850°C were performed with two different pyrolysis oils obtained at fast pyrolysis temperatures of 360 and 530°C, respectively. The oil was passed through an atomizer together with a flow of nitrogen to obtain very fine oil droplets (±50 μm) and a well-defined droplet/vapor residence time of approximately 1.2 s in the hot tube for both experiments.

Table 2.6: *Atomizing results*

Analysis	definition	Oil – 360°C	Oil – 530°C
H_2 - yield	Nm^3/kg dry oil	0.49	0.33
CH_4	Nm^3/kg dry oil	0.13	0.13
CO	Nm^3/kg dry oil	0.59	0.61
CO_2	Nm^3/kg dry oil	0.17	0.06
C_2+	Nm^3/kg dry oil	0.08	0.06
H_2+CO	Nm^3/kg dry oil	1.08	0.94
C to gas	%	103	84
C to vapours	%	0	14
C to char	%	2	5
Total Carbon balance	%	105	104

In Table 2.6, the experimental results are presented for the atomization experiments. With pyrolysis oil obtained at a pyrolysis reactor temperature of 360°C, significantly more carbon goes to the gas product: 103 vs 84% of the oil obtained at a pyrolysis temperature of 530°C. The amount of carbon that ends up in the char residue is for the 530°C pyrolysis oil approximately 2.5 times higher, when compared to the char obtained for the 360°C pyrolysis oil. No loss of carbon to the remaining (unconverted) vapors after the atomization experiments was measured for the 360°C pyrolysis oil. Consequently, the syngas (H2 + CO) production is for the 360°C oil significantly higher. Under our process conditions, the 360°C oil appears to have a better quality for the atomization unit used, and likely for gasification/combustion in general, because more carbon goes to the gas phase and less char is produced.

2.3.5 Effect of Fluid Bed Reactor Temperature on Pyrolysis Oil Quality: Hydrodeoxygenation Tests.

Three different oils, obtained at a pyrolysis temperature of 330, 530, and 580°C, respectively, were examined for their quality in the hydrotreated process to study the degree of oxygen removal and the viscosity. The pressure inside the autoclave was 192 bar, and the temperature was 300°C for all three experiments. The results of the hydrogenation of the three different oils can be found in Table 2.7.

Table 2.7: *Hydrodeoxygenation results*

Analysis		Pyrolysis temperature (^{o}C)						
		Pyrolysis oil 330	Deoxygenated oil 330 top	Deoxygenated oil 330 bottom	Pyrolysis oil 530	Deoxygenated oil 530 bottom	Pyrolysisoil 580	Deoxygenated oil 580 bottom
Elemental composition (wt%,dry)	C	51.8	71.1	72.2	55.4	71.7	54.1	70.9
	H	7.1	9.5	10.0	6.4	9.4	6.4	9.6
	O	41.0	18.6	16.9	38.1	18.0	39.4	18.6
Water content (wt%)		30.9	4.9	7.6	31.0	6.8	29.2	8.4
Yield deoxygenated oil (wt%,dry oil)			20.1	20.2		51.4		50.6
Viscosity (cP)		17	23	74	46	290	27	261
Density (kg/m^3)			0.96	1.01	1.30	1.05		1.05

The deoxygenated oil obtained after treatment of the low pyrolysis temperature (330°C) oil has a top phase and a bottom phase. The other two oils have only a bottom phase. All three deoxygenated oils differ not much in composition; the top phase of the 330°C pyrolysis oil contains somewhat less water. The oxygen content of the three deoxygenated oils was in addition reduced to around 18 wt%, and the water content was reduced from about 30 wt% to 5-9 wt%. The total yield of deoxygenated oil obtained from hydrodeoxygenation of the 330°C oil is significant lower, mostly in expense of more gases being produced during hydrodeoxygenation. The viscosity of the three deoxygenated oils increases significantly. This is most likely due to polymerization reactions. In Figures 2.7 and 2.8, the increase of the viscosity is reflected by an increasing molecular weight. It is important to notice that there is a relation between the lower viscosity of the 330 and 580°C deoxygenated oil and the lower viscosity of the incoming original pyrolysis oils; see Figure 2.8.

2.4 Conclusions

Fast pyrolysis of pine wood was studied using a 1 kg/h fluid bed pilot plant for temperatures from 330 to 580°C. The mass balance closure was very good, and the trends in product (gas, oil, char) yield and oil composition with operating temperature were established. Moreover, the oil produced at different temperatures was tested in two different standard test applications (hydrodeoxygenation and atomization) to test its suitability.

With increasing pyrolysis temperature, gas yield increases monotonously while char yield sharply decreases and becomes constant above 500°C. The decrease in char yield is believed to be due to increased lignin conversion. The oil yield is approximately constant between 450 and 530°C, as well as the elemental composition (C, H, O) of the oil. As water (and CO_2) production mainly proceeds during early stages of pyrolysis (at lower temperatures), the water content of the oil produced is nearly constant between 400 and 530°C. At 360°C, still acceptable pyrolysis oil yields of 58 dry wt% can be obtained when applying long enough residence time of the biomass particle. Therefore, the conventional view on pyrolysis taking place between 400 and 550°C to maximize oil yields must be reconsidered when pyrolysis oils obtained at temperatures below 400°C have a better quality for a certain application. Possibly practical disadvantages can arise when trying to accommodate the required long residence/conversion times of biomass particles because this can result in relatively larger reactor volumes for a set biomass throughput.

With increasing temperature, the average molecular size, the content of heavy “water insolubles”, and the viscosity of the oil increases significantly. In the temperature range of 330-450/480°C, this phenomenon can be explained by increasing conversion/volatilization of the lignin fraction of wood. At higher temperatures, the amount of water insoluble compounds in the oil stay constant but the viscosity and average molecular weight of the pyrolysis oil keeps on increasing most likely by the contribution of polymerization reactions. However, at the high end of the range investigated (when going from 530 to 580°C), the viscosity as well as the number average molecular size and the amount of produced water insoluble compounds (Figure 2.8A) decreases again, presumably due to enhanced vapor cracking. The observed viscosity reduction is remarkable as the water content is lower and the amount of water insolubles is the same as in the oil produced at 530°C. It is likely that apart from the reduced amount of produced water insoluble compounds probably also cracking of other compounds (±80 wt%) present in the analyzed oils are responsible.

Hydrodeoxygenation tests with oils produced at 330, 530, and 580°C show that hydrodeoxygenation reduces in all cases the oxygen content of the oil to around 18 wt%, reduces water content to 5-9 wt%, and increases viscosity significantly when compared to the untreated pyrolysis oil. Low viscosity pyrolysis oil will result in lower viscosity oil after treatment. The yield of the deoxygenated oil obtained from the 330°C pyrolysis oil is, however, significantly lower. From the different behavior of the three pyrolysis oils, it is not yet possible to draw a conclusion which oil is the better one for hydrodeoxygenation and use in subsequent applications.

Testing the oils produced at 360 and 530°C in an atomization unit at 850°C revealed that the oil produced at the lower temperature seems more suitable for atomization, as it leads to less char formation and higher carbon to gas yields.

Together with chemical and physical analyzes of the pyrolysis oils, feeding the pyrolysis oil into a test unit relevant for applications, can give direct information on the effect of varied pyrolysis process parameters on the quality and applicability of the pyrolysis oil.

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Chapter 3

Step-wise Fast Pyrolysis of Pine Wood

Abstract

This chapter reports the yield and product composition obtained from the step-wise pyrolysis of pine wood in a fluidized bed reactor. The first step temperature was varied between 260 and 360^{o}C. The average biomass particle residence time in the hot reactor for the first and second step was approximately 25 minutes. After the first step pine wood was cooled down to ambient temperature and pyrolyzed again at 530^{o}C. The accumulative yields (step 1 + 2) of char, gas, oil, water and of lumped compound groups; mono-phenols, lights, sugars, furans and lignin oligomers (water insoluble fraction) were compared with the yields obtained when the biomass was pyrolyzed in a single step at 530^{o}C. Although, it was possible to concentrate some groups of compounds and individual species (e.g. levoglucosan, acetic acid) in the oils obtained in one of the pyrolysis steps, it generally resulted in significant yield losses. If the first step temperature was below 290^{o}C no changes in accumulated yields were observed. This means that the reactions and phenomena happening at temperatures below 290^{o}C does not lead to chemical and structural changes affecting the outcome of the reactions at 530^{o}C. When the first step temperature was higher than 310^{o}C the accumulated yields (step 1 + 2) of char, water, lights and furans were higher than those obtained if the pyrolysis was conducted in a single step at 530^{o}C. The extra-char formed was likely to be produced from the poly-condensation of heavy pyrolytic products (lignin oligomers, hydrolysable oligomer sugars and cross-linked compounds) many of which are liquid intermediates when the temperature of the first step exceeded 290^{o}C. A new mechanistic model that includes explicitly the condensation of heavy liquid intermediate to form extra-char was proposed. The poor volatility of the heavy liquid intermediates formed during the first step seems to be an important factor controlling the yield and composition of products obtained.

3.1 Introduction

Fast pyrolysis is a technology that converts bulky inhomogeneous biomass into a liquid, often called pyrolysis oil or bio-oil. At the time of this writing, one commercial plant is in operation[1] and several demonstration projects are ongoing[2-4]. However, there is optimism about the future of this technology, which resulted in the start of several large development programs funded by governments and supported by industry[4-6]. Current research is predominantly focusing on process development[7-10], improving the quality of the oil[11-15], oil up-grading by hydro-deoxygenation[16,17] and development of pyrolysis oil derived products like syngas and bio-ethanol[18-21]. The yield and composition of pyrolysis oil depends, among other, on feedstock composition, on the particle size[22] and on the temperature[23-25].

Most fast pyrolysis reactors have to operate with (very) small particles to achieve high bio-oil yields. For grinding of the raw biomass a significant amount of energy is required. A thermal treatment (torrefaction) step could help to reduce the grinding energy significantly[26] and improve the economic viability of these technologies. However, it is not known how torrefied biomass will behave during pyrolysis. Furthermore, pyrolysis oil obtained from a one step fast pyrolysis process has some adverse properties like high acidity, high water content, high oxygen content, low heating value and the inherent complexity related to being a multi-component mixture[27,28]. Bio-oil performance parameters in a given application are often related to the presence of certain compounds[23,28,29], for example: acidity: is related to the presence of acetic acid, viscosity: is controlled by the content of water and (lignin) oligomers, combustion performance: depends mostly of water content and charring compounds, stability: is mainly dependent of (lignin) oligomers, aldehydes and guaiacols[13,28]. Step-wise pyrolysis (torrefaction followed by pyrolysis) could be an interesting process to produce pyrolysis oils with lower content of acids, concentrated in desired compounds and with improved properties.

Broido and co-workers[30] found that when cellulose was pyrolysed step-wise first at a low temperature of 275°C for 21 hours and in a second step at 370°C, the accumulative char yield was 27.6 wt% which was more than 2 times higher compared to the char yield obtained by one step pyrolysis at 370°C. In another study, Broido found that when a cellulose sample was held for a day at 250°C it formed three times as much char at 400°C as a similar sample heated directly to 400°C[31]. Antal et al.[32] pretreated cellulose for 2 hours at 240°C and then the sample was heated (5°C/min.) till 500°C. The char yield increased only with 0.5wt% for the pretreated cellulose compared to the char yield obtained from one step 500°C. When the cellulose was pre-heated at 270°C for 2.5 hours before heating it to 500°C the char yield increased only 1.5 wt%. An extensive research on the effects of cellulose thermal pretreatment on char yields without cooling between the thermal pretreatment steps (step one between 250-290°C for 0 till 999 minutes, step two at 370°C for 60-999 minutes and the final step at 500°C for 25 minutes) was performed by Varhegyi et al.[33]. From this work Varhegyi et al.[33] and Antal et al.[34] came to the important conclusion that the kinetic parameters of the depolymerization reactions of cellulose stay essentially unchanged even after 16 hours of pretreatment and that extra char formation due to thermal pretreatment requires extreme long pre-treatment times.

The evolution of phenols was studied by Roy et al[35] by vacuum step-wise pyrolysis of a mixture of birch bark (ca. 46 %) and birch sapwood (ca. 54 %). The biomass was pyrolyzed in five steps; 25-200, 200-275, 275-350, 350-450, 450-550°C. The hold-time of each step was 1 hour. The biomass was also pyrolyzed in one step 25-550°C. Most of the mono-phenols were produced between 275-350°C.

Step wise pyrolysis of hybrid poplar and the wood constituents hemicellulose, cellulose and lignin was also studied by Jones et al.[36] by analytical pyrolysis in a batch-wise micro pyrolyzer. The temperature of the wood at the start of the experiment was 200°C and proceeded in 25°C steps up to 300°C, followed 10°C steps up to 500°C. The hold-time for each temperature was 90 seconds. The wood was also pyrolyzed in one step to 500°C. After each exposure the wood sample was cooled down and analyzed using FTIR-PAS (Fourier Transform Infrared Photo Acoustic Spectrometry). The order of disappearance of the building blocks was consistent with literature: first hemicellulose degradates then cellulose (but overlapping) and lignin is the most resistant, but reacting over a wide temperature range (from 280 - 500°C)[36] The pyrolysis products were analyzed by DART-MS (Direct Analysis in Real Time Mass Spectrometry). An interesting finding was diminishing of two ring carbohydrate derivatives in the step-wise pyrolysis mode compared to one step pyrolysis.

Step-wise pyrolysis of biomass beech, poplar, spruce and straw was recently studied by De Wild et al.[37] in an auger reactor at temperatures between 250-300°C (step one) and 350-400°C (step two). They found that when beech wood was pyrolyzed step-wise in a fluidized bed from 20-280-350°C or in one step from 20-350°C the char yield did not change and that there was only little decrease in produced organic liquids. Their results showed difficulties in concentrating chemicals by step-wise pyrolysis.

In the current contribution, we report step-wise pyrolysis experiments of pine wood in a fluidized bed reactor while stretching the temperature range of the first step, as compared to De Wild and co-workers, to 360°C. By taking this wider range it is anticipated that more information is obtained about the reaction mechanisms, the particular char formation pathways. It is discussed how the observed pyrolysis behavior in the step-wise concept can be understood by combining the data with existing theoretical approaches and modifications of those. In addition of having practical implications, the step-wise pyrolysis experiments herein reported were designed to provide information on how important certain processes (reactions and transfer processes) are at certain temperature levels in the trajectory from ambient temperature to a typical fast pyrolysis temperature (in our case 530°C). Thus, the main goal of this paper is to identify the potential of step-wise pyrolysis for pyrolysis oil improvement, for maximizing the production of targeted compounds and to gain insight into the pyrolysis mechanisms.

3.2 Experimental Methods

3.2.1 Step Wise Pyrolysis tests

Experiments were performed in a 1 kg/hr fluidized bed (sand) pyrolysis plant. Details on the experimental set-up can be found in chapter 2 and 6. The fluidized bed reactor is equipped with an overflow to remove the majority of char from the bed. A knock-out vessel and two cyclones collect the remaining char fines entrained from the reactor. The pyrolysis vapors are condensed in two identical wall cooled counter-current spray columns and one intensive cooler installed to condense the very light vapors. Process conditions and biomass properties are listed in table 3.1. By controlling the biomass feed rate and sand feed rate, the (average) particle residence time in the well-mixed fluidized bed is set to ca. 25 minutes.

Table 3.1: *Experimental conditions*

Operating conditions	Values	Dimension
Biomass (Pine) feeding rate	1	kg/hr
Biomass elemental composition	C=46.6, H=6.3, O=47.0	wt% dry ash free
Biomass bio-chemical composition	Cellulose =35, hemicellulose =29, lignin =28, others =8	wt%, dry ash free
Biomass moisture content	8	wt%, as received
Biomass ash content	0.5	wt%, as received
Biomass particle size	~1	µm
Biomass residence time step 1/2	25	min
Sand particle size	220	µm
U/U_{mf}	2.5-3	-
residence time vapors hot part	1.6-1.9	sec
$T_{reactor}$ Step one	260, 290, 310, 330, 360, 530	^{o}C
$T_{reactor}$ Step two	530	^{o}C
Temp condenser 1	20	^{o}C
Temp condenser 2	20	^{o}C
Temp intensive cooler	0	^{o}C
Experimental run time	120	min

An important part of the set-up in controlling the pyrolysis time of the particles is the water cooled overflow vessel for char collection which is kept at 20^{o}C during an experiment. In this way, immediate cooling of the char after leaving the reactor is achieved. At the end of the first pyrolysis step experiment (260-360^{o}C) the partial converted biomass (char) left in the reactor is quickly cooled down to room temperature by feeding large volumes of cold sand to the fluidized bed reactor in order to freeze further pyrolysis reactions. The solid residue of first step (char / partly converted biomass) is obtained in a mixture with sand then stored in a sealed vessel to prevent moisture uptake. Prior before the second pyrolysis step the partial converted biomass is separated from the major part of the sand by sieving. A sample of the left-over char/sand mixture is combusted to determine the minerals (ash) content enabling the calculation of the actual char concentration in the feed of the second step at 530°C. The partly converted biomass can be fed without size reduction. Product yields of the first and second pyrolysis step is calculated on dry ash free biomass (fed during the first step) basis. The liquids collected in condenser 1 condenser 2 and the intensive cooler are added and this mixture is used yield calculations and analysis.

3.2.2 Pyrolysis oil analysis

The analytical methods used are shown in table 3.2. The water content of the pyrolysis oil was quantified by the Karl Fisher Titration method. The cold water precipitation method described by Garcia-Perez[38] was used to determine the water insoluble oligomers. The water insoluble compounds were further extracted by CH_2Cl_2. The CH_2Cl_2 soluble compounds are mostly LMM (low molecular mass water insoluble) compounds and the water insolubles and ether insolubles are ascribed to the HMM (high molecular mass water insoluble) compounds.

Table 3.2: *Analytical Methods employed*

Compounds	Analysis method	Reference
Water	Karl Fisher Titration	23
Water insoluble fraction (oligomers)	Cold water precipitation	38
Lights: Acetone, Ethanol, Methanol	GC/FID	13
Lights: Acetic acid, Propionic acid, Acetol, Glycolaldehyde	GC/MS	20,38
Mid-boilers: 2-furaldehyde, β-methoxy-(S)-2-Furanethanol, Guiaiacols: 2-methoxy-Phenol, Eugenol, methyl-quiaiacol, vanillin, 2-methoxy-4-(1-propenyl)-(E)-Phenol, Catechols: pyrotechol, 4-methyl-catechol, 3-methyl-cathecol, 4-Ethylcatechol, substituted phenols: phenol, O-Cresol, p-Cresol, m-Cresol, 2,4-dimethyl-phenol, 2,5-dimethyl-Phenol, 4-ethyl-Phenol, 3,4-dimethyl-phenol	GC/MS	20,38
Sugars: Levoglucosan, Glucose, Xylose/Mannose, Fructose, Arabinose and Galactose	GC/MS (levoglucosan) & acid hydrolysis followed by IEC	20
Non-condensable gasses	GC	23

The sugar content of the oils was quantified by Ion Exchange Chromatography (IEC) after hydrolysis with sulfuric acid. After neutralization of the solution, the oil was analyzed using a Dionex ICS-3000 system equipped with an AS 50 auto-sampler, GP50 gradient pump, and ED50 electrochemical detector. Separating sugars was performed with a Carbopac PA20 column. The mobile phase was an aqueous NaOH solution at a flow rate of 0.50 mL/min. Hydrolysable oligo-sugars are calculated as follows: levoglucosan is subtracted from the glucose obtained after hydrolysis. This procedure is justified by the observation that the oil before hydrolysis does not contain glucose and the fact the other mono-sugar do not hydrolyze and form glucose under the applied hydrolysis conditions[20].

An Agilent 6890N Gas Chromatograph coupled with an Agilent Technologies inert XL Mass Spectrometry Detector with a capillary column (Agilent HP-5 MS, HP19091S-433) was used to quantify part of the lights, mid-boilers and levoglucosan. A GC/FID Shimadzu GC-2014 with AOC-5000 auto injector was used to detect acetone and methanol. The column was an HP-INNOWax (30 m long, 0.25 mm inner diameter, coated with 0.25 µm film). The split and FID temperature was set at 180^{o}C and 210^{o}C. The carrier gas (helium) had a constant velocity of 27.9 cm/s, 0.5 gram of pyrolysis oil sample was incubated at 85^{o}C for 5 min. 250µL of gas was then introduced into the GC-FID with a split ratio of 1:25. The non-condensable gas composition was analyzed by GC (Varian CP 4900). A more detail description of the analysis methods can be found in chapter 7.

3.3 Analysis of Results

3.3.1 Yield of products (Oil, organic liquids, water, char and gas)

Good mass balance closures of 96-101 wt% is obtained for each experiment. Figure 3.1 shows the yields of oil, char and gas obtained in the first and second pyrolysis step as well as the accumulative char yield predicted by a single particle model described by Kersten et al.[39]. All experimental data obtained from step-wise pyrolysis is compared with the experiment performed in one-step at 530^{o}C. The cumulative yield (sum of step one and step two) of step-wise pyrolysis is used as parameter to study the pyrolysis reactions. It is our hypotheses that if we find no difference between accumulated step-wise pyrolysis yields and yields from the one-step 530^{o}C experiment, the reactions at the pretreatment temperature are not of significant importance for fast pyrolysis at 450 – 550°C. Interpretation of the step-wise results with respect to one-step fast pyrolysis at 530^{o}C, for which the particles stay only a short period of time in the range of 260-360^{o}C, gives only information regarding a maximum influence of a certain temperature in the fast pyrolysis temperature trajectory. Hence, if the effect is small at 25 minutes of thermal treatment in step 1, it is for sure small under fast pyrolysis conditions.

If, however, there is a significant effect of pretreatment it is not known if this effect is as important at fast pyrolysis (one step 530^{o}C), in which the time the reacting particle is at the pretreatment temperature is much smaller.

In qualitative agreement with previous findings in the studied temperature range, [8,23,25] as the first step temperature is increased, the liquid and gas yield increases and the yield of solid residue obtained decreases (see Figure 3.1). It is remarkable that the accumulative yields of pyrolysis oil produced in step one and two is almost constant for all investigated step-wise tests and that it is approximately equal to the one-step test at 530°C. The cumulative yields (sum of step one and two) of char and gas in the step-wise experiments at 260 and 290°C are identical (considering the error margin) to the one-step experiment at 530°C. It means that the thermo-chemical reactions responsible for the formation of extra char were not greatly affected. Our results are in accordance with previous findings. For example, Varhegyi and Antal[33] performed experiments in which cellulose, after thermal pre-treatment of 2 hours at 250-290^{o}C, was heated to 500^{o}C. No effect on the accumulated char yield of the two steps compared to one step 500^{o}C char was found[33].

Step-wise tests with 310-360°C as first step temperature clearly show higher accumulative char yields and a lower gas yield compared to one-step at 530°C. To the best of our knowledge, this has not been observed before for lignocellulosic biomass.

A large fraction of the lower accumulated volatiles yield is due to gases. The decrease in gas in this regime can be explained by the fact that many of the vapors derived from hemicelluloses do not actually “see” 530^{o}C (in the second step), but only 310-360^{o}C in which the rate of vapor cracking is lower. The gas comes either directly from the primary reactions in the reacting particle or from vapors that are unstable and are cracked.

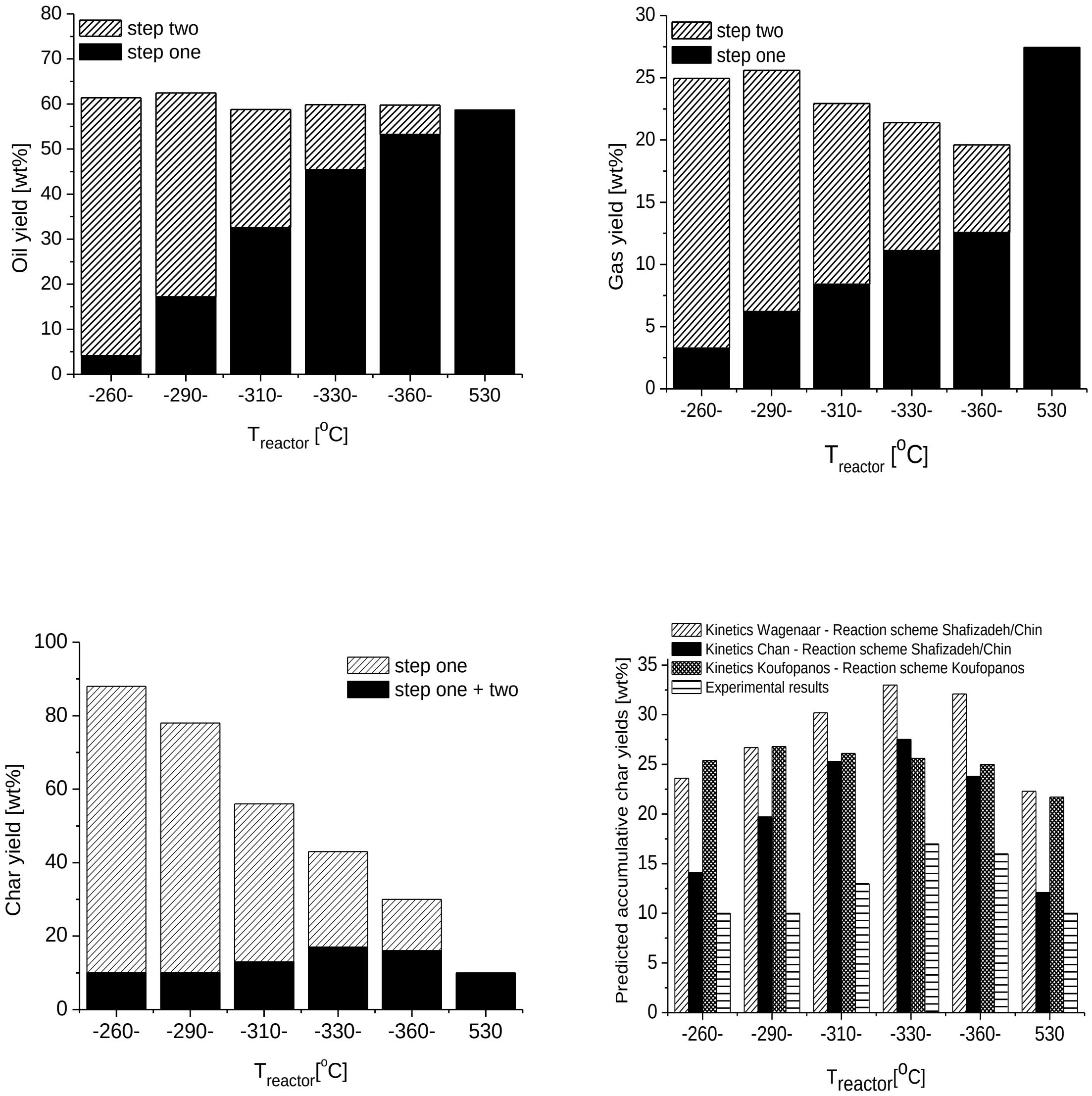

Figure 3.1: *The oil, char and gas yields obtained from step-wise pyrolysis of pine wood (kg/kg biomass (d.a.f) * 100%). The first step temperature (pre-treatment) is depictured on the x-axis. The second step was always at 530^{o}C. 530 ^{o}C on the x-axis denotes the single step experiment. A single particle model is used to predict the trends of the accumulative char yields. Predicted accumulative char yields must be compared with "step one + two" char yields.*

Figure 3.1 shows a graph with calculated values of the accumulated char yield obtained by several models. The model input is primarily based on the properties of the biomass used and the known heat transfer coefficient of the fluidized bed; reported elsewhere[39]. Simulation results obtained from a single particle model (Kersten et al.[39]) indicate that the pyrolysis at the pre-treatment conditions is practically kinetically controlled. Hence, there are hardly temperature gradients inside the particle and the reactions proceed for a very large extent at the temperature of the surrounding fluidized bed. By performing step-wise tests in a range of pretreatment temperatures (260-360°C) and comparing their cumulative yields with the yields of the experiment performed in one-step at 530°C information is obtained about the importance of the pyrolysis reactions at the pretreatment temperatures. The Shafizadeh/Chin[40] and the Koufopanos[41] mechanisms predict that the char yield of the single step experiment is lower than all the step-wise experiments. The modeling results show an increase in accumulative char yield between temperatures of 260 and 290°C, this was not observed for the experimental results. A maximum in predicted accumulative char yield can be observed at 330°C when the scheme of Shafizadeh/Chin and the kinetics of Wagenaar[42] and Chan[43] were used. These modeling results are in agreement with the experimental results. However, the predicted accumulative char yields are always much higher compared to the experimental accumulative char yields. In the "mechanism" section this will be discussed further.

Figure 3.2 shows the yield of water obtained. It was obtained after multiplying the yield of oil by the concentration of water in the oil. The yield of organics was determined by difference. Water production in the first step goes through a maximum, as was also observed earlier[23]. This result clearly indicates the acceleration of cross-linking and dehydratation reactions responsible for water formation when the material is subjected to thermal pretreatment at temperatures over 310°C. The yield of these products in the second step decreases as the pretreatment temperature increases. It is interesting to note that with 330-360°C in the first step, in the second step less organic liquid is produced relative to gas.

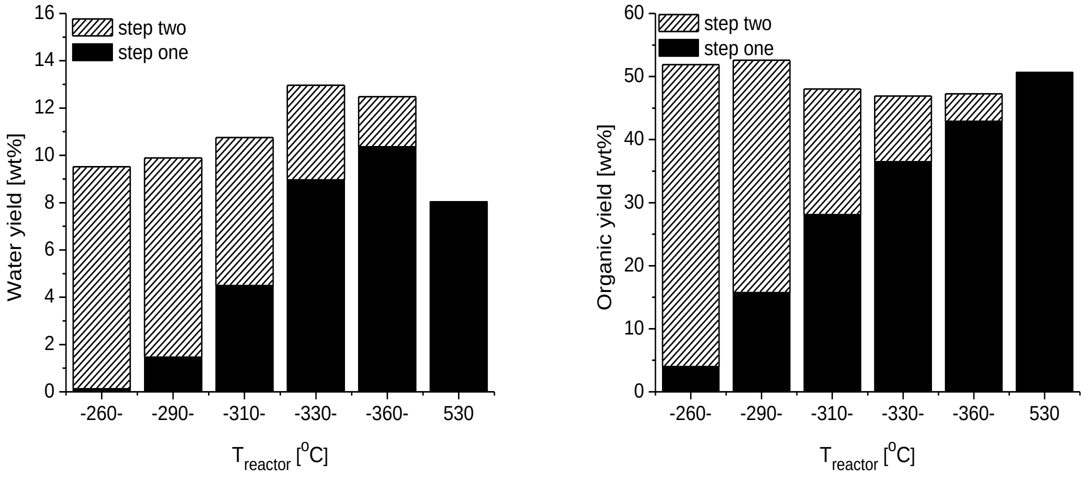

Figure 3.2: *Yield of Water and Organic Compounds*

3.3.2 Yields of light compounds (Normal boiling point < $154^{o}C$)

Cellulose decomposes in two parallel reactions namely depolymerization to form anhydro-sugars[44,45] or by ring scission to produce mainly glycolaldehyde, acetol, linear carbonyls, linear alcohols, esters and some other small products[46-49]. Lights obtained from hemicellulose are generally acetic acid, acetone, glycolaldehyde and 1-hydroxy-2-propanone[45,49,50]. Lignin can produce methanol, and minor amounts of acetic acid, formaldehyde and formic acid[51,52]. From the lights, we identified and quantified glycolaldehyde, acetic acid, acetol, propionic acid, methanol and acetone. Figure 3.3 shows the yields of lights as function of the first step pyrolysis temperature. In the first step, yield of light compounds increase with increasing first-step temperature, whereas the yield decreases in the second step. The data indicate that the production of lights is finished above ca. 360^{o}C at reaction times of 25 minutes. From the lower lights yield of the one-step tests compared to the accumulative yield of tests with first step temperatures in the range of 290-360°C, the presence of vapor cracking reactions responsible for the conversion of light compounds (formed at relatively low temperatures) into gas (at higher temperatures) becomes apparent.

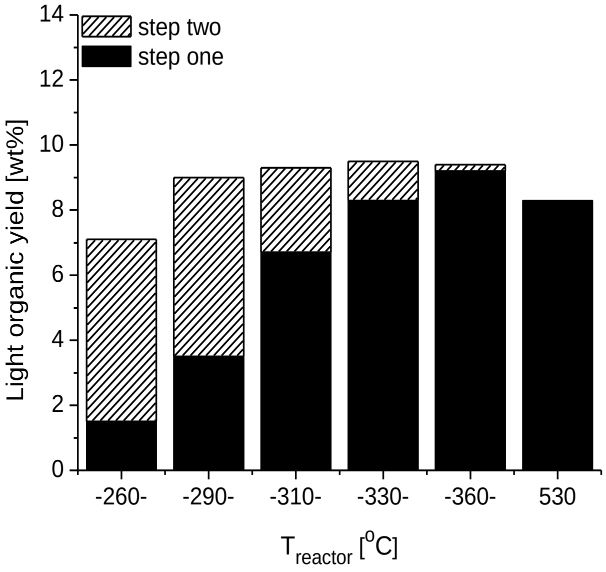

Figure 3.3: *The lights yield obtained from step-wise pyrolysis of pine wood (kg/kg biomass (d.a.f) * 100%). The first step temperature (pre-treatment) is depictured on the x-axis. The second step was always at 530°C. 530 °C on the x-axis denotes the single step experiment.*

3.3.3 Yields of Mid-boilers (Normal boiling point = 154-300°C)

Most of the phenols, guaiacols and catechols are lignin derived compounds and belong to the group of mid-boilers. In the first step, the yield of guaiacols, a primary product of lignin decomposition[51], increases as the temperature increases (See Figure 3.4). For one-step pyrolysis at 530°C the (accumulative) guaiacol yield is lower compared to pyrolysis at the pretreatment step of 330-360°C. Catechols and phenols are only collected in the second step and when pyrolyzing in one step at 530°C. No trend is observed in the accumulative yield of mid-boilers as a function of the pretreatment temperature. The results confirm the proposed mechanism[53] in which guaiacols are primary products of lignin decomposition and that at temperatures higher than 360°C they start to decompose into catechols and phenols.

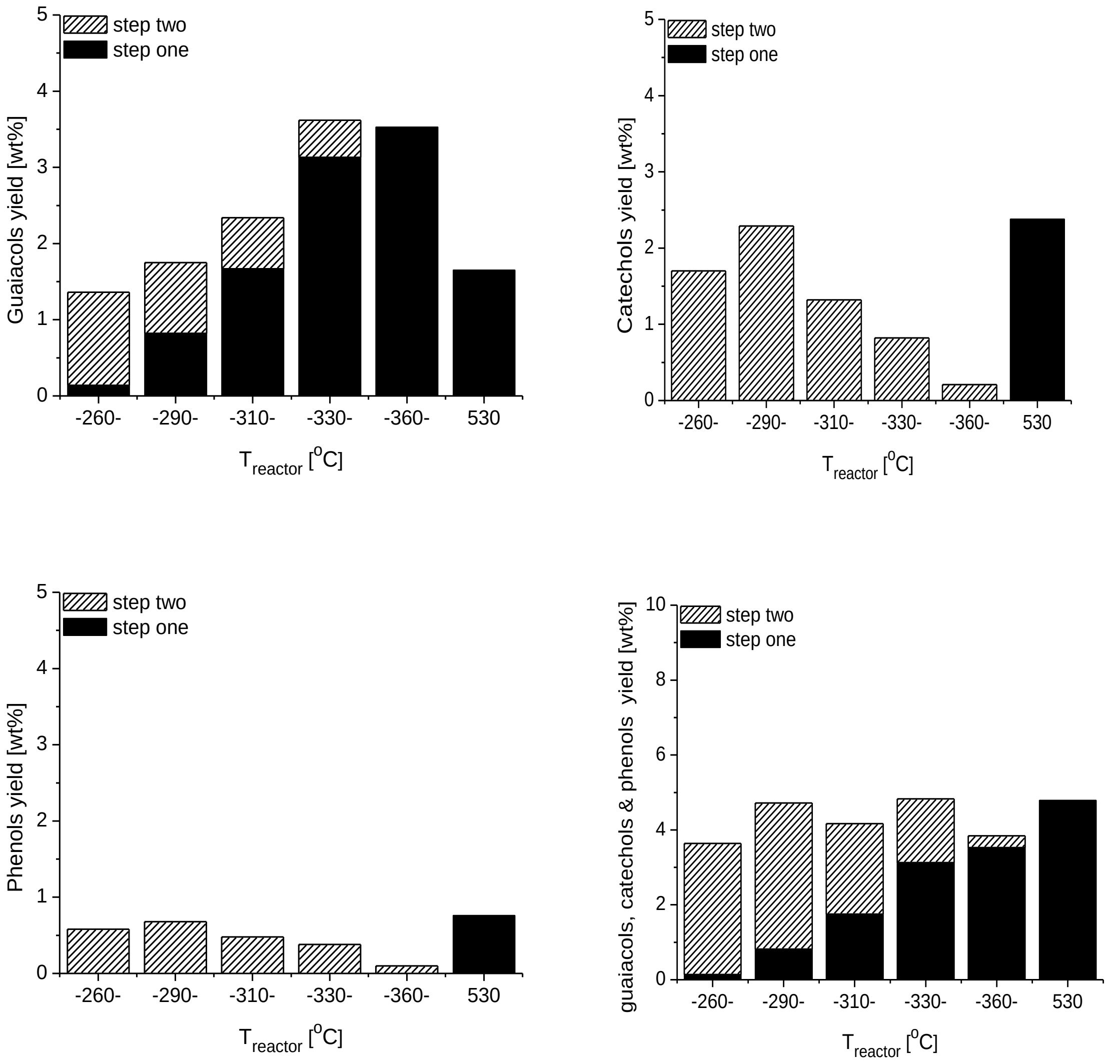

Figure 3.4: *The guaiacols, catechols, phenols and the sum of the three groups obtained from step-wise pyrolysis of pine wood (kg/kg biomass (d.a.f) * 100%). The first step temperature (pre-treatment) is depictured on the x-axis. The second step was always at 530^{o}C. 530^{o}C on the x-axis denotes the single step experiment.*

The accumulated yield of furans depictured in figure 3.5 follow the same trend as the yield of water, which could mean that these furans are a side product of intermolecular dehydratation which is known to be the predominating reaction mechanism during torrefaction[54]. Zhang et al.[55] found that furans come from pyrolysis of the amorphous part of the cellulose and did not observed any furans from the crystalline part of cellulose. The amorphous part of the cellulose is likely to be depolymerized to form oligomeric materials which easily dehydrate to form 5-HMF. While furfural is mainly produced from pentoses, 5-HMF is mostly derived from amorphous cellulose.

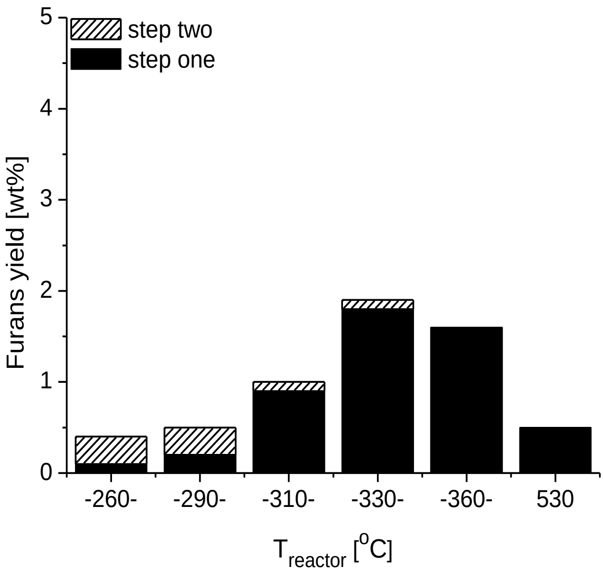

Figure 3.5: *The furan yield obtained from step-wise pyrolysis of pine wood (kg/kg biomass (d.a.f) * 100%). The first step temperature (pre-treatment) is depictured on the x-axis. The second step was always at 530^{o}C. 530 ^{o}C on the x-axis denotes the single step experiment*

3.3.4 Yields of (hydrolysable) sugars:

Figure 3.6 shows the yield of sugars (levoglucosan, hydrolysable oligo-sugars, xylose/mannose, and total sugars). Our data show that mono sugars (levoglucosan, xylose and mannose) are produced and can leave the biomass already at 290°C. The removal of these sugars happens according to their volatility[56,57]. Oligo-sugars are found in the collected liquids at temperatures as low as 310^{o}C. Our data suggest that perhaps oligo-sugars are formed earlier (at lower temperature) or simultaneous with mono-sugars but cannot leave the particle because of their low vapor pressure[56]. In the liquid phase these oligo-sugars are prone to dehydratation reactions[57]. At higher temperatures they can leave the particle via evaporation, because the reaction temperature approaches to the boiling point (581^{o}C for cellobiosan[58]). Larger molecules / fragments could also leave the particle via physical entrainment. This sweeping effects of produced vapors and gasses inside the particle as well as re-condensation in the condensers may well influence the measured yield of oligo-sugars[13].

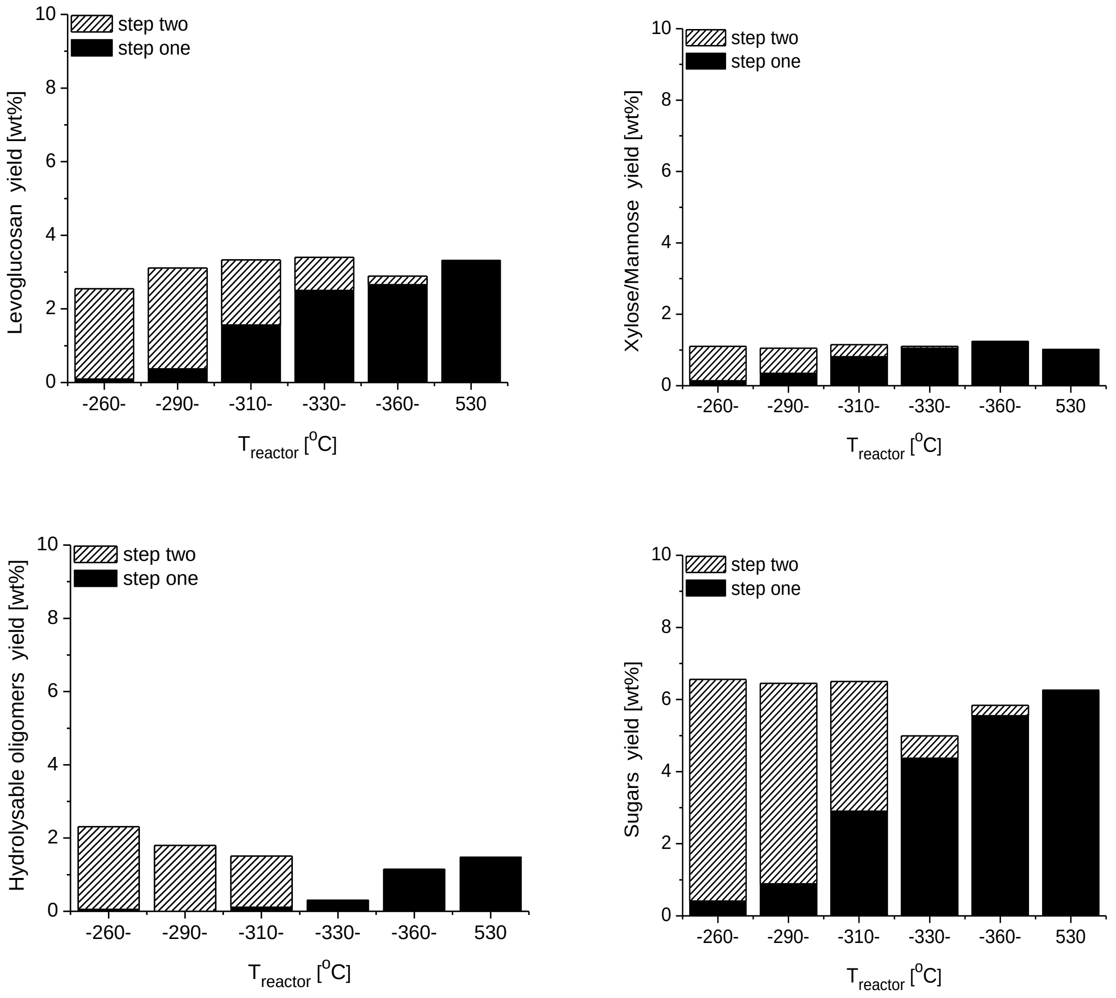

Figure 3.6: *The yields of Levoglucosan, Mannose/Xylose, hydrolysable oligomers and sugars obtained from step-wise pyrolysis of pine wood (kg/kg biomass (d.a.f) * 100%). The first step temperature (pre-treatment) is depictured on the x-axis. The second step was always at 530^{o}C. 530 ^{o}C on the x-axis denotes the single step experiment.*

The accumulative yield of levoglucosan is not influenced much by the pretreatment conditions. This may be due to the low boiling point of levoglucosan (304^{o}C) which allow it to be removed even at the pretreatment conditions used[59]. Mamleev[57] proposed that part of the char forming mechanism is ascribed to reactions proceeding in a liquid phase inside the reacting particle, which has been observed visually by Haas et al.[60]. This liquid seems to be formed not only from cellulose but also from lignin. In our tests, levoglucosan could have been in the liquid state for 25 minutes in the first pyrolysis step. Levoglucosan is quite volatile (bp 304^{o}C) and could leave the reacting particle fast via the vapor phase but heavier hydrolysable oligo-sugars and cross-linked sugars are not and do form (extra) char, therefore the two phase model of

Mamleev could be plausible for these heavier sugars. The accumulative yield of hydrolysable oligo-sugars decrease slightly when the first step temperature is at 330-360°C compared to one-step 530°C, while char increases in this region. This effect might point towards dehydratation (to form extra water and furans) or cross-linking reactions of hydrolysable oligo-sugars to char.

3.3.5 Yields of water insoluble compounds (lignin oligomers).

Figure 3.7 shows how the yield of the water insolubles varies as a result of torrefaction temperature. A sharp drop in accumulative yield can be seen when the biomass is first pretreated at 330 and 360°C while the accumulative char yield increases (See Figure 3.7). This result indicates that the pyrolytic lignin, both HMM and LMM lignin (not shown), is susceptible to char forming reactions. It is well known that the lignin starts to depolymerizes at low temperature (120-280°C)[61]. Part of this depolymerized lignin is in the liquid stage already from 250°C[51] and can thus easily react to form a char (the liquid shown by Haas et al.[60] in pyrolyzing particles is likely lignin). Hence, re-polymerization of lignin at temperatures over 300°C with the formation of stable C-C bonds (fixation of lignin to the matrix) explains the reduction in yield of pyrolytic lignin obtained when the first step is 330 – 360°C.

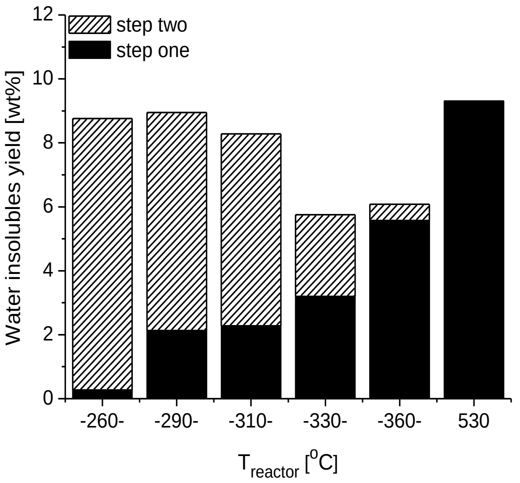

Figure 3.7: *The water insolubles yields obtained from step-wise pyrolysis of pine wood (kg/kg biomass (d.a.f) * 100%). The first step temperature (pre-treatment) is depictured on the x-axis. The second step was always at 530°C. 530 °C on the x-axis denotes the single step experiment.*

3.3.6 Unidentified

The yield of compounds that could not be identified increases with increasing first step temperature and decreases in the second step (figure 3.8). Several researchers suggested that this fraction consists of cross-linked dehydrated structures predominantly originating from cellulose[27,40,62,63].

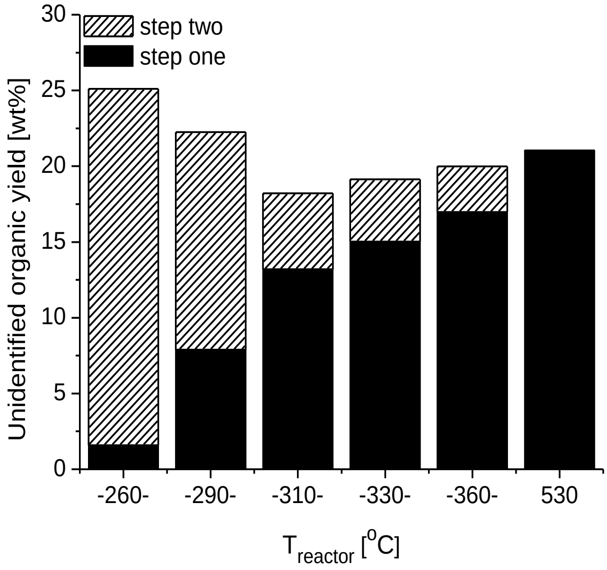

Figure 3.8: *The yield of the unidentified obtained from step-wise pyrolysis of pine wood (kg/kg biomass (d.a.f) * 100%). The first step temperature (pre-treatment) is depictured on the x-axis. The second step was always at 530°C. Pyrolysis time of the pine wood particle in the fluidized bed reactor was 25 minutes for both steps.*

All the experimental evidences reported in the literature show that this fraction: i) cannot be hydrolyzed (indicating cross-linked sugars and not C-O-C bonded oligo-sugars, ii) is soluble in water and iii) can be related to sugars based on the mass balance[27,64]. The latter statement is supported by the results shown in Table 3.3, which shows that using conservative estimates on the lignin and sugar origin of lights, water, char and gas the lignin in feed can be almost completely accounted for in the products while for sugars a large fraction is missing. Hence, also our data point towards a cross-linked structure and a primarily sugar origin. According to Molton and Demmitt[65] cross linking seems to occur by simply dehydratation reactions between hydroxyl groups on adjacent chains to form ether which need the presence of carboxyl groups derived from oxidation reactions or from levoglucosanone intermediates. An interesting result is the accumulative yield of this fraction reaches a minimum at 310-330°C, while the overall char is maximal in this range. This point towards further poly-condensation (cross-linked) of this fraction to form char.

Table 3.3: *Mass balance over the decomposition products of lignin and cellulose, hemicellulose and others (e.g. extractives, ash) to clarify the origin of the unidentified fraction.*

Lignin kg/kg d.a.f. wood *100%		Cellulose + hemicellulose + others kg/kg d.a.f. wood *100%	
Pine wood	**28**	Pine wood	**35 + 29 + 8**
Product yields obtained after pyrolysis			
Phenols	4.8	Phenols	-
Water insolubles	9.4	Water insolubles	-
Sugar	-	Sugar	6
Lights [25% of lights]*	2.1	Lights [75% of lights]	6.3
Furan	-	Furan	0.5
Water [25% of water]*	2.0	Water [75% of water]	6.1
Char [25% of char]*	2.6	Char [75% of char]	7.9
Gas [25% of gas]*	6.9	Gas [75% of gas]	20.6
Sum	**27.8**	**Sum**	**47.4**
Missing from the lignin balance	**0.2**	Missing from cellulose, hemi-cellulose and others balance	**24.6**
Unidentified	0.2	Unidentified**	24.6

* Conservative estimates

** Unidentified= not quantified compounds in the oil (21 wt%) and products missing from the overall mass balance (3.5 wt%)

3.3.7 Concentrating target compounds

In Figure 3.9, concentrations of selected lumped component classes and individual compounds in the oils collected in the first and second pyrolysis steps are plotted versus the fractional yield. Fractional yield is here defined as the yield obtained during step 1 or step 2 over the accumulative yield of the considered compound (sum of step one and two). By plotting the data in this manner it can be quickly evaluated what fraction of the whole compound is collected and at what concentration. This is a very good indicator of the separation efficiency achieved by step-wise pyrolysis. For instance: Figure 3.9 & 3.10 shows that i) the concentration of lights is 12 wt% in the liquid produced with single step fast pyrolysis at 530°C, ii) this concentration can be increased to 16 wt% in the liquid produced in the first step at 310°C and iii) for this particular step-wise test (310 – 530°C) 70% of the lights are collected in the first step and 30% in the second step (this liquid has a lights concentration of 10 wt%).

Although, it will depend on the economics, losing more than 30 – 40% of a target compound to a liquid containing less of it by concentrating it in the other will be presumably not acceptable. The data show that, like de Wild[37] concluded, stepwise pyrolysis does not achieve clean separation of several targeted compounds. However, the results shown in Figure 3.9 & 3.10 point to the following interesting observations:

i) obviously step-wise pyrolysis can remove moisture (water present in the feed biomass) from the oil; this water is recovered in the first-step liquid. Pretreatment at 310°C can result in the removal of more than 40 mass % of the reaction water formed, see Figure 3.9.

ii) lights can be concentrated (compared to one-step 530°C) in the first step liquid by a factor 1.3 [~16 wt% in 1st step liquid / 12 wt% single step] by step-wise pyrolysis at 310°C with a yield loss of 30%. The maximum concentration faction of acetic acid observed is 1.4 in the first step liquid at 330 °C, see Figure 3.9

iii) When the first step temperature is 290°C the concentration of phenols in the second step is 1.25 times higher with a yield loss of 20% to the first step [~9 wt% in 2nd step liquid / 9 wt% single step], see Figure 3.9.

iv) guaiacols can be concentrated 2.4 times [~6wt% in 1st step liquid / 2.5 wt% single step] and recovered for 100% in the first step 360°C, see Figure 3.10.

v) levoglucosan and the total hydrolysable sugars and can be concentrated in the second step liquid by pretreatment at 290 °C up to a factor 1.4 [levoglucosan: ~6wt% in 2nd step liquid / 4.25 wt% single step, hydrolysable: ~12.5 wt% in 2nd step liquid / 9 wt% single step] with a yield loss of 14% and 12% respectively, see Figure 3.10.

vi) water insolubles can be concentrated in the second step liquid by pretreatment at 310°C up to a factor 1.6 [~24 wt% in 2nd step liquid / 15 wt% single step] with a yield loss of 28%, see Figure 3.10.

How these (concentrated) oils perform in applications is subject of further research. Although the separation of individual or groups of compounds obtained is not very clean or as good as what can be obtained by two step condensation of pyrolysis vapors[11,13], the liquids obtained in the first step at temperatures below 300°C are in general rich in light compounds. The corresponding liquids obtained in the second step are heavier. These fractions can possibly also find new applications. It is envisaged that better separations can be achieved by combining step-wise pyrolysis with staged condensation. This is investigated at present and the results will be reported in a follow-up paper.

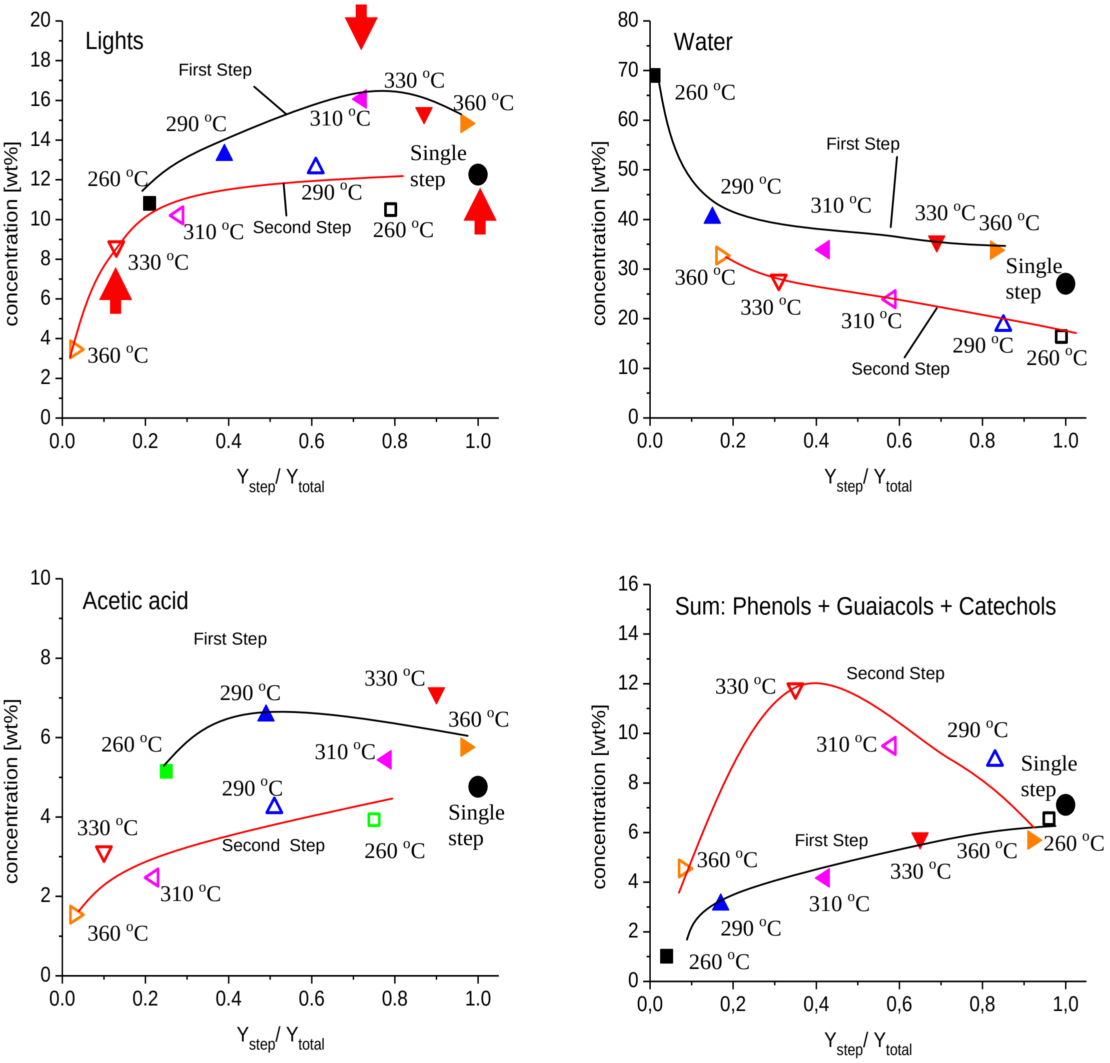

Figure 3.9: *The concentration of compounds (wt% of the oil) and lumped groups of compounds as function of the ratio between the yields collected in a single step and the cumulative yield of both steps. Solid symbols represent the first step and open symbols the second pyrolysis step: ■ 260oC, ▲ 290 oC, ◀ 310 oC, ▼ 330 oC, ▶ 360 oC, ● 530 oC (one step).*

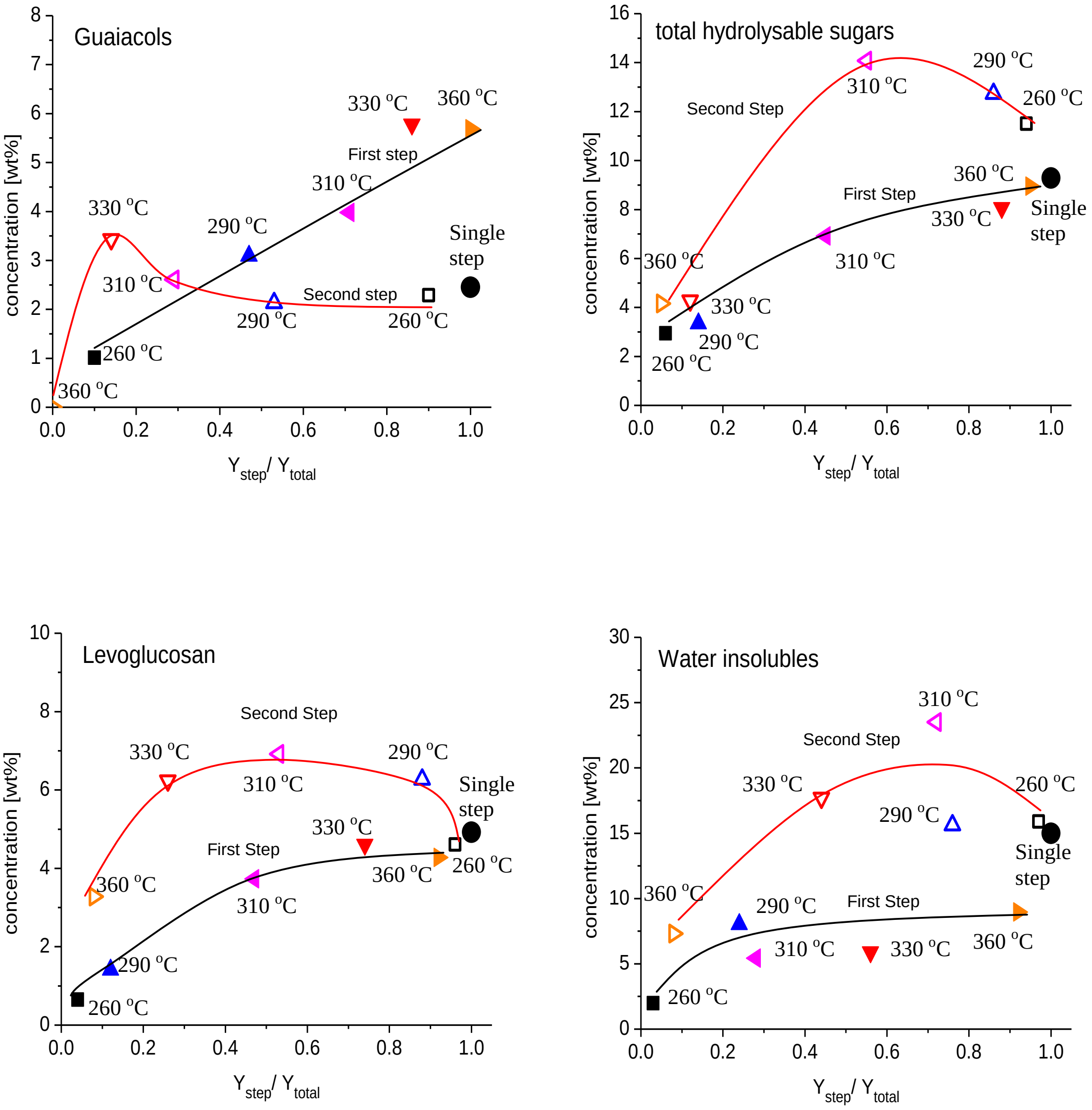

Figure 3.10: *The concentration of compounds (wt% of the oil) and lumped groups of compounds as function of the ratio between the yields collected in a single step and the cumulative yield of both steps. Solid symbols represent the first step and open symbols the second pyrolysis step: ■ 260^{o}C, ▲ 290 ^{o}C, ◀ 310 ^{o}C, ▼ 330 ^{o}C, ▶ 360 ^{o}C, ● 530 ^{o}C (one step).*

3.4 Mechanism of reaction

The accumulated yields of step one and two, as illustrated in Figures 3.1 and 3.2, show the presence of two pyrolysis regimes. The first regime (pretreatment temperature (TPT) =260-290^{o}C for 25 minutes followed by a second step at 530^{o}C) does not show any difference in product yields compared with the products from one-step 530^{o}C. In the second regime (TPT=290-360^{o}C for 25 minutes followed by a second step at 530^{o}C) the pyrolysis product distribution changes significantly compared to one-step 530^{o}C.

3.4.1 First temperature regime (TPT = 260-290^{o}C)

In the first step at 260^{o}C, almost no water or organic liquids are produced. At 290^{o}C, weight loss does happen. However, little water is produced 1.5 wt% (daf) and organic liquids are produced at a level of 15.7 wt% (daf) biomass. This finding is in contradiction with the results presented by Broido et al.[30], who found that pure cellulose reacts to form anhydro-cellulose with the loss of only water at temperatures of 200-280^{o}C during a reaction time of 24 hours. The cellulose resistance to dehydratation observed can be due to the stabilizing effect of the lignocellulosic matrix and the ash.

In this range of temperature the so called “active cellulose” should be formed[66]. The theory of active cellulose formation also comes from Broido[67] and was later confirmed and simplified by Shafizadeh and coworkers[68], in the so called Broido-Shafizadeh scheme. They proposed an initial cracking of the weak amorphous zone in cellulose chains to yield nano-crystals with a degree of polymerization between 151-400 without significant weight[65]. The Broido-Shafizadeh scheme suggest that the “active cellulose” formed in the thermal pretreatment step will influence the outcome (increased yield of organic liquid and decrease of bio-char) of the second pyrolysis step at 530^{o}C. None of this happens in our experiments; the accumulative product yields in step-wise pyrolysis at 260 and 290^{o}C stay the same compared to one step pyrolysis at 530^{o}C. Based on these results we can conclude that the initial step of the formation of active cellulose in the Broido-Shafizadeh scheme is too slow or irrelevant for the pyrolysis of pine wood under the conditions studied (at 530^{o}C).

3.4.2 Second temperature regime (TPT = 290-360^{o}C)

Table 3.4 summarizes the effect thermally treating biomass in the range of temperature between 310 and 360^{o}C could have on the accumulative yield of targeted groups of compounds. A drastic reduction in the yield of gases was observed perhaps due to the mitigation of secondary reactions of hemicelluloses products. The reduction in the yield of the heavy oligomeric fractions from cellulose and lignin (water insoluble, hydrolysable sugars, unidentified sugars) can be due to the difficulty of their reactive liquid intermediate precursors to evaporate. It is argued that the larger molecules [water-insolubles, unidentified) have difficulties in leaving the particle at low temperature because of their low vapor pressure[56] and other mass transfer limitations. While being trapped in the particle they have more time to be transformed to "final" char structures. As observed by Haas et al.[60] the droplet formed inside the cell is transformed into a special form for char deposited inside cell walls. The increased solid residue production of the step-wise tests at 310-360^{o}C is accompanied by more water, lights and furans and less water - insolubles and larger sugars (unidentified) in the collected liquids.

Table 3.4: *An example of the absolute and relative changes in accumulative step-wise product yields in the region 290-360^{o}C (data from the first step temperature 330^{o}C) compared to one step 530^{o}C.*

Lumped compound groups	$\left(Y_{T->stepwise} - Y_{one\ step\ 530}\right)$ [kg/kg d.a.f .wood *100%]	$\dfrac{\left(Y_{T->stepwise} - Y_{one\ step\ 530}\right)}{Y_{one\ step\ 530}}$ [*100%]
Phenols	0	0
Water insolubles (lignin oligomers)	-3.6	-38
Hydrolysable Sugars	-1.3	-21
Gas	-6.0	-22
Unidentified (likely cross-linked sugars)	-3.0	-8
Sum	**-13.9**	
Lights	+1.2	+15
Furans	+1.4	+280
Water	+4.9	+61
Char	+6.7	+65
Sum	**+14.2**	

In one-step fast pyrolysis at 530°C the liquid explicitly stays only seconds in the range of temperature between 290 and 360^{o}C and at high temperature they can evaporate and leave the particle resulting in less char. At temperatures over 300^{o}C it seems that the hydrolysable sugars and the cross-linked sugars will likely form a liquid phase intermediate which will accelerate dehydratation reactions (responsible for the formation of more water and furans) and may also enhance the formation of more cross-linked structures if oxidizing agents are present. The same holds for lignin. The formation of a reactive liquid intermediate from cellulose and lignin should be incorporated to the kinetic models of cellulose depolymerization.

In this regime, the accumulated yields of char and water are higher and the accumulated yield of volatiles is lower compared to one-step pyrolysis at 530°C. The models of Shafizadeh/Chin and Koufopanos with the associated kinetic constant predict this trend in char yield (see Figure 3.1). Some of these models[40] consider char as an end-product from unconverted virgin biomass. Other models[41,69,70] do include a route to form char from intermediate products, but for these reactions no kinetic data are available. The potential formation of reactive intermediates (different to the active cellulose) during the second temperature regime could explain part of the effect of thermal pretreatment in this range of temperature on the outcome of the pyrolysis process.

To identify the nature of these reactive intermediates additional experiments were performed. The solid residue obtained after pretreatment at 290^{o}C was extracted with a water/acetone mixture at 90^{o}C for 1 hour giving a yellowish solution. This shows that there are liquids present in the reacting biomass at 290^{o}C and that we could speak of a “molten” biomass state in the decomposition pathway. The extracted compounds turned out to be soluble in acetone but insoluble in water. This indicates that these compounds are lignin derived. The presence of very large sugars in water could not be completely excluded. Wu et al[71] have proved that very large sugars (DPs>5), are poorly soluble in water.

Based on the findings we concluded that a mechanism should ideally comprise several stages of the reacting particle ranging from fresh biomass to a completely devolatilized structure, that we could call “final” char. A particle can be read here as a real small particle that reacts spatially uniformly or a uniform region in a (larger) particle that has spatial density gradients. The solid residue obtained after one-step pyrolysis at 530^{o}C already contains a quite some “final” char. We can conclude this, because tests have turned out that one-step pyrolysis at 800^{o}C only gives slightly less solid residue than at 530^{o}C[72].

We present here a mechanism (see Figure 3.11) that finds its bases in the mechanisms of Broido & Weinstein[73], Antal[70], Radlein[74] and Mae[75] that recognizes the formation of extractable reactive liquid intermediates from both the cellulose and lignin. We recognize that indeed the experimental determination of the kinetics of these types of mechanisms will require more extensive experimental programs. For the time being such models are for learning and qualitative interpretation and not yet for quantitative predictions.

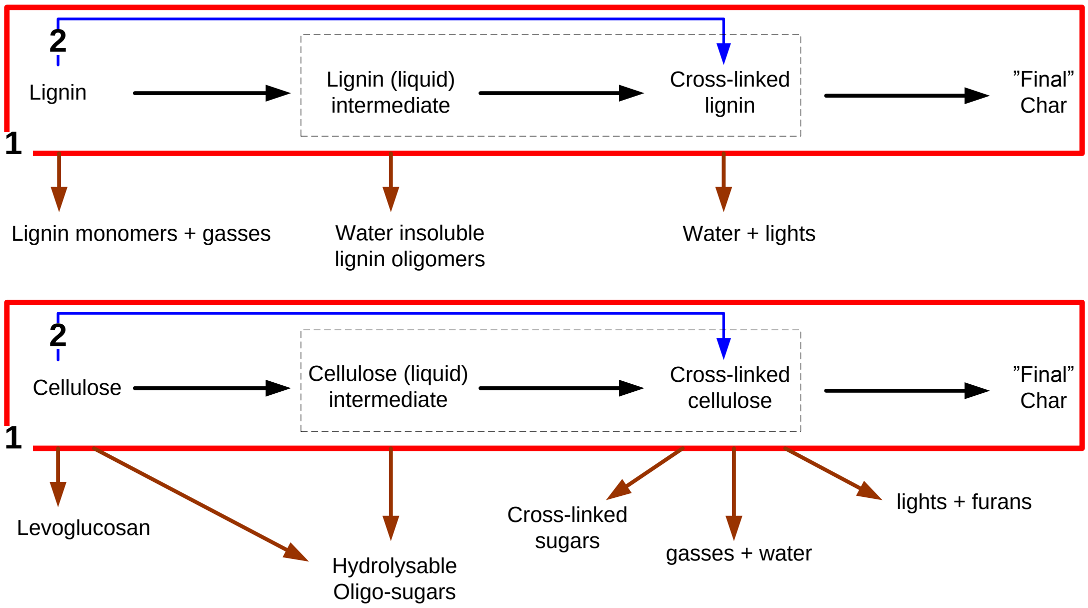

Figure 3.11: *Pyrolysis mechanism of lignin and cellulose. The thick line (1) represents the reacting biomass particle. The state of the reacting biomass particle depends in our study on the temperature/time history. The arrow (2)inside the particle represents the direct route of cellulose or lignin cross-linking. Arrows outside the particle represents the release of compounds by evaporation, sublimation or physical entrainment from the reacting biomass particle.*

Notice, that the arrows show the escape of certain compounds or lumped groups of compounds by volatilization/sublimation/physical entrainment from the whole biomass particle possibly containing all four stages but each individual arrow does represents the most important place of release of compound groups describing our data. However, the release of compound groups is not always exclusively for this single stage. Further, we want to point out that for biomasses with other ash content these mechanisms could change. Reasoning based on this mechanism could explain the higher volatiles yield and lower char and water yield of the one-step experiment compared to step-wise 310-360^{o}C.

Being at 310-360^{o}C for ca. 25 minutes, the liquid (cross-linked) intermediates have more time to polymerize towards final char at the expense of the removal of molecules and fragments from the particle which is slower at lower temperatures (evaporation/sublimation and physical entrainment). This shows that essentially chemical kinetics have to be combined with transfer models for adequate description of pyrolysis. In our view, mechanism for removal of biomass fractions from the particle have to be incorporated in future models of pyrolyzing particles. It is also likely that the pretreatment at 310-360°C brings the biomass in a (intermediate) state that is more susceptible towards polymerization during the second step. This is grounded by the observations that in the second step from 330-360^{o}C to 530^{o}C a relatively large amount of water is formed which is a side product of char forming reactions.

3.5 Conclusion

Step-wise pyrolysis [first step: 260-360°C for 25 minutes, second step 530°C] of pine-wood in a fluidized bed reactor has been investigated. Single compounds and lumped groups cannot be concentrated in the step-wise oils to a large extend, at least not without major yield losses. However, lighter and heavier oils can be produced and combining step-wise pyrolysis with staged condensation might ultimately lead to significant higher concentrations of target compounds. Step-wise pyrolysis has turned out to be an interesting approach to study pyrolysis mechanisms, especially when combing it with detailed analysis of the liquids. For instance, it has been found that reactions below 300°C do not influence the accumulated product distribution of step-wise pyrolysis. Based on this finding we concluded that below 300°C the presence and reactions of depolymerized and cross-linked biomass do not influence the pyrolysis reactions at higher temperature. The reactions running in the range of 310 – 360°C have a profound effect on char formation in the step-wise approach; more accumulative char and water is produced at the expense of organic volatiles. The presence of reactive (liquid) intermediates at this temperatures is expected to have an important impact in the outcome of pyrolysis reactions. A mechanism is proposed that includes several stages of the reacting solid and in which the main emphases lies on the competition between routes that lead to char and routes that release compounds from the biomass particle.

3.6 Acknowledgement

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3.7 References

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Chapter 4

Heterogeneous and homogeneous reactions of pyrolysis vapors from pine wood

Abstract

To maximize oil yields in the fast pyrolysis of biomass it is generally accepted that vapors need to be rapidly quenched. In this chapter, the influence of the heterogeneous and homogeneous vapor phase reactions on yields and oil composition were studied using a fluidized bed reactor. Even high concentrations of mineral low char (till 55 vol%) appeared not to be catalytically active. However, the presence of minerals, either in biomass or added, does influence the yields, mostly by the occurrence of charring/polymerization reactions. Contradictory, in the absence of minerals, homogeneous vapor phase cracking reactions were dominant over polymerization/charring reactions (400–550^{o}C, 1-15 s). With increasing vapor residence time, the oil yield reached an asymptotic value, which decreased with temperature. At a vapor temperature of 400^{o}C no decrease in oil yield was observed, but dedicated analysis showed that homogeneous vapor to vapor reactions had occurred.

4.1 Introduction

Fast pyrolysis is the thermo-chemical decomposition of organic material (moisture content typically < 10 wt%) at 400 – 600^{o}C in the absence of oxygen[1-3]. In this process, biomass is converted into char (typically 15-25 wt%), permanent gases (typically 10-20 wt%) and pyrolysis oil (typically 60-70 wt%)[1-3]. Besides direct use for combustion[3] and flavor production[4] pyrolysis oil is considered to be an intermediate to be used in subsequent processes[4]. For example, pyrolysis oil could be i) upgraded so the resulting oil can be co-refined in a standard refinery unit to (blending compounds for) fuels[3] ii) gasified to syngas followed by Fischer Tropsch synthesis to fuels/waxes or methanol synthesis[2,4] and iii) used as source for the extraction of chemicals (glycolaldehyde, levoglucosan, phenolics)[3,4]. The potential of fast pyrolysis as biomass pre-treatment step is directly related to the significantly higher density of the oil (~1200 kg/m^3) compared to the original biomass (~150 kg/m^3) and the resulting transportations benefits[2,4].

Pyrolysis oil is a mixture of water and hundreds of (oxygenated) organic compounds[1]. Over the past three decades, extensive research on the development of fast pyrolysis processes has been carried out. In order to obtain high oil yields it is generally accepted that 1) high heating rates are required 2) the pyrolysis reaction temperature needs to be controlled around 500 ^{0}C and 3) pyrolysis vapors/aerosols need to be rapidly quenched (< 2s)[1-6]. In the last decade increased fundamental insight in pyrolysis has been obtained[7-12] with also quite some experimentally observed exceptions to the aforementioned general 'design rules'[9,10,12] For example, Scott et al.[12] found no significant influence of the vapor's residence time on oil yields at up to 10 s and temperatures between 400 and 450^{o}C. A critical assessment of the 'design rules', their theoretical background and experimental verification seems therefore appropriate.

Pyrolysis products are formed by decomposition reactions of the biomass matrix (cellulose, hemicellulose and lignin) followed by reactions of produced gases, vapors, aerosols, liquids and solids. The vapors and aerosols form, after condensation, the liquid product called 'pyrolysis oil' or 'bio-oil'. In our experiments, it is not known what the nature of the oil is at the pyrolysis temperature, viz. vapors, aerosols or a combination of those. In the remainder of the text, both vapors and aerosols are denoted as vapors, but the reader should realize that "vapors" represent any combination of vapors and aerosols. Reactions of vapors are known to reduce the oil yield[13-20] by both homogeneous and heterogeneous reaction pathways. However, there is only limited information on the effect of these reactions on the oil composition[14,20]. Heterogeneous reactions can proceed when produced vapors leave the reacting biomass particle, vapors encounter other particles (char, ash, catalysts) or when vapors are in contact with the (hot) reactor material. The extent of vapor reactions is reported to depend, amongst others, on the temperature of the vapor phase, on the nature of the solid surfaces and the exposure time to high temperatures and/or surfaces,[13-20] but possibly on the concentration of the vapors as well[14,21]. Some researchers reported a significant influence of the presence of char on the extent of heterogeneous vapor phase reactions,[13,22] while others did not observe such an influence[9]. The controversies in these results are probably related to i) char composition, and ii) difficulties in separating the individual effects of biomass decomposition and homogeneous and heterogeneous vapor phase reactions while interpreting the results.

The objective of this chapter is to obtain more unequivocal insight on the influence of a). the vapor phase residence time and temperature and b) char and minerals, on the oil yield and composition. In the last part of this paper, the results are discussed in relation to kinetic model development and the engineering aspects of pyrolysis units.

4.2 Equipment and procedure

4.2.1 Feedstock materials

The feedstock materials used and their properties are summarized in Table 4.1. Pine wood with a low mineral content (Lignocel 9, purchased from Rettenmaier & Sohne GmbH, Germany) was used for the majority of the experiments. Some experiments were carried out with feedstocks high in mineral content. The presence of potassium is known to have a strong effect on the pyrolysis process[2,28,29]. For this reason we have chosen to impregnate pine wood with KCl (Sigma, P9333, purity > 99.0 %) by mixing pine wood rigorously with a KCl solution and subsequently evaporating the water. Straw (purchased from DIVRO) was used as biomass which, by nature, has a high mineral and especially potassium content.

Table 4.1: *Biomass properties*

	Pine Wood	Pine Wood + KCl	Straw
ash [wt%, dry]	0.6	1.34	6.0
C [wt%, daf]	47.9	47.9	49.8
H [wt%, daf]	5.9	5.9	6.0
O [wt%, daf]	46.2	46.2	44.2
Water [wt%]	2 – 10	0.7	0.4
K [ppm,dry]	400	6500	12000
Na [ppm, dry]	100	100	85
Particle size [mm]	~ 1	~ 1	1-2

4.2.2 Pilot Plant: analysis of in-bed char and minerals

A fluidized sand bed fast pyrolysis unit was used to study the effect of char and mineral hold-up in the bed. The reported char and mineral hold-ups (vol% and wt%) are expressed on total solid (char + sand + minerals) basis. The set-up consisted of a continuous feeding system (0.5–0.9 kg/hr), a fluidized bed reactor ($< 200\ d_{sand} < 300\ \mu m$), three cyclones and a condensation train (spray column and intensive cooler) placed in series. The complete set-up including a comprehensive validation is described in detail elsewhere[chapter 2&6, 10,30]. The standard deviations for the char, gas, oil and water yield were 1.0, 0.9, 1.3 and 1.0 wt% respectively showing that the reproducibility of the experiments is good[30]. Information about the operating conditions is listed in Table 4.2 and Table 4.3. This set-up will further be referred to as ‘pilot plant’.

Table 4.2: *Experimental specification for experiments in pilot plant (T ~ 450-490 ^oC)*

Name	Biomass*	Additives	Char Hold-Up [vol%]		K+ Na Hold-Up
			Pine	Straw	[wt%]**
20 vol% char	pine	none	20	0	0.005
55 vol% char	pine	none	55	0	0.021
KCl impregnated	KCl[a], pine	none	50	0	0.176
straw	straw	none	0	35	0.167
Na/K additive 0.7 wt%	pine	Na_2CO_3[b],K_2CO_3[c]	40	0	0.709
Na/K additive 0.1 wt%	pine	Na_2CO_3[b],K_2CO_3[c]	31	0	0.110
straw char additive	pine	straw char	25	20	0.111

*) Properties listed in Table 4.1 **) Mineral is minerals char plus minerals additives

[a]) Sigma-Aldrich, P9333, purity > 99.0% [b]) Sigma-Aldrich S7795, purity > 99.0% [c]) Sigma-Aldrich 23653-412 K_2CO_3, purity = 99.0%

Table 4.3: *Operating conditions pilot plant and lab-scale fluidized bed reactor*

Properties		Pilot Plant	FB+T-reactor
General	Run Time [min]	90 - 120	60
Feeding	$\Phi_{m,sand}$ [kg/hr]	1.6 - 4.1	No sand fed to reactor
	$\Phi_{m,biomass}$ [kg/hr]	0.5 - 0.9	0.15
	$\Phi_{v,N2} / \Phi_{m,biomass}$ [Nl/g]	~ 2.5	~ 4.5
Fluidized bed reactor	Char Hold-Up [vol%]	20 – 55 (~ stationary)	0–25 (increasing)
	$T_{reactor}$ [^{o}C]	400 - 530	500
	τ_{vapors} [s]	1.6 - 1.9	~ 1.5
	$\tau_{particles}$ [min]	20 - 40 min	No removal of particles
	U / U_{mf} [-]	4	3
	Char separation	three cyclones in series	9 μm and 5 μm filters in series
Tubular reactor	$T_{tube\ system}$ [^{o}C]	no tubular reactor incorporated	400, 500, 550
	$T_{tube\ system}$ [s]		1.1 - 15.3
	Vapors + gases [vol%]		~ 9
	Re [-]		~ 275 - 385
	Pé [-]		~ 20 - 260
Condensation System	$T_{first\ condensor}$ [^{o}C]	20 (spray column)	< 24 (ESP)
	$T_{second\ condensor}$ [^{o}C]	0	< -8

In the pilot-plant it was possible to control the char and mineral hold-up during the course of an experiment. A schematic overview of the reactor including the char/mineral hold-up regulation system is shown in Figure 4.1. The fluidized bed reactor (D = 10 cm, H = 40 cm) was equipped with an overflow to remove the sand/char/mixture mixture on top of the bed to keep the bed level constant ($V_{reactor}$ = 1.8 l). Biomass and sand were fed by two separate feeding screws. Additives like minerals and char could be added to the sand flow. The amount of char and minerals inside the fluidized bed reactor was controlled by adapting the sand/additives composition and feeding rate and by the biomass type and feeding rate. It was assumed that all solids in the fluidized bed were ideally mixed. For the “20 vol% char” experiment (estimated value, based on assumption ideal mixing), the char hold-up inside the fluidized bed reactor was experimentally determined after the experiment to validate the assumption. A value of 19 vol% was obtained which shows good agreement. Cold flow experiments did show that it was possible to fluidize sand/char mixtures up to 63 vol% of char so no problems concerning the fluidization behavior/mixing were to be expected during our experiments (up to 55 vol% char).

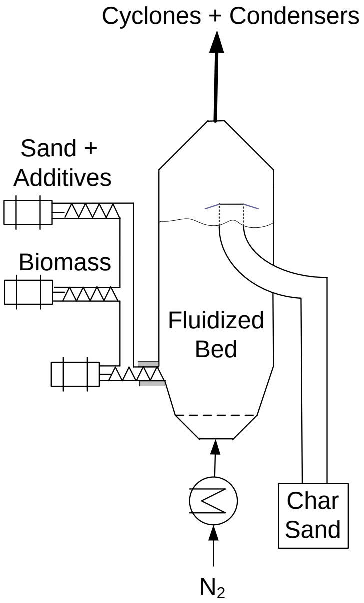

Figure 4.1: *Char/mineral hold-up regulation system pilot plant*

4.2.3 Fluidized bed with tubular reactor placed in series (FB+T-Reactor): analysis of homogeneous vapor reactions

4.2.3.1 Set-ups used in literature

In literature, a variety of set-ups is reported to have been used to study homogeneous pyrolysis vapor reactions. Although interesting results were obtained, many of the set-ups had some limitations making interpretation and extrapolation of results difficult. In several studies a batch type of pyrolysis reactor was coupled to a tubular reactor making continuous operation of the tubular reactor impossible[13,14,16,17,31,32]. In literature the vapor residence times was varied either by changing the carrier gas flow rate[34-36] or by changing the reactor volume[13,14,16-18,35,36]. Variation of the residence time by variation of the carrier gas flow rate varies the concentration of the vapors, which could cause a change in the reaction pathways of the vapors and therewith yields and compositions[14,21]. Furthermore, in most set-ups the carrier gas flow rate and thus residence time can only be varied to a limited extent to prevent de-fluidization or excessive entrainment of solids. In some studies, the reactor volume was varied (and so vapor residence time) by changing the fast pyrolysis reactor volume[21,36] or by placing a second reactor in series[13,14,16,17]. This last option makes it possible to decouple the fast pyrolysis - and vapor phase temperature and was therefore used in this study together with a continuous vapor source.

4.2.3.2 Our set-up

The fluidized bed reactor was identical to the one used in the pilot plant (section 4.2.2), however, in this set-up no feed and withdrawal of sand was applied to ease operation. A flow sheet of the set-up is given in Figure 4.2. The whole set-up including the fluidized bed reactor and tubular reactor will further be referred to as "FB+T-reactor" which is an abbreviation for "Fluidized Bed + Tubular"-reactor.

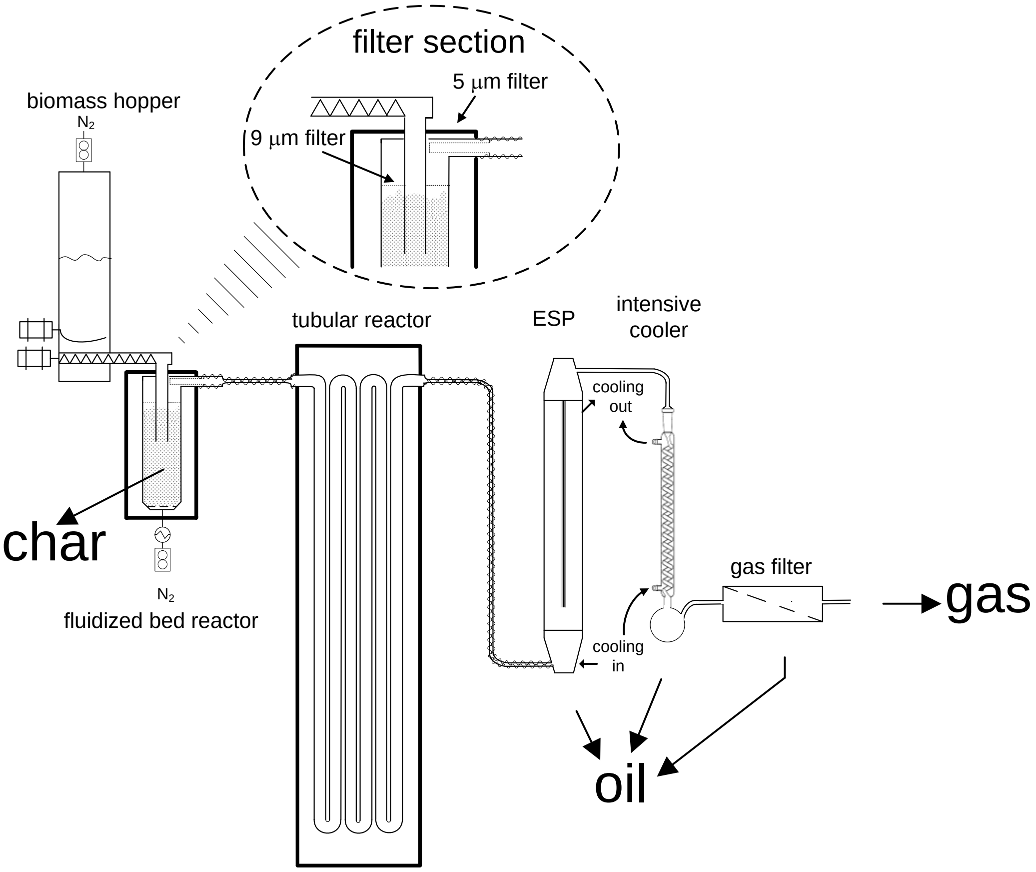

Figure 4.2: *Fluidized bed and tubular reactor placed in series (FB+T–Reactor)*

Lignocel 9 was fed via a screw into the fluidized sand bed (at a height of ~ 80% of the total bed height). The fluidized bed reactor was always operated at 500°C. The operating conditions of the standard run are summarized in Table 4.3. Preheated nitrogen gas ($3 \cdot U_{mf}$) was fed through a sintered plate. Because this set-up was not operated continuously with respect to the solids phase, char built up in the course of an experiment (up to 25 vol% in 60 minutes). A custom made wire-mesh filter section (material purchased from Dinxperlo, Wire Weaving)[(chapter 5)8] was used to remove char from the gas/vapor stream. A schematic representation of this filter section is shown in the upper side in Figure 4.2. The first filter had a pore size of 9 μm and was placed just above the fluidized bed. A second filter with a pore size of 5 μm, length of 8.5 cm and diameter of 2.2 cm was placed at the fluidized bed reactor exit (just before tubular reactor inlet). The solids content of the pyrolysis oil obtained without the use of the tubular reactor was always below the detection limit (< 0.002 wt%) indicating that a virtually solids-free gas/vapor stream was generated by using the filters. The temperature of the vapors leaving the fluid bed was controlled by heat tracing wrapped around the pipe (ID: 0.75 cm) connecting the fluidized bed and tubular reactor. The average deviation of the entrance tubular reactor temperature from the set-point of the tubular reactor (400, 500 or 550°C) was 6°C. The residence time of the pyrolysis vapors inside the fluidized bed reactor itself was approximately 1.5 s.

In the tubular reactor system (placed after the pyrolysis unit) four different tubular reactors constructed of AISI 316 steel with lengths of 1, 2.5, 8 and 11 m and an inner diameter of 3 cm were used. The additional vapor phase residence time in these tubular reactors varied from 1 till 15 s and its temperature was maintained at 400, 500 or 550°C. The temperature of the tubular reactor was regulated within 3°C by an electrical oven in which four heating zones could be controlled independently. The Reynolds number of the gaseous stream was in the range of 275 (550°C)-385 (400°C) indicating that the flow was laminar. The Péclet number as calculated from $\langle v \rangle L/D_{ax}$ varied from about 20 (400°C, 1 m) till 260 (550°C/ 11 m), indicating near plug flow behaviour.

The vapor stream leaving the tubular reactor was condensed in a custom made jacketed electrostatic precipitator (ESP tube ID: 6.2 cm / L: 44 cm) operated at 17-21 kV. The temperature of the outgoing stream of this condenser was kept below 24°C by pumping tap water through the annular space of the ESP. To the best of our knowledge, we are the first who are using a cooled ESP as main condenser directly after the reactor. Hereafter, the remaining uncondensed gas/vapor stream was sent to an intensive cooler (T <8°C) and a gas filter placed in series. About 97 wt% of the condensed organics was captured in the ESP, 2.7 wt% in the intensive cooler and 0.3 wt% in the gas filter. The oil was stored in a freezer at -20°C to prevent aging reactions[37].

4.2.4 Product collection and analysis

4.2.4.1 Biomass

The elemental composition (Fisons Instruments 1108 CHNS-O), ash content (NPR-CEN/TS 15403 – 550°C), water content (drying in an oven at 105°C for 24 hours[30]) and alkali/alkaline content (measured at vTI, Germany using ICP-OES) of the biomass feeds are reported in Table 4.1. The amount of dry ash free (daf) biomass fed during a run was determined by adjusting the mass difference of the biomass hopper before and after an experiment for the water and ash content of the feed.

4.2.4.2 Gases

The procedure to determine the gas yield in the pilot plant reactor (section 4.2.2) is described in detail in an earlier publication[30]. In the FB+T-Reactor the nitrogen flow rate was set by a calibrated mass flow controller (Brooks). Gas samples were taken every 10 minutes. These samples were analysed in a gas chromatograph for H_2, CH_4, CO, CO_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8 (Varian Micro GC CP-4900 with two analytical columns, 10 m Molsieve 5A and 10 m PPQ, using Helium as carrier gas). The sum of C_2H_4, C_2H_6, C_3H_6 and C_3H_8 will further be referred to as C_{2+}. The total outgoing mass of an individual gaseous compound was calculated by multiplying its gaseous mole fraction by the total flow rate ($\phi_{v,total} = \phi_{v,N2} \bullet (100/(100-\Sigma mol\%_{gases}))$) and molecular mass of that compound and subsequently integrating over time. The total gas yield on dry ash free basis was calculated by summing the yields of the individual gas compounds and dividing this value by the amount of daf biomass fed during the run.

4.2.4.3 Pyrolysis oil:

The procedure to determine the oil yield in the pilot plant reactor (section 4.2.2) is described in detail in chapter 6. For the FB+T-Reactor the daf oil yield was determined by a) summing the weight of oil collected in the ESP, intensive cooler and filter b) subtracting the amount of water which was already present in the feed c) dividing the resulting weight by the amount of daf biomass fed during the run. The composition of the oil was determined by various techniques as listed in Table 4.4.

4.2.4.4 Char

The procedure to determine the char yield in the pilot plant reactor (section 4.2.2) is described in detail in an earlier publication[30]. The char yield (daf) for the FB+T-reactor was determined by dividing the mass of char collected inside the bed and on the filters minus the amount of minerals present in the feedstock by the amount of daf biomass fed during the run. So, it was assumed that all minerals present inside the feedstock end up in the char phase. It should be noted that the char yield determined as described above is independent of the conditions in the tubular reactor that is placed after the pyrolysis reactor.

Table 4.4: *Techniques used to analyze pyrolysis oil*

Compound	Technique	Analyzed Oil	Ref.
Water	Karl-Fischer titration	All condensers	(chapter 2), 8
C,H,O,N	Elemental Analyzer	ESP FB+T-reactor	(chapter 2), 8
Pyrolytic Lignin (water insolubles)	Cold water (~ 0 ^{0}C) precipitation	ESP FB+T-reactor	23,24
Solids Content	Gravimetry	ESP FB+T-reactor	25
M_w-distribution (> 100 g/mol)	SEC (RID-detector)	ESP FB+T-reactor Spry column pilot plant	(chapter 2), 26
Aromatic and unsaturated conjugated compounds	SEC, ratio UV and RID detector	ESP FB+T-reactor	26
Volatile compounds	GC/MS (FID and MS detector)*	ESP FB+T-reactor	27

* Analysis carried out by vTI (Germany)

4.3 Heterogeneous vapor phase reactions

To study the influence of the contact of vapors with char and minerals a series of experiments (Table 4.2) was carried out using the pilot plant. In these experiments the char content and mineral (Na + K) content was varied. The oil (organics and water), char and gas yields are plotted in Figure 4.3. The corresponding molecular weight distributions of the oils can be found in Figure 4.5. The organic and char yield as function of the K+Na hold-up for all experiments is plotted in Figure 4.4. It should be kept in mind that the char and mineral hold-up (vol% and wt%) are expressed on total solid (char + sand + minerals) basis (see section 4.2.2).

4.3.1 Effect of char hold-up: feedstock (500 ppm Na+K) derived char

In the pilot plant, two experiments using Lignocel 9 (with only 500 ppm Na + K) as feedstock and a char hold-up in the fluidized bed of 20 and 55 vol.% were carried out. The extent of possible vapor-char interactions was expected to increase with rising volumetric char hold-up. However, similar gas, oil and char yields were obtained, while also the amount of produced water was similar (Figure 4.3). No differences in molecular weight distribution of the oil phase could be observed either (Figure 4.5A). The experiments were repeated at a lower temperature of 400^{o}C and higher temperature of 530^{o}C (no data shown). Again no influence of char hold-up was observed in those cases. Data obtained in the FB+T-Reactor supported these observations. In this set-up the char hold up linearly increased during the course of an experiment from 0 till about 25 vol%. However, no change in the permanent gas concentration and composition was observed as function of the experimental progress/char hold-up (Figure 4.6). These observations are in line with data obtained by Shen et al[9], who performed similar experiments, but contradictory to earlier observations of Boroson et al[13] and Ahuja et al[22] who did observe an effect of char. Our data indicate that vapor-char interactions from an (almost) mineral free feedstock do not influence the product yields in our pilot plant noticeably.

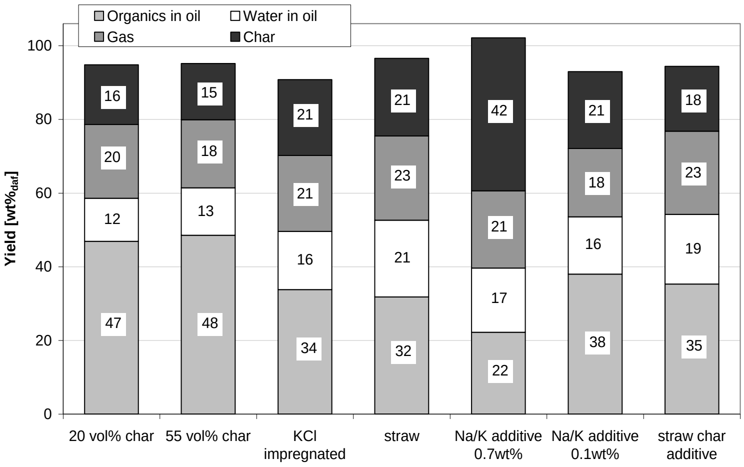

Figure 4.3: *Yields, experimental conditions reported in Table 4.2*

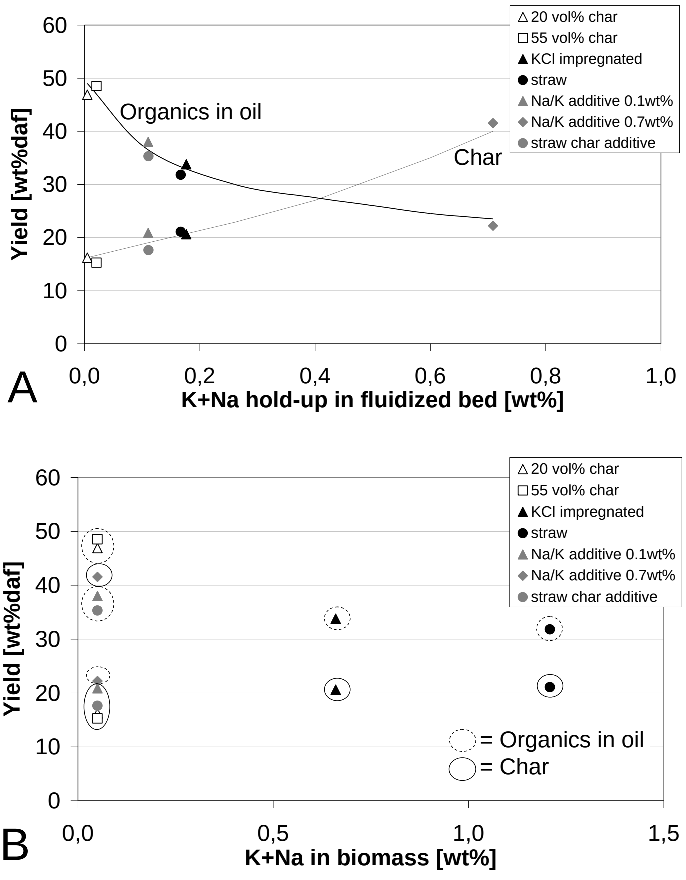

Figure 4.4: *Organic yield as function of the wt% of the K +Na inside the fluidized bed and biomass particles.*

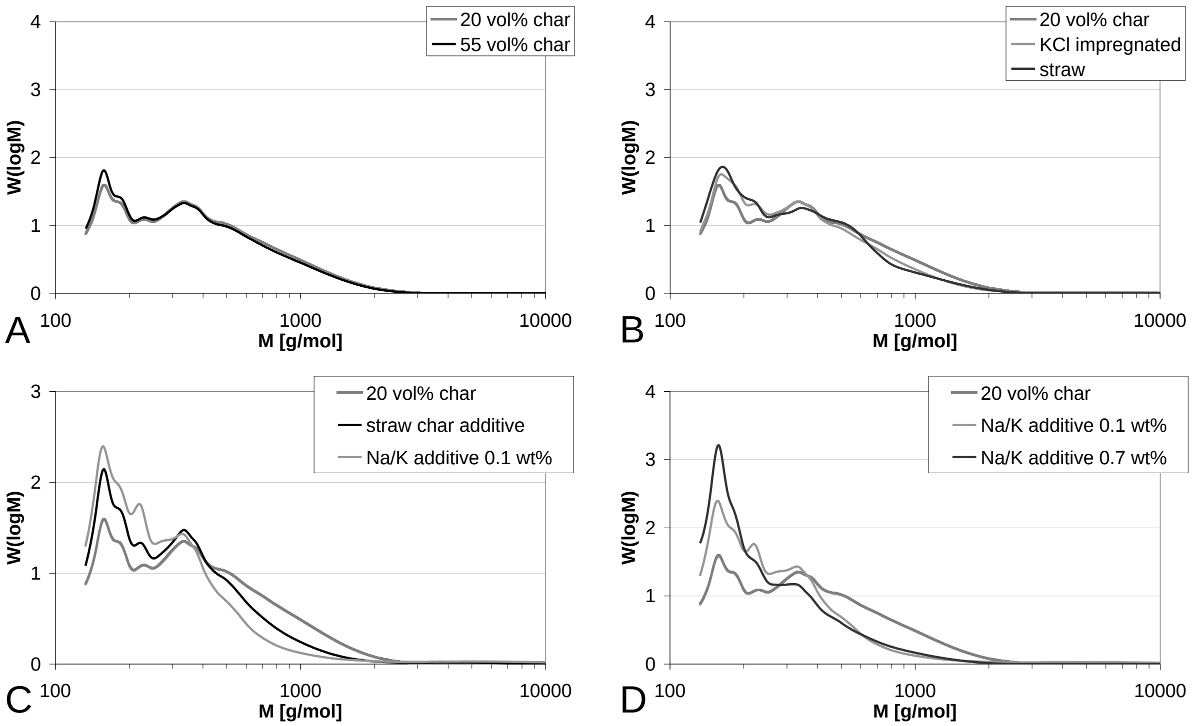

Figure 4.5: *M_w-distribution of oils produced in pilot plant*

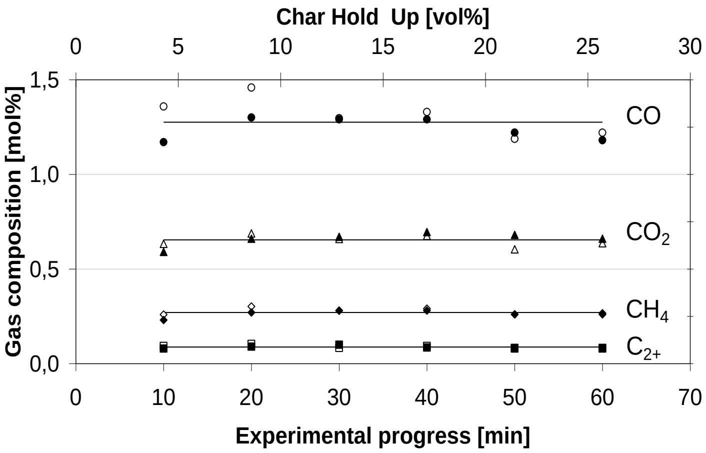

Figure 4.6: *Gas composition as function of char-holdup/timein FB+T reactor. No tubular reactor installed, closed and open symbols denote two separate experiments.*

4.3.2 Effect K + Na in feedstock

Two experiments using different feedstocks high in K/Na content were carried out. One experiment was carried out in the pilot plant using Lignocel 9 impregnated with KCl. Because impregnation is an artificial way of increasing the mineral content of the feed, straw was also used as feed (Table 4.1). In both cases, the liquid organic yield dropped, the char and water yield increased (Figure 4.3) and the average molecular weight of the oil decreased (Figure 4.5B) compared to experiments carried out using untreated Lignocel 9. In addition, a slight increase in gas yield was observed for the "straw" experiment. Our data and the results reported in literature[2,28,29] clearly show that the mineral content (especially Na and K) inside the biomass has an important effect on the product yields and product characteristics. Because the use of a mineral rich feedstock also results in the formation of mineral rich char, it is not clear whether the observed effects are due to differences in reactions (rate, pathway) inside the reacting biomass particle (internal) or because of reactions of produced vapors with already existing char (external). This will be discussed in the following sections.

4.3.3 Effect "external" K + Na on heterogeneous vapor phase reactions

To reveal whether 'external minerals' can affect the extent of vapor phase reactions an additional series of experiments was carried out. In these experiments, untreated Lignocel 9 was used as feedstock, however mineral rich additives were added to the feed of the fluidized bed. These additives were either Na/K salts (using two hold-ups, viz. 0.1 and 0.7 wt%) or a mineral rich char originating from straw (straw char hold-up 25 vol.%, Na/K hold-up 0.1 wt%). The organic oil yield decreased, while the char and produced water yield increased as compared to the "20 vol% char" experiment (Figure 4.3). More gases were produced in the "straw char additive" experiment and the average molecular weight decreased for all experiments (Figure 4.3 and 5C, D), both phenomena suggesting some form of cracking. One experiment was carried out with a much larger amount of added salts to the bed: "Na/K additive 0.7 wt%". The results in Figure 4.3 show that less oil and more gasses, water and char were produced and the average molecular weight of the oil was decreased in comparison with the experiment using 0.1 wt% Na/K. The yield of char even doubled to 42 wt%.

Our results clearly show that after leaving the biomass matrix vapors react on the (internal) surface of particles with inorganic matter to form additional char, water and an oil with a lower molecular weight. Heterogeneous vapor phase charring/polymerization reactions were more important than cracking reactions of vapors to gas.

4.3.4 Na+K in biomass versus Na+K in the reactor (FB)

A decline in organic yield and an increase in char yield were observed with increasing total Na + K hold-up inside the fluidized bed reactor (Figure 4.4A). However, no relationship could be observed between the amount of Na + K present inside the biomass feedstock and the yields of organics and char (Figure 4.4B). From these experimental data it can be concluded that in the studied range (Table 4.2+3) external interactions between the vapors and Na/K rich solids do play a more significant role than the interactions between Na/K and the (decomposing) biomass (internal). However several TGA (heating rate 10 ^{0}C/min)[29,38] and Py-GC/MS[39,40] (heating rate > 2000^{o}C/s) studies report that minerals like K and Na have an effect on the decomposition "weight loss" reactions of biomass, cellulose and hemicellulose. When adding for instance KOH to pine wood the temperature at which the highest weight loss rate was observed reduced significantly from 353 to 275°C[38]. Although minerals influence the initial decomposition reactions this could not be established in this study because of the predominance of external interactions between the vapors and Na/K rich solids. More research is necessary to elucidate the effect of minerals on a (decomposing) biomass particle in absence of vapor-particle interactions.

4.3.5 Concluding remarks

The results clearly show that char itself, viz. the organic C,H and O atoms in it, appear *not* to be catalytically active inside the fluidized bed reactor. However, the presence of minerals (Na/K) –either in the biomass matrix (native or impregnated) or external (as salt or in char), does influence the fast pyrolysis process. Heterogeneous vapor phase charring/polymerization reactions were more important than cracking reactions of vapors to gas. From these results it is evident that the contact between minerals and vapors needs to be minimized to be able to obtain high oil yields.

4.4 Homogeneous vapor phase reactions

Homogeneous vapor phase reactions from char free pyrolysis vapors were studied in the FB+T reactor system. It is important to realize that the pyrolysis vapors that were introduced in the tubular reactor were already exposed for ~ 1.5 s to the temperature in the fluidized bed reactor (500^{o}C). The gas and oil yield as function of the tubular reactor conditions and the corresponding char yield in the fluid bed are shown in Figure 4.7. The mass balance closure is plotted in the same figure, and is around 90 wt% for all experiments. This gap is expected to be related to the loss of some volatile compounds which might be stripped from the condensation system due to the high $\Phi_{v,N2} / \Phi_{m,biomass}$ ratio applied (Table 4.3). Three identical runs were carried using the fluidized bed reactor alone to get an indication of the experimental error and are plotted as reference (designated as "0.0 s"). The product yields and oil composition show good reproducibility (Figures 4.7-4.13).

4.4.1 Heterogeneous reactions on reactor wall

In the downstream tubular reactor, heterogeneous reactions of vapors in contact with the (hot) stainless steel reactor wall cannot be excluded. Minor char deposits were visually observed on the tubular reactor wall. This is in accordance with previous results which showed that some char can be formed on various surfaces from a solids-free vapor stream[9]. An estimation of the amount of char deposited on the tubular reactor wall was made after finishing all experiments. The 1 m tubular reactor was weighed, cleaned (by burning) and subsequently reweighed. Assuming the weight difference to be caused by only deposited char, this amount appeared to be only 0.1 wt% (daf) (average over all runs with 1 m tubular reactor). To study the influence of a fivefold larger steel area on the vapor phase reactions the 1m tubular reactor was filled with steel wool. The results were similar to these obtained without steel wool (Figure 4.7-4.10). Assuming that the increase in mass of the steel wool afterwards was due to char formation, this was again a negligible percentage (+ 0.05 wt%, daf) It can thus be concluded that the possible catalytic effect of the steel tubular reactor wall is insignificant.

4.4.2 Yields: oil, gas, char

The measured char yield in the fluid bed should of course be independent on the process conditions in the tubular reactor placed after the fluid bed. This was indeed the case, about 12 wt% (daf) of char yield was obtained in all experiments. Char formation inside the tubular reactor could only be quantified indirectly. No solids were detected inside the pyrolysis oil (<0.002 wt%) and, as already shown in section 4.4.1, an insignificant amount of char was deposited on the reactor wall. These results indicate that for the process conditions applied negligible amounts of char were formed from homogeneous vapor phase reactions.

The oil and organic yield did follow the same trend since the water production was constant for all tubular reactor conditions (section 4.4.3). The oil and gas yield remained constant and were independent on residence time if the tubular reactor was operated at 400^{o}C. At 500^{o}C and in the first 5 s, a slight decrease in oil yield (~ 5 wt%, daf) and a similar increase in gas yield was observed. The oil and gas yield remained nearly constant hereafter. At 550^{o}C, the oil yield decreased and gas yield increased with slightly more than 10 wt% (daf). The yields appeared to be almost completely stabilized with time up to 12 s. In literature it is regularly reported that the oil yield decreases continuously with increasing residence time (studied up to 3.5 s[18,19,41]). Our results show that this trend cannot be extrapolated to higher residence times. Boroson et al.[14] postulated the existence of such a temperature dependent asymptote based on a measured constant oil yield at 800^{o}C for residence times between 1.6 and 2.0 s. Although their maximum residence time of 2 s was not long enough to observe the asymptotes at typical pyrolysis temperatures, our data show that their postulation is indeed correct for temperatures between 400 and 550^{o}C. Graham et al[15] studied the vapor phase reactions during the pyrolysis of cellulose and also in that case asymptotic oil yields were obtained, but much faster than Boroson observed: within 1 s for temperatures in the range of 650 – 800^{o}C. These results show that a temperature dependent asymptote is present provided that long enough vapor residence times are applied. With increasing temperature an increasing part of the pyrolysis vapors can crack to gases via homogeneous vapor phase reactions.

The effect of the vapor residence time and temperature on the yields of the individual gas compounds (CO, CO_2, CH_4, C_{2+}) is shown in Figure 4.8. Based on thermodynamic calculations (RGibbs reactor in Aspen Plus) and experimental data of Lanza et al.[21], water gas shift and methane reforming reactions are not expected to play a significant role in the temperature range used (400 – 550^{o}C). Therefore, the change in especially CO_2, CO H_2O, CH_4 and H_2 must originate directly from pyrolysis vapor reactions. According to Figure 4.7, no change in gas yield was observed if the tubular reactor was operated at 400^{o}C and also the gas yield of the individual compounds remained constant. The gas yields for all individual compounds increased with reactor severity for temperatures above 500^{o}C. Especially the yield of CO was increasing with increasing reactor severity (~ 70 % of additional formed gases on weight basis), while the yield of CO_2 increased only marginally (~ 10 % of the additional formed gases on weight basis). The C_{2+} yield showed the largest relative increase, almost tripling at 550^{o}C/12 s. The CH_4 yield doubled under those conditions. The increase of the CO/CO_2 ratio with the extent of vapor phase reactions (i.e. temperature, residence time) is in line with previous results obtained using batch wise operated pyrolysis reactors with subsequent tubular reactor using wood[14,16,17] and model compounds[42-44] as feedstock.

Although the pyrolysis oil yields do not (400^{o}C) or marginally (500^{o}C) change as a function of the residence time in the tubular reactor, it is not clear whether changes in composition by vapor to vapor reactions occur for these experiments. Additional analytical techniques were used to study these possible changes.

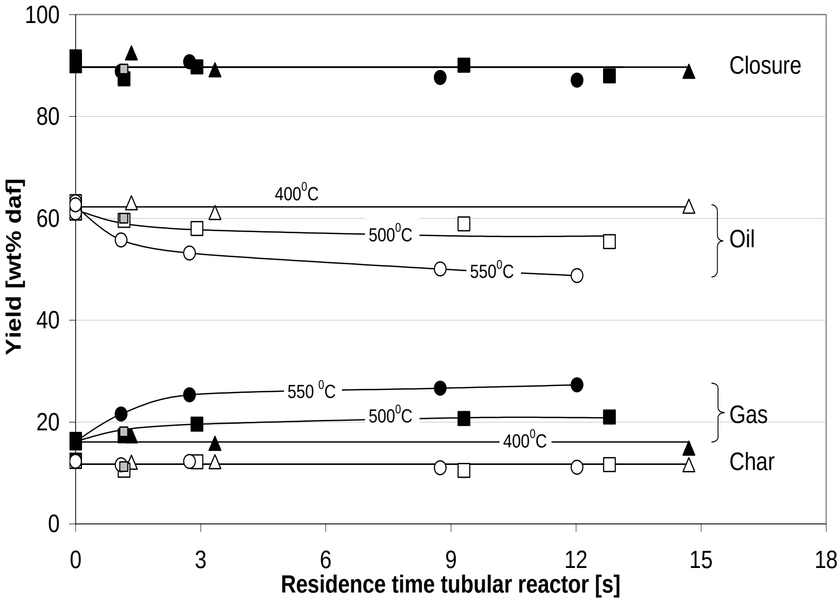

Figure 4.7: *Yields at different tubular reactor temperatures and residence times, residence time in fluid bed ~ 1.5 s (▲△= 400 ^{o}C, ■□ = 500 ^{o}C, ●○ = 550 ^{o}C, ▨ = steel wool 500 ^{o}C.*

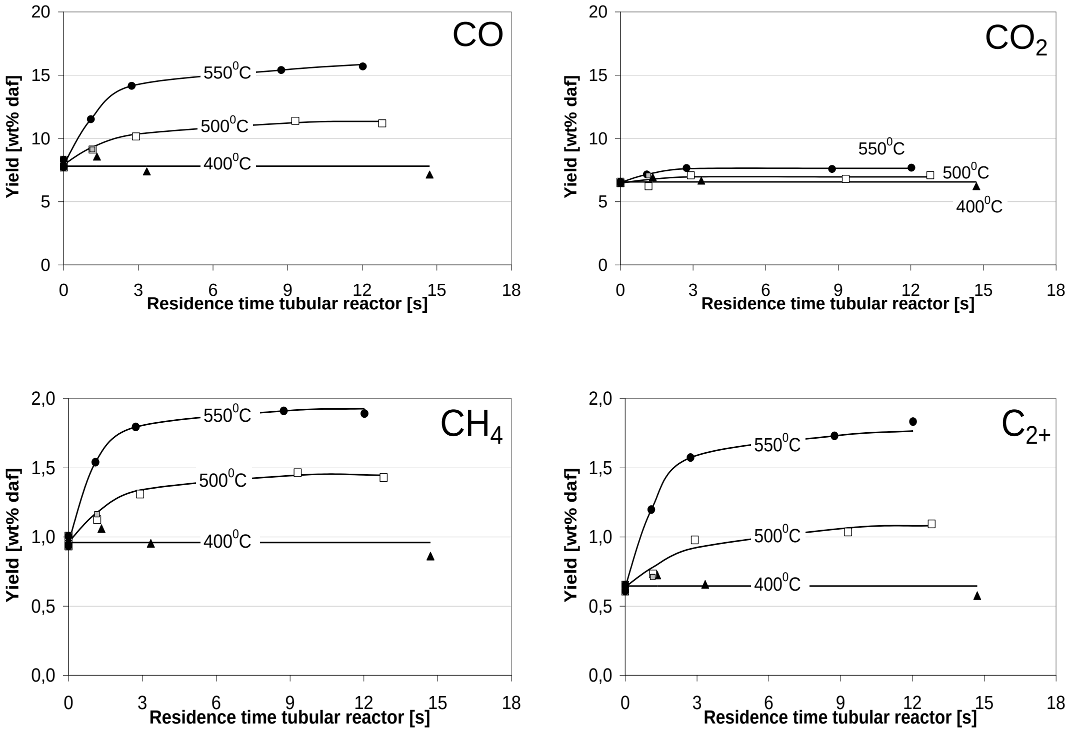

Figure 4.8: *Gas yields at different tubular temperatures and residence times (triangle = 400 ^{o}C, square = 500 ^{o}C, circle = 550 ^{o}C, ■ = steel wool 500 ^{o}C).*

4.4.3 *Water production*

According to literature, several dehydratation reactions of pyrolysis vapors can occur, for example during the formation of iso-eugenol[42], furans[43-45], ketene-structures[43] (which can rehydrate to form acids) and several mono-saccharides[48] and anhydrosugars[46]. Condensation reactions of pyrolysis oil are known to take place even at room temperature[46]. Possibly, water can also be formed via (bimolecular) condensation reactions inside the vapor phase. However, no differences in water production could be observed between the various experiments (Figure 4.9) indicating that dehydratation reactions occurred mainly inside the fluidized bed reactor ($\tau \sim 1.5$ s). An average water production value of 10.5 wt% was measured, with a standard deviation of 1.0 wt%.

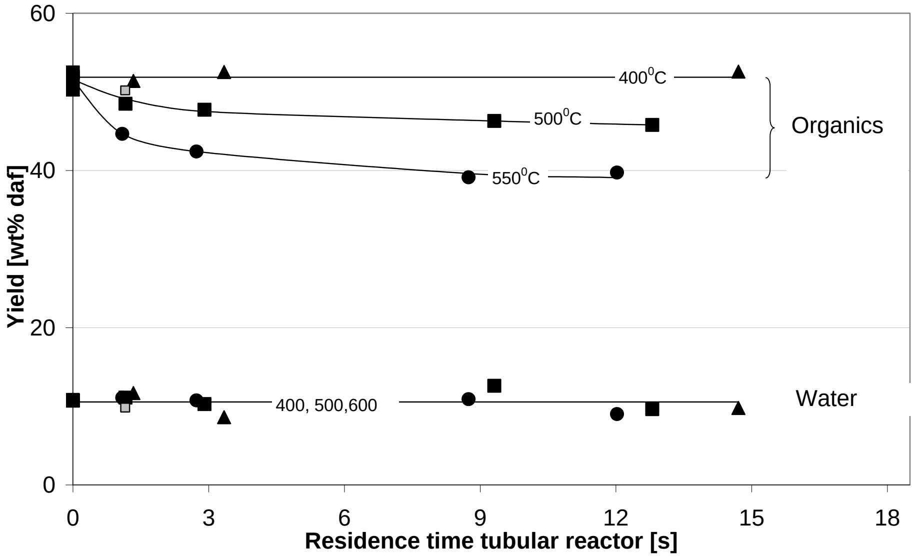

Figure 4.9: *Yields of organics and produced water as a function of tubular temperature and residence time (triangle = 400 °C, square = 500°C, circle = 550 °C, ▰ = steel wool 500 °C)*

4.4.4 *Elemental composition of oil (organics)*

Considering that the water and char production were independent of the conditions in the tubular reactor, the change in elemental composition of the oil should directly be related to the change in elemental composition and yield of the gas phase. For the most severe conditions –11 m tube, 550°C – a calculated change in elemental oil composition of only +1.1, +0.3 and -1.4 wt% for C, H and O would be expected. In line with these expected small changes, the measured elemental composition appeared to be independent on the process conditions in the tubular reactor and similar to the one of the oil obtained directly after the fluidized bed reactor: C = 57 ± 0.8 (stdev), H = 6 ± 0.9 and O = 36 ± 0.2 wt% (daf).

4.4.5 *Molecular weight distribution*

The molecular weight distributions of the oils produced in the shortest (1 m, τ = 1s) and longest (11 m, τ = 12-15 s) tubular reactor operated at 400, 500 and 550^{o}C are plotted in Figure 4.10. The oil produced in the fluidized bed reactor alone is plotted as reference in the same figure (0.0 s). The area under the SEC curves is normalized to 1, so the peak heights/area are not related to the actual yield of a molecular weight fraction, but to (a certain extent to[26]) the relative presence of it inside the oil.

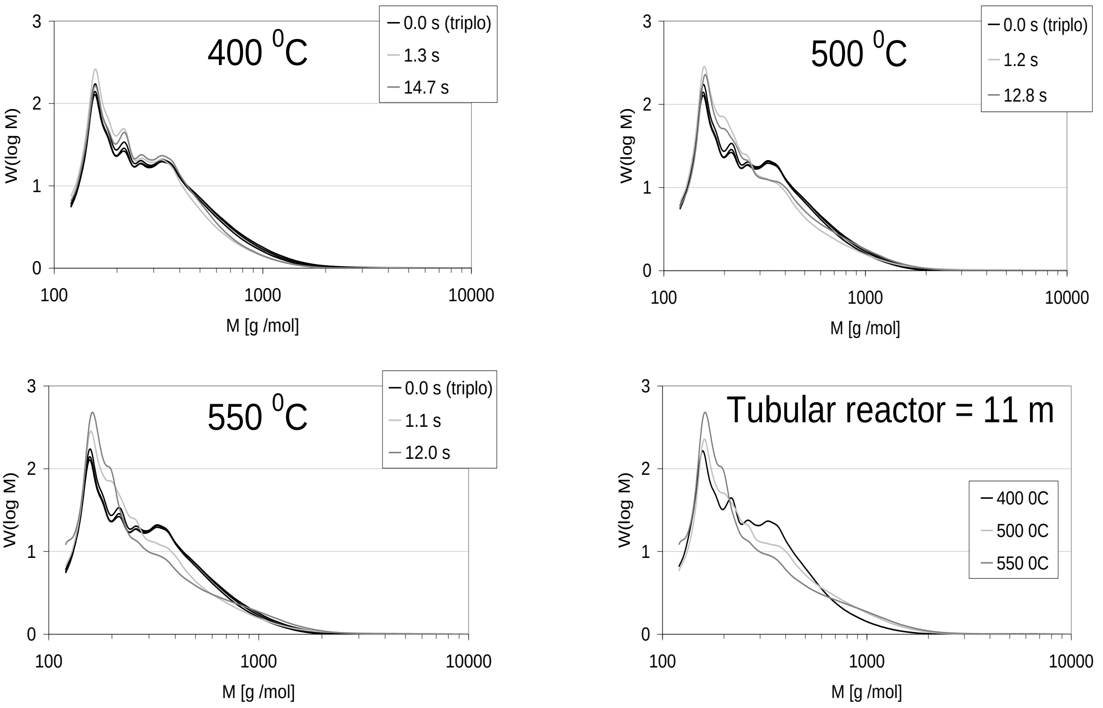

Figure 4.10: *M_w-distribution of pyrolysis oil. Time gives residence time in tubular reactor system.*

A small decrease in average molecular weight with respect to the reference oil was observed for the experiments carried out in the tubular reactor operated at 400^{o}C. It was shown before (Figure 4.8) that no additional gases were formed at this temperature, so vapor molecules are likely to have rearranged and cracked to smaller ones that end up in the oil phase upon condensation.

A significant reduction in the peak intensity around 200-350 g/mol was observed when the tubular reaction system was operated at 500^{o}C. The centre plateau at 200-350 g/mol disappeared completely at 550^{o}C and a vapor phase residence time of 12.0 s indicating cracking reactions. The occurrence of cracking reactions is supported by the aforementioned increase in gas yield at the expense of oil yield (section 4.4.2). The oil produced with the tubular reactor operated at 500 and 550°C did contain relatively more compounds with higher molecular weight (>1000 g/mol) than the reference oil and the oil produced in the FB+T at 400°C. It cannot be unambiguously concluded whether these compounds are really formed by polymerization reactions or if it is only a relative increase which can be explained by the disappearance of low molecular weight compounds due to the formation of gases. Because no increase in pyrolytic lignin content (see next paragraph) and no noticeable increase in water production (condensation reactions) was observed, the second explanation is favored.

4.4.6 Pyrolytic lignin content

In Figure 4.11 the pyrolytic lignin yield (water insolubles) is plotted as function of the vapor phase residence time. Pyrolytic lignin is known to account (partly) for the high molecular weight compounds present in pyrolysis oil[10]. The pyrolytic lignin content dropped at 400°C which is in line with the M_w-distribution results. This supports the aforementioned finding that vapor molecules do crack at 400°C to smaller molecules, although no oil yield changes were observed. The pyrolytic lignin yield dropped further upon increasing the tubular reactor temperature to 500 and 550°C, which is in line with the observed decline in average molecular weight of the oils. These results and the results on the M_w-distribution of the oils suggest that cracking reactions were dominant over polymerization reactions in the studied range (400–550°C / 1–15 s).

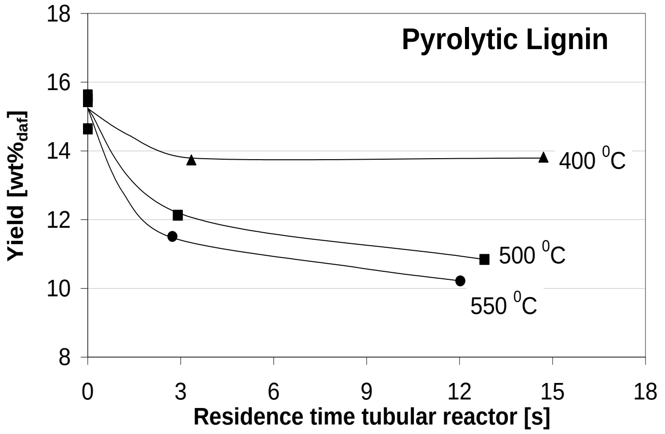

Figure 4.11: *Pyrolytic lignin (water insolubles)*

4.4.7 Aromatic and conjugated (AC) compounds

The ∫UVdv/∫RIDdv ratio which is associated with the relative content of the aromatic and conjugated (AC) compounds in the oil[26] is plotted as function of the tubular reactor severity in Figure 4.12. The ∫UVdv/∫RIDdv ratio for the oil remained constant for the experiments carried out at 400^{o}C. The amount of AC compounds appeared to increase with increasing tubular reactor severity. In literature it is regularly reported that pyrolysis oil produced at higher temperatures contains more aromatics[18,35,47]. Aromatization reactions are reported to take place at higher temperatures[47]. A second explanation opposite to the formation of AC compounds is that non AC compounds might be gasified which should be accompanied by an oil yield decrease and a relative higher abundance of AC compounds. Although it is unknown if a linear relation exist between the ∫UVdv/∫RIDdv ratio and the concentration of AC compounds, the yield corrected ∫UVdv/∫RIDdv ratio's are plotted as well in Figure 4.12 (open symbols). The yield corrected ∫UVdv/∫RIDdv ratio was independent of the tubular reactor severity. This suggests that higher concentrations of aromatics as often observed in the oil with an increase in pyrolysis severity does not necessarily imply the net formation of aromatics, but can also be explained by the net disappearance of the non-aromatic fraction from the oil.

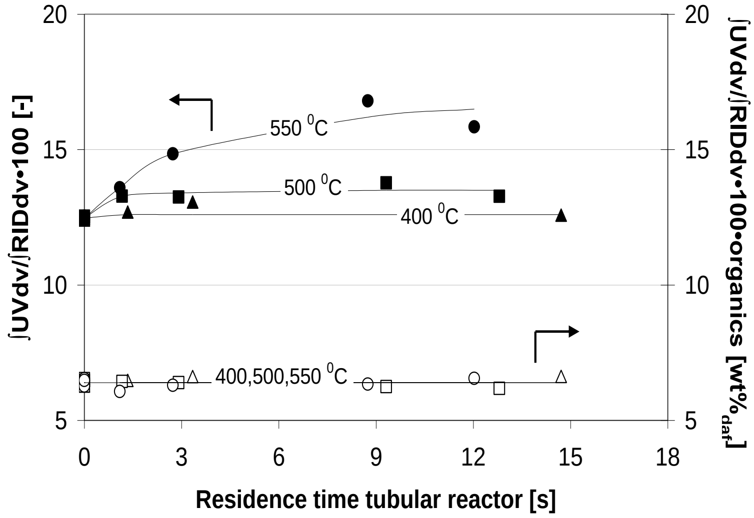

Figure 4.12: *∫UVdv/∫RIDdv ratio for pyrolysis oil (associated with aromatic and conjugated compounds)*

4.4.8 GC/MS: volatile compounds

An indication of the fraction of volatile compounds in the pyrolysis oil was obtained by using GC/MS. The total yield of volatile compounds, levoglucosan and the yield of four lumped groups (non-aromatic aldehydes, pyrans, guaiacols, lignin derived phenols) are plotted in Figure 4.13 as function of the tubular reactor temperature (400, 500, 550^{o}C) and residence time (0-15 s). The detected and quantified compounds in these four groups are listed in Table 4.5.

At 400^{o}C, the sum of total GC/MS detectables (~volatiles) increased with residence time, while no oil yield changes were observed at this temperature. This shows that also at 400°C vapor to vapor reactions occur and heavier molecules are likely to be cracked to more volatile ones. This is in line with the SEC analysis result and the pyrolytic lignin content (section 4.4.5 and 4.4.6). At higher temperatures (500 and 550°C), the yield of volatile compounds decreased with residence time, but also an increase in gas yield was observed for these experiments. Summing the gas and volatile yield showed that its value increased with residence time for all temperatures. So, overall, heavier molecules were cracked to smaller ones (either volatiles or gases) for all temperatures. From this we conclude that the overall formation of GC/MS detectable volatile compounds from heavier vapor components is slower than the overall cracking of GC/MS detectable volatiles to gases at 500 and 550°C.

Non-aromatic aldehydes are reported to mainly originate from pyrolysis of hemicellulose and cellulose[43,44]. The yield of non-aromatic aldehydes initially (up to ~3 s) increased for all temperatures after which a decline was observed for the two highest temperatures only. Aldehydes appear to be formed from heavier molecules during pyrolysis vapor phase reactions even at temperatures as low as 400°C for which no oil yield changes were observed. Since an increase in CO yield was observed only at 500 and 550°C and aldehyde type of compounds are reported to be cracked to CO[43,44], it is likely that the decline in aldehyde yield can be explained by subsequent decarbonylation reactions. Overall, part of the heavier hydrocarbons seem to be converted to non-aromatic aldehydes (>400°C) and CO (>500°C).

Pyrans originating from the degradation of several (poly)saccharides[48] appeared not to be stable in the range of 400 to 550°C, as is shown in Figure 4.13. These results proof again that at 400°C internal rearrangement reactions took place although no changes in yields were observed.

Levoglucosan is one of the most abundant products in pyrolysis oil and originate primarily from cellulose[43,48,49]. Figure 4.13 shows that the levoglucosan yield was constant at 400°C. At higher temperatures, the small increase in levoglucosan yield might be explained by further cracking of cellulose decomposition products (e.g. cellobiose). In literature several reactions schemes of levoglucosan are reported. Cracking reactions of levoglucosan to lower molecular weight products like furans and aldehydes[43,49] but also polymerization reactions of levoglucosan to form polysaccharides[49] are included in those schemes. Our results did show that such kind of reactions do not take place inside a homogeneous vapor phase at temperatures between 400 and 550°C.

In literature it is reported that softwood lignins typically degrade to guaiacol-type of compounds[50] and guaiacols are reported to be converted to phenols and catchols[35,42,50]. The methoxy group (–OCH_3) was suggested be an important source for the formation of the small volatile species (CO, CO_2 and CH_4)[42]. 2.3 wt%, daf of guaicaols were detected inside the pyrolysis oil collected just after the fluidized bed reactor. Although at 400°C guaiacols appeared to be stable, they disappeared almost completely with increasing severity in the tubular reactor. An increase in gas yield and lignin derived phenols was observed simultaneously at 500 and 550°C which is expected based on the reaction pathway proposed in literature.

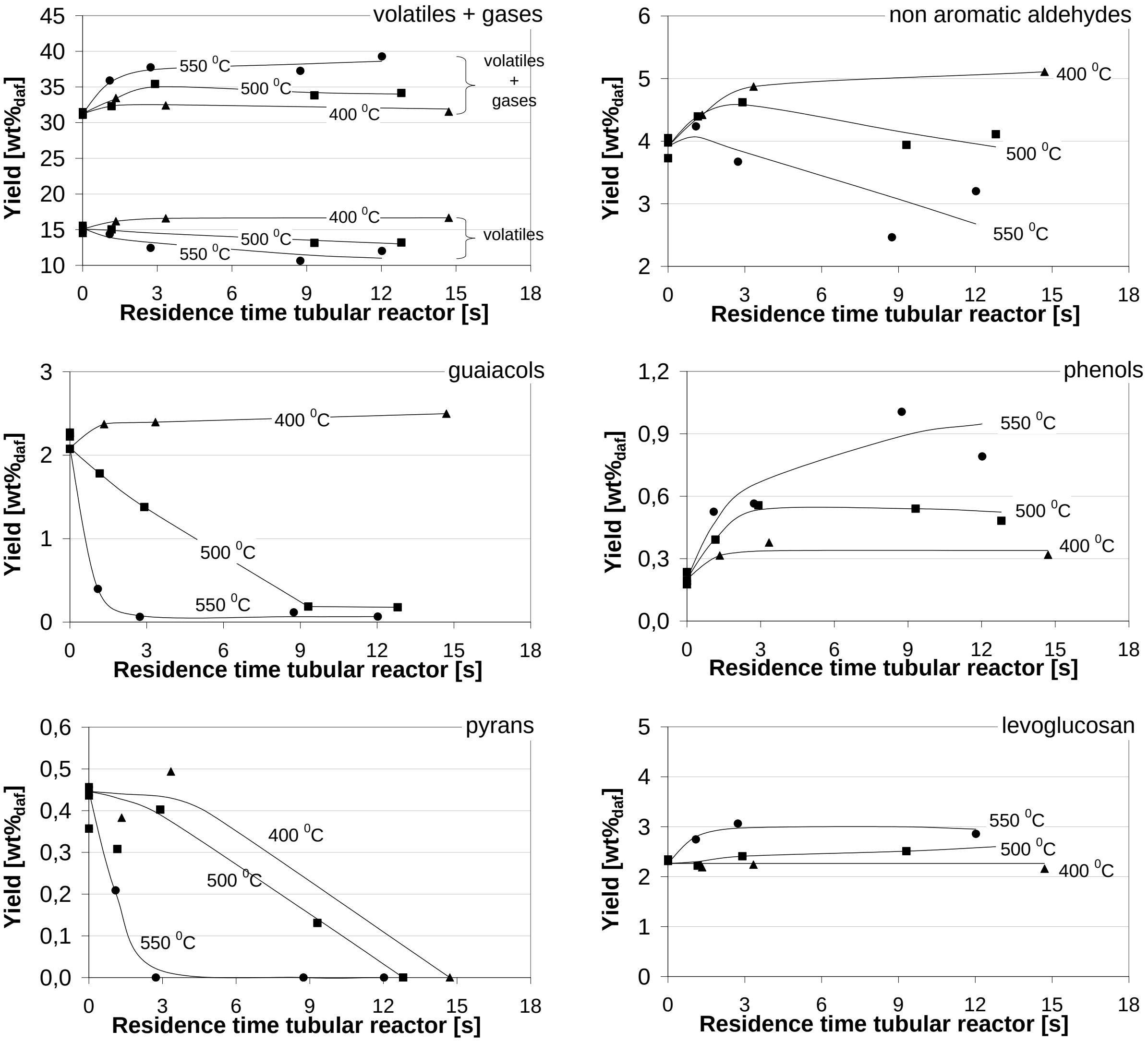

Figure 4.13: *Yields of GC/MS detectable volatile compounds (denoted as volatiles in figure) in FB+T reactor (triangle = 400 °C, square = 500 °C, circle = 550 °C)*

Table 4.5: *Lumped classes of pyrolysis liquid compounds, quantified by GC/MS (denoted as volatiles in Figure 4.13)*

Class	Quantified compounds
Non aromatic aldehydes	hydroxy-acetaldehyde, 3-hydroxy-propionaldehyde, crotonaldehyde, butandial, 2-methyl-propanal
Pyrans	3-hydroxy-5,6-dihydro- (4H)-Pyran-4-one
Phenols	phenol, cresol (o,m,p), dimethyl-phenol (2,5 and 2,6), trimethyl-phenol (2,3,6 and 2,4,6), ethyl phenol (2 and 3 and 4), trimethyl-derivative of phenol, (2,3,4- of 2,4,5-), 2-hydroxy-benzaldehyde, 2-hydroxy-4-methylbenzaldehyde
Guaiacols	guaiacol, 4-methyl-guaiacol, 4-ethyl-guaiacol, 4-vinyl-guaiacol, 4-allyl-guaiacol, (eugenol), 4-propenyl-(cis/trans)-guaiacol, (=isoeugenol), vanillin, homovanillin, coniferyl alcohol, acetoguajacone, propioguaiacone, guaiacyl acetone, coniferylaldehyde, 4-hydroxy-3-methoxy-benzoic acid methyl ester

4.4.9 Effect concentration on polymerization reactions

The results described in section 4.4.2 till 4.4.8 suggest that cracking reactions were dominant over polymerization reactions in the studied range ($C_{\text{gases+vapors}}$ = 9 vol%, 400 – 550°C/ 1 – 15 s). No increase in char yield, water production (linked to condensation reactions), pyrolytic lignin content and absolute molecular weight was observed which are all indicators for the occurrence of polymerization reactions. It should be emphasized that nitrogen diluted pyrolysis vapor streams were used (because of the fluid bed technology) and the concentration of the vapors is thus low. Polymerization reactions are expected to be bi-molecular and its rate thus expected to be concentration dependent. Since in literature no data are reported about the effect of pyrolysis vapor concentration on homogeneous vapor phase reactions some preliminary tests were carried out with a three times higher concentration ($C_{\text{gases+vapors}}$ = 27 vol%, τ = 3 s, T = 400 and 500°C). The higher concentration was reached by reducing the reactor diameter (ID 5.5 cm versus 10 cm) and by reducing the minimum fluidization velocity ($d_{p,\text{sand}}$ = 200 μm versus $d_{p,\text{sand}}$ = 200-300 μm). No decrease in oil yield was observed for the 27 vol% compared to the standard runs with a vapor and gas concentration of 9 vol%. The molecular weight distributions of the resulting oils are shown in Figure 4.14. No additional polymerizations reactions appeared to occur for the more concentrated pyrolysis vapor stream (27 vol%). So, the findings reported in this study are expected to be valid for more concentrated vapor streams as well.

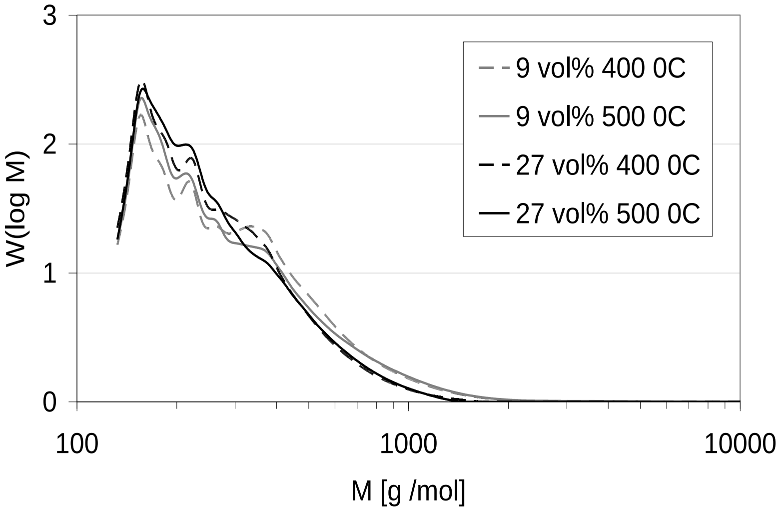

Figure 4.14: *Effect of vapor/gas concentration on the M_w-distributions of the oils*

4.5 Kinetics, mechanism and modeling of vapor phase reactions

The degradation of biomass is traditionally described via three parallel first order reactions to gas, oil and char[51,52]. More comprehensive pyrolysis reaction models include homogeneous vapor phase reactions. The background of some of these models is discussed below in relation to the results obtained in this study.

Homogeneous vapor to gas reactions are often modelled using simple first order kinetics[19,20,41]. Baumlin et al.[19] constructed an Arrhenius plot of the first order rate constants of vapor to gas as reported in literature. The calculated Arrhenius constants for our own results (500/550°C, first 2 s, isothermal plug flow model, $k_0 = 1.8\times10^5\ s^{-1}$, $E_a = 9.7\times10^4$ J/mol) lie within the range of literature data. However, the spread in reported k-values was large with differences up to a factor 15. This spread in reported k-values was attributed to the difference in feedstocks (type, particle size), reactor (type, heating rate, reactor material) and calculation procedures[14,19]. Although the aforementioned model can predict the trend for short vapor residence times, it cannot predict the asymptotes in oil yield we did observe at prolonged vapor residence times (Figure 4.7). These asymptotes can be predicted if not the actual oil yield, but the difference between the actual and the stable oil yield (i.e. minimum oil yield at a specific T) is used in the kinetic expression. However, such models appear to underpredict the conversions at short vapor phase residence times[14] probably due to the presence of vapors with different reactivities.

Some researchers[14,16-18] extended the concept of first order oil vapor to gas reactions by introducing several parallel first order vapor to gas cracking reactions. Boroson et al.[14] and Stiles et al.[18] assumed an infinite number of reactions to occur (distributed activation energy model) while Rath et al.[16,17] divided the pyrolysis vapors into three reactive fractions. Such models are able to predict the asymptotes as observed in this study, but do not take into account any type of vapor to vapor reactions which were proven to occur in this study (section 4.4.2). Antal[31] took those types of reactions into account in his model by including two parallel first order vapor reactions: one to permanent gases and the other one to stable vapors. Missing in Antal's model is a distinction between the reactivity of the different type of vapors originating from the biomass matrix (cellulose, hemicellulose and lignin).

Combination of the work of Boroson et al.[14] and Antal[31] would yield a model that represents the homogeneous vapor phase reactions better. However, our work has shown that heterogeneous vapor reactions have a large influence on oil yield and composition as well. So far, and to our knowledge little to nothing has been done on the description and modeling of these heterogeneous vapor phase reactions.

The systematic approach dealing with the heterogeneous and homogeneous vapor phase reactions as carried out in this study can not only help to obtain a better understanding of the complex pyrolysis system but also elucidate the feasibility of modelling such system reliably. We believe that a *generic* mathematical description of the pyrolysis reactions either leads to a dangerous oversimplification or to a model with far too many (unknown) fit parameters. To our opinion, and at this point in time, simple models based on measurable parameters supported by good understanding of the actual phenomena taking place (decomposition and vapor phase reactions) allows for the most reliable prediction / extrapolation of the performance just outside the measured area for which the models were derived.

4.6 Engineering viewpoint

Several reactor types for fast pyrolysis processes have been and are being developed like i) bubbling fluidized bed ii) transported bed iii) circulating fluidized bed iii) ablative pyrolysis iv) auger and v) vacuum pyrolysis. Their advantages and disadvantages are described extensively in literature[1,2,5,12,53]. Three statements which are important from an engineering point of view are formulated based on our experimental results.

1. It is not necessary to remove ash poor char (C,H,O) directly from the hot pyrolysis vapor stream

No changes in yields and oil composition were observed as function of (mineral poor) char hold-up (section 4.3.1). Consequently it is not necessary to remove pure char (C,H,O) from the vapors. It should be noted that it is only possible to obtain an ash poor char from an ash poor feedstock. For this, either a clean feedstock like pine wood needs to be used or the minerals present in the biomass needs to be removed beforehand by a pre-treatment step. Research did show that minerals can be removed by a relatively simple washing step using water[28].

2. The contact time between vapors and minerals needs to be minimized

Minerals, whether incorporated in the char matrix or not, appear to be detrimental for the pyrolysis oil yield. Contact between minerals and pyrolysis vapors should be avoided to prevent a decrease in oil yield. This can either be done by reducing the mineral concentration inside the reactor (for example prevent accumulation in continuous circulating processes) or by reducing the residence time of the vapors in the mineral rich part of the pyrolysis unit.

3. Pyrolysis vapors (mineral poor) can be exposed to temperatures up to 400 ^{0}C for long times

At 400^{o}C, homogeneous vapor phase reactions do not influence the fast pyrolysis process in terms of oil yield. Rapid cooling of the vapors to ambient temperatures as typically reported in literature is thus not necessary[1-6]. Although some extent of vapor to vapor cracking was observed at 400^{o}C, this was not accompanied by changes in oil yield. It should be noted that the pyrolysis vapors were produced at a typical pyrolysis temperature of 500^{o}C and statement 3 may not be valid for lower pyrolysis temperatures.

4.7 Conclusions

Heterogeneous and homogeneous reactions of pyrolysis vapors from pine wood were studied using respectively a fluidized bed reactor (500 ^{0}C, ~ 0.8 kg/hr) and a fluidized bed reactor (500^{o}C, 0.15 kg/hr) connected to a tubular reactor (1-15 s, 400–550 ^{0}C).

Char itself, viz. the organic C, H and O atoms, appeared *not* to be catalytically active inside the fluidized bed reactor. However, the presence of minerals (Na/K) – either in the biomass matrix (native or impregnated) or external (as salt or in char), does influence the fast pyrolysis process. Heterogeneous vapor phase charring/polymerization reactions were more important than cracking reactions of vapors to gas.

Pyrolysis vapors were also found to be reactive in the absence of minerals. With increasing temperature an increasing part of the pyrolysis vapors cracked to gases via homogeneous vapor phase reactions. Our results show that a temperature dependent oil yield asymptote is reached provided that long enough vapor residence times are applied (400°C: 62 wt% (daf) 500°C: 57 wt%, 550°C: 49 wt%). At a vapor temperature of 400°C, the oil and gas yield were independent on the residence time, but homogeneous vapor to vapor reactions were proven to occur. In the studied range (400-550°C, 1-15 s) homogeneous cracking reactions were dominant over polymerization reactions. A decrease in average molecular weight, lignin content and an increase in gas yield (especially CO) and phenols (GC/MS) was observed which are all indicators for cracking reactions while no increase in char yield and water production was observed which are indicators for the occurrence of polymerization reactions. It was shown that literature models consider the homogeneous and heterogeneous vapor phase reactions only to a limited extent.

Based on this work three statements which are important from an engineering point of view could be formulated:

1. It is not necessary to remove ash poor char (C,H,O) directly from the hot pyrolysis vapor stream,
2. The contact time between vapors and minerals, whether or not incorporated in the char matrix, needs to be minimized,
3. Pyrolysis vapors (mineral poor) can be exposed to temperatures up to 400°C for long times.

4.8 References

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Chapter 5

Effect of Particle Geometry and Micro-Structure on Fast Pyrolysis of Beech Wood

Abstract

The influence of particle geometry and micro-structure in fast pyrolysis of beech wood has been investigated. Milled wood particles (<0.08-2.4 mm) and natural wood cylinders (2-14 mm) with different lengths (10-50 mm) and artificial wood cylinders (D_p = 0.5-14 mm) made of steel walls, filled with small milled wood particles (<0.08-0.140 mm), have been pyrolyzed in a fluidized bed at 500°C. From the results of the experiments, the influence of particle geometry and micro-structure on char, gas and pyrolysis oil yield and pyrolysis oil composition has been derived.

The product yields of large cylinders with diameters of 6-14 mm are primarily determined by the outer diameter and resulting heating rate. The micro-structure of these cylinders, being either natural channels or randomly packed small milled wood particles, has turned out to be much less important. For the smaller milled wood particles the micro-structure does have a profound effect on the product yields. The smallest particles (<0.140 mm), which consist only out of cell wall material and have lost their typical wood channel structure, show a clearly higher oil yield and lower char yield. It is postulated that the high pyrolysis oil yield can be explained by larger mass transfer rates of pyrolysis products from these smallest particles, as compared to mass transfer from particles containing channels.

5.1 Introduction

Fast pyrolysis of biomass is a thermo-chemical conversion method to obtain a pyrolysis oil, along with a solid char and non-condensable gas, by fast heating of the biomass in the absence of oxygen. Pyrolysis oil is a complex mixture of many oxygenated compounds like sugars, acids, furans, phenols, aldehydes, ketones and water insoluble lignin derived oligomers[1,2,3]. Water is one of the most abundant compounds in pyrolysis oil[4,5]. Water lowers the viscosity and the heating value of the oil and at high concentrations it causes the oil to phase separate[6,7,8,9]. Levoglucosan is an interesting mono-sugar that can be hydrolyzed to form glucose or can be directly fermented to produce ethanol[10]. The water-insoluble lignin derived oligomers present in pyrolysis oil have the potential to be used for the production of transportation fuels[11].

In the last three decades many pyrolysis reactors have been developed. Generally, these reactors can be divided in bubbling fluidized beds, circulated fluidized beds, ablative reactors, screw reactors, rotating cone and vacuum reactors[12,13,14]. Design and optimization of these pyrolysis processes requires insight and understanding of the chemical reactions and physical processes involved during the conversion of the biomass particles. One area that still needs further research is the effect of the biomass particle shape and size on char, gas and pyrolysis oil yield and composition. Wang et al.[15] have shown that variation of the diameter of wood cylinders between 0.7 and 14 mm ($L_p/D_p > 3$) has a minor effect on the total liquid yield. It was observed experimentally in their study that the water production increased as the diameter of the cylinder increased. Shen et al.[16] studied the effect of mallee wood particle size (18-5.6 mm) on the yield and composition of pyrolysis oil using a fluidized bed reactor operated at 500^{o}C. It was found that the bio-oil yield decreased as the particle size increased from 0.3 to 1.5 mm. Shen et al.[16] postulated that destruction of the wood particle structure by milling could be a reason for higher oil yields for smaller particles. In the particle size range of 1.5 to 5.6 mm no further decrease of oil was found by these researches. Salehi et al.[17] pyrolyzed three fractions of milled wood particles: <0.59 mm, 0.59-1 mm and 1-1.4 mm in a fluidized bed operated at 500^{o}C and noticed that the oil yield decreased rapidly from 62-52 wt% as the saw dust size was increased from <0.59 mm to 0.59-1 mm. For larger saw dust sizes the decrease in oil yield leveled off.

Since the costs associated with biomass grinding increase with decreasing particle size[18], there is need to identify the optimal particle size for which acceptable oil yields are obtained and if the oil still satisfies the specifications for further usage.

One of the important characteristics of the pyrolysis process is the heating rate of the biomass particle[19,20,21,22]. Heating rate and final pyrolysis temperature both have a large impact on the pyrolysis product yields and pyrolysis oil quality[6,23,24]. For particles larger than ~1 mm the external heat transfer and/or thermal diffusivity controls the conversion rate. For beech wood particles smaller than ~1 mm, decomposition is said to take place very close to the reactor temperature and is more likely to be controlled by its kinetics[19].

In addition to heat transfer and final pyrolysis temperature, the time needed for the (partial) de-polymerized biomass, being in the liquid or solid state, to leave the reacting particle by vaporization / sublimation of vapors or physical entrainment of aerosols is seen as an important issue determining the product distribution[6,16,24,25]. Haas et al.[25] performed real-time microscope analysis of poplar wood undergoing pyrolysis. The poplar wood was heated with 150^{o}C / min to 500^{o}C. It was clearly visualized that liquid droplets exist inside the decomposing wood structures and that some of the droplets were trapped inside the particle. This is a clear indication on limitations for newly formed liquid (partly depolymerized biomass) to leave the particle. Vapors / aerosols created inside the biomass particles find their way out mainly via channels inside the biomass structure (anisotropic vapor outflow)[25]. When these compounds do not leave the hot biomass particle fast enough, they will cross-link and eventually form char[24].

There are two main objectives in the present paper. The first objective concentrates on the effect of beech wood geometry (shape & size) on the char, gas, water, organics, water insolubles and levoglucosan yield. Wood cylinders of 2-14 mm and milled particles of 0.25-2.5 mm were pyrolyzed in a fluidized bed at 500^{o}C.

The second objective of this study is focused on the effect of wood micro-structure and vapor/aerosol outflow patterns (anisotropic/isotropic) on the char yield. Artificial wood cylinders with solid walls (1, 6, 10 or 14 mm inner diameter) and wire-mesh end caps at both sides, filled with milled particles (<0.08 mm), were used to study the effect of micro-structure on pyrolysis. The results will be compared with those obtained with artificial cylinders completely made from wire mesh (6, 10, 14 mm), filled with milled particles of 0.140 mm to investigate the effect of isotropy / anisotropy in outflow of the produced vapors.

5.2 Experimental

5.2.1 Wood particles

Beech wood (660 kg/m^3) was used as feedstock in the pyrolysis experiments. The ash content was determined to be between 0.5-0.6 wt% and elemental composition was: N=0.5 +/-0.1, C=46 +/-1, H=7 +/-0.5 and O=46 +/-1 wt%. The biomass was dried for 24 hours at 105^{o}C prior to the experiment. The residual moisture content is below 1 wt%. In this paper, we changed both the geometry (shape and size) and micro structure of the wood. Wood cylinders (D_p= 2-14 mm) and milled particles (L_s = < 0.08 mm – 2.4 mm) were used. The length of the cylinders was always 50 mm resulting in an aspect ratio larger than 3, which made the particles one-dimensional (the diameter) with respect to internal heat transfer. Milled wood particles were obtained by extensive milling of the wood cylinders followed by sieving (using sieves of 0.08 – 2.4 mm) into several fractions. The size of the milled wood (L_s) is herein defined as the middle value of the upper and lower size limits of the sieve meshes. This definition of the particle size is about the same as the one Shen[16] used to allow for comparison. It must be noted that the smallest dimension of a particle in a certain sieve fraction, the one being most important for heat transfer, can be smaller than the size of the smallest sieve. The shape of the milled wood particles can vary a lot and is difficult to define. From microscope analysis it became clear that most milled particles have rectangular or (almost) round shapes. The effects of the wood geometry on pyrolysis has been studied by comparing the pyrolysis product yields of wood cylinders and milled particles of varied sizes.

The effect of the micro-structure of milled particles and wood cylinders on the char yield was also studied. The micro-structures used in this work are schematically visualized in Figure 5.1. For wood cylinders the micro-structure consists out of longitudinal channels (cells). The outflow of vapors, aerosols and gases is anisotropic; these products leave the biomass mainly via the channels. Figure 5.2 shows that for the milled particles of 1 mm the wood still consist of channels. Milled particles of around 0.1 mm however (shown in Figure 5.3) consist only out of cell wall material. Microscopic analysis of the sieve fractions showed the fractions of 0.14 mm and below only consisted out of cell wall material. Hence, the micro-structure of these particles is different compared to the cylinders and the larger milled particles.

The milled particles (< 0.08 mm) are also inserted in metal (stainless steel) cylinders with a solid cylindrical wall (D_p=0.5, 6, 10, 14 mm, internal diameter) and wire-meshes at the bottom and top. These cylinders are called further artificial solid wall (sw) cylinders. The micro-structure of these artificial wood cylinders is very different compared to the natural wood cylinders: randomly packed particles versus highly structured longitudinal channels. By comparing the char yields of natural wood cylinders with those of artificial cylinders while varying the diameter it can be evaluated whether cylinder diameter or internal micro-structure is dominant with respect to the char yield.

Also artificial cylinders (filled with milled particles of 0.14 mm) completely made out of wire-mesh were used. Produced vapors, aerosols and gases flow out of the particle in an isotropic manner. These cylinders are called further artificial wire-mesh (wm) cylinders. Comparison of the char yield of these cylinders with char yield of identical artificial cylinders with a solid cylindrical wall provides information on the importance of the outflow pattern.

Artificial wood cylinders of 0.5 mm ID and varied length (10-50 mm) were filled with small milled particles (< 0.08 mm) consisting only of cell wall material. By comparing the char yields of the cylinders with different length, it is investigated if the contact time of produced vapors and aerosols with char has influence on the char yield. Comparing the results of these artificial cylinders to natural particles of 0.5 mm gives information on the influence of the micro-structure.

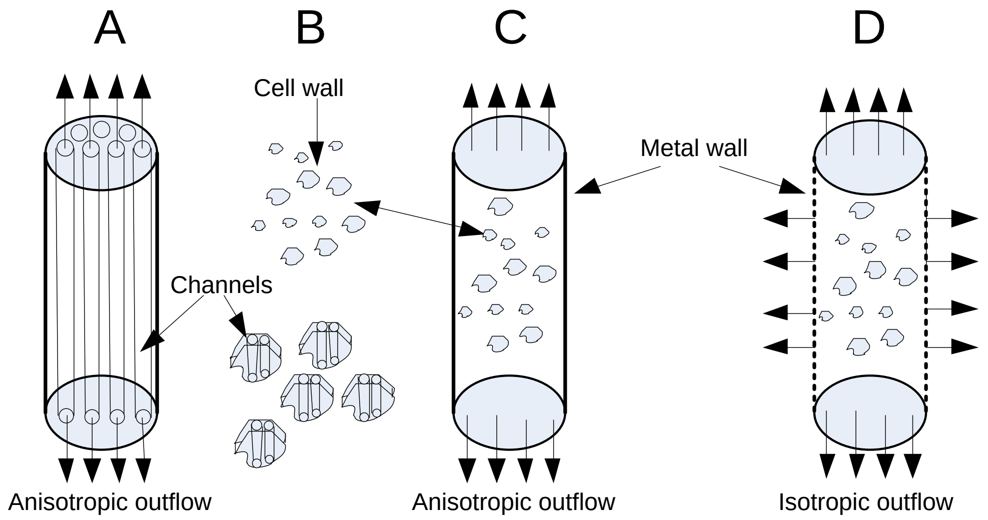

Figure 5.1: *Particles used. A) Wood cylinders having channels in longitudinal direction, B) Milled particles containing channels or existing only out of cell wall material, C Milled particles inserted in metal cylinders with anisotropic outflow, D) milled particles in metal cylinders with isotropic outflow. Arrows out of the particles indicate the direction of the outflow of produced gases, vapors and aerosols.*

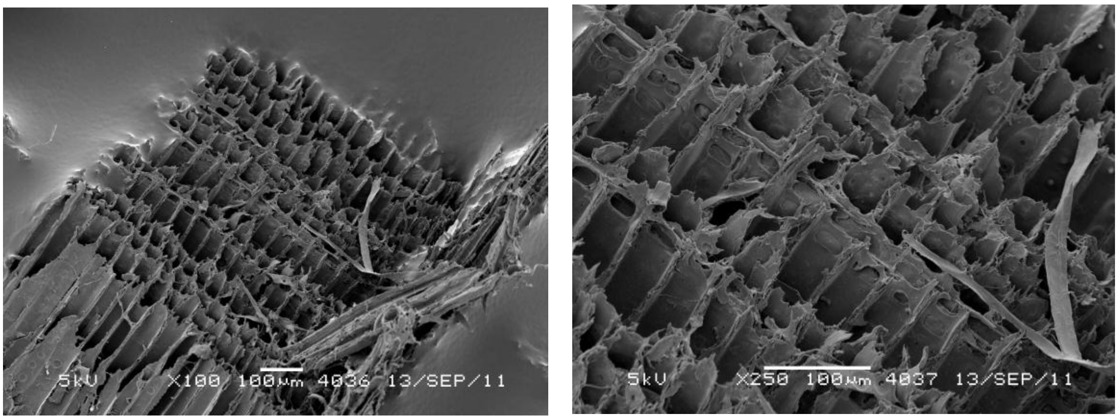

Figure 5.2: *SEM pictures of 1 mm beech wood particles.*

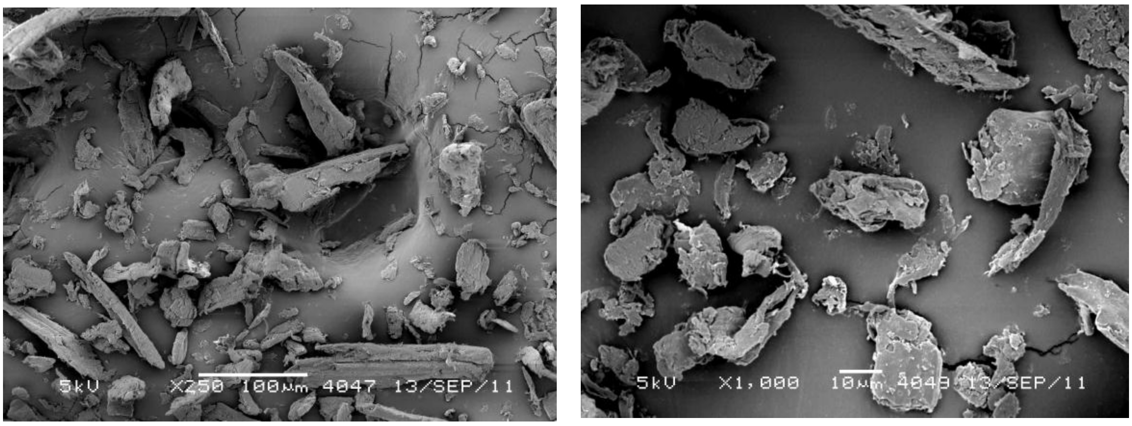

Figure 5.3: *SEM pictures of beech wood particles smaller than 80 micron.*

5.2.2 Preparation and characteristics of the metal cylinders

Metal walled cylinders with varied diameter were prepared. The bottom and top of the solid wall cylinders were covered with wire-mesh to ensure the anisotropic outflow of vapors. The cylinders with a diameter (ID) of 6, 10 and 14 mm had a constant length of 50 mm. The length of the 0.5 mm artificial metal cylinder was varied between 50 and 10 mm. The solid cylindrical wall was made of a double layer of 0.025mm thick metal foil and the 0.5 mm internal diameter cylinder was made of a 0.25 mm thick metal wall. The thermal resistance of the metal walls can be neglected ($\alpha > 10^4$ W/m^2/K) with respect to heating of the particle if the contact between the metal wall and the internal milled particles is sufficient. For the artificial cylinders of 6 mm and more, the mass of metal represents less than 0.1% of the total mass and can also be neglected. The mass of metal of the 0.5 mm artificial cylinders is >99% of the total mass leading to slower heating as compared to the 0.5 mm milled particle.

The overall density of the wood inside the artificial cylinders was set to 660 kg/m^3 (mass wood / internal volume artificial cylinder); identical to the natural wood cylinders.

Wood cylinders of 14 mm were inserted in the solid wall and wire mesh steel cylinders with an internal diameter of 14 mm. After pyrolysis of the wood cylinder, both fed as wood cylinder and inside the metal cylinders, the char yield was determined. By comparing the char yields of the wood cylinders enclosed by the wire mesh and solid wall cylinders with the separately pyrolyzed wood cylinders, possible heat transfer limitations and/or catalytic effects of the stainless steel cylinder walls would become visible. The char yield of the wood cylinders and wood cylinders of the same size inserted in the artificial solid wall and wire-mesh cylinders was identical, 23.0 , 23.1 and 23.0 wt% respectively. Hence, no influence on the heating rate nor catalytic effects of the metal wall of the artificial wood cylinder was observed.

In another experiment, the heating rate of the 14 mm wood- and artificial cylinder filled with milled particles in a fluidized bed at 500^{o}C was measured with a thermo-couple inserted in the center of the cylinders. The initial heating rate (2.5^{o}C/s) and the time to reach 95% of the fluid bed temperature (210 seconds) of the wood- and artificial cylinder filled with milled particles turned out to be nearly the same. It can be concluded that also the milled particles have sufficient contact with the wall of the artificial wood cylinder to experience an equal heating rate as the wood cylinder.

The mesh used for the artificial cylinders (wall in wire mesh cylinder & bottom and top in both cylinders) was 9 μm. Because of possible attrition of char inside the wire mesh and solid cylindrical wall cylinders during the pyrolysis experiment, resulting char loss could be a problem. The char loss from the wire mesh and solid cylindrical wall cylinders was determined experimentally, by fluidizing the cylinders filled with char for two hours. The attrition loss of all artificial solid wall cylinders was found to be less than 0.4% of the initial char for the 140 and 300 μm particles. Due to too high char loss (1-3 wt%) for the artificial wire mesh cylinders including milled particles of <80 μm, experiments with these smallest sizes (<80 μm) were only performed with solid wall cylinders. No sand entered the wire mesh cylinders, as determined by measuring the ash content of the char before and after the two hour experiments. No difference between the ash contents per unit weight char was found. Experiments with the artificial cylinders were always performed in triple to check the reproducibility.

5.2.3 Experimental setup

Fast pyrolysis experiments were performed in a fluidized bed reactor made of stainless steel and placed in an electric furnace. The set-up used is shown in Figure

5.4. The reactor temperature was kept at 500°C for all experiments. The incoming fluidization gas (nitrogen) was preheated to 500°C.

As bed material 1.1 kg silica sand with a particle size of 212-300 μm was used. This size fraction was used in order to prevent entrainment of sand particles from the reaction section into the bio-oil recovery section of the set-up, while minimizing the required volumetric flow of fluidization gas. The nitrogen flow was set to 12 normal liters per minute, resulting in a vapor/gas residence time of less than 2 seconds in the hot part of the set-up.

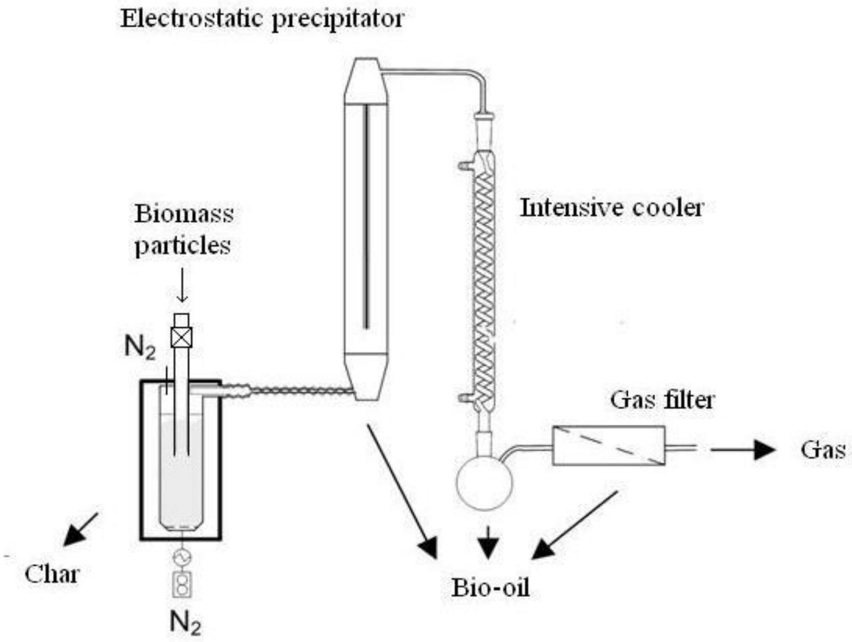

Figure 5.4: *Fluidized bed fast pyrolysis set-up.*

Hundred gram of milled particles or wood cylinders was fed manually in batches of 4-8 gram together with 2 gram sand with a valve system into the fluidized bed reactor. The temperature drop of the reactor bed during feeding of the cold wood/sand mixtures never exceeded 10°C.

A 5 μm filter at the reactor outlet was used to remove char/ash from the hot pyrolysis vapors. The pyrolysis liquid was collected by two sequential condensers. The first condenser was an electrostatic precipitator (ESP) operated at 17-21 kV and cooled externally with tap-water at 20°C. The remaining vapors, mostly lights, were further led to a glass wall intensive cooler (IC) operated at -5°C. A tubular cotton gas filter (10μm) was introduced to capture the remaining liquid. A dry gas meter was used to measure the gas flow before it was sent to the main ventilation system. A more detailed description of the set-up can be found elsewhere[26]. The only modification in this study is the replacement of the continuous feeding system by a valve, batch wise, feeding system.

For experiments with saw dust and wood cylinders, the whole set-up was used. An important feature of the set-up is that it can facilitate enough biomass particle residence time, even for the 14 mm cylinders, to achieve full conversion. The total liquid yield was determined gravimetrically by weighing the condensers and the gas filter before and after the experiments. Gas samples were taken frequently during the experiments and the gas composition was determined. On the basis of the GC analysis and the known amount of nitrogen added, the produced non-condensable gases could be calculated. The char yield was measured as difference between the bed and filter mass before and after experiment.

For the experiments with the artificial cylinders only the char yield was determined as the small number of cylinders fed to the reactor is insufficient for accurate oil- and gas yield determination. The experiments with the artificial cylinders were performed in triple to ensure good reproducibility of the obtained char yields.

After the ESP, the remaining gases and vapors were sent to the main ventilation system. The operating conditions of the batch pyrolysis unit are summarized in Table 5.1.

Table 5.1: *Operating conditions batch pyrolysis unit.*

operating conditions pyrolysis unit	**Beech wood**	**dimension**
experimental run time	30	min
mass sand	1.1	kg
diameter sand	212-300	μm
mass wood fed	100	gr
total mass milled particles in artificial cylinders fed	0.07 – 16	gr
bed height	0.20	m
U/U_{mf}	2-3	-
residence time vapors	<2	s
temperature reactor bed	500	°C
temp gas out 1st condenser	20	°C
temp gas out Intensive cooler	-5	°C

5.2.4 Analyses

The water content of the oil is determined by Karl Fischer titration. Hydranal Composite 5 was used as titer. The elemental composition of the different wood cylinders and milled particles is determined by an elemental analyzer EA 1108 CHNS-O. The composition in terms of carbon, nitrogen, hydrogen and oxygen (calculated) was obtained. Gas samples were analyzed in a gas chromatograph for H_2, CH_4, CO, CO_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8 (Varian Micro GC CP-4900 with two analytical columns, 10 m mole sieve 5A and 10 m PPQ, using Helium as carrier gas).

The water insolubles are determined by cold water precipitation method described by Garcia-Perez[27]. Solids content[7] (char and traces of some possibly entrained sand) where determined by gravimetric. The ash content of the biomass was determined by NPR-CEN/TS 15403-550°C. The levoglucosan content in the pyrolysis oil was determined by HPLC (p.n. PL1170-6820 Agilent Technologies), Column PL Hi-PLex-Pb 9µm., 7.7 x 300 mm. The eluent used was DDI water (0.6 ml/min). The injection volume was 10µl and the temperature of the column was 70°C. The HPLC detectors used were the RID (55°C) and VWD (210 nm).

5.3 Results

Pyrolysis experiments were conducted on milled wood particles (d_p=0.25-2.5 mm) and wood cylinders (D_c=2-14 mm, L=50 mm). The obtained closure of the mass balances was always between 92% and 97%. Pyrolyzing very small particles of $\leq$ 0.3 mm in a fluidized bed reactor is difficult. Therefore, three identical experiments with these small particles were performed to check its reproducibility. The product yields were as follows; Oil 71% +/- 1%, gas 15% +/- 1%, char 10% +/- 1% showing that the experiments could be reproduced well. Only the pyrolysis of <0.08 mm particles led to major experimental difficulties. Therefore, the pyrolysis data of the < 0.080 mm particles is excluded from this research. The terminal falling velocity (26 cm/s) of the 0.3 mm beech wood particles was always much higher than the applied fluidization velocity (8 cm/s). Because of the filter installed at the reactor outlet the partly decomposed biomass will remain in the reactor anyway and decomposes further at 500°C. Large particles > 6 mm can float on the top of the bed, but if they do, the heat transfer rate is still high enough to achieve fast pyrolysis because of the hot sand splashing at the top of the fluid bed. A detailed study on this phenomenon is described elsewhere[15]. The 9 micron solid filter positioned in the outlet of the reactor worked well. The amount of solids in the pyrolysis oil never exceeded the 0.05 wt% and there were no operational problems. The experiments with the artificial wood cylinders were always performed in triple. The standard deviation between the char yields of experiments of identical artificial cylinders was always smaller than 0.3%.

In Figure 5.5, the pyrolysis oil, organics in the pyrolysis oil, gas and char yields are plotted versus the milled particle- and wood cylinder size. In Figure 5.5, also the char yields of the artificial cylinders with solid- and wire mesh wall are included. Figure 5.6 shows the water, levoglucosan and water insolubles yield as function of the particle size.

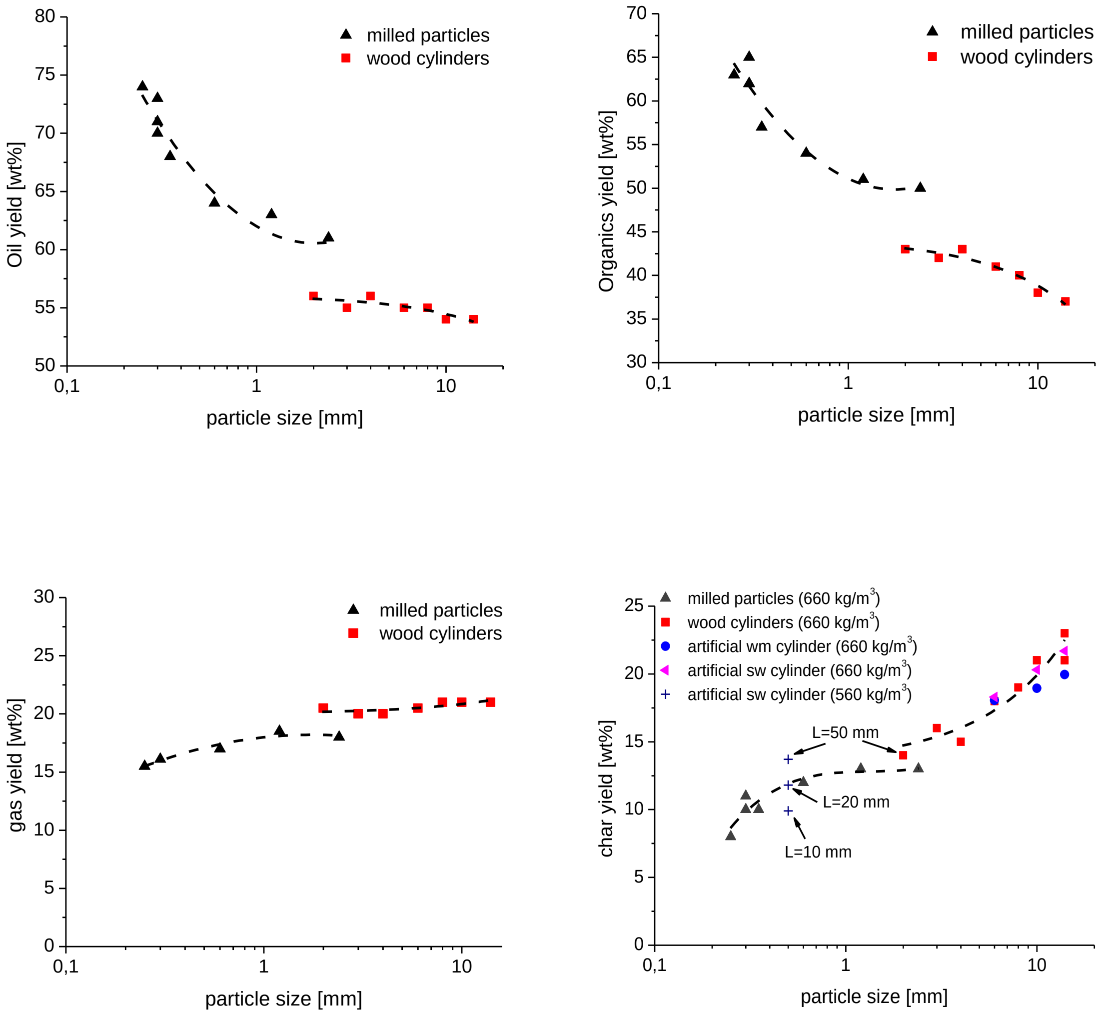

Figure 5.5: *Pyrolysis oil, organics in pyrolysis oil, gas and char yields (daf) are plotted as function of the particle size. The char yield of the artificial solid wall (sw)- and wire mesh (wm) cylinders are plotted as function of various sizes. The length of the artificial- and wood cylinders was 50 mm. Only for the 0.5 mm cylinder the length was varied between 10-50 mm.*

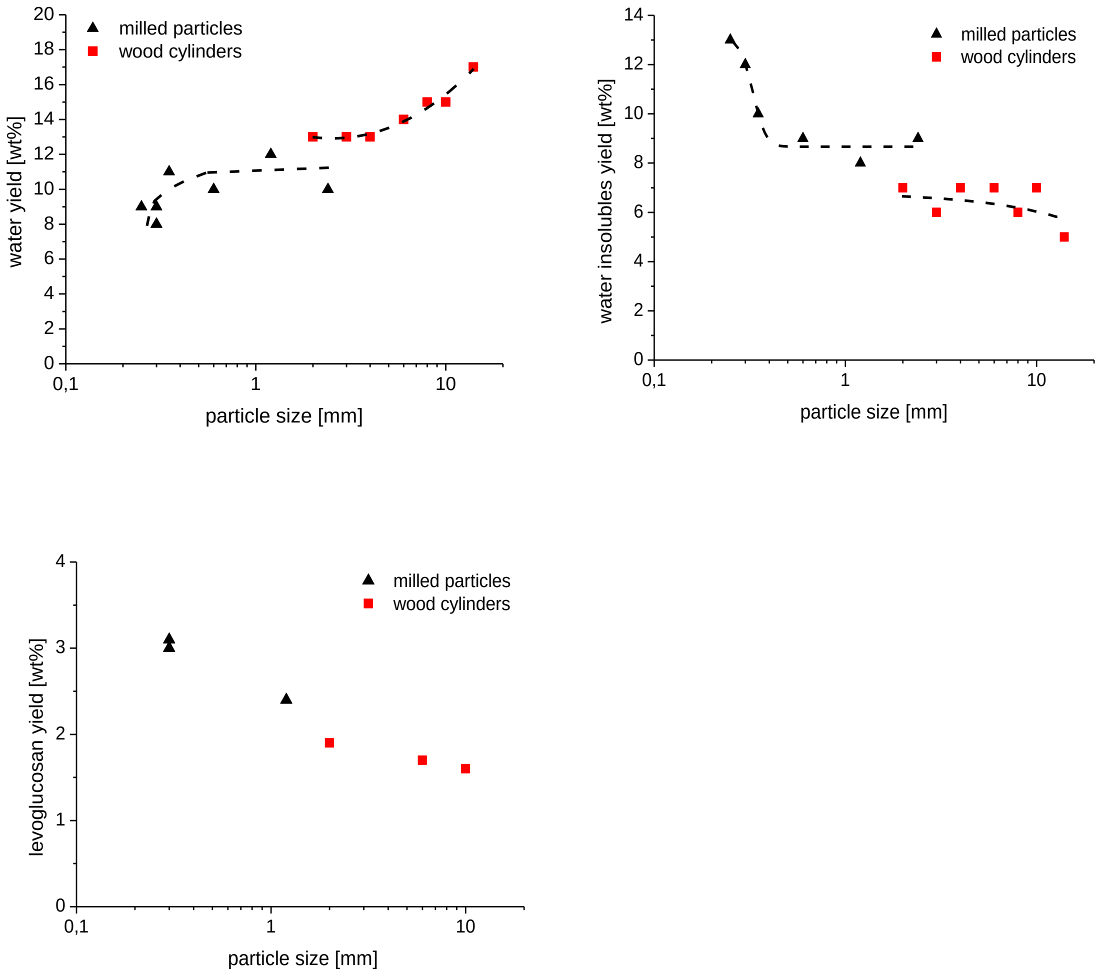

Figure 5.6: *The yields (daf) of water, levoglucosan and water insolubles as function of the milled particle- and wood cylinder size.*

According to Figure 5.5 & 5.6, for wood cylinders with a diameter between 2 and 14 mm, the yields of pyrolysis oil and gas is almost constant, while the yield of char and water increases as the particle size is increased. These results are in line with the results obtained by Wang[15] for beech wood cylinders. The organics yield remains almost constant between 2 and 5 mm and decreases as the wood cylinder diameter is further increased. The yields of levoglucosan and water insolubles decrease only slightly with the size of the wood cylinders between 2 and 14 mm.

A discontinuity between all the product yields obtained from wood cylinders and milled particles can be seen between 2 and 2.4 mm: the milled particles have higher oil and organics yields and lower char and gas yields. An explanation could be the shorter length of the milled particles compared to the wood cylinders. Another explanation is faster heating rates of the milled particles because of smaller aspect ratio's and the presence of particles with smaller characteristic heat transfer lengths compared to the sieve size. A third explanation could be partly destruction of the particles by milling resulting in different micro-structures compared to the wood cylinders[16] (See Figures 5.2 & 5.3).

For the milled particles the yields of the pyrolysis oil, organics in the pyrolysis oil, levoglucosan and water insolubles decrease rapidly as the particle size increases from 0.25 to 1 mm. The char yield increases drastically when the particle size is increased, while a less sharp increase in water and gas yield is observed. As the size of the milled particles is further increased from 1 to 2.4 mm, the decrease and increase of these aforementioned products tend to level of. It should be noted that similar results were obtained by Shen for milled particles of mallee wood[16].

The sharp decrease in the yields of pyrolysis oil and organics in the pyrolysis oil as the milled particle size is increased from 0.25 to 1 mm could be caused by differences in micro-structures. As can be seen from Figure 5.2 & 5.3, for very small particles only cell wall material is visible while the 1mm particles still have the original structure of the wood cells containing wood channels.

During pyrolysis of only the cell wall material (Figure 5.3), resulting droplets can vaporize much faster than inside a channel of a large particle. Slower vaporization processes of droplets under high temperature pyrolysis conditions result in the formation of more char by cross-linking reactions instead of the outflow of produced vapors / aerosols from the reaction particle(s). This outcome is underpinned by a lower yield of high boiling point molecules like the water insolubles for the larger milled particles and an increasing yield of water, a component that is known to be formed as a side product of cross-linking and poly-condensation reactions. This competition between the formation of char and the release of vapors / aerosols was clearly pointed out in our previous study on step-wise pyrolysis of pine wood[24].

It is worthwhile to mention the observation that for the smallest milled particles with diameter ≤0.140 mm, the sand bed turned black, while only very little char particles were visually observed after the experiment. This is not observed for pyrolysis of larger biomass particles that result in clearly identifiable char particles and clean sand. This could mean that “explosions” or (complete) disruption of the wood structure takes place during pyrolysis so that these particles could not be found back. Another explanation could be that very large molecules leaving the small particle as aerosol or vapor, adhere or re-condensate on the sand particles. Our data show (see Figure 5.6) that indeed more heavies (water-insolubles) are produced from the smallest particles. A third explanation could be that liquid intermediates, on the border of the biomass particle, (droplets) attach to the sand. From the observations made by Haas et al.[25] it was found that these droplets originate from the middle lamella where most of the lignin fraction of the wood is situated[28]. If these droplets can find sand particles, they may adhere on these particles. A recent study on lignin pyrolysis clearly pointed out that lignin melts and adheres to the sand to eventually form lumps[29].

Scott and Piskorz[23] reported oil yields as high as 75-80 wt% from pyrolysis of low ash Aspen-poplar and Maple. These values have been often used as reference in defining the maximal pyrolysis oil yield that can be obtained. However, these high oil yields are seldom, if at all, achieved by other researchers. In light of our results an explanation for the high oil yields reported by Scott and Piskorz is the use of very small particles <595 micron, including considerable amounts of fines even smaller than 88 micron.

The gas yield decreases rapidly for particles <1 mm. For the smallest particles, pyrolysis does take place at the reactor temperature due to almost instantaneous heating. So, practically the whole pyrolysis process takes place at the highest temperature. Still they have the lowest gas yields. This is rather surprising, given that most studies report that higher pyrolysis temperatures favor the production of gas[6,18,30]. A plausible explanation for the lower gas yield for the smallest particles is that gas is not only a product from vapor phase cracking but also a side product of cross-linking and poly-condensation reactions inside the particles. For smaller particles cross-linking reactions proceed to a lesser extent indicated by a decrease in production of char and water.

Figure 5.5 includes the char yield data of the artificial wood cylinders as function of the cylinder diameter. First the experimental data of the artificial wood cylinders with a solid metal wall (called artificial sw cylinder in the further text and in the figure) with diameters between 6 and 14 mm are discussed and later the data of the artificial wood cylinders made completely from wire-mesh (called artificial wm cylinder in the further text and in the figure). It appears that the char yields of the artificial sw cylinder and the wood cylinders of equal diameter are comparable and could be considered equal, within the accuracy of the data. We have shown that the internal heating rate for a cylinder with a certain diameter is almost identical for the wood cylinders and the artificial sw cylinders (see section 5.2.2. Preparation and characteristics of the metal cylinders**)**. Hence, comparing the results for a fixed diameter should indicate the effect of the difference in micro-structure. It can be concluded that the micro-structure has no notable effect on the char yield of large cylinders (6-14 mm). The experimental results (see Figure 5.5) show that char yield of the wood and artificial wood cylinders is predominantly determined by the outer cylinder diameter; larger particles have a lower heating rate giving a lower average temperature at which the pyrolysis reactions run, leading to more char.

Artificial wm cylinders with diameters of 6-14 mm, filled with 140 micron milled particles, were used to study the effect of outflow pattern by comparison with the artificial sw cylinders (isotropic vs. anisotropic outflow). The hypotheses was that if vapors / aerosols can escape from the artificial cylinder in an isotropic manner, this results in overall less contact of the formed vapors/aerosols with char, because of the shorter outflow distances, and therewith less total char due to less (poly)-condensations of these vapors / aerosols on char. This is not contradicted by our data (the char yields of artificial wm cylinders of 10 & 14 mm lay below the yields of the artificial sw cylinders), but the observed effect is not very strong.

The length of the artificial sw cylinders with a diameter (ID) of 0.5 mm was varied between 10-50 mm. As can be seen from Figure 5.3, the milled particles of < 0.08 mm inserted in the artificial cylinders only consist out of cell wall. The milled particles of 0.5 mm actually contains both particles with intact channels and some particles that consist only out of cell wall material. For the 0.5 mm artificial sw cylinder with lengths of 50 and 20 mm, the char yield is higher compared to the 0.5 mm milled particles. This may be ascribed to the longer outflow distance of the vapors leading to more polymerization (char formation) on the internal milled particles, as compared with the milled particles used as such which had a length much shorter than 5 mm.

When the length of the 0.5 mm artificial sw cylinder is 10 mm, the char yield decreases further and is below the char yield of the 0.5 mm milled particles. This cannot be explained on basis of the outflow distance of vapors/aerosols. The length of 10 mm (artificial sw cylinder) is much longer than the length of the 0.5 mm milled particles . If polymerization of vapors/aerosols in the pores (of the milled particles) or over the internal milled (char) particles of the artificial sw cylinder is dominant, this would lead to more char for the artificial sw cylinder. We observed the opposite experimentally. As mentioned before, the heating rate of this artificial cylinder is considerably lower than the corresponding natural wood cylinder because of the high mass of the steel wall. Lower heating rates are typically reported to result in more char. Again, we observed the opposite. Based on these two observations it is argued that, if polymerization of vapors/aerosols and heating rate are not dominating phenomena, the micro-structure of the 0.5 mm artificial sw cylinder (filled with < 0.08 mm milled particles) remains as an important factor controlling the char yield.

5.4 Conclusion

The effect of particles geometry and micro-structure on the fast pyrolysis of beech wood was investigated in a fluidized bed reactor operated at 500^{o}C. When the particle size is decreased from 1 to 0.25 mm, the pyrolysis oil yield and organic yield increases rapidly mostly due to the increase in production of levoglucosan and water insolubles. In contrary the char and gas yield decreases rapidly. The wood microstructure is a major factor controlling the release of vapors/aerosols from the converting wood of 1 to 0.25 mm. For the very small particles pure cell wall material is pyrolyzed resulting in less transport resistance of vapors / aerosols leaving the particle compared to particles that are intact and have their original cell structure which includes channels. For particles sizes between 1 and 5 mm, only little changes in all product yields were observed. When the particle size is further increased the oil and organic yield decreases further while the char and gas yield increases. In this particle size regime the release of the vapors is almost not influenced by the microstructure and vapor outflow pattern, but mostly by internal heat transfer limitations.

5.5 References

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Chapter 6

Controlling the Water Content of Biomass Fast Pyrolysis Oil

Abstract

Several methods to control the water content of pyrolysis oil from fast pyrolysis of biomass were evaluated experimentally. Parameters varied were the operating temperature of the condenser, the gas load of the condenser, and the moisture content of the feedstock. Experiments were performed in a continuous bench scale plant (1 kg/h intake) equipped with a fluidized bed reactor. Pine wood with moisture contents between 0 wt% and 20 wt% (as-received basis) was used as feedstock. The mass balance closure was between 94 wt% and 102 wt%, and the reproducibility of yields of identical experiments was good. Increasing the condenser temperature (15-90°C) and increasing the gas load (2.0-4.1 kg of gases/kg of vapors in the condenser feed) of the condenser are both well suited to control the water content. However, decreasing the water content by these measures always results in a loss of organic vapors, leading to a lower oil yield in the condenser. Deep drying of the feedstock is beneficial; a lower moisture content of the feed results in less loss of organic vapors for the same water content of pyrolysis oil. Experimental results were compared with the predictions of an equilibrium flash condensation model. Predictions of this equilibrium model are in good agreement with the experimental results. All input parameters of the model (reactor yields and composition of the organics in pyrolysis oil) can be measured, or are known, with sufficient accuracy.

6.1 Introduction

Fast pyrolysis is a promising process to produce transportable oil with a high volumetric energy density from bulky and inhomogeneous biomass.[1-3] There are several applications foreseen for pyrolysis oil. It has been tested as a substitute for fuel oil or diesel in boilers, furnaces, engines, and turbines for heat and power generation [2,4-6] and has been considered as a precursor for transportation fuels and chemicals.[2,7,8] Water is the most abundant component in pyrolysis oil; typically it is present in the range of 15-35 wt%[1,4,9]. Probably all applications require different specifications with respect to the water content of pyrolysis oil. For fueling into a diesel engine, for instance, Oasmaa et al.[5] and Oasmaa and Czernik[10] reported that the water content should be below ca. 30 wt% to decrease emissions of particles and to prevent ignition delay and phase separation, but that there should be also a minimum amount of water present to limit NO_x emissions and to ensure a uniform temperature distribution in the cylinders. For co-feeding pyrolysis oil in a mineral oil refinery, nearly all water and most organically bound oxygen must be removed. [7,8] Generally, less water is beneficial for the energy density, transportation costs, stability, and acidity of pyrolysis oil[10]. Below 15 wt%, the viscosity (at 20°C) increases exponentially. Oil containing 4 wt% water, for example, has a viscosity of ca. 80 000 cP (at 20°C), which could cause problems in pumping and processing.

The objective of this paper is to evaluate several options, available within the pyrolysis process, to control the water content of pyrolysis oil. The temperature and gas load (kilograms of gases per kilogram of vapors in the condenser feed) of the condenser are tested as process variables to steer the water content of pyrolysis oil. Pine wood with moisture contents between 0 and 20 wt% is used as feedstock.

Pyrolysis experiments have been performed in a continuous bench scale pyrolysis plant (intake = 1 kilogram of biomass per hour) equipped with a fluidized bed reactor. The experimental results obtained are compared with the predictions of an equilibrium flash condensation model.

6.2 Experimental Section

6.2.1 Materials.

Silica sand with a mean diameter of 250 μm and a particle density of 2600 kg/m^3 (bulk density = 1600 kg/m^3) was used as bed material. Pine wood was purchased from Rettenmaier & Söhne GmbH, Germany. The pine wood particle density was 570 kg/m$_{particles}^3$, and the number-average particle size was 1 mm (maximum size = 2 mm). The composition of the pine wood used is listed in Table 6.1.

Table 6.1: *Composition of pine wood.*

Bio-chemical composition (wt%, dry)	
Cellulose	35
Hemicellulose	29
Lignin	28
Ultimate analysis (wt%, daf)	
C	46.58
H	6.34
O (by difference)	46.98
N	0.04
S	0.06
Alkali metals (mg/kg, dry)	
K	34
Mg	134
Ca	768
Total ash	2600

The moisture content of the wood was adjusted by the following methods. To obtain 0 wt%, the pine wood was dried completely in an oven at 105°C[11] for at least 24 h. To achieve a moisture content of 12 or 20 wt%, biomass was contacted with a demineralized water spray in a closed vessel. This method is described in detail by Diego et al.[12]. Moisture contents within the following ranges could be realized: 12 ± 1 and 20 ± 1 wt%. All biomass feeds were analyzed for moisture content by drying in an oven at 105°C for at least 24 h. Water contents are always reported on an as-received basis (ar).

6.2.2 Continuous Bench Scale Plant.

A continuous fast pyrolysis bench scale plant with an intake of 1 kg/h biomass (ar) has been designed, constructed, debugged, and operated. This plant is schematically shown in Figure 6.1.

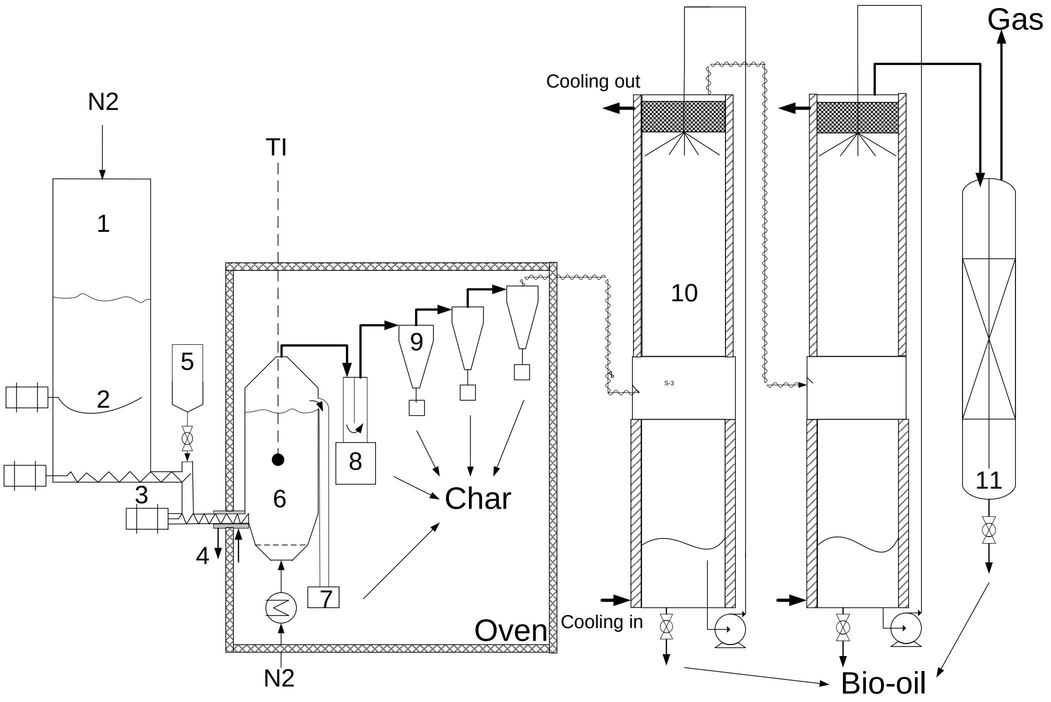

Figure 6.1: *Schematic drawing of the pyrolysis plant; (1) Biomass storage hopper, (2) Mechanical stirrer, (3) Feeding system, (4) Cooling jacket, (5) Sand storage/feeding system, (6) Fluidized bed reactor, (7) Overflow, (8) Knock-out vessel, (9) Cyclones, (10) Counter current spray condensers with cooling jackets, (11) Intensive cooler.*

The biomass was stored in a hopper with a capacity of 4 kg. A slowly rotating stirrer inside this hopper prevented biomass particles from sticking together and forming bridges. A small nitrogen gas flow was fed to the biomass hopper, creating a slight overpressure, which prevented vapors and gases from flowing from the fluidized bed pyrolysis reactor to this hopper via the double screw feeding system. The first screw of this feeding system was used to transport the biomass from the biomass hopper and to mix this biomass with sand. Sand was stored in a second hopper and was fed to the screw with a calibrated valve. The second screw transported the biomass/sand mixture into the reactor. A water-cooled stainless steel jacket at the end of this screw (at the connection with the reactor) prevented biomass from pyrolyzing already inside it. Sand was added to control the char holdup in the fluidized bed. By feeding 2 kg of sand per kg of wet biomass, the char holdup in the reactor could be kept between 0.15 and 0.20 m^3 of char/m^3 of sand. The char holdup was measured by analysis of the reactor content after an experiment for the mass and density of char and sand. It is important to control and know the char holdup as char catalyzes the cracking of pyrolysis vapors leading to a lower oil yield13 and influences the fluidization behavior.

The fluidized bed reactor was made from stainless steel 316 with a main diameter of 100 mm and a total height of 420 mm. It had a conical bottom part to ensure fluidization while minimizing the use of additional preheated fluidization gas (N_2), which was fed through a sintered metal plate. A mass flow controller was used to set the feed rate of the fluidization gas. The biomass was fed, in the conical bottom (see Figure 6.1). Typical superficial gas velocities (fluidization gas, vapor, and produced gas) in the cylindrical part were in the range of 0.09-0.17 m/s. Other operating conditions and parameters are listed in Table 6.2.

Table 6.2: *Operating conditions fluidized bed.*

parameters	**values**	**units**
Experimental time	120	min
$M_{sand, initial}$	2.1	kg
Bed height	0.250	m
Bed diameter	0.1	m
U	0.09-0.17	m/s
U/U_{mf}	3-5	-
$\tau_{reactor}$	0.57-1	s
τ_{hot}	0.97-1.66	s
$T_{reactor}$	480	^oC
$T_{cyclones}$	500	^oC

In the fluidized bed, five thermocouples were installed at different heights to monitor the temperature. During a run, the difference in temperature between these thermocouples never exceeded 20°C. The temperature at the center of the bed was defined as the reactor (fluidized bed) temperature, $T_{reactor}$ (see Figure 6.1). A solids overflow tube kept the bed level constant. Sand and char particles removed via this tube were collected in a vessel. The vapor/gas stream leaving the reactor contained sand fines and about 20 wt% of the produced char. In a knockout vessel, all of the sand and most of the char particles were removed and collected. A downstream series of three cyclones, equipped with collection vessels, removed almost all residual char particles. The reactor, the solids overflow vessel, the knockout vessel, and the cyclones were thermostated in the same oven. The fluidized bed temperature ($T_{reactor}$) was used as the set point for the oven's control loop.

The nearly particle-free hot vapor/gas stream was condensed in a jacketed counter-current spray column (length 1.68 m, diameter 0.07 m). The temperature of this condenser could be controlled with an accuracy of 1°C by pumping thermostated BP thermo-oil (Transcal SA) through the jacket. An on-line pressure indicator registered the pressure in the condenser during the run. The temperature was measured in the outgoing vapor/gas stream just after leaving the condenser. Shell Ondina 941 oil was used as spraying and startup liquid, because it has a low solubility in pyrolysis oil and therefore facilitated nearly full decantation of the pyrolysis oil produced. The circulation rate of Shell Ondina 941 oil was 5 L/min. The first condenser is hereafter referred to as the main condenser or simply as the condenser. With this condenser, the effects of operating temperature and gas load on the water content of pyrolysis oil have been investigated. The outgoing vapor/gas flow of the First condenser was led through another condenser (identical design to the first one) operated at 20°C and an intensive cooler kept at 0°C placed in series. These were installed to collect the remaining liquid in order to complete the mass balance. The volumetric flow rate of the gas leaving the intensive cooler was measured with a dry gas flow indicator. A small sample of this stream was pumped through a gas analysis unit. On-line analyzers were used to measure CO, CO_2, CH_4, and H_2. A gas chromatograph was used to analyze C_2 and C_3 hydrocarbons off-line.

6.2.3 Analysis of Produced Pyrolysis Oils.

The oils collected in the condensers and the intensive cooler were analyzed for water content by Karl Fischer titration (titrant: Hydranalcomposite 5). On some oils, extraction experiments were performed by contacting demineralized water and pyrolysis oil at different phase ratios while stirring at room temperature. After agitation, the samples were allowed to settle for 2 h at room temperature in closed bottles to avoid evaporation of volatile components. Each of the phases was decanted in a separatory funnel, weighted, and analyzed for water content.

6.2.4 Mass Balance and Yield Calculations.

Product yields *Y* were determined on both as-received basis (ar) and dry basis (dry). These yields are related by:

$$Y_{dry} = \frac{Y_{ar}}{(1 - f_{w,\,biomass})} \tag{1}$$

$$Y_{\text{dry}} \equiv \frac{\text{kg of product formed}}{\text{kg of biomass(ar) consumed} \cdot (1 - f_{\text{w, biomass}})} \qquad (2)$$

Hereafter, only the formulas on dry basis are given. The amount of biomass fed to the reactor during a test was known by measuring the amount of biomass present in the hopper before and after the test. After an experiment, the char present in the reactor, the overflow vessel, the knock-out vessel, and the collecting vessels of the cyclones was collected and weighed. The char yield was defined by:

$$Y_{\text{char, dry}} = \frac{\sum\limits_{\text{reactor, overflow, knock-out, cyclones}} \text{kg char collected}}{\text{kg of biomass(ar) consumed} \cdot (1 - f_{\text{w, biomass}})} \qquad (3)$$

The amount of gas leaving the setup (after the intensive cooler) and its composition were measured continuously by a dry gas meter and on-line infrared and thermal conductivity detector (TCD) analyzers (CO, CO_2, CH_4, H_2), respectively. C_2 and C_3 hydrocarbons were measured at intervals of 15 min with a gas chromatograph (GC). On the basis of these data and the known flow rate of nitrogen fed to the fluidized bed, the gas yield was calculated:

$$Y_{\text{gas,dry}} = \frac{\int_{t_0}^{t_{\text{end}}} \left(\left(\Phi_g \cdot \frac{P}{R \cdot T} \right)_{\text{out}} - \left(\Phi_g \cdot \frac{P}{R \cdot T} \right)_{\text{in}} \right) \cdot \sum\limits_{\text{gas components}} (X \cdot M) \, dt}{\text{kg of biomass(ar) consumed} \cdot (1 - f_{\text{w, biomass}})} \qquad (4)$$

During an experiment, the condensed liquids remained in the condensers and intensive cooler. After an experiment, the liquids removed from the condensers and intensive cooler and the produced oil were separated from the Shell Ondina 941 oil. Hereafter the produced oils were weighed and analyzed for water content. These data provided the yields of pyrolysis oil,

$$Y_{\text{organics in pyrolysis oil, dry}} = \frac{\sum\limits_{\text{condensers, intensive cooler}} \text{kg liquid collected} \cdot (1 - f_w)}{\text{kg of biomass(ar) consumed} \cdot (1 - f_{\text{w,biomass}})} \qquad (5)$$

$$Y_{\text{pyrolysis oil, dry}} = \frac{\sum\limits_{\text{condensers, intensive cooler}} \text{kg liquid collected}}{\text{kg of biomass(ar) consumed} \cdot (1 - f_{\text{w, biomass}})} \qquad (6)$$

$$Y_{\text{producedwater, dry}} = Y_{\text{pyrolysisoil,dry}} - Y_{\text{organicsin pyrolysisoil,dry}} - \frac{f_{\text{w,biomass}}}{1 - f_{\text{w,biomass}}} \tag{7}$$

The sum of $Y_{\text{char, ar}}$, $Y_{\text{gas, ar}}$ and $Y_{\text{pyrolysi oil, ar}}$ defines the mass balance.

The moisture content in the condensable feed stream of the first condenser (f_{w}, feed) is calculated from the amount and water content of the liquids collected in the first and second condenser and the intensive cooler:

$$f_{\text{w,feed}} = \frac{\sum [\text{kg of liquid collected} \times f_{\text{w}}]_{\substack{\text{1st condenser,}\\ \text{2nd condenser,}\\ \text{intensive cooler}}}}{\sum\limits_{\substack{\text{1st condenser,}\\ \text{2nd condenser,}\\ \text{intensive cooler}}} [\text{kg of liquid collected}]} \tag{8}$$

6.3 Condenser Model

The condenser is modeled as an equilibrium flash separator. In this unit, the hot reactor effluent is cooled and partially condensed at constant temperature and pressure leading to phase separation. Because the qualitative and quantitative composition of pyrolysis oil is not known, the assumption of reaching equilibrium is a conjecture that is difficult to prove experimentally. However, whether the design of the condenser allows reaching equilibrium between the outgoing liquid and vapor stream can be checked by performing tests with model feeds. Nitrogen/steam and nitrogen/steam/ethanol vapor mixtures with flow rates corresponding to the ones in the pyrolysis experiments (steam and ethanol representing pyrolysis oil) were fed to the condenser at different temperatures. The amounts of water and liquid ethanol that were collected from the condenser after these tests corresponded well with the predictions of the model described below. This result shows that reaching phase equilibrium between the outgoing streams is possible for model feeds in the condenser. It is assumed further that this also holds for pyrolysis vapors.

The product compositions and flow rates of the vapor (y_i, V) and liquid (x_i, L) streams leaving the condenser are predicted with the so-called Rachford-Rice equation:[14]

$$f\left(\frac{V}{F}\right) = \sum_{i=1}^{C} \frac{z_i \cdot (1 - K_i(T,p))}{1 + \frac{V}{F} \cdot (K_i(T,p) - 1)} = 0 \tag{9}$$

Besides thermal ($T_L = T_V$) and mechanical ($p_L = p_V$) equilibrium, the model assumes phase equilibrium and ideal behavior of both vapor and liquid phases such that the partition ratios (K_i) are independent of composition:

$$K_i(T,p) \equiv \frac{y_i}{x_i} = \frac{p_i^{\bullet}(T)}{p} \tag{10}$$

This is probably a reasonable assumption because the weight fraction of most individual components in the oil hardly exceeds 1%, as a result of which each component could behave as a diluted species in a bulk liquid that contains all the other components. For water, which is present up to 35 wt%, this reasoning does not hold. Nevertheless, it was assumed that water also behaves ideally.

In equation 9 and 10, the molar composition (z_i) and molar flow rate (F) of the condenser feed as well as the condenser temperature (T) and pressure (p) should be specified. Temperature and pressure were measured. The amounts of water, fluidization gas (N_2), and the amount and composition of product gases in the condenser feed were known from the overall measured mass balance. Gases are defined here as species that cannot condense at the condenser temperatures tested (15-90°C). The amount of organic vapors (species that can condense at the used condenser temperature range) in the condenser feed is also known from the mass balance, but the composition of this organic fraction is not measured. Our laboratory is not equipped with advanced liquid analysis apparatus. Therefore, the composition of the organic fraction in the condenser feed is collected from literature data. To fill in the organic fraction in the model, we have chosen pyrolysis oils from the literature that (i) represent almost all organics produced in the pyrolysis reactor (i.e., liquid condensed at low temperature in a condenser operating at equilibrium or the blend of liquids collected in several condensers), and (ii) were produced from the same feedstock (pine wood) in similar reactor configurations (fluidized/ transported bed) under comparable operating conditions. About 40 wt% of the organics in pine wood pyrolysis oil produced by Dynamotive (fluidized bed, $T_{reactor}$ = 460°C) have been identified on a component level by a round robin study[15]. It should be mentioned here that the quantitative chemical analysis results at the level of individual components of the laboratories involved in the round robin were not very consistent. For the condenser model, the identified and quantified components are grouped into normal boiling point ranges; see Table 6.3.

Table 6.3: *Organic component groups used in the condenser model*

Group	Normal Boiling Point [K]	Components	Vapour pressure component (N.b.p. [K])	Molecular weight [g/mol]	Appearance in organic condenser feed [wt%, daf]
IO1	250-300	formaldehyde, acetaldehyde	formaldehyde (253.9)	31.4	1.2
IO2	300-330	propionaldehyde, glycolic acid, glyoxal, acetone	Propionaldehyde (322)	65.4	0.9
IO3	330-360	Methanol, 2-oxobutanoic acid, ethanol, MEK, 2-propanol, (5H)-furan-2-one	Ethanol (351.6)	48.4	3.3
IO4	360-390	formic acid, hydroxyacetaldehyde, 5-hydroxymethylfurfural	formic acid (373.9)	61.6	9.2
IO5	390-420	acetic acid, butanol, lactic acid, 4-propylguaiacol, propionic acid, acrylic acid, acetol	propionic acid (414.2)	71.0	18.0
IO6	420-450	isobutyric acid, 2-hydroxy-2-cyclopentene-1-one, 2-hydroxy-1-methyl-1-cyclopentene-3-one, 1-hydroxy-2-butanone, furfural, methacrylic acid, N-butyric acid, coniferylaldehyde	n-butric acid (436)	105.8	2.9
IO7	450-500	Phenol, crotonic acid, valeric acid, 3-hydroxypropanoic acid, o-cresol, tiglic acid, 4-methylpentanoic acid, p-creosol, m-creosol, hexanoic acid, guaiacol, 4-hydroxybenzaldehyde, 4-methyl guaiacol, vinylguaiacol	p-cresol (475)	125.3	2.5
IO8	500-550	4-ethyl guaiacol, 1,2-benzendiol, levulic acid, benzoic acid, eugenol, syringol, vanillin, isoeugenol (cis + trans)	Eugenol (526)	150.9	2.4
Sugar constituents 1		Levoglucosan, glucose, xilose, cellobiosan, hydroquinone, ...	Hydroquinone (558)	160 (levoglucosan)	17.3
Sugar constituents 2	∞	Some components identified, no qualitative data on component level[a]	$p^{\bullet} = 0$	320	17.3
LMM Lignin	∞	Idem[a]	$p^{\bullet} = 0$	450	18
Extractives	∞	Idem[a]	$p^{\bullet} = 0$	460	3
HMM lignin	∞	Idem[a]	$p^{\bullet} = 0$	1050	4

[a] From reference 16.

A group is represented in the condenser model by its vapor pressure and molecular weight. For the vapor pressure curve a component in the middle of the boiling point range is selected; the group's molecular weight is the mass-average molecular weight of the components within the group. At the level of these groups the results of the round robin were more dependable. We used average values from laboratories 3 and 9 if available; if not, the results from laboratory 12 were taken.

The missing 60 wt% of the organics are defined as sugar constituents, extractives, low molecular weight lignin, and high molecular weight lignin as obtained from fractionation experiments done on pine wood pyrolysis oil produced by VTT (transported bed, $T_{reactor}$ = 520°C, residence time of pyrolysis vapors is 1-2 s)[16]. According to VTT analysis these component groups add up to about 65 wt% (daf) of the organics in pine oil. We copied their measured weight percent of extractives, low molecular weight lignin, and high molecular weight lignin. The average molecular weight of these groups is known[16,17] and is high enough to allow the assumption of a zero vapor pressure in the condenser. The sugar constituents fraction as measured by VTT is lowered by 5 wt% (making the total 100%) while assuming that some of these components are already present in the round robin list. These sugar constituents are split into two equal parts: one with the vapor pressure of hydroquinone and one with zero vapor pressure. In Table 6.3, the groups of organic components used in the condenser model together with their characteristics are listed.

6.4 Results

6.4.1 Mass Balance Closure and Reproducibility.

In total, 41 experiments were performed without operational problems. It was decided beforehand that the mass balance closure must be between 94% and 102% for proper interpretation of the results. Of the 41 experiments, 7 were outside the desired mass balance closure limits and have been rejected consequently.

Reproducibility was checked by repetition of nine experiments under identical reactor conditions and using the same feedstock (12 wt% moisture), but different operating temperatures of the first condenser.

Of these tests the average yields on dry basis are 14, 72, and 24 wt% for char, pyrolysis oil, and gas, respectively. These yields lie in the range of fluidized bed fast pyrolysis yields reported in the literature[18]. Our process conditions were, however, not optimal for maximizing the pyrolysis oil yield. Due to the fact that both the reactor and the char separation units (knock-out vessel + cyclones) were placed in the same oven, the temperature of these units was ca. 500°C while the temperature in the fluidized bed was 480°C. At 500°C, cracking of pyrolysis vapors to gases can be significant,[19-21] lowering the pyrolysis oil yield and increasing the gas yield.

The statistics of the nine identical tests provides an estimate of the reproducibility of an individual experiment (see Figures 6.2 and 6.3). Table 6.4 lists the average yields, standard deviations, and the relative spread $(\frac{\sigma_{Y_{dry}}}{\overline{Y}_{dry}} \cdot 100\%)$. The relative scatter on the char, gas, and pyrolysis oil yield is less than 8%, showing that the reproducibility of the experiments is good. The relative spread on the yield of produced water is somewhat larger (11%), but is still low enough for trend detection on the basis of single experiments. In this work, trends in yields based on single measurements as a function of the operating conditions are considered sound only if they exceed σ of the repetitive measurements reported in Table 6.4.

These nine experiments also show that the condensation train of two condensers and one intensive cooler in series Works well: with this train we can collect all the products ultimately, under all conditions of the first condenser (see Figures 6.2 and 6.3).

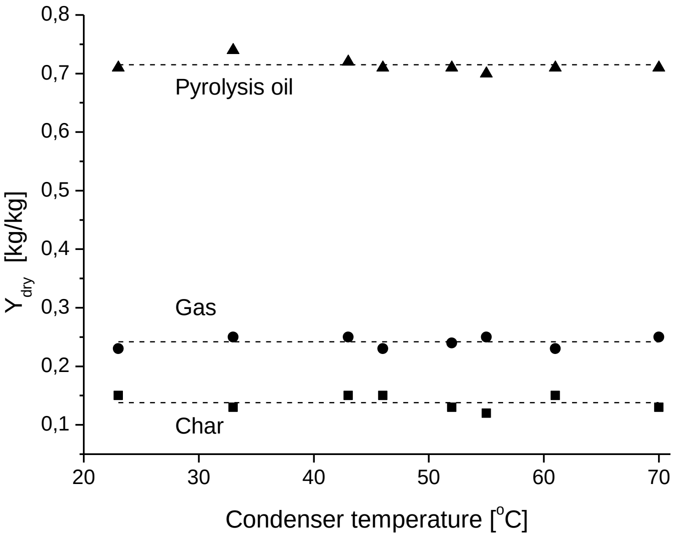

Figure 6.2: *Yields of char, gas and pyrolysis oil of 9 identical experiments with respect to the reactor conditions, but different temperatures of the condenser. Conditions:* $T_{reactor} = 480\ ^oC$, $T_{cyclones} = 500\ ^oC$, $\tau_{hot} = 1.32$ s, $\tau_{reactor} = 0.78$ s, *moisture content feed = 12 wt%. The dashed lines represent the average value of the 9 experiments.*

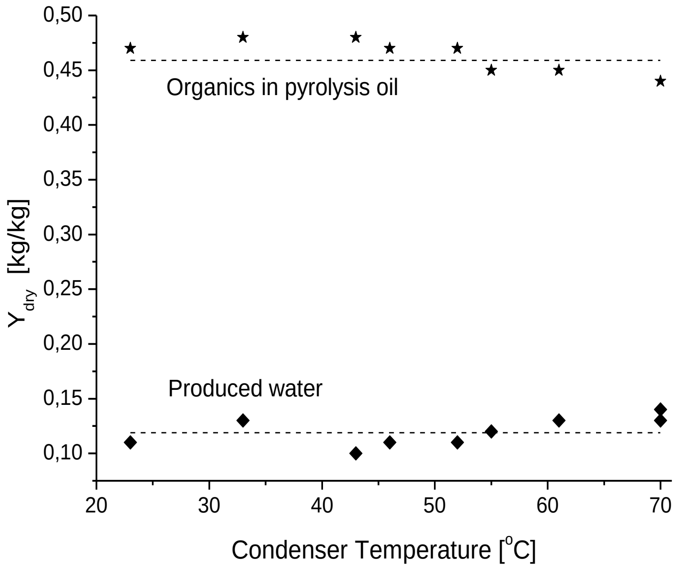

Figure 6.3: *Yields of organics in pyrolysis oil and produced water of 9 identical experiments with respect to the reactor conditions, but different temperatures of the condenser. Conditions:* $T_{reactor}$ *= 480* °C*,* $T_{cyclones}$ *= 500* °C*,* τ_{hot} *= 1.32 s,* $\tau_{reactor}$ *= 0.78 s, moisture content feed = 12 wt%. The dashed lines represent the average value of the 9 experiments.*

Table 6.4: *Reproducibility of 9 identical experiments with respect to the reactor conditions* $T_{reactor}$ *= 480* °C*,* $T_{cyclones}$ *= 500* °C*,* τ_{hot} *= 1.32 s,* $\tau_{reactor}$ *= 0.78 s, moisture content feed = 12 wt%* [a]

Products	Average yield $\overline{Y}_{dry}$ [kg/kg]	Standard deviation $\sigma_{Y_{dry}}$ [kg/kg]	*Relative spread* $\frac{\sigma_{Y_{dry}}}{\overline{Y}_{dry}} \cdot 100\%$ *[%]*
Char	0.14	0.010	*7.6*
Gas	0.24	0.009	*3.7*
Organic in pyrolysis oil	0.46	0.017	*3.7*
Produced water	0.12	0.013	*11.4*
Pyrolysis oil (organics + total water)	*0.72*	*0.01*	*1.4*

[a] The condenser temperature varied 15-70°C.

6.4.2 Effect of the Operating Conditions on the Yields.

The reactor yields of gas, organics in pyrolysis oil, and produced water are input parameters for the condenser model. In this section, it is reported if and how these yields are affected by the varied operating conditions.

6.4.3 Moisture Content of the Feedstock.

The effect of the moisture content of the feedstock (range 0-20 wt%) on the yields of char, gas, and pyrolysis oil, the latter subdivided into the organic fraction and produced water, is shown in Figure 6.4. All data points presented are averages of at least three experiments. In this experimental series, the reactor conditions were kept constant (T_{reactor} = 480, τ_{hot} = 1.32 s), but the operating temperature of the condenser varied. It has been shown, however, that the latter variation does not affect the yields (see section 6.4.1, "Mass Balance Closure and Reproducibility"). With increasing moisture content of the feedstock, it has been observed that the char and gas yield increase, the produced water yield decreases, and the yield of organics in pyrolysis oil remains constant (see Figure 6.4). Gray et al.[22] also observed that more moisture in the feed results in an increased char yield. The increase in char and produced water yield can be explained partly from the pyrolysis process at the particle level. Our single particle pyrolysis model[3] shows that the effective pyrolysis temperature of a biomass particle with a characteristic length between 1 and 2 mm and reacting at ca. 500°C decreases upon increasing the moisture content, because of the energy consumption of water vaporization. The effective pyrolysis temperature is the volume-averaged value of the local temperature at which the reaction rate is maximal. If there are heat transfer limitations to or within the particle, the effective pyrolysis is lower than the reactor temperature. Kersten et al.[3] have shown that evaluation of the intrinsic kinetics at the effective pyrolysis temperature provides a good estimate of the yields predicted by a full model including, next to kinetics, also transport parameters. Several kinetic studies[23-25] have shown that, starting from a pyrolysis (fluidized bed) temperature of 480°C, a lower pyrolysis temperature increases the char yield. Combining this trend of the intrinsic kinetics with the model predictions regarding the lower effective pyrolysis temperature for wetter biomass explains the measured increase of the char yield for feeds with a higher moisture content. However, the absolute effect predicted by the model is only half of the measured effect. Bridgwater et al.[26] collected experimental data indicating that a decreasing temperature in the range of 500-400°C results in a lower yield of produced water. The increase in gas yield and the constant yield of organics in pyrolysis oil cannot be explained unequivocally by the present knowledge of fast pyrolysis.

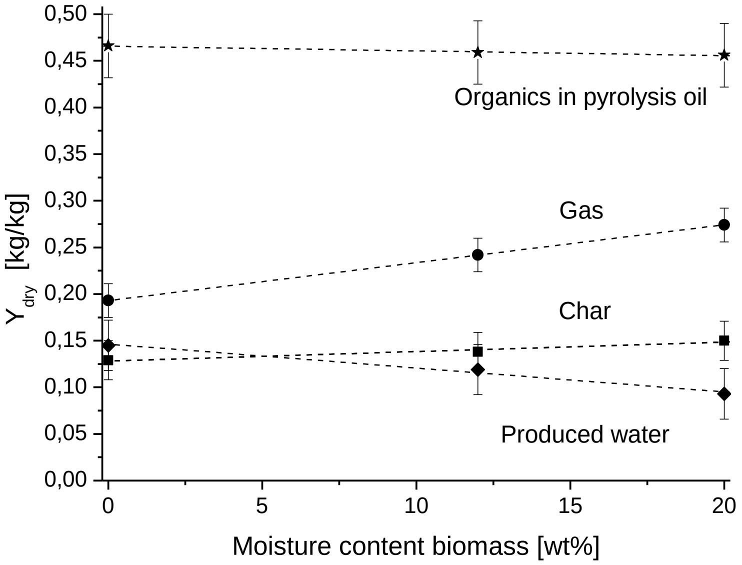

Figure 6.4: *The effect of the moisture content of the feedstock on the yields of char, gas, produced water, and organics in pyrolysis oil. Conditions:* $T_{reactor} = 480\ ^oC$, $T_{cyclones} = 500\ ^oC$, $\tau_{hot} = 1.32$ s, $\tau_{reactor} = 0.78$ s, *moisture content feed = 0-20 wt%. The condenser temperature varied between 15-90* ^oC. *Condenser feed: 2.90 - 3 kg gasses / kg vapours. Dashed lines represent trends.*

6.4.4 Vapor Residence Time.

To steer the water content of pyrolysis oil, variation of the gas load (sweep gas) of the condenser is tested (see section 6.4.8, “Gas Load of the Condenser”). The additional gas was fed to the fluidized bed reactor which influenced the residence time of the produced pyrolysis vapors at high temperature. A higher residence time of vapors might influence the product distribution through cracking reactions (overall first order) of these vapors. In this experimental series the residence time of vapors varied between 0.97 and 1.66 s. From the results obtained, it can be concluded that within this range the yields are not affected by the vapor residence time (see Figure 6.5), especially when considering the scatter on individual data points (see section 4.1, “Mass Balance Closure and Reproducibility”). Also, Scott et al.[27] found that, at temperatures of 500°C and below, the vapor residence time studied does not have a significant effect on the yield of pyrolysis oil.

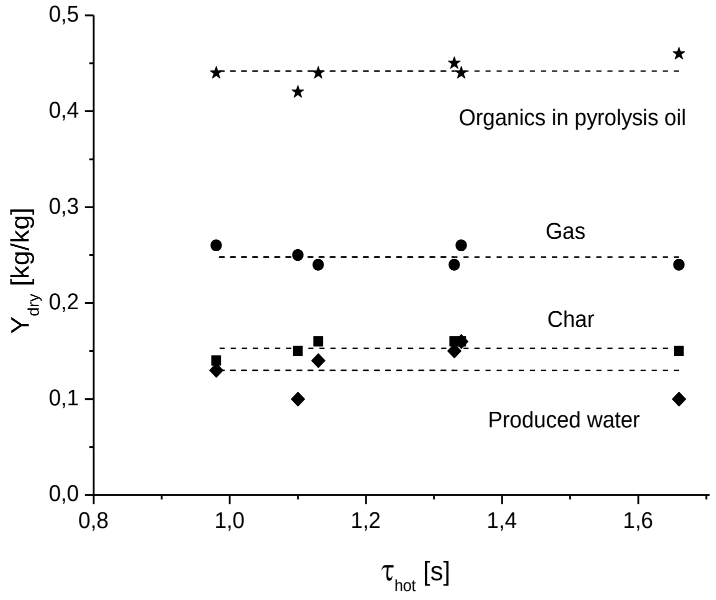

Figure 6.5: *The effect of residence time on yields of gas, char, organics in pyrolysis oil, and produced water. Conditions:* $T_{reactor}$ *= 480* ^{o}*C,* $T_{cyclones}$ *= 500* ^{o}*C, moisture content feed 12 wt%. The condenser temperature = 50* ^{o}*C. Dashed lines represent average values.*

6.4.5 Steering the Water Content of Pyrolysis Oil.

Below, the results of the investigated methods to manipulate the water content of pyrolysis oil are reported and discussed.

6.4.6 Extraction of Pyrolysis Oil.

As reference for the other methods investigated to remove water from pyrolysis oil, extraction of pyrolysis oil with water has been investigated experimentally. The conclusion concerning this method, though, could have been drawn also on the basis of phase diagrams of pyrolysis oil presented in the literature[1,10]. If single phase pyrolysis oil is extracted with enough water (ca. 30 wt% water in the total liquid), phase separation occurs. Just after decantation, the obtained hydrophobic phase contains 20 wt% water, independent of the initial water content, showing that the water content (can be up to 35 wt% initially) can be decreased by extraction. However, from the offset of phase splitting, the organics in pyrolysis oil are distributed with a partition ratio that hardly depends on the amount of water added over the hydrophilic phase (containing ca. 45% of the organics) and hydrophobic phase (containing ca. 55% of the organics). Concluding, although the water content of pyrolysis oil can be lowered by extraction with water, it is not a feasible method because the pyrolysis yield decreases too much (50% of the organics end up in the water phase).

6.4.7 Varying the Temperature of the Condenser.

Oasmaa et al.[17] reported some exploratory results on the effect of the condenser temperature on the water content of pyrolysis oil. We present a more detailed analysis covering a broad range of condenser temperatures from 15°C to 90°C. In Figure 6.6 the water content of pyrolysis oil is plotted versus the condenser temperature in the range 15-90°C for various moisture contents of the feedstock (0, 12, 20 wt%). The used moisture contents in the feedstock correspond to 22.5, 35.7, and 42.9 wt% moisture in the condensable condenser feed ($f_{w,feed}$), respectively. All results described in this section were obtained with a gas load of the condenser of 2.90-3 kg of gases/kg of vapors in the condenser feed.

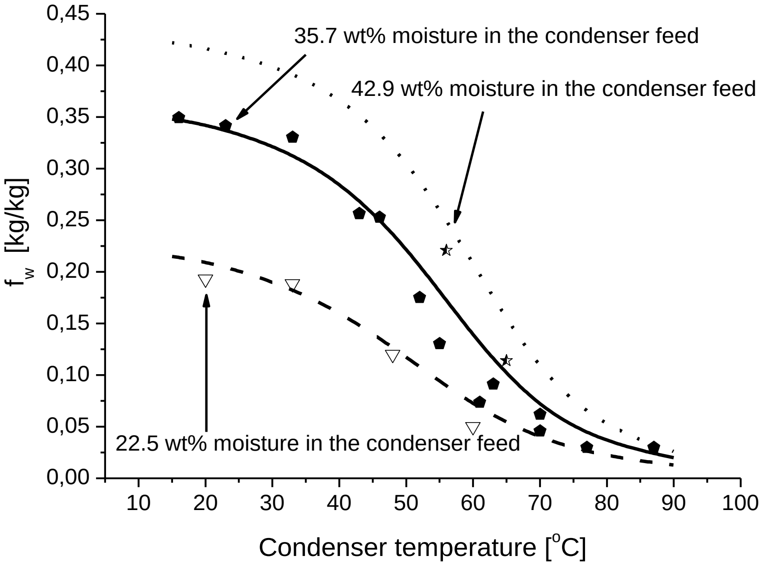

Figure 6.6: *Water content of the pyrolysis oil obtained in the (first) condenser as function of the condenser temperature. Experimental results (presented by points) are compared with model predictions (presented by lines). Conditions:* $T_{reactor}$ *= 480 °C,* $T_{cyclones}$ *= 500 °C. Condenser temperature varied between 15-90 °C.*

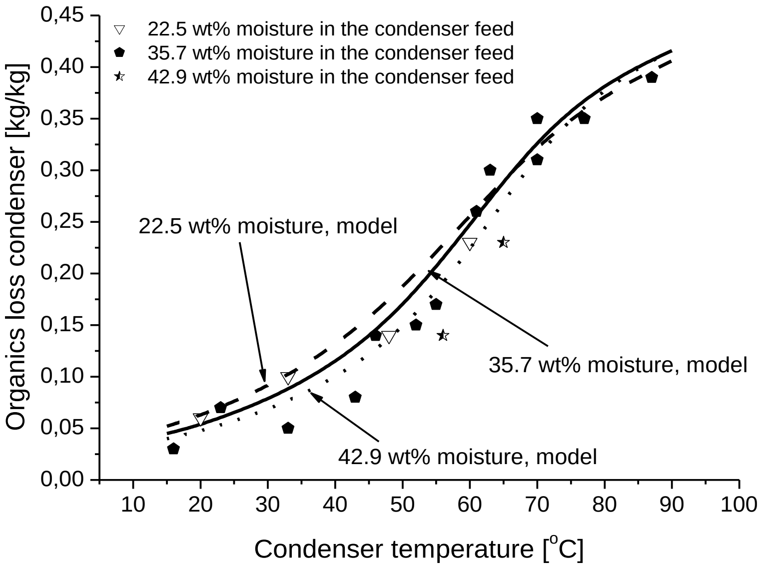

Figure 6.7: *Loss of organics from the pyrolysis oil obtained in the condenser as function of the condenser temperature. Experimental results (presented by points) are compared with model predictions (presented by lines). Reactor:* $T_{reactor}$ *= 480 °C,* $T_{cyclones}$ *= 500 °C. Condenser temperature varied between 15-90 °C.*

The water content of pyrolysis oil hardly depends on the condenser temperature in the range between 15 and 35°C (see Figure 6.6). Between 35 and 70 °C, the condenser temperature affects the water content significantly. Above 70 °C, the influence of the condenser temperature on the water content is minimal. The pyrolysis oil obtained at a condenser temperature of 90°C (water fraction of 0.03) is very viscous (viscosity = 80 000 cP) at 20°C. The agreement of the model predictions with respect to the moisture content of pyrolysis oil collected in the condenser is very good.

The average residence time of produced liquid in the condenser was ca. 1 h. Storage at elevated temperature for 1 h may affect the composition of pyrolysis oil. However, this has not been observed unequivocally in our study. The total yields of organics in pyrolysis oil and produced water are not affected by the condenser temperature (see Figure 6.3). Apparently, 1 h residence time of pyrolysis oil at temperatures of 90°C and lower is not enough to have significant condensation (polymerization) reactions in the liquid phase, yielding water and lowering the yield of organics. These results are in line with experimental results reported by Czernik et al.[28] concerning storage of pyrolysis oil at elevated temperature. They found only a slight increase in viscosity and molecular weight (5%) after storage at 90°C during 1 h. It is known that the main physicochemical changes of stored pyrolysis oil take place in the first 6 months after production and that water is formed as a by-product of condensation reactions[29]. The pyrolysis oils produced in our study were analyzed just after production and after 6 months. Over this period no significant increase in water content is observed for all pyrolysis oils (see Table 6.5).

Table 6.5: *Water content of pyrolysis oil as function of the condenser temperature and storage time.*

Condenser temperature [°C]	Water fraction pyrolysis oil just after production f_w [kg/kg*100%]	Water fraction pyrolysis oil after 6 months f_w [kg/kg*100%]
33	33.1%	34.1%
43	25.7%	25.1%
50	17.7%	17.7%
56	21.9%	22.1%
70	4.5%	4.3%

Obviously, starting with a wetter feedstock at otherwise identical operating conditions results in pyrolysis oil with higher moisture content (see Figure 6.6). This effect is small at condenser temperatures above 70°C, because then most water leaves the condenser in the vapor phase anyway. With increasing condenser temperature, not only water but also light organic volatiles are removed from the pyrolysis oil, thus decreasing the total amount of oil. The loss of these lights can be expressed as the fraction of total produced organic vapors in the condenser feed that is not collected in the first condenser. Figure 6.7 shows that, for different moisture contents of the feedstock, resulting in different moisture contents of the condenser feed, this loss increases with increasing condenser temperature. Above 80°C, the effect of the condenser temperature on the loss of organics diminishes, because most lights have left as vapors already and the heavy organics (e.g., heavy sugars, LMM and HMM lignin, extractives) still completely condense due to their high molecular weights. Also, for the loss of organic vapors from the condenser the agreement between the model predictions and the experimental data is good. At the same condenser temperature, it appears that the moisture content of the feedstock only has a slight effect on the organics fraction collected in the First condenser. In fact, below 70°C at otherwise the same conditions, a higher moisture content of the condenser feed results in a lower loss of organics vapors in the condenser. This can be explained by a lower concentration of organic vapors in the condenser inlet at increasing steam load. From the list of compounds used in our condenser model (see Table 6.3), it can be seen that the organic compounds leaving condenser 1 are low molecular weight acids, aldehydes, and ketones. Etherification and esterification reactions between hydroxyl, carbonyl, and carboxyl groups are partly responsible for the aging reactions[28]. It has been suggested by Oasmaa et al.[17] that in removing these light compounds the pyrolysis oil becomes more stable.

Maintaining the same water content of pyrolysis oil when the condenser feed contains more water (wetter feedstock) requires a higher condenser temperature at otherwise identical conditions (compare Figure 6.6 and Figure 6.7). As a result of this higher temperature, the loss of organics increases. Another method to maintain the same water content is to increase the gas load of the condenser. This is discussed in the next section.

6.4.8 Gas Load of the Condenser.

In the experimental series, the temperature of the condenser was maintained at 50°C and the load of sweep gas was varied (2.0-4.1 kg of gases/kg of vapors in the condenser feed). In the pyrolysis process this sweep gas can be (i) gas that is also led through the pyrolysis reactor (e.g., fluidization gas) or (ii) after further cooling, the gas stream leaving the condenser. In the latter recycle options further cooling of the recycle stream is required to lower the water vapor content of this gas relative to the equilibrium prevailing in the condenser. The experimental results are shown in Figure 6.8, together with model predictions. There is always a minimum amount of gas entering the condenser due to gas production in the pyrolysis process; this is indicated by the vertical dashed line in Figure 6.8. Clearly, the use of a sweep gas in the condenser lowers the water content of pyrolysis oil. However, as by increasing the condenser temperature, a decrease in water content also always results in a loss of light organics. Next to the results at a condenser temperature of 50°C, also model predictions for other condenser temperatures are included in Figure 6.8 together with individual data points. The model predictions show that at low gas loads (<1 kg/kg) a condenser temperature of at least 70°C is needed to decrease the water content of pyrolysis oil significantly. At low gas loads and such high temperatures, a small change in sweep gas load will largely affect the water content of the pyrolysis oil. This could lead to difficulties in controlling the water content. For high gas loads (>2 kg/kg), the water content can be decreased significantly at a relatively low condenser temperature of 50°C.

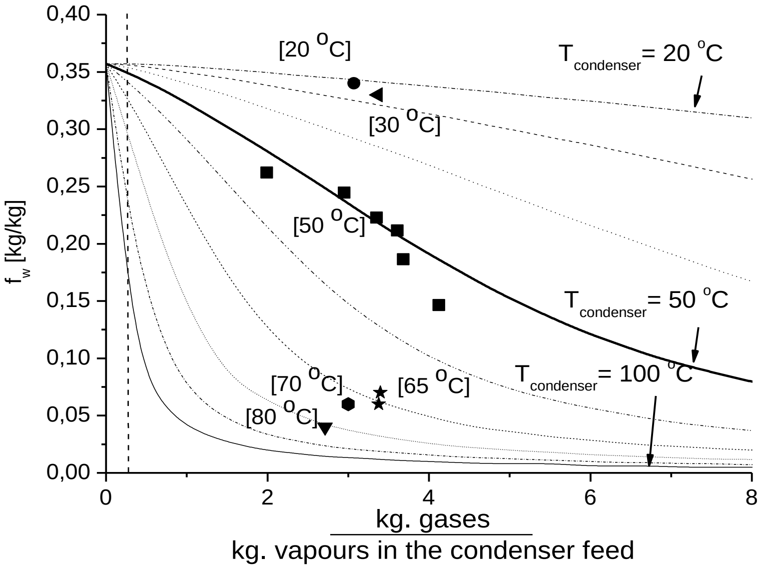

Figure 6.8: *Water fraction of the pyrolysis oil obtained in the (first) condenser as function of the gas load of the condenser. Experimental results (condenser temperatures are indicated near the data points) are compared with model predictions for condenser temperatures in the range of 15 to 100 °C. Conditions:* $T_{reactor}$ *= 480 °C,* $T_{cyclones}$ *= 500 °C, moisture content feed 12 wt%.*

6.4.9 Condenser Model Sensitivity

In this section, the condenser model sensitivity is evaluated. For this analysis, only the organic composition of the condenser feed is varied. Non-condensable gases and water in the condenser feed are (can be) known accurately enough. Gases follow from the mass balance and the water content can be estimated precisely by operating the condenser (first) at low temperature (<30°C). Figure 6.6 shows that at such low temperatures the water content of the obtained oil in the condenser (first) is nearly identical to the water content of the condenser feed, if the condenser operation approaches equilibrium. The organic components in the condenser feed are divided in three groups according to their boiling points (lights, middles, and heavies). Three cases have been defined relative to the base case: more lights, more middles, and more heavies. Deviations relative to the base case are based on the maximum spread reported by the round robin study[15]. The weight fraction of the groups in the considered cases is listed in Table 6.6. Simulations are done for three different gas loads (0.4, 1, and 3 kg of gases/kg of vapors) and two different water contents (22.5 and 35.7 wt%) in the condenser feed.

Table 6.6: *Composition (wt% dry) of the organic condenser feed in the cases used in the condenser model sensitivity study.*

	Base case	More lights	More middles	More heavies
Lights (IO1-IO4)*	14.6	20	12	12
Middles (IO5-IO8)*	25.8	23	31	23
Heavies (IO9-IO13)*	59.6	57	57	65

*See Table 6.3 for details on IO1 to IO13

The model simulations show (see Figure 6.9) that the predicted water content of pyrolysis oil in the condenser (first) is almost independent of the (assumed) organic composition of the condenser feed within the ranges defined in Table 6.6 and for all considered gas loads and water fractions in the condenser feed. This can be explained by the fact that water is by far the major compound on molar bases (mole fraction) 0.77-0.82) present in the condenser feed in all cases. The absolute spread in loss of organics compared with the base case rises to maximal 0.05 kg/kg at higher condenser temperature.

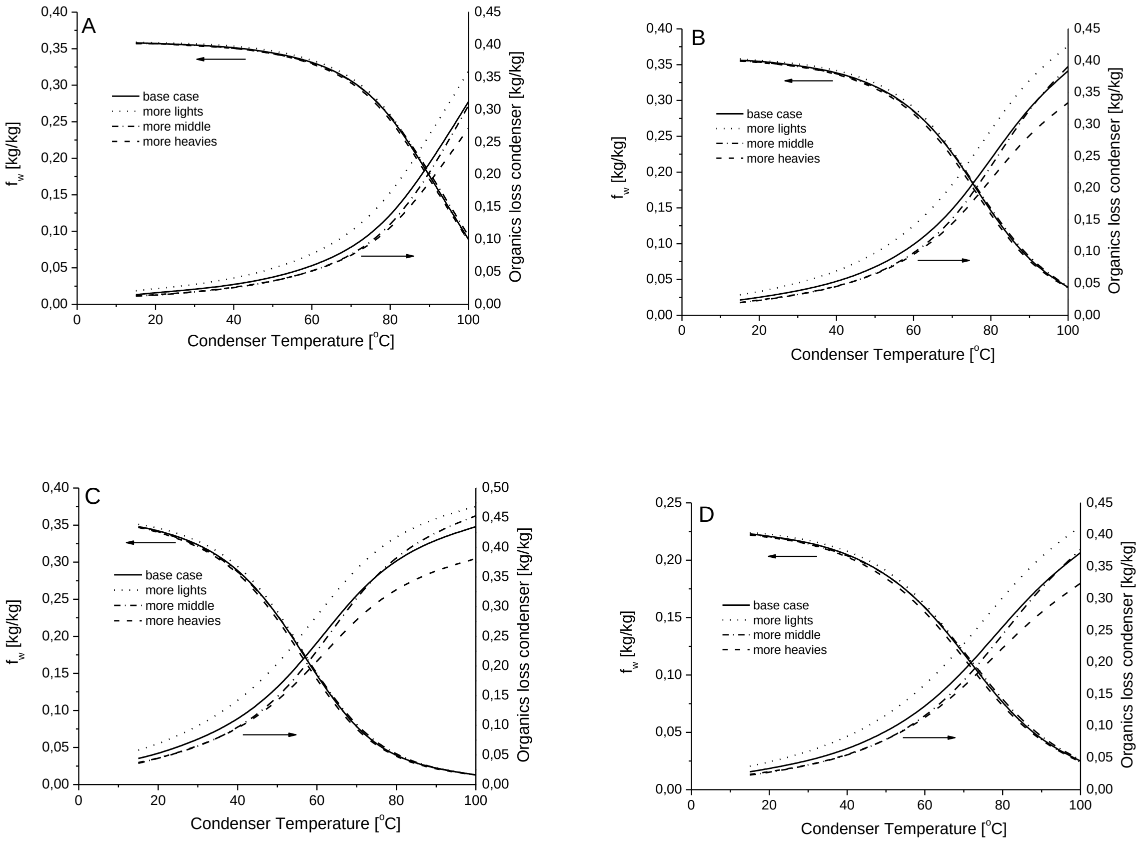

Figure 6.9: *Model sensitivity: 8A) Inert gas flow 0.4 kg gasses/kg vapours and water content of the condenser feed 35,7 wt%. 8B) Inert gas flow 1 kg gasses/kg vapours and water content of the condenser feed 35,7 wt%. 8C) Inert gas flow 3 kg gasses/kg vapours and water content of the condenser feed 35,7 wt%. 8D Inert gas flow 1 kg gasses/kg vapours and water content of the condenser feed 22,5 wt%.*

6.5 Discussion and Conclusions

In this paper, several process options to steer the water content of pyrolysis oil are evaluated. Downstream extraction of pyrolysis oil with water does reduce the water content, but it is not a viable approach because the yield of pyrolysis oil is reduced too much. The temperature (15-90°C) and the load of sweep gas (2-4.1 kg of gases/kg of vapors in the condenser feed) of the condenser are both well suited to lower the water content of pyrolysis oil. However, removing water is always accompanied by the loss of organic vapors in the condenser via entrainment with the outgoing gas stream. No negative effects with respect to yield and no increased aging of oil condensed at elevated condenser temperature have been observed at an average liquid residence time of 1 h. The influence of the operating conditions of the condenser on the water content of the collected pyrolysis oil and the loss of organic vapors can be predicted with sufficient accuracy for process design using a simple equilibrium model. This model assumes that the outgoing streams of the condenser are at equilibrium, which can be achieved in practice by providing enough contact area and contact time to condense the vapors. Inputs for the model are the yields of the pyrolysis products and the composition of the organic fraction of the pyrolysis oil. The yields can be measured, and from round robin studies in the literature sufficient accurate and reliable data on the composition of oils derived from various feedstock materials are available. In Figure 6.10 the loss of organic vapors in the condenser is plotted versus the obtained water content of pyrolysis oil.

Results of varying the condenser temperature and water content in the condensable condenser feed (22.5, 35.7, 42.9 wt% corresponding in our process to a biomass feedstock moisture of 0, 12, and 20 wt%) at constant sweep gas load are compared with results of varying sweep gas load at otherwise identical conditions. Figure 6.10 shows that, for a condenser feed with 35.7 wt% water, the amount of organic vapors lost in the condenser to reach a certain water content of pyrolysis oil is fixed, irrespective of whether the water is removed by raising the temperature or increasing the gas load of the condenser (the data representing these scenarios are indistinguishable). In a practical pyrolysis plant, a well-considered combination of a sweep gas load and the condenser temperature can be used to control the water content.

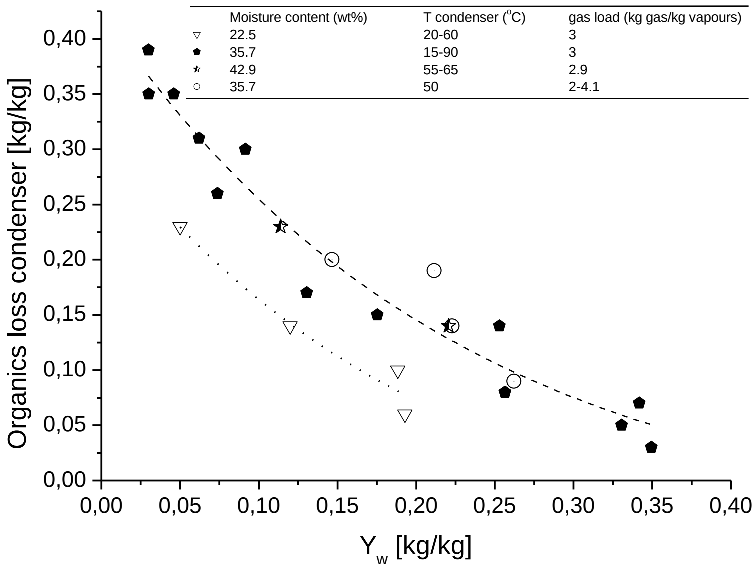

Figure 6.10: *operating regime map of the condensers on the basis of the water content of pyrolysis oil and the loss of organic vapours produced by pyrolysis. Results of varying condenser temperature for feeds with 22.5, 35.7 and 42.9 wt% H_2O at constant sweep gas load (kg gases / kg vapours) are compared with results of varying sweep gas load at otherwise identical conditions. Conditions: $T_{reactor}$ = 480 °C, $T_{cyclones}$ = 500 °C.*

The results of feeds with 35.7 and 42.9 wt% water in the condenser feed are identical in view of the scatter in the experimental data. Drying the feedstock to very low moisture levels (approaching zero) leading to a low water content of the condenser feed (22.5 wt%) is beneficial, because it reduces the amount of organic vapors lost in the condenser over the whole range of desired water contents of pyrolysis oil. From a practical point of view such dry feedstock materials are, however, not realistic due to the high costs of the dryer.

6.6 Nomenclature

M_{sand} = Amount of silica sand, kg.
U = Superficial velocity, m/s.
U_{mf} = Minimal fluidization velocity, m/s.
Y = Yields, kg/kg.
f_w = Water content of the pyrolysis oil, kg/kg.
$f_{w,biomass}$ = water content of the biomass, kg/kg.
t = experimental time, min.

V = Vapour flow that left the 1st condenser, mol.
L = Liquid pyrolysis oil, mol.
F = Condenser feed, mol.
K = Partition ratio
p = Pressure, bar or mm Hg.
z = Fraction of a component in the 1st condenser feed.
T_L = Temperature of the pyrolysis oil in the 1st condenser, °C.
T_V = Temperature of the vapour that left the 1st condenser, °C.
y = Fraction of a component in the vapour phase.
x = Fraction of a component in the liquid phase.
p_i^0 = Partial pressure of a component, bar or mm Hg.
l = Length, m.
d = Diameter, m.
Q_g = Gas flow l/min
X = mol fraction in the gas phase
M = mol mass

Greek symbols

τ_{hot} = Residence time of vapours and gases in the hot part of the set-up, s.
$\tau_{reactor}$ = Residence time of vapours and gases in the reactor bed, s.
σ = Standard deviation.

Subscript

dry = On dry feedstock basis.
daf = On dry-ash free basis.
Initial = At the start of a experiment.
0 = At time point zero.
i = A single component.
ar = As received.

Terminology

LMM = Low Molecular Mass.
HMM = High Molecular mass.
N.b.p. = Normal boiling point

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Chapter 7

Fractional Condensation of Biomass Pyrolysis Vapors

Abstract

In this chapter, we have investigated the possibilities to steer the composition and, thus, the quality of pyrolysis liquids by the reactor temperature and the pyrolysis vapor condenser temperature. Pine wood was pyrolyzed in a 1 kg/h fluidized-bed pyrolysis reactor operated at 330 or 480°C. The pyrolysis vapors produced were condensed using a condenser train of two counter-current spray columns arranged in series. In this paper, the temperature of the first condenser was varied between 20 and 115°C, while the second condenser temperature was kept at 20°C. To describe the composition of the oils, we have integrated several analytical techniques into a novel characterization scheme that can account for 77-82 wt% of the oils. The effects of the condensation conditions on fractions of light compounds in the oils can be predicted with a simple equilibrium stage condensation model. It has been observed that pyrolysis at 330°C gives a light oil with a low amount of mid-boilers [normal boiling point (nbp) of 150-300°C] and heavy compounds (water insolubles and mono-and oligo-sugars). Sugars, mid-boilers, and water-insoluble lignin derived oligomers are more present in the oil obtained at 480°C, while the yields of light organics are approximately the same for 330 and 480°C. It can be concluded that fractional condensation is a promising cheap downstream approach to concentrate compounds (classes) and, thus, to control the quality of pyrolysis oils. For instance, operating the first condenser around 70-90°C gives an aqueous liquid in the second condenser containing 40 wt% light organics, which are interesting for extraction (e.g., 10 wt% acetic acid) and supercritical water gasification to produce hydrogen. Under these conditions, the oils from the first condenser have a high content of sugars (20 wt%) and lignin-derived oligomers (40 wt%), which are attractive fractions for fermentation/sugar chemistry and gasoline production via fluidized catalytic cracking (FCC)/hydrotreatment, respectively.

7.1 Introduction

Fast pyrolysis is a process in which biomass is converted in the absence of oxygen into a liquid, often called pyrolysis oil or bio-oil. Pyrolysis oil has the potential to become an important intermediate energy carrier for the production of bio-based chemicals, transportation fuels, heat, and electricity. Recently, there has been a shift in research attention from maximizing bio-oil yield to approaches and process designs aiming to improve bio-oil quality. It is now recognized by the stakeholders that our capacity to control oil quality is very important for realizing the introduction of large volumes of pyrolysis oil into the market and to facilitate its further refining. Quality can relate to storage, transport, and processing characteristics of the oil. For example, oxidative and thermal stability and vapor pressure are important properties for storability and transportation. Quality criteria (indicators) will depend upon the final application. In the case of gasification and combustion of the oil, water (heating value of the fuel) and coke formation during evaporation (atomization) are considered important quality parameters. For co-processing stabilized bio-oil in standard crude oil refinery units, molecular weight (distribution), oxygen content, hydrogen/carbon (H/C) ratio, total acid number, corrosivity, and thermal stability are key characteristics[1-3]. These quality indicators are directly related to the chemical composition of these oils. For example, the amount of carbonyl, carboxyl, and hydroxyl groups in the heavy part of the oil [water-insoluble fraction (lignin derivatives) and mono-and oligo-sugars] is directly related to the tendency of these oils to form carbonaceous residues.

One of the options to steer the bio-oil composition is by controlling the pyrolysis conditions (reactor temperature and residence time of vapors and solids)[4-9]. Another option is fractionation of the vapors produced. Downstream fractionation of the whole pyrolysis oil obtained after condensation by, e.g., distillation is an option, but the high reactivity of some bio-oil fractions typically result in the formation of cross-linked solid carbonaceous residues when bio-oil is heated. In this paper, it is investigated if fractionation can be achieved during condensation in the pyrolysis unit. Using a serial condenser train, instead of a single condenser, creates the opportunity to produce different liquids (oils) optimized for different applications. Fractional condensation of biomass pyrolysis vapors is not discussed much in the literature. Effendi et al.[10] describe the application of fractional condensation to concentrate phenolic compounds. Removal of light fractions from the pyrolysis oil by fractional condensation and replacement of this fraction by an alcohol has shown to increase the oil stability[11]. In our previous research,[4,12] the effect of condenser operation on the water content and loss of total organics from the oil obtained in the first condenser was studied. Parameters varied were the condenser temperature, sweep gas load, and initial moisture content of the biomass.

In this paper, we integrate experimental and modeling tools to investigate strategies to optimize oil composition and, thus, quality by variation of both the reactor temperature (330 and 480°C) and the temperature of the first condenser (20-115°C) in a serial train of three condensers (second at 20°C and third at 0°C). The effect of these changes on the concentration of individual components (e.g., water, acetic acids, acetol, and levoglucosan) in the oil, on the concentration of lumped fractions (e.g., light fractions, acids, water insolubles, sugars, and water-insoluble fractions), and on other quality indicators, such as heating value and viscosity, was studied.

The experimental data obtained describing the effect of condensation conditions on the yield, composition, and quality of these oils are compared to the predictions of a simple equilibrium stage condensation model. This model needs as input an overall description of the composition of pyrolysis vapor entering the first condenser in the form of a discrete distribution of boiling points. A novel bio-oil characterization scheme is proposed to obtain this information.

7.2 Experimental section

7.2.1 Fluidized-Bed Reactor.

Pine wood ($D_{particle}$ = 1 mm, with a moisture content of 10 wt%) was pyrolyzed in a fluidized-bed continuous fast pyrolysis plant. A detailed description of the plant can be found elsewhere[chapter 2&6,4,5]. Sand ($D_{particle}$ =220 μm) was used as fluidized-bed particles, and nitrogen was used as fluidization gas. The fluidization velocity was always kept at $2U_{mf}$, resulting in an inert gas flow of 2 kg/kg of wet biomass when the reactor temperature was 480°C and 2.17 kg/kg of wet biomass when the reactor temperature was 330°C. The biomass feed rate was 1.0 kg/h for all experiments. Char was separated from the vapor/gas stream by a knockout vessel and cyclones, which were kept at a constant temperature of 400°C. The total residence time of the vapors in the hot part of the pilot plant was approximately 1.3 s. The average residence of the biomass particles in the hot reactor was 20-25 min, which was long enough for >95% conversion of the particles at both 330 and 480°C, according to the measurements and calculations by Kersten et al.[13].

The char yield was determined by collecting all of the solid material from the knockout vessel, cyclones, reactor, and overflow. The weight difference between the sum of all of the collected material and the amount of sand initially in the system was the amount of char produced. With the gas composition (CH_4, CO_2, CO, H_2, and C_2-C_3 hydrocarbon content) determined by gas chromatography (GC) (Varian CP 4900) and the measured difference between the in- and outgoing gas flow rate (in m^3/s), the gas produced by pyrolysis (in kg/s) was calculated.

7.2.2 Condenser System.

The vapors (vapor temperature entering first condenser = 400°C) were condensed in two counter-current spray condensers placed in series (see Figure 7.1). The temperature of the first condenser was varied between 20 and 115°C, and the temperature of the second condenser was kept at 20°C. During the experiments, the temperature of the vapors leaving the condenser and the liquid accumulated in the condenser was measured. The temperature of these vapors could be controlled within ± 1°C of the set point. The temperature differences between liquid and vapor in a condenser were never more than 2°C.

The residence time of the liquid produced in the collector underneath the condenser at the temperature of the condenser was approximately 1.5-2 h. Shell Ondina oil 917 was used as spraying liquid in the first and second condensers. The pressure in the condensers was monitored during all of the experiments and was always 1.1 ± 0.01 bar. More information on the condenser system can be found elsewhere[chapter 6, 4]. An intensive cooler, packed with steel wool, was used to collect the remaining light vapors. In this intensive cooler, the light oil droplets are collected by a knockout principle by quick change of the gas flow direction. The temperature of the stream leaving the intensive cooler was 0°C.

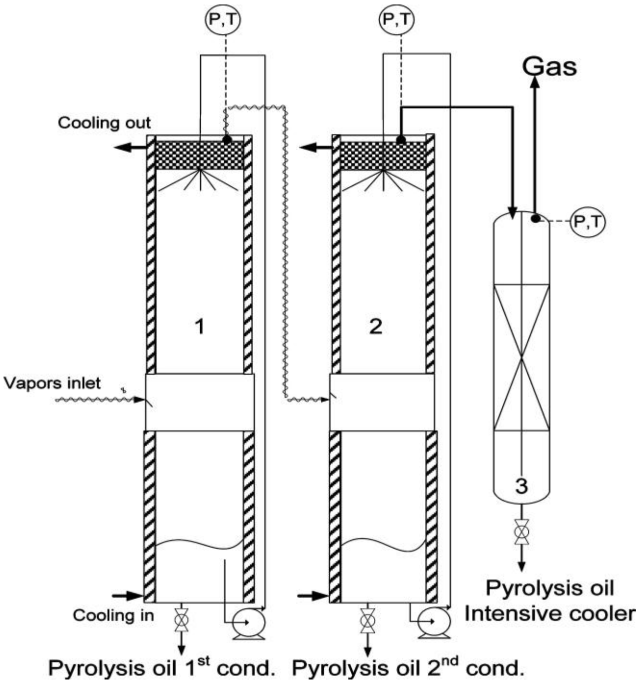


Figure 7.1: *Condenser system with two counter-current spray columns and an intensive cooler in series.*

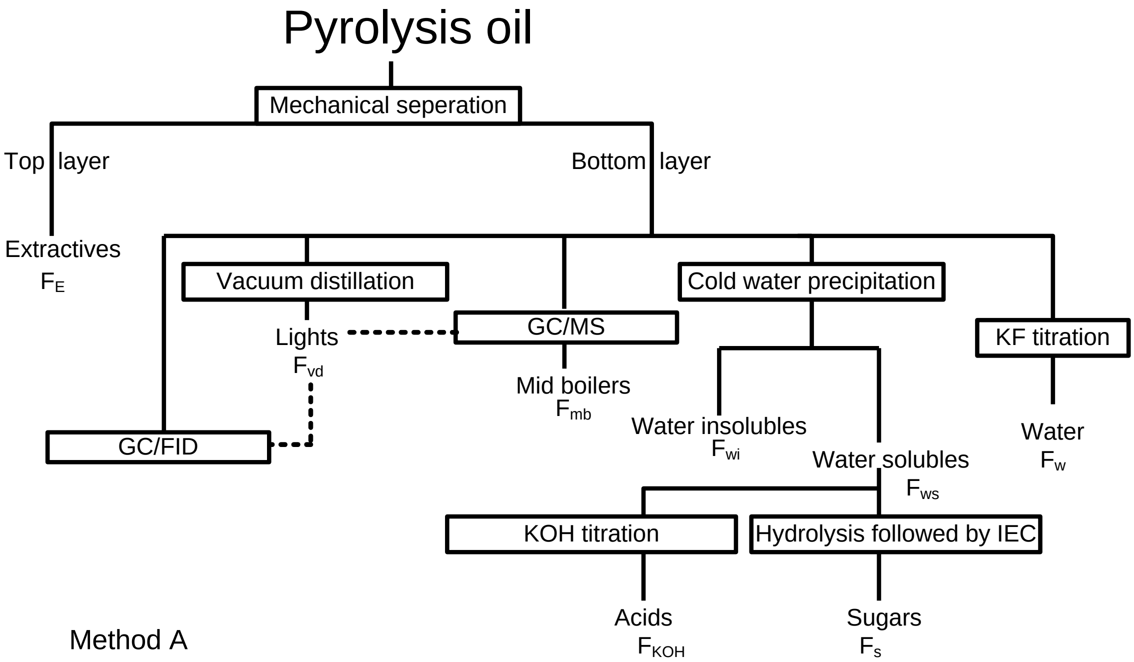
7.2.3 Condenser Model.

Earlier work[4] has shown that our condensers can be described by single-stage equilibrium units. Therefore, the first condenser is modeled as a single-stage equilibrium flash drum. The model was previously used by us for prediction of the water content of pyrolysis oil by operating the first condenser between 15 and 90 °C with varying inert sweep gas flows (2.0-4.1 kg of gases/kg of vapors in the condenser feed) and different moisture contents (0-20 wt%) of the biomass[4]. In this paper, we will use the same model but to predict the evolution of individual species of lumped groups and of some properties of the oil as a function of the operational conditions of the first condenser. To do so, the inlet stream to the first condenser (stream leaving the pyrolysis reactor) was described as 12 discrete organic boiling point groups, H_2O, N_2, and non-condensable gas (see Table 7.3). The relative amounts (kg of group/kg of wet oil × 100%) of the organic groups and H_2O in the feed stream of this condenser were derived from oil characterization schemes shown in Figure 7.2. To define the model (first condenser) input, these schemes were applied to the sum of the oils collected in the first condenser, second condenser, and the intensive cooler when the temperature in the first condenser was 20°C. N_2 (fluidization gas) and produced non-condensable gases entering the first condenser were also inputs to the model and were determined experimentally.

One representative compound of every group was chosen to define the vapor pressure of that group. The Antoine constants for the vapor pressure calculation were taken from well-known compounds, with boiling points in the same range of the group (formaldehyde, ethanol, formic acid, acetic acid, propionic acid, p-cresol, eugenol, and hydroquinone; see Table 7.3). It is important to point out that efforts were made to choose a model compound that was actually present in the bio-oil, but in some cases (groups 6 and 9), it was not possible to find model compounds belonging to that group in practice with known Antoine constants. n-Butyric acid and hydroquinone were chosen as model compounds for these groups (see Table 7.3). A more detailed description of the condenser model can be found in chapter 6.

7.2.4 Oil Characterization Scheme.

Pyrolysis oil has been reported to contain more than 200 compounds, covering a wide range of molecular weights, boiling points, and functional groups. Characterizing these oils by single analytical techniques is thought to be impossible. To describe the composition of the oil, it is necessary to integrate analytical techniques to analytical schemes. In this paper, we propose to integrate several analytical techniques into an analytical scheme to obtain the content of individual compounds, an overall lumped composition of oils, and some quality properties of the oils. We have tested two versions (methods) to obtain an overall description of the pyrolysis oil. The second method is a downsized version of the first and requires significantly less analytical input.



Method A

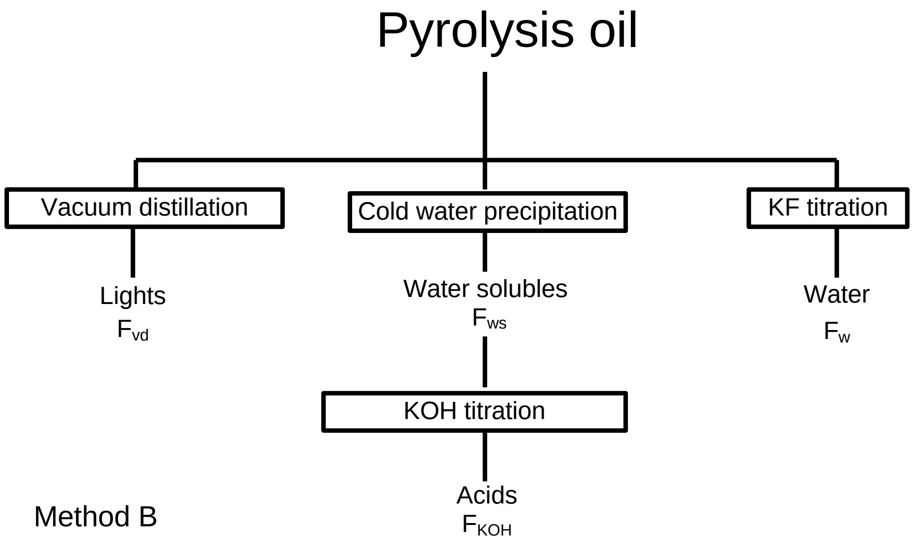


Figure 7.2: *Analytical scheme for pyrolysis oil characterization.*

The scheme (Figure 7.2) is applied to the liquids collected in the first and second condensers and the intensive cooler and result in fractions (F, kg of fraction/kg of wet oil × 100%) of certain chemical families in the oil per condenser and in the total oil (sum of the first condenser, second condenser, and intensive cooler). The fractions are assigned to the discrete boiling groups in the condenser model (see Table 6.3 for the relations between the groups and the fractions and numerical values of the groups). The first method (hereafter called method A) is presented in Figure 7.2.

This method first extracts a top layer of the oil. The remaining bottom layer is subjected to vacuum distillation, gas chromatography/mass spectrometry (GC/MS), Karl Fisher (KF) titration, and cold-water precipitation. The aqueous phase obtained after cold-water precipitation is subjected to ion-exchange chromatography (IEC) and KOH titration. Method B (see Figure 7.2) is simpler and does not include information about mid-boilers and the heavy fractions (water insolubles and sugars).

The individual analysis techniques used as part of this analytical scheme are described below.

The content of the extractive-rich upper layer (F_E) formed as a very thin top layer was determined by decanting the oil collected in the first condenser[15].

Gas Chromatography/Flame Ionization Detector (GC/FID). A Shimadzu GC-2014 with an Aoc-5000 auto injector was used to detect acetone and methanol. The column was a HP-INNOWax (30 m long and 0.25 mm inner diameter, coated with 0.25 µm film). The split and FID temperature was set at 180 and 210°C. The carrier gas (helium) had a constant velocity of 27.9 cm/s. A total of 0.5 g of pyrolysis oil sample was incubated at 85°C for 5 min. A total of 250 μL of gas was then introduced into the GC/FID with a split ratio of 1:25. The column temperature was held at 45 °C for 1 min, then warmed with a heating rate of 5°C/min to 70°C, and held at this temperature for 2 min. The column was then heated to 200°C with a heating rate of 65°C/min and held constant at this temperature for 5 min for cleaning purposes.

KF Titration. The water content (F_w) of the pyrolysis oil was measured by KF titration (Metrohm 787 KF Titrino). The titrant was Hydranal Composite 5.

GC/MS. The identity of several pyrolysis oil volatile chemical compounds was performed using an Agilent 6890 N gas chromatograph coupled with an Agilent Inert XL mass spectrometry detector with a capillary column (Agilent HP-5 MS, HP19091S-433). The following compounds were detected and quantified. Light fractions: Glycolaldehyde, acetic acid, acetol, propionic acid, toluene, and cyclopentanone. The mid-boilers (Fmb) were quantified by adding the content of furfural, furfuryl alcohol, *p*-xylene, *o*-xylene, 2-methyl-2-cyclopenten-1-one, 2(5H)-furanone, β-methoxy-(S)-2-furanethanol, 1-ethyl-2-methylbenzene, phenol, 1-methyl-2-(1-methylethyl)-benzene, o-cresol, p-cresol, *m*-cresol, guaiacol, 2,4-dimethyl-phenol, 2,5-dimethyl-phenol, 4ethyl-phenol, 3,4-dimethyl-phenol, 2-methoxy-4-methyl-phenol, pyrotechol, 3-methyl-1,2-benzenediol, 4-ethyl-2-methoxy-phenol, 4-methyl1,2-benzenediol, eugenol, syringol, 2-methoxy-4-propyl-phenol, 4-ethyl-catechol, vanillin, tetradecane, 2-methoxy-4-(1-propenyl)-(E)-phenol, and pentadecane. Sugars: levoglucosan. For calibration, at least five standard solutions for each of these compounds were prepared. The response factor of each of the standards was calculated using phenanthrene as an internal standard. It was not possible to obtain standards for all of the compounds identified by the GC/MS chromatograms. Consequently, the response factors for some compounds were considered equal to that for the standard of the closest chemical structure. Methanol solutions containing 5 wt% pyrolysis oil and 0.2 wt% phenanthrene (internal standard) were used to quantify the chemical compounds of interest. The particles in the pyrolysis oil/methanol solution were removed with a microfilter (0.45 μm) prior to injection into GC/MS. A total of 1 μL of sample was injected into the injection port set at 200°C, with a split ratio of 10:1. The column was operated in a constant flow mode using 1 mL/min of helium as a carrier gas. The mass spectrometer was operated at the electron ionization mode and scanned from 28 to 400 amu. Identification of each compound was based on retention times and matching the mass spectrum recorded with those in the spectral library (NIST/EPA/NIH Mass Spectral Library, Version 2.0d, FairCom Corporation).

Cold-Water Precipitation. The amount of water-insoluble compounds (F_{wi}) typically associated with pyrolytic lignin was determined by the cold-water precipitation method described by Scholze and Meier[16]. Besides pyrolytic lignin, this method also yielded an aqueous-phase product.

IEC. The content of hydrolyzable sugars (F_s) in the oil was quantified by IEC. Approximately 10 g of the aqueous phase obtained after cold-water precipitation was hydrolyzed at 120°C with sulfuric acid solution at 500 mM final concentration under reflux for 4 h. This was performed to convert the hydrolyzable oligosugars in IEC-detectible monosugars. The aqueous phase was then diluted with distilled water to about 100 times the original volume. The content of sugars after neutralizing the solutions was quantified by high-performance anion-exchange chromatography using a Dionex ICS-3000 system equipped with an AS 50 auto-sampler, GP50 gradient pump, and ED50 electrochemical detector. Separation of sugars was performed with a Carbopac PA20 column. The mobile phase was an aqueous NaOH solution at a flow rate of 0.50 mL/ min. Deionized water was used to prepare the mobile phase. A 10 mM sodium hydroxide storage solution was added postcolumn to maintain a pH of 10.4 in the detector. The injection volume of the sample was 10 μL, and the column temperature was constant (35°C). The calibration curves for all sugars (levoglucosan/sorbitol arabinose, galactose, glucose, mannose/xylose, fructose, and ribose) analyzed were linear in the range of concentrations studied. The sugar fraction is defined as the mono-sugars measured after hydrolysis of the aqueous phase of the liquids obtained. After hydrolysis, oligo-(anhydro-) sugars with glycosidic bonds (C-O-C) between the monomers are converted to a large extent to monosugars, which are detectable by IEC. C-C bonded sugars cannot be hydrolyzed and cannot be quantified. Also, mono-anhydrosugars can be hydrolyzed (e.g., levoglucosan). Hence, the sugar fraction is a measure of the sum of monosugars and oligo-(glycosidic) hydrolyzable sugars present originally in the liquids.

Acid Fraction and pH. The acid fraction (F_{KOH}) was measured by dissolving (0.5 – 2 g) pyrolysis oil in (0.5 - 2 g) water. The aqueous phase was dissolved in (approximately 80 g) of demineralized water. Titration was performed with a Metrohm Titrino model 798, and the reagent was 1 M KOH. The titration was stopped at the second equilibrium point when all strong and weak (carboxylic) acids, representing most of the acids in the oil, were neutralized. The very weak acids (e.g., phenols) were thus not taken into account. Acetic acid was chosen as a representative model compound for the calculation of the acid fraction (on the basis of the KOH titration) in the pyrolysis oil.

The pH was measured with a Metrohm electrode (pH 0 - 14) connected to a Metrohm Titrino model 798 titrator.

Vacuum Distillation. This technique was used to determine the amount of light fractions (F_{vd}). Vacuum distillation was performed at 98°C and 0.06 bar. Light fractions were defined here as compounds that have a lower normal boiling point (nbp) than that of butyric acid ($T_{nbp} < 154°C$). Using the Clausius-Clapeyron equation, the boiling point of butyric acid was estimated to be around 98°C at 0.06 bar (pressure of the vacuum distillation). We performed additional experiments on the reactivity of the pyrolysis oil that showed that neither significant water production nor viscosity increase because of the observed polycondensation reactions for 0.5 h residence time at 98°C. The organic light fraction removed from the oil by vacuum distillation was determined as the difference between the yield of vacuum distillate and the fraction of water in the distillation feed.

Viscosity. The viscosity (Brookfield DV-E viscometer) was measured as the dynamic viscosity (cP).

The elemental composition of the wet pyrolysis oil was analyzed using a Fisons Instruments 1108 CHNS-O apparatus. From this composition, the higher heating value was calculated from Milne's formula[17].

The data obtained by the analytical scheme shown in Figure 7.2 was used to formalize the chemical composition of the oil in 13 lumped groups (method A) or 7 lumped groups (method B) (see Table 6.3). The first five groups and group 13 (water) are the same for both methods. The content of organic light fractions (containing groups 1-5) was obtained by subtracting the water (determined by KF titration, group 13) to the vacuum distillate. Because group 4 (the acids) was measured by KOH titration, the content of each of the groups 1, 2, 3, and 5 was calculated as the difference between the light organic fractions and the acids. In this paper, the content of groups 1, 2, 3, and 5 was considered to be the same; thus, the content of each of these groups was calculated by dividing the unknown light fractions by 4.

In method A, groups 6-9 represent compounds with moderate boiling point. The overall content of the mid-boiler groups (6-8) was determined by GC/MS. The content of each of these individual groups was calculated by dividing the overall content of mid-boilers in three equal parts. The fraction of hydrolyzable sugars (from IEC) is placed in group 9. Water-insoluble lignin-derived compounds (measured by precipitation) are represented by group 10, and the top layer (extractives) of the oil is represented by group 11. Group 12 is a group of unknown compounds with no vapor pressure in the temperature range studied, which may be associated with poorly C-C bonded sugars[14]. In the formalization method A, this fraction is determined by the difference.

Method B is simpler because it describes the overall composition of the oils by only making use of the information obtained by KF titration (water content, F_w, group 13), KOH titration (total acids, F_{KOH}, group 4), cold-water precipitation to obtain the aqueous phase, and vacuum distillation (overall content of the light fractions, F_{vd}). All mid-boilers and heavy fractions are assigned to group 12, which is assumed to have no vapor pressure in the temperature range studied.

7.3 Results

7.3.1 Mass Balance.

Mass balance results of the experiments at 330 and 480°C are listed in Table 7.1. Average results of all experiments at the same reactor temperature but varying temperature of the first condenser are presented. The relative scatter (standard deviation divided by the mean) is also included in the table for both sets of experiments and is lower than 8%, showing that the reproducibility of the experiments is good and the condensers are working properly. As expected, in comparison to 330°C, at a reactor temperature of 480°C, the oil and gas yield are higher and the char yield is lower. It should be noted that, despite the long particle residence time of the pyrolyzing particle in the reactor (approximately 30 min), it is well-possible that the char obtained at 330°C is not fully converted biomass. The char yields are in line with data obtained by other studies[9].

Table 7.1: *Mass balance (yields, Y: kg product / kg wet biomass * 100%) of pyrolysis temperatures of 330°C and 480°C.*

Products	Average yield		Standard deviation		Relative spread	
	$\bar{Y}$ [wt%]		σ_Y [wt%]		$\frac{\sigma_{Y_t}}{\bar{Y}} \cdot 100$ [%]	
	$T_{reactor}$ [°C]		$T_{reactor}$ [°C]		$T_{reactor}$ [°C]	
	480	330	480	330	480	330
Char	14.0	44.3	1.0	1.5	7.1	3.4
Gas	18.4	7.4	1.3	0.6	7.2	7.7
Pyrolysis oil (incl. H_2O)	62.7	45.2	1.7	3.4	2.7	7.5

7.3.2 Composition of the Whole Oil.

The average oil composition is shown in Table 7.2. In this table, also, the ratio of the yields at 480 and 330°C per fraction is listed. This ratio shows that, at 330°C, water, mid-boilers, and heavier fractions (water insolubles and mono-and oligosugars) are significantly less released from the feedstock compared to 480°C. Possible explanations for this are a lower degree of lignin degradation at 330°C (water insolubles) and thermodynamic and kinetic limitations of heavier fractions toward leaving the solid matrix at a lower temperature. Light fractions are also less removed from the biomass at 330°C, but here the yield difference is minor. As a result of producing significantly fewer heavy fractions at 330°C, oil with 56-58% vacuum-distillable compounds and only 5-6% water insolubles are obtained. In upcoming publications discussing stepwise pyrolysis, we will elaborate more on reaction/mass-transfer mechanisms in relation to the oil composition.

As mentioned before, the fraction of acids in the oil was determined with KOH titration under the assumption that acetic acid is the representative compound for all acids in the oil. This fraction of acids obtained from KOH titration is close to acetic acid (HAc) determined by GC/MS ($T_{reactor}$ =480°C: F_{KOH} = 5.4 wt% and F_{HAc} = 4.6 wt%; $T_{reactor}$ = 330°C: F_{KOH} = 7.3 wt% and F_{HAc} =5.5 wt%; see Figure 7.5), indicating that the assumption is reasonable. The difference in acid fraction can largely be ascribed to propionic acid measured by GC/MS.

Table 7.2: *Composition (expressed as fractions) of the whole pyrolysis oil (condenser 1 + 2 and intensive cooler) and the ratio of the yields (Y, kg fraction in whole oil / kg wet biomass * 100%) at 480°C over 330°C. Averaged values over 6 (480°C) and 4 (330°C) experiments.*

Group	$T_{reactor}$=480^{o}C		$T_{reactor}$=330^{o}C		$\frac{Y_{480^\circ C}}{Y_{330^\circ C}}$
	Average all experiments (wt%)	T_{cond}=20^{o}C one run (wt%)	Average all experiments (wt%)	T_{cond}=20^{o}C one run (wt%)	
F_{wi}	15.9	17.1	5.1	6.1	4.4
F_s	9.9	7.7	8.0	6.4	1.7
F_w	29.2	28.4	31.7	31.2	1.6
F_{mb}	8.8	11.4	6.4	8.2	1.9
F_{KOH}	5.4	6.1	7.3	7.4	1.0
F_{vd}	47.7	47.8	57.8	56.1	1.2
F_E	0.1	0.1	0.0	0.0	-

As explained before, the experimental data obtained was used to define the chemical composition of the oils in term of lumped families with properties of an assigned representative compound. Two methods were used to define the oil composition. This formalization is critical to describe phase equilibrium of the bio-oil in the condenser. Results of this are listed in Table 7.3.

Table 7.3: *Model inputs: formulas (relating groups and fractions) and numerical values of the groups (wt% wet oil basis, between brackets).*

		$T_{reactor} = 480$, $T_{cond1} = 20^{o}C$		$T_{reactor} = 330$, $T_{cond1} = 20^{o}C$	
Group	Normal BP range (K) (representative vapor pressure compound)	Method A (model input)	Method B (model input)	Method A (model input)	Method B (model input)
1	(250-330) (Formaldehyde)	$0.25*(F_{vd}-F_w-F_{KOH})$ (3.3)	$0.25*(F_{vd}-F_{KOH}-F_w)$ (3.3)	$0.25*(F_{vd}-F_w-F_{KOH})$ (4.4)	$0.25*(F_{vd}-F_{KOH}-F_w)$ (4.4)
2	330-360 (ethanol)	$0.25*(F_{vd}-F_w-F_{KOH})$ (3.3)	$0.25*(F_{vd}-F_{KOH}-F_w)$ (3.3)	$0.25*(F_{vd}-F_w-F_{KOH})$ (4.4)	$0.25*(F_{vd}-F_{KOH}-F_w)$ (4.4)
3	360-390 (Formic acid)	$0.25*(F_{vd}-F_w-F_{KOH})$ (3.3)	$0.25*(F_{vd}-F_{KOH}-F_w)$ (3.3)	$0.25*(F_{vd}-F_w-F_{KOH})$ (4.4)	$0.25*(F_{vd}-F_{KOH}-F_w)$ (4.4)
4	391 (Acetic acid, representative for all acids)	F_{KOH} (6.1)	F_{KOH} (6.1)	F_{KOH} (7.4)	F_{KOH} (7.4)
5	392-427 (propanoic acid)	$0.25*(F_{vd}-F_w-F_{KOH})$ (3.3)	$0.25*(F_{vd}-F_{KOH}-F_w)$ (3.3)	$0.25*(F_{vd}-F_w-F_{KOH})$ (4.4)	$0.25*(F_{vd}-F_{KOH}-F_w)$ (4.4)
6	427-450 (n-butric acid)	$(1/3)*F_m$ (3.8)	-	$(1/3)*F_m$ (2.7)	-
7	450-500 (p-cresol)	$(1/3)* F_m$ (3.8)	-	$(1/3)* F_m$ (2.7)	-
8	500-550 (eugenol)	$(1/3)* F_m$ (3.8)	-	$(1/3)* F_m$ (2.7)	-
9	Hydrolys-able sugars (hydroquinone)	F_s (7.7)	-	F_s (6.4)	-
10	Pyrolytic lignin $p^{\bullet}=0$	F_{wi} (17.11)	-	F_{wi} (6.08)	-
11	Extractives $p^{\bullet}=0$	F_E (0.1)	-	F_E (0)	-
12*	Non-volatiles (unknown) $p^{\bullet}=0$	$1-F_{vd} - F_s - F_m - F_{wi}-F_E$ (15.9)	$1-F_{vd}$ (52.2)	$1-F_{vd} - F_s - F_m - F_{wi}-F_E$ (23.3)	$1-F_{vd}$ (43.9)
13	Water	F_w (28.4)	F_w (28.4)	F_w (31.2)	F_w (31.2)

* by difference

7.3.3 Effect of the Temperature of the First Condenser.

This section, reports on the effects of the temperature of the first condenser on (i) the overall oil distribution over the condensers, (ii) the concentration of lumped fractions [e.g., light fractions (F_{vd}), mid-boilers (F_{mb}), hydrolyzable sugars (F_s)] in the oils obtained in the first and second condensers, (iii) the concentration of individual compounds (e.g., acetic acid, acetol, and glucose) in the oils obtained in the first and second condensers, and (iv) the reactivity of some compounds in the condenser.

Figure 7.3 shows the distribution of the bio-oil produced over the condensers as a function of the temperature in the first condenser. The temperatures in the second and third condensers were kept constant in all of the experiments. Obviously, with an increasing temperature of the first condenser, the amount of liquid collected in this condenser decreases, while the amount collected in the second condenser increases. The liquid collected from the intensive cooler increases slightly. Actually, when operating the first condenser at 20°C, more than 80% of the produced vapors condense in this condenser, while at temperatures of 70-80°C, this is less than 50% (see Figure 7.3).

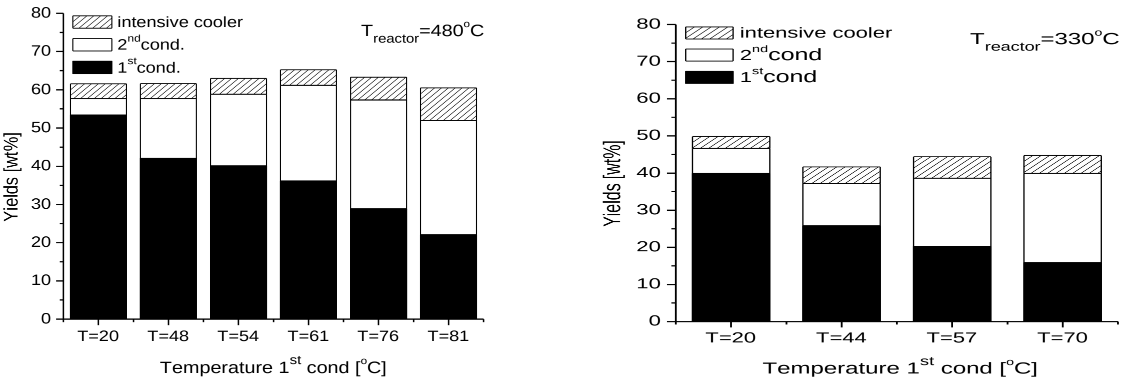


Figure 7.3: *Oil recovered in the 1st & 2nd condenser and intensive cooler as a function of the temperature of the 1st condenser.* $T_{reactor}$ *= 480 °C or 330 °C. Yields in kg oil (per condenser) / kg wet biomass *100% are plotted.*

In the sections below, the effects will be described in more detail per lumped fraction and for two reactor temperatures.

Light Fractions (nbp < 154°C).

Figure 7.4 shows the evolution of the concentration of light compounds (F_{vd}), water (F_w), and the acids (F_{KOH}) in the oil obtained in the first condenser as a function of the condensation temperature.

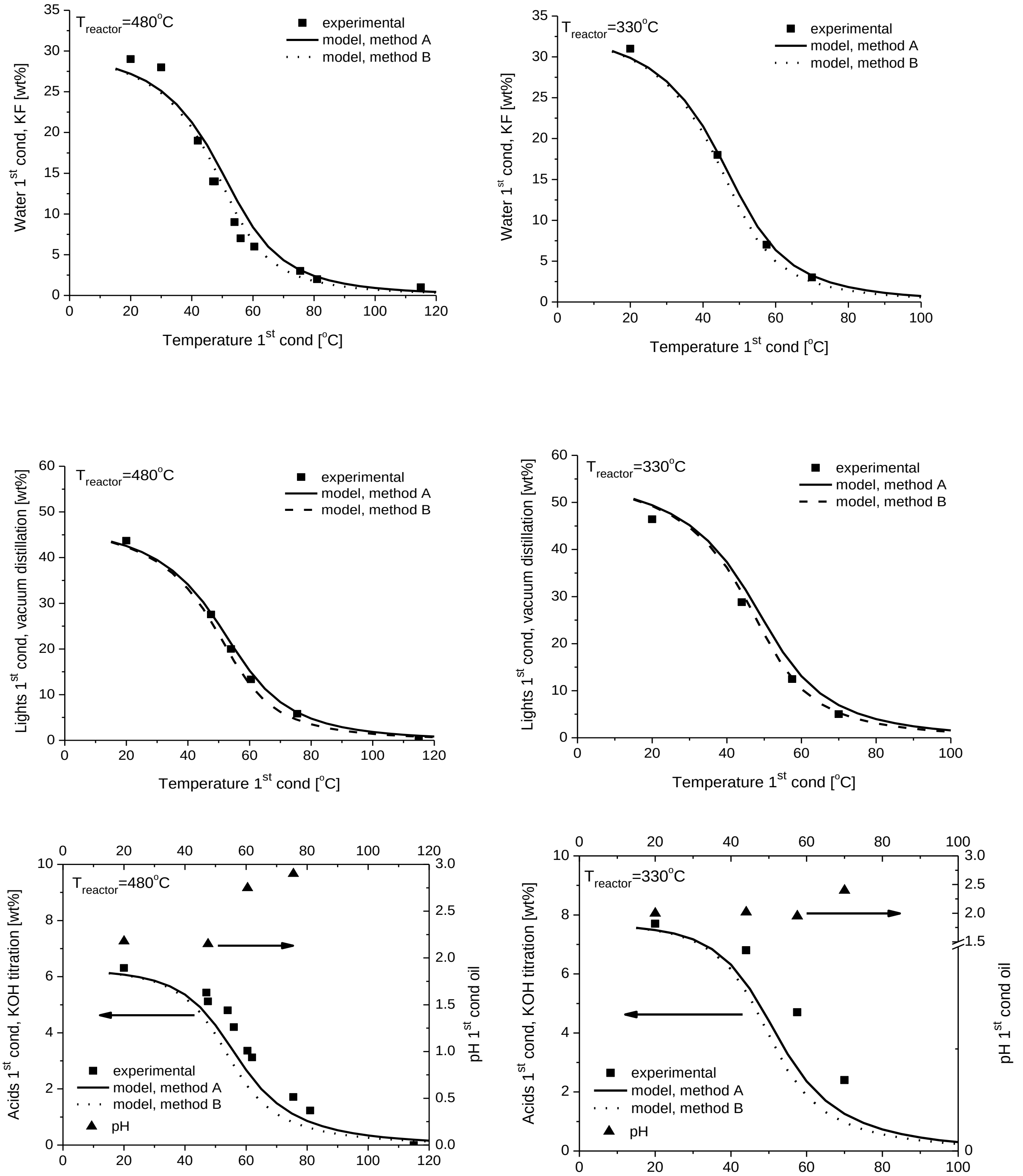
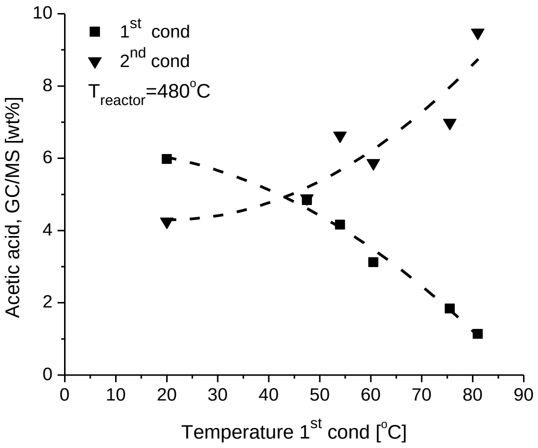
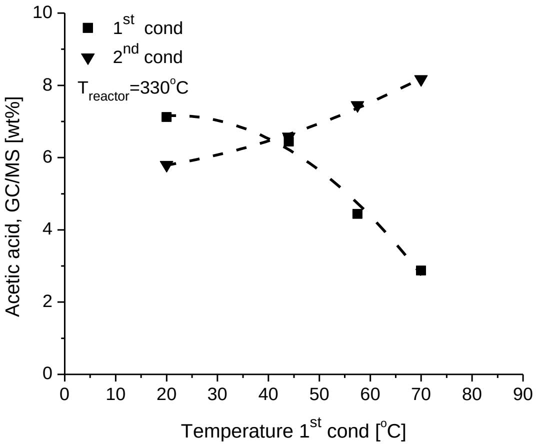


Figure 7.4: *Effect of the temperature of the 1st condenser on the lights fraction (vacuum distillation), acids fraction and pH (KOH) and water content (KF) of the oil collected in the first condenser.* $T_{reactor}$*=480°C or 330°C. Lines are model predictions.*

The content of light compounds, water, and the acids decreases rapidly at an increasing condenser temperature for both reactor temperatures. Above a condenser temperature of 80°C, the light fraction is below 5 wt%. The light fraction in the oil produced at a reactor temperature of 330°C is somewhat higher than in oil produced at a reactor temperature of 480°C. The water content drops below 10 wt% at condenser temperatures above 50°C. It should be noted that the fractions of light components also significantly depend upon the "sweep" gas load of the condenser[4]. More gas going through the condenser will entrain more light fractions. At a temperature of the first condenser of 80 °C, the acid fraction is only 2 wt%, coming from 8 wt% at 20°C. This results in pH values ranging from 2 to 3. The equilibrium condenser model well predicts the trends in light fractions, water, and acids. Moreover, also, the absolute values are predicted reasonably; only the prediction of the acid fraction at a reactor temperature of 330°C shows some deviation. Deviations can be due to the equilibrium assumptions made to build the model, simplifications made to formalize the chemical composition of these oils, and the reactivity of some compounds at higher condenser temperatures (see below).

The predictions based on the input from oil composition obtained by method B (with no detailed information on the mid-boiler and heavy fractions) are as good as those based on method A, which uses measured values for the heavy fractions and subdivides them into several subgroups. This indicates that, for accurate prediction of the light fractions, detailed information on the heavy fractions is not required for the condenser model.





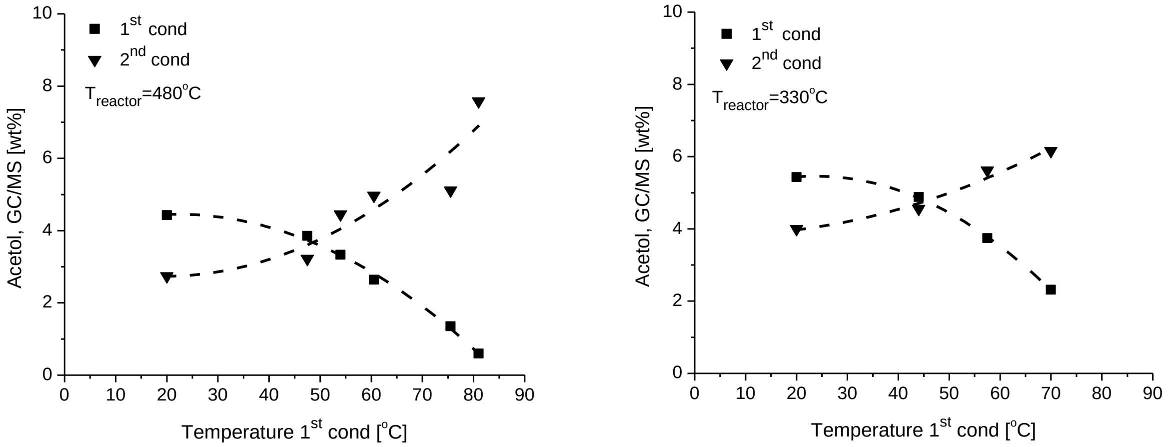


Figure 7.5: *Acetic acid and Acetol fraction in the oils obtained in the 1st and 2nd condenser as a function of the temperature of the 1st condenser.* $T_{reactor}$*=330 or 480°C. Lines are trend lines.*

Organic compounds belonging to the light fraction, detected and quantified by GC/MS and GC/FID, are methanol, acetone, glycolaldehyde, acetic acid, acetol, propionic acid, toluene, and cyclopentanone. Figure 7.5 presents the evolution of the content of acetic acid and acetol (interesting compounds for extraction) found in the first and second condenser oil. When the first condenser is operated at 80°C, the fractions of acetic acid and acetol in the second condenser liquid increase to 10 and 8 wt%, respectively, while their fraction in the first condenser oil drops considerably.

At 80°C, more than 90% of the acetic acid produced is recovered in the second condenser (see Figure 7.6). Extracting these compounds from the second condenser liquid is beneficial because the recovery of organic compounds at these high concentrations may be economically viable, especially in an aqueous stream containing no oligomers, which makes the extraction process easier.

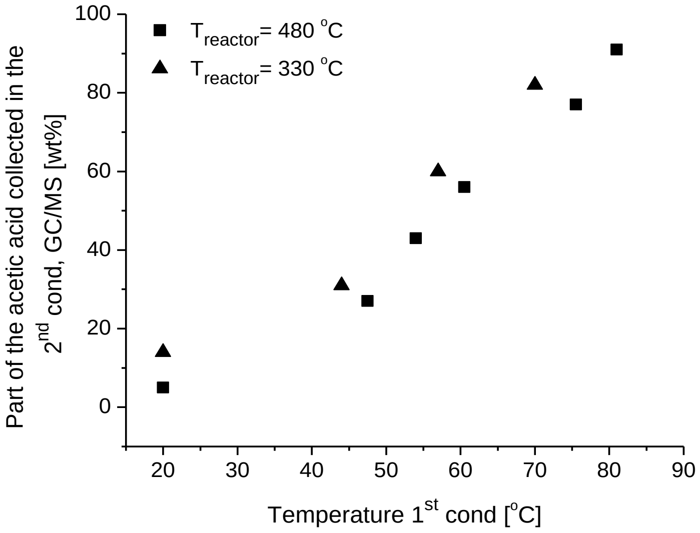


Figure 7.6: *Fraction * 100% of relative amount of acetic acid collected in the 2nd condenser as a function of the temperature of the 1st condenser.* $T_{reactor}$*=330 or 480°C.*

Light compounds can be reactive. From the analyzed compounds in the light fraction, glycolaldehyde has been taken as an example to illustrate the possible reactivity of some compounds in the condenser. Figure 7.7 shows the amount of glycolaldehyde produced as function of the temperature of the first condenser. Up to 55°C, the amount of this compound collected is constant; as the temperature increases, the amount of this compound decreases drastically. This result can be explained by the reactions occurring during the time the oils are inside the condenser (1.5 - 2 h). Decreasing the residence time of the liquid in the condenser (by, e.g., fast cooling or product removal) will lower the extent of reactions in the liquid phase at an elevated condenser temperature. The equilibrium model proposed, which does not consider chemical reactions, will, for our experimental conditions in which the residence time is relatively high (1.5 - 2 h), tend to overestimate the content of these reactive compounds.

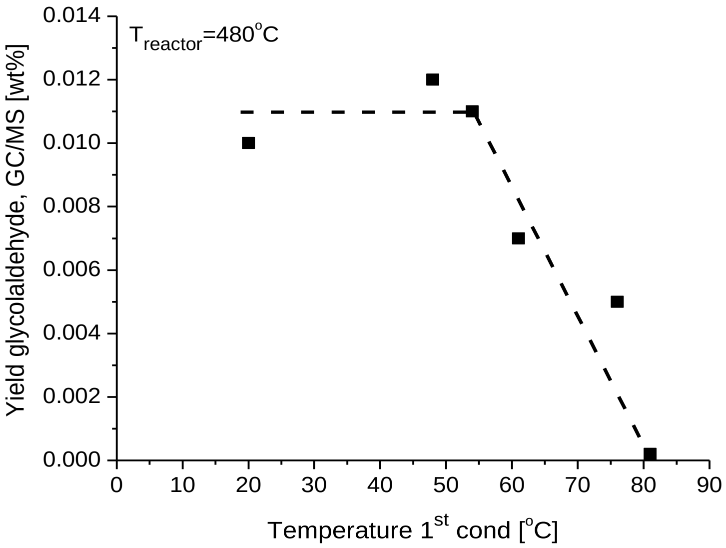


Figure 7.7: *Total yield (kg/kg wet biomass * 100%) of glycolaldehyde collected (condenser 1+ 2+ 3) versus the temperature of the 1st condenser (reactivity). 1.5-2 Hours residence time of the oil in hot 1st condenser.* $T_{reactor}$*=480°C.*

Mid-boilers (nbp of 154 to 300 °C).

The mid-boiler fraction contains mainly phenols and some furans (see analysis section on GC/MS). It is expected that, when the temperature of the first condenser is increased from 20 to 80°C, the concentration of the mid-boilers in the liquid obtained in this condenser will increase. This is because at increasing temperature, removal of light compounds from this condenser takes place, while the mid-boilers remain because of their low vapor pressure. In practice, however, this increase in concentration is only observed at a reaction temperature of 330°C and not at a reaction temperature of 480°C (see Figure 7.8). One of the possible explanations for this may be the differences in chemical composition of both oils (see Figure 7.9).

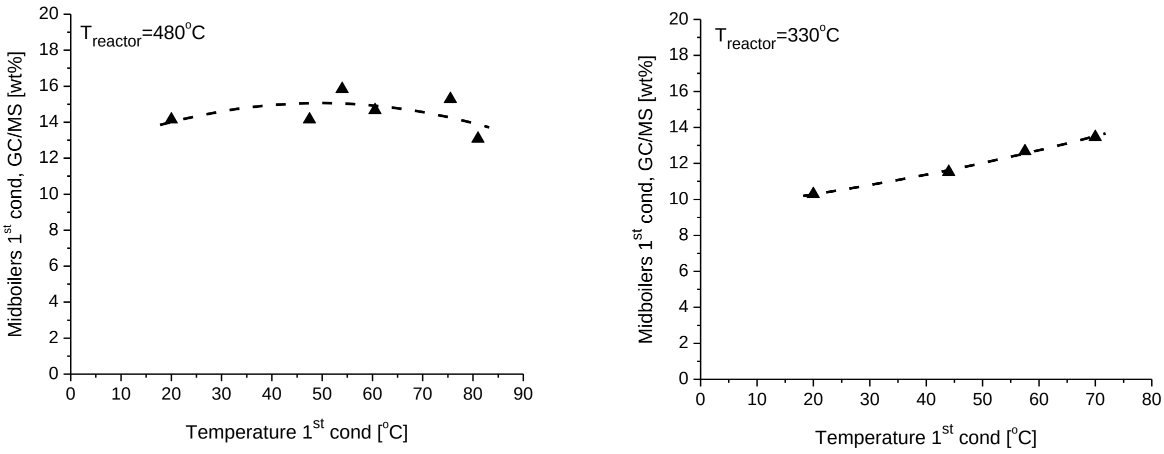


Figure 7.8: *Effect of the temperature of the 1st condenser on the fraction of mid-boilers (GC/MS) of the oil collected in the first condenser.* $T_{reactor}$*=480°C or 330°C (Lines are trend lines).*

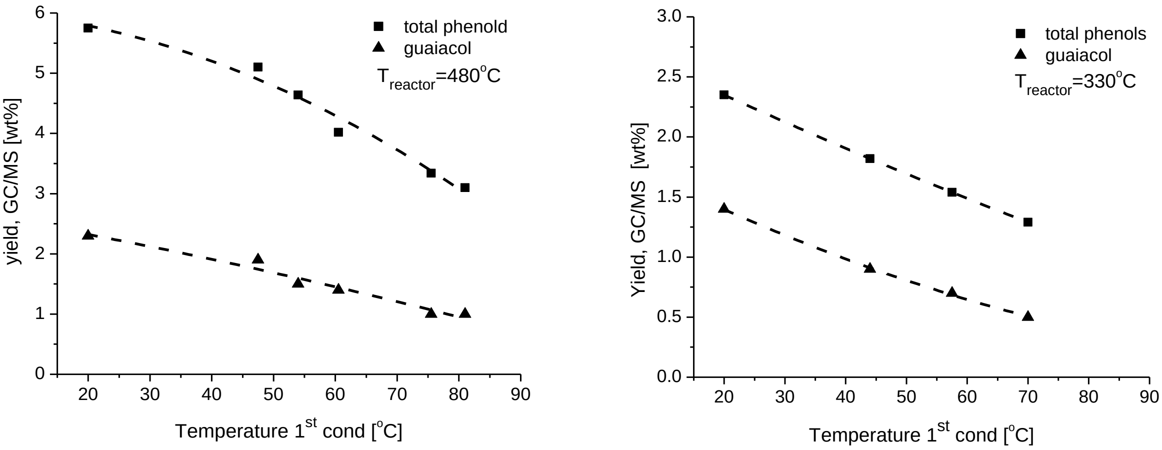


Figure 7.9: *Total yields (kg/kg wet biomass * 100%) of phenols and guaiacol versus the temperature of the 1st condenser (reactivity). 1.5-2 Hours residence time of the oil in hot 1st condenser.* $T_{reactor}$ *= 480°C*

To illustrate the reactivity of mid-boilers, the total yield (condensers 1 + 2 + intensive cooler) of monophenols (a major fraction of the mid-boilers) is plotted in Figure 7.9 as a function of the condenser temperature. A clear decrease in the yield of phenols can be seen. The most reactive group of compounds belonging to the phenols is the methoxy-substituted phenols (guaiacols). Approximately 2/3 of the initial yield of guaiacols, collected at a temperature of the first condenser of 20°C, disappeared by reaction at a condenser temperature of 81°C. One example is guaiacol itself; its disappearance with increasing temperature of the first condenser and is also pictured in Figure 7.9. A more detailed model taking into account droplet size distribution, heat and mass transfer to and from the droplet, and the kinetics of chemical reactions is needed to describe the behavior of reactive species. The results reported are useful because it allowed for identification of the reactive species under the condensation conditions studied. However, a more elaborated experimental design is needed to obtain the kinetics of these reactions.

Sugars (F_S).

The levoglucosan concentration in the oil collected in the first condenser (measured by GC/MS) almost doubled from 5 to 10 wt% as the temperature in the first condenser increased (see Figure 7.10). Levoglucosan has been identified as an interesting biochemical that can be easily converted by hydrolysis into glucose[13].

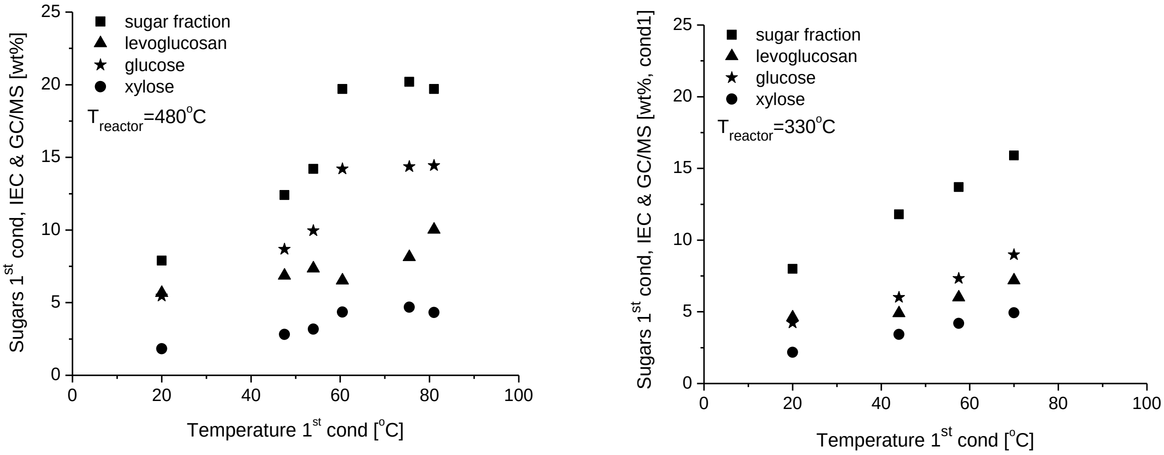


Figure 7.10: *Effect of the temperature of the 1st condenser on the sugar fractions of the oil collected in the first condenser.* $T_{reactor}$*=480°C or 330°C.*

Figure 7.10 also shows the evolution of the concentration of products of hydrolyzable sugars (glucose and xylose) in the first condenser as its temperature increases. As we saw earlier, upon increasing the temperature of the first condenser, many light compounds and water are removed from this condenser, which results in higher concentrations of heavier compounds, e.g., sugars.

After hydrolysis, glucose is the most abundant sugar (ca. 70%), making this stream of interest for fermentation to ethanol or to produce other valuable compounds. Xylose (approximately 20% of the sugar fraction), a more difficult to ferment sugar, can serve as a platform for the production of other high-value products (xylitol, furfural, and lipids).[18,19]

At a reactor temperature of 480°C and condenser temperatures of 60-80°C, the fraction of total sugars in the first condenser oil is as high as 20 wt%. Producing oils with high contents of hydrolyzable sugars could open the door for the separation and further use of this fraction to produce biofuels and high-value products.

Figure 7.11 shows the total yield of sugar as a function of the temperature in the first condenser. Our results indicate (shown particularly from the data at $T_{reactor}$ = 330°C; see Figure 7.11) that this fraction is not affected much by the condenser temperature and that the reactivity of the sugars is minimal in the range of the condenser temperature studied. Comparing the yields of levoglucosan and xylose in the oil with the sugar fraction/glucose yields after hydrolysis, it is possible to state that the yield of hydrolyzable oligosugars is low, viz., ca. 1.5 and 0.4% at 480 and 330°C, respectively. Concentrations of these oligomeric sugars can nevertheless be significant in oils condensed at higher temperatures (e.g., ca. 6 wt% at $T_{reactor}$ = 480°C and temperatures of the first condenser between 60 and 90°C). This result suggests that perhaps some of the hydrolyzable oligosugars may be formed after condensation.

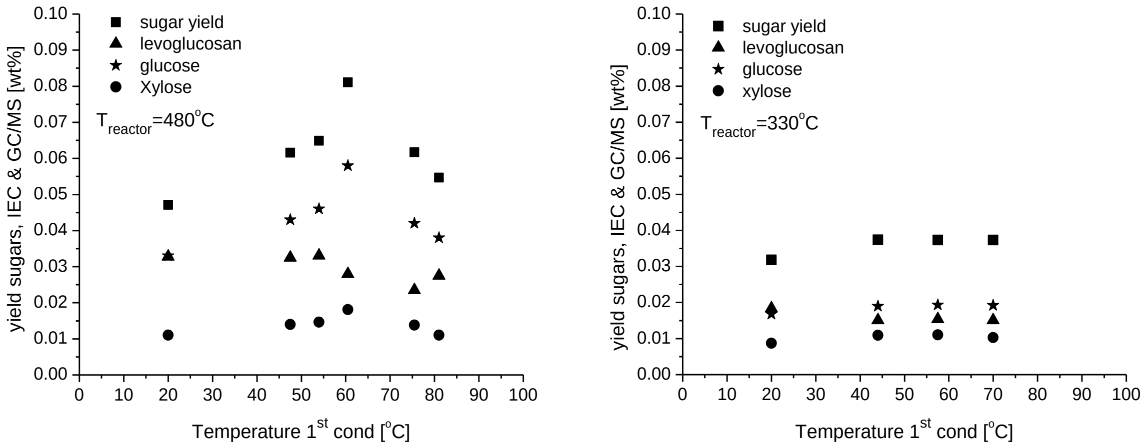


Figure 7.11: *Yield (kg/kg wet biomass * 100%) of all the sugars, levoglucosan, glucose and xylose versus the temperature of the 1st condenser (reactivity). 1.5-2 Hours residence time of the oil in hot 1st condenser.* $T_{reactor}$*=480°C or 330 °C.*

Water Insolubles.

Water insolubles consist primarily of lignin derivates[16]. The effect of the condensation temperature on the heavy fraction of the pyrolysis oil in the first condenser is illustrated in Figure 7.12. The concentration of water-insoluble compounds increases with an increasing condenser temperature. In fact, the fraction of water insolubles takes up a large part of the pyrolysis oil (obtained in the first condenser) when the condenser temperature is increased while operating the reactor at 480°C. This fraction increases up to 35 wt% when the condenser temperature is increased to 81°C. At a reactor temperature of 330°C, the fraction of water insolubles is much lower; only 13 wt% at a condenser temperature of 70°C. This is due to the lower production of lignin oligomers at lower temperatures.

The measured amount of water insolubles compares well to the model prediction. In the second condenser, no water insolubles have been found for the whole condenser temperature range studied. This result shows the effectiveness of the spray droplet condenser system to collect aerosols that are presented.

A comparison of the model predictions shown in Figure 7.12 for $T_{reactor}$ = 480 and 330°C shows the importance of the model input (yields of organic groups) for accurate predictions. Using the yields (composition) of the oil obtained at $T_{reactor}$ = 480°C as the model input for predictions of experiments carried out at $T_{reactor}$ = 330°C would result in 3-4 times overprediction of the water-insoluble fraction. The model input is also important for the light fractions (see Figure 7.4) but less sensitive when compared to the heavy water-insoluble fraction, which is shown to change dramatically with the pyrolysis temperature.

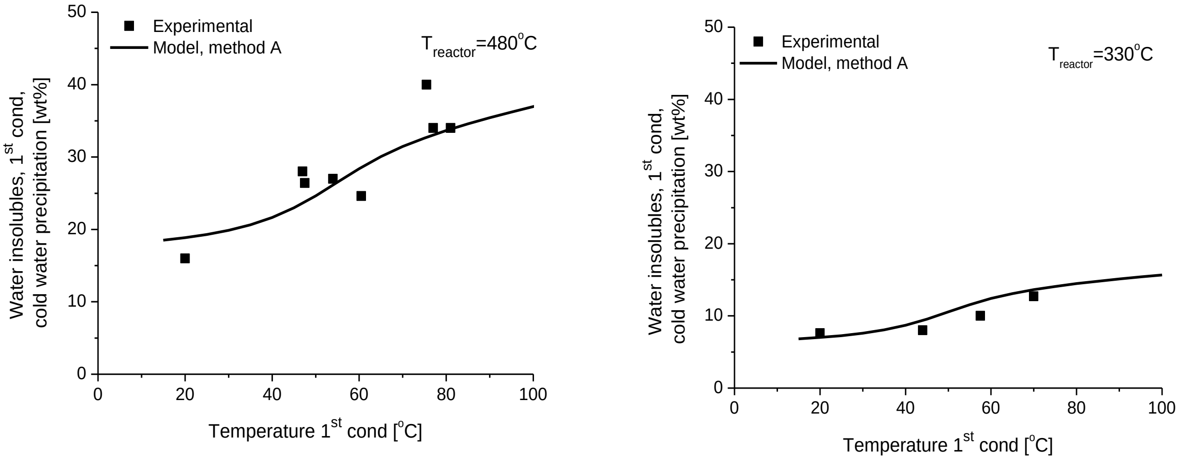


Figure 7.12: *Effect of the temperature of the 1^{st} condenser on water insolubles fraction of the oil collected in the 1^{st} condenser. $T_{reactor}=480^oC$ or 330^oC. Lines are model predictions.*

7.3.4 Overall Composition and Properties of the Oil.

Elemental composition, viscosity, and phase stability tests were performed on the oils produced at different condensation temperatures[4]. Figure 7.13 shows the evolution of the elemental composition and the high heating value of the bio-oil collected in the first condenser as a function of the condensation temperature. The high heating value (calculated from the elemental composition) of the pyrolysis oil increases from 14 to 24 MJ/kg on a wet oil basis ($T_{reactor}$ = 480°C) when the condenser temperature is increased from 20 to 70°C. The high heating value on a dry oil (organic) basis increases from 20 to 25 MJ/kg. This can be explained by the increase of the concentration of lignin-derived compounds in the oil, which have a relative low oxygen content compared to the light organic compounds removed from the first condenser oil.

While the carbon content increases from around 52 to more than 62 wt%, the content of oxygen decreased from 42 to almost 35 wt% (both on a dry basis). This decrease in the content of oxygen and the concentration of molecules with more than six carbon atoms in the oil could help to reduce the amount of hydrogen needed for the hydrotreatment of these oils.

Figure 7.14 shows the viscosity of four of these pyrolysis oils as a function of the temperature at which the viscosity is measured. At higher condenser temperatures, the viscosity of the oil measured at 20°C increases rapidly because of the loss of water and light organic compounds from the first condenser. The viscosity of the pyrolysis oil can be reduced significantly by heating (see Figure 7.14). These heavy oils can therefore still be very interesting for further applications or upgrading when they are preheated before usage. Actually, pyrolysis oil with 1.5 wt% water (T_{cond} = 80°C) has, at room temperature, a viscosity of 80 000 cP, and after heating to 80°C, it only has a viscosity of 300 cP. Phase stability tests were performed by adding 10 wt% water to the first condenser oils obtained at condenser temperatures of 20, 49, 57, and 63 °C ($T_{reactor}$ =480°C). In this series of experiments, the measure for the stability is the tendency to phase separate into two layers (an aqueous phase and a heavy-oil phase). Only the oil condensed at 20°C phase separated almost immediately into two layers; the others did not. Visual inspection of the other oils during 4 years of storage has been carried out. These heavier oils still appear visually to be a single-phase liquid after 4 years. From this, it can be concluded that removal of light organic polar compounds and water (happens when condensing at higher temperatures) does not cause instability of the oils. In fact, adding water could be an excellent way to reduce the viscosity of oils collected at high condensation temperatures during its further refining.

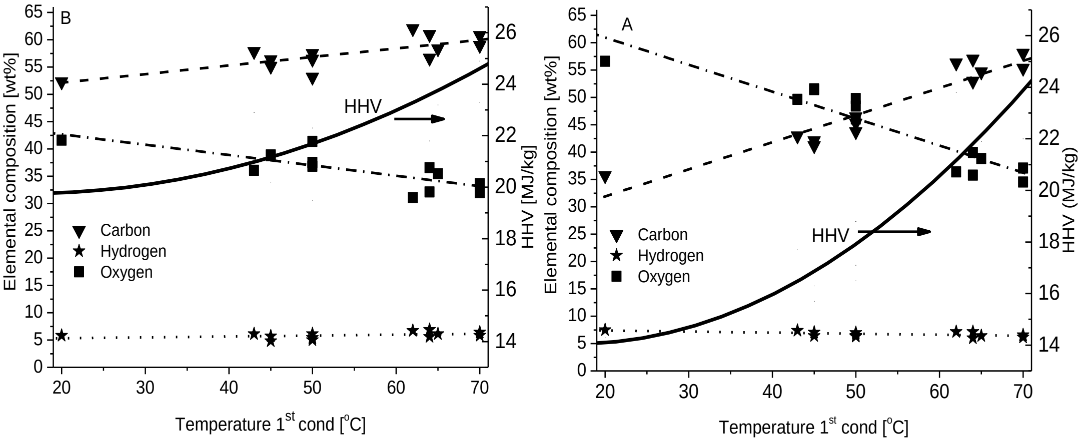


Figure 7.13: *The elemental composition and High Heating Value of the pyrolysis oil collected in the 1^{st} condenser (A wet oil basis and B dry oil basis) as a function of the temperature of the 1^{st} condenser. $T_{reactor}$=480°C. Lines are trend lines.*

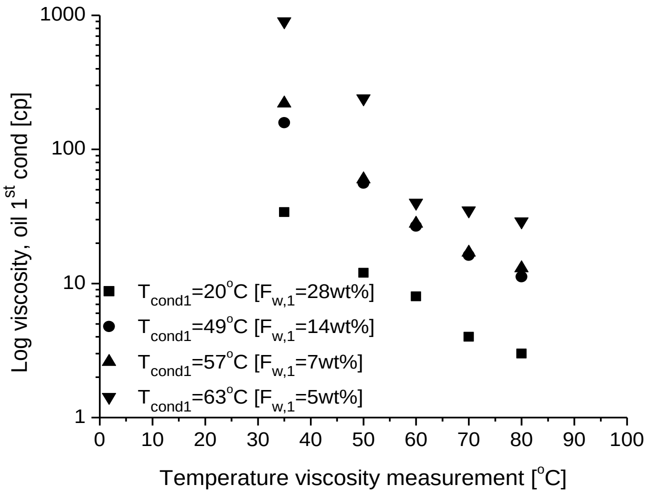


Figure 7.14: *Viscosity of the oils collected in the 1st condenser versus the temperature of the oils during the measurement. The reactor temperature was 480°C.* $F_{w,1}$ *is the water fraction (wt%) of oil in the 1st condenser.*

7.4 DISCUSSION AND CONCLUSION

Controlling reaction and condensation conditions to produce pyrolysis oils suitable for upgrading to transportation fuel and chemical production is still in the research and development stage. Meanwhile, research establishing experimentally validated relations between oil composition and performance (quality) in downstream processes is emerging[5].

In this paper, we have investigated the possibilities to steer the composition and, thus, quality of the produced liquids by the reactor temperature and the temperature of the first condenser.

To describe the composition of the oil, we have integrated several analytical techniques into a novel characterization scheme. Two methods of this scheme (one being a less detailed version of the other) are developed. With the detailed method, it is possible to account for 77-82% of the oil. The rest of the oil is likely to be formed by C-C bonded sugars that are difficult to quantify by conventional analytical approaches. Because no solvents are used (except for cold-water extraction) in our scheme, interpretation of the result is not troubled by the partition of (lumped) component classes over different solvent phases.

Fast pyrolysis has been optimized toward maximum oil yield, resulting in an operating window of 400-550°C[5,6]. Reducing the pyrolysis temperature from 480 to

330°C results in a significantly lower amount of mid-boilers and heavy compounds being released from the feed, resulting (after condensation) in a light oil. It has been shown that this oil has a low coking tendency[5] during atomization and better steam-reforming characteristics[20]. Sugars, mid-boilers, and water-insoluble lignin-derived oligomers are more present in the oil obtained at 480°C (1.7, 1.9, and 4.4 times more than at 330°C, respectively), while the yields of light organics are approximately the same.

When the temperature of the first condenser is increased in a serial condenser train, the concentration of target compounds (classes) can be increased in either the first or second condenser. A well-designed spray condenser has shown to be very effective in collecting aerosols. When the first condenser is operated around 70-90°C, the light fractions are collected for more than 90% in the second condenser. Under these conditions, aqueous solutions containing up to 10 wt% acetic acid can be obtained in the second condenser, which is beneficial for extraction of this compound. The aqueous liquid collected from the second condenser contains generally 40% light organics and could be an interesting feedstock for aqueous-phase reforming and gasification in supercritical water. Oils from the first condenser operated at 70-90 °C contain significantly less water (10-4 wt%) and less (acetic) acid (3-2 wt%), which results in a pH of 2.5-3 compared to 2-2.2 at 20°C, making it more suitable for further refining to produce transportation fuels and chemicals. The heating value of the oils collected in the temperature range of 20-90 °C (hereafter called heavy oils) increased from 14 to 24 MJ/kg on a wet oil basis. The viscosity of these oils at room temperature is very high (up to 8000 cP). However, the viscosity is decreased drastically at higher temperatures (oil containing 5 wt% water has a viscosity of 1000 cP at 20°C, dropping to 40 cP at 80°C). Heavy oils contain ca. 20 wt% sugars (monosugars plus hydrolyzable oligomers), which can be an interesting fraction for fermentation[21] and sugar chemistry. Next to sugars, this oil contains large amounts (especially at $T_{reactor}$ = 480°C) of pyrolytic lignin (water insolubles), which can be separated from the sugars by precipitation. This lignin-derived fraction has been considered for co-feeding in hydrotreaters and fluidized catalytic cracking (FCC) units for gasoline production.

Overall, it can be concluded that fractional condensation is a promising cheap downstream approach to concentrate compounds (classes) and, thus, to control the quality of pyrolysis oils, making it more suitable for further upgrading and/or direct applications.

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Main Conclusions

Biomass, potentially an environmental friendly and sustainable resource, is widely recognized as a promising way of addressing the problems of climate change by substituting for finite fossil fuel reserves. One of the more options is the conversion of biomass, in the absence of oxygen, to obtain a liquid called pyrolysis oil. Pyrolysis oil differs from conventional mineral oils in terms of composition and properties. This creates particular challenges in making direct use of pyrolysis oil in those end-applications and conversion processes that were originally developed for fossil fuels.

The main goal of the research described in this thesis was to evaluate the options for pyrolysis oil quality and yield improvement within a pyrolysis process that consisted of feed pretreatment, reactor and condenser system. Results obtained in specific tests were used to gain insight in the pyrolysis mechanism, in particular the complex phenomena of simultaneous chemical reaction, mass transfer and heat transfer within a pyrolyzing particle.

The influence of pretreatment was studied by varying the particle size (0.25-14 mm), the water content (0-20 wt% of biomass), the ash content and the micro-structure of the feed, which was mostly pine and beech wood in this work. Micro-structural effects were investigated by comparing the pyrolysis results obtained using: (i) natural wood cylinders; (ii) milled wood particles; and (iii) artificial wood cylinders that had a thin steel wall and were filled with milled wood particles.

Within the reactor, variations were made to the temperature (260-560^{o}C), ash/char hold-ups and vapor/aerosol residence time (2 – 15 s). It was investigated whether it is possible to concentrate single compounds or groups of compounds in the oils by applying a step-wise pyrolysis approach. In step-wise pyrolysis, biomass is first pre-treated at 260-360°C where after the solid residue of the first step is cooled down to ambient temperature and re-processed at a higher temperature of 530°C, while the gaseous and condensable products are collected during both steps. The condenser system, consisting of two counter-current spray columns, was operated at various temperatures between 20 and 115˚C and sweep gas load (2.0-4.1 kg of gasses / kg of vapors) to see if controlled fractional condensation of the pyrolysis vapors is possible.

To perform the required experiments sufficiently accurately, a 1 kg/h pyrolysis plant was developed that allowed the study of the effects of a wide range of process parameters, under stable operating conditions and with high mass balances closure (typically between 94 and 101%) and good reproducibility, even at the level of single compounds in pyrolysis oil. A custom fluidized bed reactor was developed especially for this research, which was found to operate highly effectively. However, its design would need to be reconsidered for scaling up. The counter-current spray condensers allowed for well-controlled fractional condensation, because they achieved near-equilibrium and the spray principle was very effective in collecting aerosols by applying a sufficiently large contact surface. The condensor performance could be accurately described by a single-stage equilibrium model that used the vapor composition, and thus its boiling point distribution, as input.

To describe the composition of the pyrolysis oil obtained, we combined several discrete analytical techniques into a novel, single characterization scheme that subdivides the oils in groups such as: (i) lights; (ii) mid-boilers; (iii) water-insolubles; and (iv) hydrolysable sugars. Within these groups, individual compounds were identified using KF, GC/MS and Ion-Exchange Chromatography. Two versions of this scheme were developed, one more detailed than the other. Using the detailed scheme, it was possible to characterize ca. 80% of the oil, although the exact composition of the remaining 20% could not be established. However, it was found that this unidentified fraction of the pyrolysis oil is sugar-derived, has a boiling point higher than 154˚C, is water-soluble, but not hydrolysable. Most probably this important fraction that could not be analyzed contains cross-linked (c-c bonds) oligomeric sugars.

With respect to the pyrolysis mechanism at the particle level the following conclusions are drawn. (i) Reactions below 300˚C do not influence the accumulated (sum of step one and two) product distribution in step-wise pyrolysis with a final pyrolysis step at 530˚C. This means that reactions below this temperature are not important for typical fast pyrolysis conditions of 450-550˚C. (ii) The reactions taking place in the range of 310-360˚C have a profound effect on char formation in the step-wise approach: more accumulative char and water is produced at the expense of organic volatiles. Larger molecules, whether in the liquid or solid phase, that are present in the pyrolyzing particle are responsible for the increased formation of char due to their high reluctance to leaving the particle. While they remain in the particle, these larger molecules undergo cross-linking and poly-condensation reactions leading to char. Facilitating long residence times for particles in this regime results in the production of bio-char. Moving rapidly through this temperature regime favors the production of pyrolysis oil. Reactions that produce lights, mono-phenols and sugars are almost completed at 360-400˚C if a sufficiently long particle residence time (in this study, 25 minutes) is facilitated. Based on the findings of the step-wise and particle size/micro structure study, we conclude that an effective pyrolysis mechanism ideally comprises several stages of the reacting particle, ranging from fresh biomass to a completely devolatilized structure that we term “final” char. The main emphasis in such mechanistic model should, in our view, be on the competition between those routes that lead to char and those routes that release decayed compounds from the biomass particle by sublimation, vaporization or physical entrainment. Another key conclusion is that — due to mass transport and energy transport limitations — even for the smallest pyrolyzing particles studied (0.25 mm), the (theoretical) maximum oil yield and minimum char yield still has not proved possible to obtain it. Indeed, it seems unlikely that truly chemically and kinetically controlled pyrolysis is feasible. Within the typical particle size range of 1 to 5 mm, mass transfer, energy transfer and chemical reaction all occur simultaneously. The extend of mass transfer effects were found to be related to the micro-structure of the particle; larger decay products can escape more easily from the smallest particles that consist only of cell wall material than they can from larger particles that have a channel structure.

A maximum oil yield of 74 wt% and minimum char yield of 8 wt% was observed for particles of 0.25 mm pyrolyzed at 500^{o}C and a vapor residence time of less than 2 seconds. Such high oil yields are not often reported.

It was observed that none of the various process parameters, methods of operation and process configurations resulted in a much higher overall production nor in the suppression (the sum of step one and two in case of the step-wise approach) of target compounds (groups) in the oil. The maximum observed effect for single compound — or class of compounds — in the oil was a factor two increase compared to one step 530^{o}C.

Both light and heavy oils can be produced by imposing suitable process conditions. Light oil was produced at lower pyrolysis temperatures and/or using larger particles. Heavy oil was obtained at higher pyrolysis temperatures, using smaller particles and during the second step in the step-wise approach with the temperature of the first step above 300˚C. The heavier oils contain more water-insoluble, lignin-derived compounds, leading to a clearly higher average molecular weight and viscosity for these oils. The complex processes occurring inside the particles during pyrolysis such as liquid intermediates that can either polymerize or leave the particle, overlapping decomposition of the wood constituents along the temperature track resulted in the observation that single compounds and lumped groups could neither be concentrated to any significant extent in oils obtained from various particle sizes nor in the step-wise oils — at least not without major yield losses in the case of the latter.

Introducing oils produced under various process conditions into a gasification or hydrodeoxygenation test unit gave direct indications about the effect of various pyrolysis process parameters on the quality (and therefore applicability) of the ultimate pyrolysis oil.

In terms of the homogeneous vapor conversion, homogeneous cracking reactions were found to be dominant over polymerization reactions. At 400˚C, the oil yields were independent of the residence time, although changes in oil composition indicated that some cracking reactions had occurred. At and above a vapor temperature of 500˚C, the gas yield increased and the oil yield decreased initially with residence time, while for longer residence times (up to 15 s) an almost stable oil yield was achieved. These results show that a large proportion of the wide variety of vapor molecules is stable enough at temperatures up to 550^{o}C not to be cracked to gases, even at relatively long residence times (>2 sec.). Only a small amount of char was formed from a char-free vapor stream on surfaces such as the reactor wall and filter material, but this amount was too small to be quantified.

In terms of the heterogeneously catalyzed vapor conversions, it was observed that in a fluidized bed pyrolysis reactor the char (of low ash biomass) appears to have no influence on the vapor yield. However, the presence of minerals (Na or K), either in the biomass matrix (native or impregnated) or externally (in the form of salt or in char), has significant influence, especially on the charring/polymerization reactions. The char yield even increases from 16 wt% (under normal conditions) up to 42 wt% when a hold-up of 0.7 wt% (of the solid material in the bed) of Na and K is present in the fluidized bed reactor.

Fractional condensation is a promising and cheap downstream approach to concentrating compounds (classes) as produced in the complex pyrolysis process and, therefore, to controlling the quality of pyrolysis oils. High boiling point compounds — such as sugars and lignin-derived oligomers — were collected in the first condenser and the lights were collected in the second condenser. Oil properties — such as viscosity, elemental composition, stability (water content) and acid number — could be controlled accurately under various sweep gas loads and feed moisture levels In conclusion, fractional condensation is a promising method of controlling key properties of the pyrolysis oil, such as water content and acidity, and therefore of controlling the oil’s quality.

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