Improving the selectivity of pyrolysis by pyrolytic acid leaching of biomass

the role of AAEMs, anhydrosugar production
and process design & evaluation

S.R.G. Oudenhoven

IMPROVING THE SELECTIVITY OF PYROLYSIS BY PYROLYTIC ACID LEACHING OF BIOMASS

THE ROLE OF AAEMS, ANHYDROSUGAR PRODUCTION
AND PROCESS DESIGN & EVALUATION

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THE ROLE OF AAEMS, ANHYDROSUGAR PRODUCTION AND PROCESS DESIGN & EVALUATION

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To friends and family

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Chapter 1

General introduction

Abstract

Firstly, a short introduction into the current energy consumption, reserves and applications is given. The challenge of producing energy for future generations in a sustainable way is explained. Hereafter, the composition and availability of biomass is discussed and conversion routes to chemicals and energy carriers are touched upon. This chapter also serves as a general introduction to biomass pyrolysis. The pyrolysis of wood is described at the level of chemistry and transport processes. Special attention is paid to the role of alkali and alkaline earth metals (AAEMs) in pyrolysis. Options to minimize the effects of the AAEMs during pyrolysis are discussed. A novel pyrolysis process, using pyrolytic acid leaching, which has been developed and evaluated in this thesis is introduced. Finally, the scope and structure of this thesis are explained.

Part of this chapter is based on:

Oudenhoven SRG, Westerhof RJM, Aldenkamp N, Brilman DWF, Kersten SRA. Demineralization of wood using wood-derived acid: Towards a selective pyrolysis process for fuel and chemicals production. J Anal Appl Pyrolysis. 2013;103:112-8.

1. The fossil fuel centuries

The earth can be regarded as a closed mass system to which continuously an amount of energy is added via the sun [1]. This energy finally leaves the earth as low temperature radiation [1]. A fraction of this sunlight is stored via photosynthesis as biomass. This process can be regarded as a closed cycle involving the creation of biomass (reduced components), which are subsequently oxidized during decay or utilization to CO_2 and H_2O . Over millions of years a fraction of the biomass has been transformed into fossil resources [2].

In the early days mankind was using food (biomass) as its sole energy source ($\sim 2000 \text{ kcal day}^{-1} = 8.4 \text{ MJ day}^{-1}$) [1]; mechanical energy was produced by man or animal power. Later biomass, mainly wood, was also used for heat generation (fireplaces), lighting, cooking food and making materials (e.g. pottery and smiting). From the 9th century mechanical energy was also produced via wind or hydro power [2]. The invention of the effective steam engine, by Newcomen (~ 1712) and Watt (~ 1765), and later the internal combustion engine (~ 1860) caused that mechanical energy produced from fossil fuels largely replaced man power (diesel contains 37 MJ dm^{-3} vs human energy consumption of 8.4 MJ day^{-1}). The development of commercial oil drilling and refining (1745 Russia [3], 1859 USA [1]) led to the production of numerous new synthetic carbon based materials like synthetic fibers (e.g. rayon, nylon and polyester), plastics, cosmetics and detergents. The production of ammonia, main source of nitrogen fertilizers, from air and natural gas via the Haber Bosch process (1909) facilitated that more food per hectare of farmland could be produced allowing the increase of the world population. Nowadays the food production consumes 5 to 15 times more energy than the energy recovered in the final food [4].

In 2011, the primary energy use per capita was 216, 387, 708 MJ day^{-1} for the world, Europe and the Netherlands, respectively [5]. Based on these numbers it can be calculated that people in the Netherlands consume around 85 times more energy than the amount required as food. Since 1970-1980, the amount of energy consumed in highly developed countries (~ 1 billion people) has stagnated due to the development of more efficient processes [4]. The coming decades the prosperity of the rest of the world (~ 5.5 billion people) is expected to increase. Combined with the expected growth in world population (9.7 billion in 2050 [6]) this shows that the demand for energy will continue to increase. Depending on the energy scenarios the world primary energy consumption will be between 600 and 1000 EJ year^{-1} in 2050 [5]. At present 86 % of our primary energy originates from fossil fuels (Figure 1). The various fossil fuel sources are used for different applications i.e. crude oil is mainly used for transportation and industrial applications (producing chemicals) whereas coal and gas are mainly used for heating and electricity production.

Figure 1: World energy consumption by energy source and world population as function of year. Data for energy consumption from [7] and data for population from [8] (before 1950) and [6] (1950 and later).

The utilization of fossil fuel as main source for energy has, next to the improvement of the standard of living, a number of disadvantages, these include:

- The combustion of enormous amounts of fossil fuel have led to an increase of the atmospheric carbon dioxide (CO_2) concentration from 315 ppm in 1958 to nearly 400 ppm in 2015 [9]. CO_2 is a greenhouse gas causing the surface and lower atmosphere of the earth to warm up. The importance of global warming, affecting our ecosystems and livelihood, is reflected by governments and industries across the world setting sustainability targets like the global pact, to keep the global temperature rise by the end of the century well below 2 °C, as agreed at the 2015 UN Climate Change Conference in Paris.
- Fossil fuels were produced from biomass, via natural processes, during time spans of millions of years. There is a huge mismatch between the time needed for its formation and the current rate of consumption. Therefore fossil fuels can be regarded as finite. Under the current consumption rate and proven reserves, we will have sufficient coal, natural gas and oil for the coming 120, 55 (excluding shale gas) and 56 (excluding unconventional oil resources) years, respectively [10].
- The uneven distribution of fossil fuel resources has led often to political tensions (security of supply).

To summarize, one of the biggest challenges for the coming decades will be to supply people's energy needs, required for a high living standard, in a sustainable way with reliability and resilience.

2. The rationale for biomass utilization

2.1. Biomass

Biomass by definition covers all organic matter derived from recent biological origin such as wood, grasses, manure and sewage. In principle any biomass source can be used to produce chemicals or transportation fuels. However, its use should not compete with the direct and indirect supply of food, as long as insufficient cheap food is available worldwide, or largely affect the biodiversity; e.g. burning down rainforest for palm oil production. Therefore, the largest and most convenient biomass stream is lignocellulosic biomass like wood, forestry residues, agricultural residues, and industrial waste streams (e.g. food or timber industry) [10, 11].

Biomass supply studies estimate the yearly available amount of biomass, in a sustainable way, to be between 200 and 500 EJ (currently 50 EJ year⁻¹ used) [5]. It should be noted that this amount of energy is based on the HHV of biomass and that fossil fuels in general are used more efficient. As an example, ethanol produced from corn consumes ~0.5 MJ of fossil fuel per 1 MJ of ethanol [12], for ethanol from sugarcane the fossil fuel contribution is around 25% [12]. Compared to the current primary energy consumption (590 EJ in 2013 [5]) it can be seen that only a fraction of the energy can be potentially supplied from biomass. Besides biomass other sustainable sources like wind, hydro and solar power can also be utilized for energy production. However, these alternative sources can produce heat and electricity but do not contain concentrated carbon (alternative is to capture CO₂), which is required for chemicals and material production. Moreover, the energy storage in liquid fuels is still much larger than the energy stored in batteries (Li-ion ~1.8 MJ l⁻¹ diesel 38.6 MJ l⁻¹) which is beneficial for long distance or heavy duty transport like trucks, ships and airplanes. It's the authors point of view that, based on the aforementioned, it should be concluded that biomass is an interesting feed for the production of chemicals and transport fuels

2.2. Lignocellulosic biomass structure

In this section the microscopic structure of softwood and the molecular structure of the building blocks of lignocellulosic biomass are discussed. Figure 2 shows the structure of softwood at various scales. It can be seen (Figure top right) that softwood is composed of two cell types; tracheids (vertical) and rays (horizontal). The axial tracheids are long cells (1 to 10 mm) and cover over 90% of the volume of softwood. These tracheids, through which the water and nutrients were transported, in wood are in the range of 20 µm - 60 µm wide [13] (~30 µm for pinewood) with an average cell wall thickness of 3 µm [7]. Water and nutrient exchange between adjacent tracheids occurs via so-called bordered pits in the cell wall,

mainly concentrated in the long tapered ends of the tracheids [8]. The cell wall is made from microfibrils, which are bundles of cellulose covered with hemicellulose. Lignin is deposited between the microfibrils to “glue” them together and protect the carbohydrates against biological degradation.

Figure 2: Structure of softwood at different scales.

Cellulose

Cellulose, the most abundant organic compound on the surface of the earth, is a straight non-branched polymer which consists of β -D-glucopyranose units linked by 1,4-glycosidic bonds [14]. The length (number of glucopyranose units) of a cellulose chain is called the degree of polymerization (DP) which can vary significantly between different kinds of cellulose [14]. Natural cellulose has a DP in the range of 2,000-15,000 [14], whereas microcrystalline cellulose, often used for model studies, has a DP of 150-300 [15]. The different strains of cellulose are bonded together by hydrogen bonds forming a crystalline (highly ordered) structure [14]. These crystalline regions are alternated with amorphous (disorganized) regions [14], which are less resistant to biologic and thermal degradation [16]. The cellulose content of lignocellulosic biomass is typically in the range of 35 %- 50 % of dry mass.

Hemicellulose

Hemicellulose is a branched polysaccharide, which is composed of different pentoses (xylose

and arabinose), hexoses (glucose, mannose and galactose) and acidified sugars (e.g. glucuronic and galacturonic acids) [17]. In contrast to cellulose the average DP is in the range of 150-300 units [17]. It has an amorphous structure, allowing less hydrogen bonds, making it less resistant to (thermal or biological) degradation [18]. As a result the isolation of pure hemicellulose, for model studies, without modifying its original structure is very difficult. The actual composition and branching frequency largely depend on the biomass type. The hemicellulose content in biomasses varies between 15-35 % on dry mass [17, 18].

Lignin

Lignin is a highly cross-linked polymer mainly made of three common monolignols, being coumaryl, coniferyl and sinapyl alcohol, which are mainly interlinked through carbon-carbon and ether bonds [19, 20]. Lignin is highly resistant to chemical and biological degradation [19]. The molecular mass of lignin molecules is in the excess of $10,000 \text{ g mol}^{-1}$. Just like hemicellulose, lignin is difficult to isolate without modifying its chemical structure. The actual composition depends largely on the biomass type, e.g. softwoods contain mainly coniferyl alcohol whereas hardwoods are made up by coumaryl and sinapyl alcohol instead [18]. The lignin content in biomasses varies between 15-45 % on dry mass [21].

Other organic compounds

Next to cellulose, hemicellulose and lignin, lignocellulosic biomass contains also nonstructural organic component. These compounds can be extracted from biomass using polar (e.g. water or alcohol) or nonpolar solvents (e.g. hexane or toluene) and are therefore termed extractives. The extractives include proteins, simple sugars, pectins, starches, resins, terpenes, fats and essential oils [17, 18]. Depending on the biomass composition it can be interesting to extract these compounds, for example proteins for animal feed from grasses or oil from sunflower seeds, before processing the lignocellulosic fraction [22].

Inorganic compounds

The inorganic content, a combination of nutrients, sand and clay, varies significantly between different biomass types; for wood typically <1 wt% while fast growing grasses and algae can contain up to 25 wt% [23, 24]. The actual inorganics composition depends on the nutrients required for the specific plant growth [23]. Major inorganic constituents besides silica include the alkali and alkaline earth metals (AAEMs), i.e. potassium, calcium, magnesium, and sodium [23, 24]. The AAEM exist partly as salts (e.g. oxide, carbonate, oxylate and chloride) deposited in cells or pores after drying [23, 24]. The other part of the AAEMs is ionically bound to the lignin or hemicellulose via the empty electron pair of the oxygen atoms in carboxyl groups and hydroxyl groups [23].

3. Biomass conversion technologies

Solid biomass can be used to produce heat or electricity via combustion. However, it is the author's view, that the preferred way to utilize (the majority of) biomass is as a feedstock for the production of transportation fuels and/or chemicals. Understanding of the current production of these products from fossil fuels can provide insights for their bio-based alternative. Crude oil is a mixture of hydrocarbons with varying molecular weights (C_5 - C_{50+}). In contrast to biomass (~50 wt% oxygen), crude oil contains almost no oxygen. In an oil refinery crude oil is: i) distilled to obtain "mixtures" (like gasoline (C_6 - C_{12}) and diesel (C_8 - C_{24})) with certain physical properties, e.g. boiling temperature (closely related to molecular weight), and octane or cetane number; ii) a large fraction of the high molecular mass fraction is cracked to meet the aforementioned fuel specification; and iii) certain (pure) compounds with a specific chemical structure like benzene, toluene, ethylene and propylene are separated as building blocks for chemical production. A part of these building blocks for chemicals are functionalized by adding oxygen into the molecules. This process is depicted in Figure 3. From this figure it can be seen that the biomass building blocks need to be depolymerized. The oxygen content needs to be removed when traditional fuels are targeted; however, for a fraction of chemicals and alternative fuels, like ethanol, no or a rather small fraction of the oxygen has to be removed.

Figure 3: Molecular weight and oxygen content of crude oil, biomass and final products. Adapted from [25]

Figure 4: Routes for biomass conversion to transportation fuels and chemicals. Reproduced from Kersten et al. [80]

Several biological, chemical and thermal conversion techniques have been investigated to depolymerize biomass, an overview of these techniques is given in Figure 4. In general two approaches can be differentiated: i) lignocellulosic biomass is first fractionated into cellulose, hemicellulose and lignin whereupon the cellulose, together with or without the hemicellulose, is further depolymerized in mono sugars. These sugars are subsequently converted via various biochemical methods into final products (see Figure 7 for overview of possible products); and ii) thermo-chemical routes in which the whole biomass is depolymerized into a bio-oil (T 150 °C - 550 °C) or synthesis gas ($T > 800$ °C). The techniques producing bio-oils, like pyrolysis, have typically low selectivity towards specific compounds. Therefore these highly complex mixtures are used directly as fuel for heat and/or power production or further processed via deoxygenation techniques to obtain transportation fuels (mixtures). The syngas, a mixture of H_2 and CO, after removing N, S and tars, can be converted in various compounds including ammonia, alcohols and alkanes. As can be seen there are many ways to convert lignocellulosic biomass into fuels and chemicals. Unfortunately, the production costs of these bio-based processes are often higher compared to the production from crude oil. At the time of writing, for each of the techniques depicted in Figure 4, advantages and disadvantages have become clear or are becoming clear. The choice which technique will be implemented will largely depends on the decisions made by policy makers (subsidies) and (petro-) chemical companies (infrastructure and economics).

In the following part the pyrolysis of biomass, which is the subject of this thesis, is discussed in more detail.

4. Pyrolysis

Biomass decomposes at temperatures above 250 °C and in the absence of oxygen into char, liquid (transported from the particle as vapors and aerosols), and gases. The exact product composition depends largely on the biomass feedstock and process conditions. Maximal liquid yields are obtained under fast pyrolysis conditions. These conditions include reactor temperatures between 450 °C and 550 °C, high heating rates of the biomass particles and rapid quenching of the produced vapors (< 2 sec) [26]. To obtain high heating rates small particles (mm) are used as feedstock. Fast pyrolysis processes are generally operated at atmospheric pressure or below. Lower reactor temperatures (200–350 °C) and low particle heating rates result in higher char yields. This process is typically known as slow pyrolysis or carbonization. The liquid, termed pyrolysis oil or bio-oil, is a complex mixture of water and a large variety of oxygenated organic compounds with different chemical functional groups. The char, solid residue, is a carbonaceous material containing the majority of the inorganic compounds naturally present in biomass. The gases mainly consist of CO_2 , CO , CH_4 and H_2 .

Figure 5: Schematic representation of a typical pyrolysis process, in which the required energy is obtained by combustion of char. Moreover, the concept of decentralized pyrolysis and centralized refining, and other possible oil applications are depicted. Figure is reproduced from Kersten and Garcia Perez [27].

The pyrolysis of biomass has been studied extensively for more than hundred years. It is worth to mention that pyrolysis is also the initial chemical conversion in gasification and combustion processes. Good reviews on various pyrolysis fields include: chemistry see Shafizadeh [28] or Antal [16, 29]; reactor concepts see Radlein [30], Bridgwater [31] or Lede [32]; pro-

cess modelling and kinetics see Di Blasi [33], Lin et al. [34] or Antal et al. [35]; and for recent developments and current challenges see Mettler et al. [36] or Kersten and Garcia-Perez [27]. From these reviews it can be concluded that the potential of process parameters or process concepts to steer the lumped product classes or certain specific compounds are known. However, detailed understanding of the chemistry and transport processes (mass and energy) is lacking at molecular, particle and reactor level. At the time of writing, several fast pyrolysis (demonstration) plants are in operation (Ensyn, KIT), or are in debugging stage (BTG-BTL, Fortum). Current research is mainly focusing, next to screening various biomasses, on developing new methods to obtain pyrolysis oils with improved quality for targeted applications. These methods include; catalyst impregnation into the biomass [37, 38], catalytic vapor upgrading [39] and fractionation techniques [40, 41].

Table 1: Typical fast pyrolysis oil composition and properties. Data based on [45].

Major components classes	Typical concentrations in pyrolysis oil (wt%)
Water	20-30
Acids	5
Furanics	3
Aldehydes	10
Pyrans	1
Mono phenolics	2
Anhydrosugars	5
Water insolubles (mainly oligomeric phenolics)	16
Extractives	5
Properties	value
pH	2-3
TAN (mg KOH g ⁻¹ oil)	70-100 [46]
Solids (wt%)	>0.5
Oxygen content (wt%)	35-45
LHV (MJ kg ⁻¹)	13-18
Viscosity (cp at 40 °C)	15-35
Density (kg dm ⁻³)	1.1-1.3

Conventional fast pyrolysis can be seen as a process that converts biomass, with 50 wt% - 70 wt% mass and 40 % - 65 % energy yield [42], into pyrolysis oil. Compared to the bulky inhomogeneous solid biomass the produced pyrolysis oil can be more easily and economically stored and transported. This may allow the decoupling of the biomass production, primary conversion, further refining and/or application locations (see Figure 5). A typical pyrolysis oil composition and its properties produced by the fast pyrolysis of wood is shown in Table 1. The produced oil can be: i) used direct as feed for heat and/or power production; or ii) upgraded to serve as feedstock for transportation fuel production [43] and, to a lesser extent, for chemical production [44]. The latter can be explained by the fact that conventional fast pyrolysis of biomass lacks selectivity to single compounds (see Table 1).

Several pyrolysis reactor configurations have been studied and implemented in industry. These configurations include among others; bubbling fluidized bed (Dynamotive), circulating fluidized bed (Ensyn and Fortum), rotating cone reactor (BTG), cyclone reactor (Latvian State Institute of Wood chemistry) and auger reactor (Lurgi together with Karlsruhe and Abritech) [31, 47]. Each of these reactor concepts has its specific parameters, i.e. particle heating rate, escape rate of formed products from the pyrolyzing particle, contact time between vapors with char and hot vapor residence time, which all influences the pyrolysis products. The role of these parameters in pyrolysis are explained in the next section.

Figure 6: Schematic of the multilevel character of wood pyrolysis ranging from a tracheid to a wood particle. Figure adapted from Kersten and Garcia Perez [27].

4.1. A closer look at the processes during pyrolysis

At microscale, wood has an inhomogeneous structure (as discussed in 2.2) consisting of cells. These cells are mainly oriented in longitudinal direction and termed tracheids; in a rectangular wood particle of 1 mm * 1 mm (depth * width) 300 – 10000 of these tracheids are present. Upon heating the solid biomass decomposes into vapors and gases. It is worth to mention that a part of the biomass, during pyrolysis, will pass through a liquid intermediate with a lower DP [48, 49], in cases of cellulose pyrolysis often termed active cellulose [50]. The chemistry will vary within the different phases, e.g. Mamleev et al. [51] stated that dehydration reactions will mainly occur in the liquid intermediate phase. Teixeira et al. showed that during the pyrolysis of small cellulose particles aerosols were ejected from the liquid intermediate [52]. They argued that mass transport via aerosols, next to vaporization of smaller molecules, is an important mechanism to transport heavy, non-volatile, products out of the reacting biomass particle [52] (see Figure 6 right). In a pyrolyzing biomass particle, the transport of gases, vapors and aerosols will proceed predominantly via these tracheids [27] (see Figure 6). The vapors and aerosols can undergo secondary reactions with the nascent char (containing the AAEMs) on their way out of the biomass particle or outside the particle in the vapor phase. These reactions can be cracking reactions leading to gases or light vapors or polymerization reactions leading to char and water. The severity of vapor reactions largely depends on the vapor temperature [53], residence time [53-55] and the presence of AAEMs [53]. Heat transfer into the particle is a multidimensional problem, however for typical biomass particles with an aspect ratio (length over diameter or width) of 3 or larger the dominant heat transfer direction is the diameter (width). Depending on the pyrolysis temperature, biomass particle size and used heat transfer the pyrolysis reactions can be i) kinetically controlled therefore the reactions occur at the temperature of the surroundings [56], this situation is the case for small biomass particles and temperatures below ~550 °C [57, 58]; ii) limited by the external heat transfer [56], which is often the case when no solid heat carrier is used; or iii) controlled by internal heat transfer [56], which is the case for larger biomass particles and temperatures above ~550 °C [57, 58]. By which of these 3 options a pyrolysis experiment is limited can be classified using the Biot, Py and Py' numbers as proposed by Pyle and Zaror [56]. The kinetic models used to describe the pyrolysis process rely on lumped components (often char, oil and gas), and can therefore not be used to predict the product composition. From the aforementioned it therefore can be concluded that pyrolysis is a multilevel (position and time scale) process (see Figure 6).

4.2. The importance of AAEMs during pyrolysis

The presence of AAEMs in biomass during pyrolysis increases the char, water, gas and light organic yield reportedly via catalyzing of ring-fragmentation [59] and dehydration [60] reactions of the carbohydrates. These two AAEMs catalyzed reactions cause, at least partly, the low selectivity towards anhydrosugars and the presence of many small oxygenated molecules in the pyrolysis oil. Producing anhydrosugars, from the hemicellulose and cellulose, together with monomeric phenolics, from lignin, via pyrolysis would be an promising concept as these compounds are precursors for the bio and/or (petro-) chemical industry (see Figure 7 and Figure 8). The high water production leads often to phase separation of the pyrolysis oil, producing an aqueous and sticky organic phase which makes it more difficult to transport and to be used in applications. In addition, AAEMs causes difficulties in the char combustor due to its low melting point. The AAEMs can be (partially) removed from the biomass by water [61] or acid leaching [59, 62]. Leaching with (hot) de-ionized water can effectively remove most of the Na and K, however Mg and Ca are only partly removed [63, 64]. During acid leaching the deposited salts react with the acid to readily water soluble compounds and the cations bound to the biomass structure are ion-exchanged. The mineral acid leaching has been employed at increased temperatures [59] as well as at (near) ambient temperature [64]. Leaching at high temperatures (90-240 °C) with mineral acid leads to degradation of the hemicellulose [59] and is hereafter referred to as hydrolysis. It is worthwhile to mention that the removal of AAEMs from biomass has also been studied to improve pulping [65], improve the combustion properties [66] and to prevent slagging and corrosion [61]. Another approach studied is the passivation of AAEMs via infusion of biomass (also referred to as impregnation/titration) with sulfuric or phosphoric acid [67, 68]. In the acid infusion experiments biomass is soaked with diluted H_2SO_4 or H_3PO_4 , subsequently the water is removed via evaporation [67]. The infused sulfuric or phosphoric acid will (partly) react with the salts to (bi)sulfates or phosphates, which will precipitate in the biomass after the water evaporation. As a result of this titration it is claimed that the AAEM salts are replaced by less active AAEM salts (e.g. sulfates) [67]. Active as in influencing the pyrolysis reactions.

In 1924, Venn already showed that the production of anhydrosugars largely increased after mineral acid leaching of the feedstock for the pyrolysis of cellulose (cotton) [69]. An excellent paper was published in 1979 by Shafizadeh and co-workers [70] showing that the main differences in pyrolysis results (oil and anhydrosugar yield) from various cellulose batches were caused by the small amounts of AAEMs in the celluloses. These differences largely disappeared after mineral acid leaching. Under the applied conditions, 2 mbar and 400 °C, glucose yields, after hydrolysis of the oil, up to 68 wt% were reported from cellulose [70]. Moreover it was shown that after mineral acid leaching high anhydrosugar yields can be obtained by pyrolysis of wood [70]. Piskorz et al reported high anhydrosugar yields from mineral acid leached cellulose and wood in a fluidized bed pyrolysis reactor. This shows that vacuum is not

required to obtain high anhydrosugars yields. Patwardhan et al. showed that relatively low concentrations of AAEMs, by adding 0.01 wt% of NaCl or KCL to cellulose, largely reduced the levoglucosan yield from 60 wt% to 30 wt% [71].

Between 1958 and 1970 a pyrolysis process was operated, at the Krasnodar hydrolysis plant (USSR), for the production of levoglucosan (75 kg h^{-1}) [72]. The lignocellulosic residues were first hydrolyzed to produce xylite or furfural from the hemicellulose fraction. The solid residue was washed with H_2SO_4 at 90°C , followed by rinsing with water and the 2nd condenser liquid. After drying, the material was pyrolyzed using superheated steam as heat supply. The pyrolysis vapors were condensed in two stages, levoglucosan was concentrated in the 1st condenser, operated at 105°C . Levoglucosan was hereafter crystalized in cold acetone. Detailed information on the exact process is however lacking.

The understanding of the pyrolysis of lignin is much less compared to that of cellulose pyrolysis. This is partly due to the complex structure of lignin, which varies by biomass type, and to difficulties with analysis of the products. Lignin pyrolysis yields a large variety of light organics and monomeric and oligomeric phenolics [73]. Especially the oligomeric structures are difficult to identify and quantify. Typical reported monomeric phenolics yields on lignin basis are around 10 wt%. Whether the AAEMs affect the lignin derived products is still under debate as there is conflicting results in the literature. (discussed in more detail in chapter 6)

Figure 7: Routes for transportation fuels and chemicals from levoglucosan and glucose. Glucose products based on [74].

Figure 8: Products from lignin.

4.3. A pyrolytic acid leaching concept

The main objective of the work described in this thesis is to develop a pyrolysis process that can thermally depolymerize the cellulose, hemicellulose and lignin into monomeric anhydrosugars and phenolics instead of, or next to, pyrolysis oil for energy applications. This would make pyrolysis a technology that produces precursors for the bio and/or (petro-) chemical industry (see Figure 7 and Figure 8). Based on the literature described in section 3.2. it can be expected that the AAEMs need to be removed or passivated before pyrolysis to obtain high anhydrosugar yields. Understanding of how to steer the pyrolysis of lignin or biomass towards monomeric phenolics production is so far still lacking.

An interesting sustainable alternative to the mineral acid leaching or infusing (both methods use H_2SO_4 or HNO_3) would be to utilize the organic acids produced during the pyrolysis process itself. These pyrolytic acids, mainly formic and acetic acid, need to be separated from the rest of the oil. Westerhof et al have shown that fractional condensation of the pyrolysis vapors can be used as a simple and cheap technique to separate these small pyrolytic acids from the anhydrosugars and phenolics products [40].

Figure 9: Function block diagram for the pyrolysis of pyrolytic acid leached biomass.

Figure 9 shows a first simplified process layout consisting of the following process steps:

- i) Fast pyrolysis of the acid leached biomass where after the pyrolytic vapors are (fractional) condensed in two spray condensers in series. Operating the condensers at 80 °C and 25 °C (or lower), the lignin derived phenolic compounds together with the anhydrosugars (mostly levoglucosan) are concentrated in the 1st condenser while an acidic aqueous fraction (containing up to 10 wt% of acetic acid) is recovered in the 2nd condenser[40].
- ii) Leaching of the (wet) biomass with the acidic aqueous stream from the 2nd condenser to remove the (alkali) minerals from the biomass feed, upfront to pyrolysis. After the leaching step, the biomass is dried / dewatered to 0-20 wt% moisture content[75].

- iii) Combustion of the char and combustible non condensable gases produced during pyrolysis, in order to generate heat and energy for the drying, acid leaching and pyrolysis process.

Other advantages of removing the AAEMs, next to the increased selectivity towards anhydrosugars, include: i) increased oil yield at the expense of gas, char and water; ii) no minerals in the pyrolysis oil and hence no mineral related problems in subsequent applications, as e.g. catalyst poisoning during catalytic upgrading of pyrolysis oil or ash deposition in engines/turbines during combustion; iii) no low temperature melting ashes in the char, no agglomerates to be formed and less corrosion problems in the combustor section and iv) no catalyst poisoning by ashes during catalytic pyrolysis, both inside the reactor or in the vapor phase between the reactor and condenser, or during regeneration of the catalyst (burning of coke).

The concept of acid leaching using “pyrolytic” acids, concentrated by fractional condensation, before pyrolysis will be further developed and evaluated throughout this thesis. It would be preferred if the following conditions can be met by the final process: i) process that is capable of processing a large variety of lignocellulosic biomasses; ii) process that is self-sufficient in required heat; and iii) broadening of the product slate, allowing the production of specific molecules instead of, or next to, heating oil.

The final design of proposed process will be based on obtained insights in the underlying processes at all relevant scales, ranging from cell wall level to the process parameters at bench plant scale.

In this thesis pinewood (lignocel 9) and cellulose (Avicel ph101) are used as main feedstock. This biomass was selected due to many years of experience in the SPT research group [40, 53, 76-79] with this biomass, allowing comparison with earlier work. Besides the pinewood tests with lignocellulosic feedstocks with more industrial potential, e.g. agricultural waste streams, are performed.

5. Outline of the thesis

The work presented in this thesis focusses on the design and evaluation of a new pyrolysis concept, in which the AAEMs are removed before pyrolysis via pyrolytic acid leaching. The products of interest are anhydrosugars together with monomeric phenolics. The work is presented in the next chapters as follow:

First, in order to get a better understanding of the potential of producing anhydrosugars via pyrolysis, the pyrolysis of microcrystalline cellulose is studied in **Chapter 2**. As discussed in section 4. of this introduction, pyrolysis is a complex process of various reactions and transport phenomena. We started with pyrolysis conditions that minimize non-isothermality and maximize the escape and quenching rates of volatile products. These condition will minimize further reactions of volatile compounds at particle level and in the vapor phase, to obtain insights in the very early processes taking place at particle level. Under these conditions the effect of temperature on the product yield and composition is studied. Since these conditions are not realistic at industrial scale the effect of higher pressures and longer hot vapor residence times are evaluated next. To be able to interpret the experimental results two interpretation models were made. Based on experiments and these models the most dominant parameters affecting the anhydrosugars yield are identified.

Since complete removal of all AAEMs will not be realistic in practice, **Appendix A** focuses on the effects of low concentration of K_2CO_3 in cellulose. Also here we started with pyrolysis conditions that minimize non-isothermality and maximize the escape and quenching rates of volatile products.

In **Chapter 3** the proposed pyrolysis concept is tested with 4 different biomass sorts. The effect of pyrolytic acid leaching on the chemical composition of the biomasses and the AAEMs removal efficiency is studied. The product yields of untreated and acid leached biomass, obtained in a bench scale fluid bed pyrolysis reactor at 530 °C, are compared. Special attention is paid to the anhydrosugars yield. Moreover, it is investigated if the pyrolysis outcome can be related to the biomass composition before and after acid leaching. The importance of AAEMs remaining in the biomass after acid leaching is studied by comparing the anhydrosugars yield with that of pure microcrystalline cellulose and K_2CO_3 impregnated microcrystalline cellulose pyrolyzed under identical process conditions.

The use of a synthetic mixture for the acid leaching of biomass instead of the real 2nd condenser liquid is validated in **Appendix B**.

In **Chapter 4** it is investigated if the process can be optimized further by varying the pyrolysis

temperature between 360 °C and 580 °C. The effect of the reactor temperature on the pyrolysis of acid leached pinewood on the product yields and oil composition is studied. The results are compared with the results for untreated pinewood. To get a better understanding of the effect of acid leaching on the pyrolysis results, it is investigated if the observed effects are mainly caused by the AAEM removal or that possible modifications of the biomass structure induced by the acid leaching also play a role. In contrast to the anhydrosugars, for monomeric phenolics it is chosen to study these lignin derived products directly from biomass, as most extracted lignin underwent severe condensation reactions during isolation. Therefore, a combination of GC-MS, GPC and UV-fluorescence analysis is used to obtain insights on the effects of AAEMs and reactor temperature on the lignin derived products including the monomeric phenolics. Finally the formation of bed agglomerates during the pyrolysis of acid leached biomass is investigated.

In **Appendix C** the acid leaching of biomass is compared with H_2SO_4 infusion of biomass as pretreatment to reduce the effect of AAEM's during the pyrolysis process. Moreover the potential of adding small amounts of H_2SO_4 to pyrolytic acid leached biomass to further improve the anhydrosugars yield is tested

In **Chapter 5** it is evaluated under which conditions the pyrolytic acid leaching of biomass before pyrolysis can help to improve the economic feasibility of the overall process. Therefore a preliminary process design, for the implementation of acid leaching at a pyrolysis plant with a feedstock capacity of 5 or 50 ton h^{-1} , is made. The feedstocks studied were: pinewood, straw and bagasse. Moreover different cases are studied to evaluate the feasibility of producing various products, being heating oil, anhydrosugars and/or phenolics. The mass and energy balances of the designed process are calculated in Aspen Plus®. The economic performance is calculated using a net present value (NPV) balance and compared with that of a pyrolysis plant using untreated biomass producing heating oil as reference technology.

In **Chapter 6** an outlook and the main conclusions of this thesis are presented.

Appendix D contains the supplementary information for chapter 2

Appendix E contains the supplementary information for chapter 4

Appendix F contains the supplementary information for chapter 5

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Chapter 2

The interplay between chemistry and heat / mass transfer during the fast pyrolysis of cellulose

Abstract

Sugar produced from biomass is expected to play an important role as a platform chemical. Herein, we have shown that in the range of 370 °C to 765 °C, a constant high yield of sugar (~70% on C-basis) can be obtained from the fast pyrolysis of Avicel cellulose while producing hardly any gas (<1% by weight) and solid residue (<1% by weight, above 450 °C and 5 seconds reaction time). This opens the opportunity to combine the advantages of thermochemical processes, such as high conversion rates & products not being heavily diluted with water, with an increased value of the product slate. In this chapter, firstly the experimental technique, used to study the very early stages of cellulose pyrolysis, is introduced and characterized. Secondly, yield data as a function of process conditions are presented and interpreted, also using mathematical models, with respect to chemistry, heat transfer, mass transfer and their interplay.

This chapter is based on:

Westerhof RJM, Oudenhoven SRG, Marathe PS, Engelen M, Garcia-Perez M, Wang Z and Kersten SRA. The interplay between chemistry and heat / mass transfer during the fast pyrolysis of cellulose. ready for submission

1. Introduction

The pyrolysis of biomass has been studied extensively for more than hundred years. Already in 1920 Clément and Rivière [1] published a book called “La cellulose” summarizing the results until then. More recently, Lédé [2] presented a historical review covering results of cellulose pyrolysis till 2012. Mettler et al. [3], Mohan et al. [4], and Kersten and Garcia-Perez [5] reviewed fast pyrolysis of biomass and identified knowledge gaps and challenges. From these reviews it can be concluded that although progress is still made in the detailed understanding, predictive models of the chemistry and transport processes (mass and energy) are lacking at molecular, cell, particle and reactor level.

For decades, fast pyrolysis has been advocated to be a promising technology for the production of a bio-based energy carrier, called bio-oil, which can replace fossil fuels in the heating and transportation sector. Yet, the slow market introduction of the technology and adverse properties of the bio-oil point out the room for improvement. Optimization could be achieved via predictive reaction & transport models from which optimal process conditions, leading to the highest value of the product slate, can be obtained. With respect to the product slate it is the authors’ view that it is worthwhile to explore the production of feeds for the fermentation (sugars) and the chemical industry (e.g. sugars, aromatics / phenols, acetic acid, glycolaldehyde) instead of, or next to, bio-oil for energy applications [5, 6].

This chapter aims at advancing the understanding of reactions and transport phenomena by pyrolysing cellulose at conditions that minimize non-isothermality, maximize the escape rate of volatile products from the pyrolyzing cellulose particles and maximize the rate of the subsequent quenching of these products. High escape rates of the volatile products will reduce the extent to which they undergo reactions while still being part of the pyrolysing cellulose sample. Fast quenching minimizes reactions in the vapour phase and in the ejected fragments (e.g. aerosols). Hence, we have attempted to study the first stages and products of the pyrolysis process. To do so a screen-heater reactor has been designed that combines a high heating rate of the biomass sample with fast removal and quenching of reaction products [7]. In order to be able to draw conclusions without being hindered by uncontrollable and poorly understood phenomena, such as the effects of alkaline and alkaline earth metals [8-10] and interactions between the biomass’ building blocks [11, 12], it was decided to start with Avicel ph101 (very pure) cellulose. Knowing that this is an oversimplification, the upcoming work will be also on real biomass.

In the current chapter, progress on the characterization of the screen-heater (e.g. temperature measurement, quenching rate), aiming at better interpretation of the experimental data, is reported. As most important result, yields of lumped component classes (gas, solid residue,

condensed product), anhydrosugars (DP_1 to $DP_{>5}$), and glycolaldehyde are determined as a function of the final temperature of the screens in the range of 330 °C to 765 °C. It is investigated if the pyrolysis is kinetically controlled [13] or if there is an interplay between heat, mass transfer and chemistry.

Studies also aiming at minimizing secondary reactions are, inter alia, those of Lédé et al. [14], Piskorz et al. [15] and Gong et al. [16]. These studies report (very) low char yields, high yields of anhydrosugars, but also significant amounts of light oxygenates (e.g. glycolaldehyde) and permanent gas, particularly at higher temperature. The production of lights and gas in these studies may be due to the secondary reactions. In our experimental set-up we attempted to eliminate these reactions even further.

2. Material and methods

2.1. Materials

Avicel ph101 (Sigma-Aldrich particle size $\sim 50\ \mu\text{m}$, 60.5% crystallinity [17], ash content 0.005% by weight, AAEM $1\ \text{mg kg}^{-1}$, degree of polymerization specified < 350 average 220 [18]), levoglucosan (1,6-Anhydro-b-D-glucopyranose carbosynth purity $>98\%$ by weight) and cellobiosan (1,6-Anhydro-b-D-cellobiose Carbosynth purity $>95\%$ by weight) were used as a feedstock for the pyrolysis experiments. The feedstocks were dried in a vacuum oven (Heraeus FVT420) at room temperature and 1 mbar for at least 24 hours. More details on the used chemicals and materials can be found in S1

2.2. Screen-heater

The screen-heater (see Figure 1) and experimental procedure are described in detail in S2 and in Hoekstra et al. [7]. Here follows a short recap. The reactor consisted of a glass vessel (250 ml) in which the sample, $\sim 50\ \text{mg}$ cellulose pressed between two (stainless steel 316) screens, was clamped between the electrodes (#5). The effect of the screen material, which turned out to be not significant, was checked by tests with gold sputtered screens (see S2). The vessel could be filled with nitrogen till a pressure of 950 mbar - 1000 mbar. A vacuum pump could be used to create a pressure of ca. 5 mbar inside the vessel. A liquid nitrogen bath (#4) was placed around the vessel to cool the wall of the vessel. A syringe to take gas samples (#9) and a pressure gauge to monitor the pressure increase during an experiment were present. A pyrometer (#12) was used to monitor the temperature. To prevent disturbance of the temperature measurement by the liquid nitrogen, a glass tube with a silicone sealing (#13) was placed in the liquid nitrogen bath. During the experiment an electrical current was passed through the screens, which served as electrical resistance heaters to supply the heat required for heating the sample and maintaining it at a constant temperature for a specified time, called the holding time (see Figure 2 for a typical temperature profile). After the holding time the screens were cooled with a rate of approximately $60\ ^\circ\text{C s}^{-1}$. Experiments at 1 second and 5 seconds holding time were performed. 5 seconds was selected to ensure complete conversion as of $\sim 450\ ^\circ\text{C}$.

During the experiment cellulose decomposes into vapors, aerosols and gases. The vapors condensed on the cold surface of the vessel and electrodes and were recovered together with the aerosols. Note, the condensed product is in principle a solid product and not a liquid at room temperature, therefore this fraction will be referred to as condensed product instead of the general pyrolysis or bio-oil. The material that remained between the screens after certain experiments is termed solid residue.

Figure 1: Schematic representation of the screen heater set-up.

Figure 2: Typical temperature profile of the screen (experiment at 5 mbar). The heating pulse is started at 0 s. The pyrometer doesn't detect temperatures lower than 200 °C. Therefore, the temperature profile is constant between 0 ms and 36 ms.

The mass of condensed product was determined by subtracting the initial weight of the vessel, tape and clamps from the weight of these components after the experiment. The vessel was then rinsed with approximately 6 mL (in batches of 2 mL) of solvent. Note, >90 wt% of these products were collected on the vessel wall and thus only <10 wt% of these products was collected on the clamps and tape. The solvent was milli-Q water for HPLC analysis or methanol for GC/MS analysis. The solution was filtered before analysis. Some small amounts of compounds were not soluble. These compounds turned out to be unconverted cellulose (<9 wt%) see S6.5. The solid residue was determined by weighting the screens before and after the experiment. Detailed experimental information is available in S2. The condensable product, removed from the vessel with solvent, was analyzed for the light oxygenate content (GC/MS) and sugar content (HPLC). The DP is referred to as the degree of polymerization of $C_6H_{10}O_5$ units. The sugars DP_1 (levoglucosan), DP_{1-2} (compounds identified between DP_1 and DP_2), DP_2 (cellobiosan), DP_3 (cellotriosan), DP_{4+5} (sum of DP_4 (cellotetrasan) and DP_5 (cellopentosan)) and $DP_{>5}$ (DP higher than 5) were analyzed using HPLC (see S4). LC/MS analysis was used to identify the degree of polymerization of compounds referred to as $DP_{>5}$ (see S4) and to obtain information on the composition of compounds termed DP_{1-2} (S6.4). Hydrolysis of the condensable product was done using the analysis method of NREL [19] (S4). By hydrolysis the hydrolysable sugars in the condensable product were converted to glucose. The glucose yield in this work is expressed on cellulose basis. See for the calculations (equation 33, in S6.3) of the glucose yield.

Table 1 shows an overview of the analysis methods.

Table 1: Overview of analytical techniques.

Composition / properties	Technique	Reference
Cellulose		
Ash content	Dry oxidation @ 575 °C	[20]
Ash composition	ICP	
Solid residue		
Functional groups	FTIR	
Condensed products		
Light oxygenates	GC/MS	[21]
Anhydrosugars	HPLC + LC/MS	
Hydrolysable sugars	Acid hydrolysis + HPLC	[19]
Functional groups	FTIR	
Gas		
Non-condensable gassen	Micro-GC	

2.3. Fluidized bed

Avicel cellulose particles of $<50\text{ }\mu\text{m}$ were introduced semi-batch wise in the splash zone of a fluidized bed operated with sand of 212 μm to 300 μm . The feed rate was 200 g h^{-1} . The fluidized bed was operated at low velocity ($\sim 2 U_{mf}$) as a result of which the cellulose particles did not back-mix into the bed, minimizing the cellulose-sand interaction. Therefore the set-up can be characterized by a pyrolysis zone with a high heat transfer coefficient (the splash zone) followed by an empty residence time reactor (the hot zone till the condensing section). More details are given in S3. The vapor residence time in the hot zone of the set-up (reactor + tubing) was ~ 1.6 seconds. In this calculation the flowrates of the nitrogen, produced vapors and gasses were considered.

3. Characterization of the equipment

In the screen-heater we performed experiments at 5 mbar and 1 bar. The results of these experiments were compared with results obtained in a 200 g h⁻¹ fluidized bed (FB) operated at 1 bar. In Table 2, the main characteristics of these experiments are listed. Temperature is important as it sets the rate of the pyrolysis reactions. The heating rate determines the time it takes to heat the cellulose from its initial temperature to its end temperature (typically the temperature of the surroundings / pyrolysis reactor). The ratio of the heating rate over the reaction rate, the Py' number, indicates whether the reactions take place after the cellulose is heated to its final temperature ($Py' > 10$ & $Bi < 1$ = kinetically controlled pyrolysis) or already in the heating trajectory [13]. A lower hot vapor residence time (higher quenching rate) will result in less secondary reactions of products outside the reacting cellulose particle. The residence time of products on the reacting cellulose, characterized here by the evaporation time of individual products, is indicative for the extent to which these products can further react while still being on the pyrolyzing cellulose particle. A low residence time (high escape rate) results in less reactions of initial decay products while being on the particle.

3.1. Temperature & Heating rate

It was assumed that the temperature of the screens could be measured with the Kleiber KGA 730 pyrometer (see S2.5). Note, during conversion the temperature of the cellulose can be lower than that of the screens. The experiments were characterized by the final screen temperature (T_{FS} , see Figure 2). It was not possible to set T_{FS} exactly on beforehand. With the employed control-system the set-point temperature could be approached within 10 °C. In our experiments, the radiation of the screens / sample travels through the glass vessel and tube (#1 and #13 in Figure 1) before reaching the pyrometer. In order to calculate the temperature from the measured radiation, the transmittance of the glass parts and the emissivity of the screens were determined (see S2.5). The emissivity of the screens was estimated to be 0.65 +/- 0.15. From the scatter on the emissivity the error on the temperature was calculated to be +/- 20 °C for 330 °C increasing to +/-45 °C for 750 °C. Spatial temperature differences of the screens were estimated to be maximally 20 °C (see S2.5).

Under the standard conditions of 5 mbar the set-point of the screens was varied between 331 °C – 765 °C. We called this temperature the final screen temperature (T_{FS}). In this temperature range, the time to reach full conversion of cellulose is reported to decrease from minutes to less than a second [16, 22-24] and an increase of gaseous products at the expense of liquid and solid products is typically observed [22, 25]. At 1 bar, experiments were performed at ~ 535 °C in both the screen-heater and fluidized bed.

The heating rate of the screens was measured to be $\sim 5000\text{ }^{\circ}\text{C s}^{-1}$ (with cellulose between the screens). Also in the fluidized bed the initial (first part of the trajectory) heating rate was estimated to be very high ($\sim 5000\text{ }^{\circ}\text{C s}^{-1}$, see S3). High heating rates were selected to approach kinetically controlled pyrolysis as much as possible. Under which conditions this was actually achieved in the screen-heater will be discussed in the results section. The employed heating rates are high in comparison with industrially relevant particles of several millimeters in size. For such particles heating rates are limited to $50\text{ }^{\circ}\text{C s}^{-1} - 500\text{ }^{\circ}\text{C s}^{-1}$ [26, 27].

3.2. Hot vapor residence time

Like mentioned before, the screen-heater has been designed to minimize the time that volatile products, once escaped from the reacting particle, are at high temperature ($>80\text{ }^{\circ}\text{C}$) in order to prevent secondary reactions of these products outside the pyrolyzing particle. The time difference between escape from the particle till quenching, is defined as the hot vapor residence time. Like mentioned before, the escaped products can be vapors as well as aerosols. Under our standard conditions of 5 mbar and the wall of the vessel being cooled with liquid nitrogen, the estimated traveling time (based on the random walk approximation) of a hot escaped molecule from screens to the cooled wall is 20 ms (see S5.1). This number is supported by analysis of the frames taken from the high speed camera movies during pyrolysis which show that $\sim 12\text{ ms}$ after the first material disappeared (see mesh in frame 2 of Figure 3) from the screens the first condensed product appeared on the vessel wall (see frame 3 of Figure 3, condensate on glass wall pointed by arrow). Figure 3 shows a test with levoglucosan. Figure 5 shows the frames of a test with cellulose. In this test the first material disappeared from the screen after 79 ms (see mesh in frame 2 of Figure 5) and after 95 ms the first condensed product appeared on the vessel wall (see frame 3 of Figure 5, condensate on glass wall pointed by arrow). From the analysis of these frames a similar estimate of the hot vapor residence time ($\sim 15\text{ ms}$) compared to levoglucosan is obtained.

Also at 1 bar and cooling of the vessel wall with liquid nitrogen the escaped products cool very rapidly due to their direct contact with the cold nitrogen gas inside the vessel. A thermocouple positioned at a distance of 0.015 m from the screen showed that the temperature was below $80\text{ }^{\circ}\text{C}$ when pyrolysis of cellulose took place at $535\text{ }^{\circ}\text{C}$ and 1 bar. Rapid cooling of the escaped products at 1 bar was confirmed by analysis of the movie frames, see Figure 4. Immediate after the first levoglucosan disappeared the first aerosols appeared in the glass vessel showing that the levoglucosan vapors had cooled down (see frame 3 and up figure 4, white clouds pointed at by the arrow). Also here, similar observations were done for cellulose (see S2.6).

Figure 3: Screen shots extracted from a high speed camera movie of levoglucosan pyrolysis/evaporation. Pressure 5 mbar, $T_{FS} = 391$ °C. The arrows show the condensed product on the glass vessel wall.

Figure 4: Screen shots extracted from a high speed camera movie of levoglucosan pyrolysis/evaporation. Pressure 1 bar, $T_{FS} = 488$ °C. The arrows show the condensed product in the glass vessel.

In the fluidized bed operated at 1 bar the hot vapor residence time was estimated to be 1.6 seconds (~ 80 times more than in the screen heater) based on the known gas phase volume of the reactor and the volumetric flow rate, which should result in significant cracking of the vapors according to previously reported data [22, 28, 29].

3.3. Residence time of products on the reacting particle (escape rate from the particle)

We cannot measure the residence time (escape rate) of individual products on (from) the reacting cellulose particles. Instead, we measured the time it takes to evaporate pure levoglucosan (DP_1) and we modelled the evaporation time of pure DP_3 as an approximation of the residence time on the particle during pyrolysis. The results are only used to indicate the differences in residence time / escape rate between 5 mbar and 1 bar. Obviously, a low evaporation time is equivalent to a high escape rate (low residence time). The evaporation time of levoglucosan in the screen-heater was measured at $T_{FS} = 391\text{ }^{\circ}\text{C}$ (see Figure 3). At this temperature the vapor pressure of levoglucosan is estimated to be 4.5 bar [30], which indicates very turbulent ejection from the sample. At 5 mbar the levoglucosan sample was heated and completely evaporated in 79 ms. Note, there is no difference in appearance of condensed product on the glass wall between 79 ms and 663 ms. As the first levoglucosan disappeared from the screens at 46 ms the evaporation time was estimated to be 33 ms. Because the aerosols blocked the view of the screens the evaporation time could not be determined on basis of the frames for levoglucosan at 1 bar and 488 $^{\circ}\text{C}$. Nevertheless, based on the high vapor pressure of levoglucosan the evaporation time is expected to be also low ($< 1\text{ s}$). Indeed an additional experiment showed that the heating plus evaporation time at 1 bar was shorter than ca. 350 ms (see S2.6).

The evaporation time of DP_3 (estimated vapor pressure of 3 mbar at 550 $^{\circ}\text{C}$) was estimated using a model (see S5.1) describing the evaporation / sublimation of the pure compound (sheet of material of 25 mm). In this model, the evaporation flux is described by diffusion (convection is excluded) with the vapor pressure at the prevailing temperature being present at the surface. This model predicts (see Table 2) that at 1 bar the evaporation time of DP_3 is 75 s as compared to 0.4 s at 5 mbar. We are aware that these are rough estimates, though the predicted difference in evaporation time will be of the correct order of magnitude. Therefore, it can be concluded that at 5 mbar DP_3 can evaporate during pyrolysis of cellulose (which takes ca. 121 ms at $T_{FS} = 610\text{ }^{\circ}\text{C}$, see Figure 5), while at 1 bar this will be hardly the case. High DP products can also leave the sample via ejected aerosols as shown by Dauenhauer [31]. Also by this mechanism the escape rate will be higher at lower pressure as a result of vigorously boiling smaller molecules entraining the aerosols and/or a lower counter pressure supporting aerosol ejection.

Figure 5: Screen shots extracted from a high speed camera movie of cellulose pyrolysis. Pressure 5 mbar, $T_{\text{FS}} = 610\text{ }^{\circ}\text{C}$. The arrow show the condensed product on the glass vessel wall.

Summarizing: i) by comparing results obtained in the screen-heater at 5 mbar and 1 bar the effect of the escape rate of larger sugars from the reacting sample is studied (quenching of escaped products is very fast for both), ii) comparison of the screen-heater at 1 bar with the fluidized bed at 1 bar shows the influence of the hot vapor residence time (escape rate from the sample is comparable).

3.4. Interpretation model

Figure 6: schematic representation of the mass and heat transport processes and interpretation models I and II.

To support the analysis of the data an interpretation model is used. The model is schematically visualized in Figure 6. Heat is transferred via the wires to the sample via direct contact with the wires. The wires have a heating rate of approx. $5000\text{ }^{\circ}\text{C s}^{-1}$ (see Figure 2). At elevated temperatures, chemical reactions will start to proceed in the solid sample. The temperature of the reacting sample can be lower than the temperature of the wires due to endothermic reactions and a finite heat transfer coefficient between sample and wires. Some decay products leave the solid matrix via sublimation. Other smaller products can form liquid regions inside the solid matrix. Such liquids have been observed in pyrolysing biomass [32]. In the liquid pools reactions can continue and products can evaporate from it. Evaporation of smaller products (e.g. DP_1) may be turbulent as the vapor pressure can be much higher than the prevailing pressure in the vessel. The work of Dauenhauer and co-workers [31] has shown that it is also possible that aerosols are ejected from reacting cellulose samples. Summarizing, products can escape from the pyrolysing particle via sublimation, evaporation and aerosol ejection.

Mathematical models are used to interpret the experimental data at the level of the observed trends in product yields as a function of final temperature of the screens.

To describe the weight loss and temperature of the cellulose sample a modified version of the model as described by L and co-workers [33] has been used including the reaction rate parameters as given by Shafizadeh [34]. In our model, the sample has a spatially uniform temperature and the state of the intermediate/active cellulose is not defined (can be liquid and/or solid). Hereafter this model is called model I (see Figure 6)

To predict the trend of the product distribution as function of the temperature, model I has been extended by: i) an intermediate / active cellulose phase that consists of heavies ($\text{DP}_{\geq 2}$) and DP_1 , ii) a reaction of heavies to lights that takes place on the sample; and iii) a lower escape rates of heavies compared to lights. Hereafter this model is called model II. Figure 6 shows the models schematically and in S5 the details are given including the kinetic constants.

4. Results

4.1. Mass balance closure and reproducibility

The closure of the mass balance of the 37 reported cellulose screen-heater experiments at the level of gas, condensed product and solid residue was in the range of 0.87 kg kg⁻¹ to 1.01 kg kg⁻¹ with a median of 0.95 kg kg⁻¹. Reproducibility was checked by taking into account 5 measurements in the range of 520 °C to 540 °C (a single constant temperature was not possible due to control issues, see below). The standard deviation in the yields of condensed product, gas and solid residue were 0.03 kg kg⁻¹, 0.005 kg kg⁻¹ and 0.002 kg kg⁻¹, respectively. The standard deviation in the yields of DP₁ to DP_{>5} was 0.02 kg kg⁻¹ (average value of the standard deviations of the individual DPs). Taking into account the small amount of sample and the tedious recovery and analysis procedure these numbers are considered quite satisfactory. The fact that 4 experimenters produced results that do not significantly differ further supports the soundness of the developed apparatus and methods. More details can be found in S2.

4.2. Yields and product composition at 535 °C

Table 2 gives the mass balance and the composition of the condensed product obtained at a final screen temperature (T_{FS}) of 535 °C. At 535 °C and 5 mbar, the yield of condensed product was 96% by weight while the yields of gas and solid residue were below 1% on weight basis (average of 5 experiments).

In literature, very low char yields ($\leq 2\%$ on weight basis) have been often reported for the fast pyrolysis of pure cellulose at temperatures of 400 °C and up [16, 36, 37]. We did not find literature data showing (close to) zero gas production at fast pyrolysis temperatures. Proposed reaction paths indicate that gas can be produced by cracking reactions in the vapor phase [25, 38] or on the reacting cellulose particle [8, 34, 36], the latter is the so-called prompt gas. In an attempt to discriminate between these two mechanisms of gas production (cracking on sample vs. in vapor phase) a comparison was made between: screen-heater at 5 mbar ($< 1\%$ by weight gas), screen-heater at 1 bar ($\sim 2\%$ by weight gas) and fluidized bed at 1 bar (12% by weight gas). The residence time of hot vapors in the fluidized bed is much higher than in the screen-heater and the escape rate of larger sugars is much lower at 1 bar as compared to 5 mbar, while the escape rate of DP₁ is high for all cases (see Table 2). Hence, increasing the hot vapor residence time while keeping the escape rate constant (compare screen-heater 1 bar with fluidized bed 1 bar) has much more impact than keeping the hot vapor residence time low (constant) and decreasing the escape rate of larger sugars (compare screen-heater 5 mbar and 1 bar). This analysis points towards cracking in the vapor phase as the dominant mechanism for the gas production during pyrolysis of Avicel cellulose. Similar observations were

done for glycolaldehyde (GA, hydroxyacetaldehyde) for which the yield was 2% by weight in the screen-heater. In the fluidized bed with a hot vapor residence time of 1.6 seconds considerably more GA was produced (6 wt%, see Table 2). It seems therefore that also GA is produced predominantly in the vapor phase. Note this might be different in the presence of AAEM salts [10, 39]. Direct formation of GA from low DP cellulose, like proposed by Richards [40] and Radlein et al. [41], does not become evident from our data. If the latter mechanism would be dominant, more GA would be expected at 1 bar in the screen-heater as compared to 5 mbar in the screen-heater, because the larger sugars have a longer residence time on the reacting sample. The low gas and GA production in the screen-heater shows that we succeeded indeed in suppressing secondary reactions outside the particle.

Table 2: Mass balances for experiments at $T_{FS} \sim 535$ °C in screen heater and fluidized bed

	Screen heater	Screen heater	Fluidized bed
Pressure (mbar)	5	1000	1000
Heating rate (°C s ⁻¹)	5000	5000	5000
Hot vapor residence time (s)	0.02	~0.02	1.6
DP1 evaporation time (s)	0.03	<0.3	<0.3
DP3 evaporation time (s)	0.4	75	75
No of experiments	4	2	1*
yields (kg kg⁻¹ cellulose)			
Gas	<0.01	0.02	0.12
Solid residue	<0.01	<0.01	0.01
Condensed product	0.96	0.83	0.85
Produced water	N.D.	N.D.	0.10
Condensed Organics	N.D.	N.D.	0.75
DP ₁ **	0.19	0.33	0.40
DP ₁₋₂ **	0.17	0.16	0.19
DP ₂ **	0.23	0.09	0.05
DP ₃ **	0.18	0.04	0.03
DP ₄₊₅ **	0.16	0.02	<0.01
DP _{>5} **	0.04	<0.01	<0.01
Total**	0.97	0.64	0.68
Total sugars ($C_{glucose}/C_{cellulose}$)***	0.69	0.50	0.50
Glycolaldehyde	0.02	0.02	0.06

* reproducibility of fluidized bed experiments has been shown in [6, 35]

** measured by hplc, total is sum of DP₁ DP₁₋₂ DP₃ DP₄₊₅ DP_{>5}

*** glucose measured after hydrolysis of condensed product

N.D. not determined

HPLC analysis gave absolute amounts of levoglucosan (DP_1), and estimated amounts of cellobiosan (DP_2), cellotriosan (DP_3), cellotetrasan (DP_4), cellopentasan (DP_5) and $DP_{\geq 5}$ from which yields and selectivities were calculated. For $DP_{\geq 2}$ the yields are estimates because it is known, or likely, that next to the anhydrosugar there are some other compounds present in the assigned peak area (see e.g. the shoulder at the right hand side of DP_2). By LC/MS, DP_1 (C_6) to DP_{11} (C_{66}) sugars were identified in the condensed product obtained from tests with the screen-heater (see S6.4). The presence of such large sugars ($DP_{\geq 5}$) was observed by several researchers but only using solvent extraction of the solid residue after cooling to ambient temperature. In this work, they were actually collected as condensed product. Only small amounts of deeper dehydrated products (e.g. 5 HMF and levoglucosenone) were presented in the condensed product. Interestingly, the lumped compounds between DP_1 and DP_2 analyzed by HPLC and identified by LC/MS turned out to be isomers of cellobiosan. These isomers were also observed by Boon and co-workers [42].

The product distribution of the condensed product, including DP_1 to DP_{11} , shows that random chain scission must play an important role as has been also concluded by Boon and co-workers [43], Lédé and co-workers [14] and Scott and co-workers [15, 25, 44], though unzipping as first proposed by Golova et al. [45] cannot be excluded as a mechanism that runs next to random chain-scission.

Typically, the sum of the compounds detected by HPLC accounted for more than 90% by weight of the total condensed product for tests at 5 mbar in the screen heater (see Table 2 and Table 8 in S6.7). Acid hydrolysis of the condensed product obtained at 5 mbar (see Figure 11) resulted in predominantly glucose (analysis by HPLC). By this method we could recover 70% of the carbon in cellulose as glucose in the condensed product. This yield of hydrolysable sugar is amongst the highest reported values in the temperature range of 400 °C - 540 °C [9, 16, 36, 46]. Note, that glucose yield is a conservative estimate because the hydrolysis efficiency was only measured for levoglucosan (93%) and cellobiosan (84%) (see S6.3). It might be very well possible that a lower hydrolysis efficiency is obtained for larger sugars which are presented in our condensed products at high yields.

DP_1 , DP_2 and DP_3 were found in similar quantities when pyrolyzing cellulose in the screen-heater at 5 mbar, viz. all their yields were around 20 wt% (see Table 2). In addition, a significant amount of DP_4 & DP_5 and $DP_{\geq 5}$ were found. When operating the screen-heater at 1 bar DP_1 became the dominating product while much less larger sugars were found. The yield of sugars and their distribution obtained in the fluidized bed and in the screen-heater operated at 1 bar were remarkably similar: DP_1 was the dominant product and $DP_{\geq 4}$ was hardly present. Because of the large difference in hot vapor residence time between these experiments (screen-heater and fluidized bed at 1 bar), hot vapor residence time is excluded as an important factor affecting the DP distribution. The main difference between the

— P = 93 mbar (500°C)
 --- P = 939 mbar (500°C)

DP₂

DP₁

HPLC Response (a.u.)

Time (min)

Studies comparing the composition of the condensed product with that of molecules extracted from partly converted particles (after quenching) also show that mass transfer dictates the composition of the condensed product. L and co-workers [14] and Wu and co-workers [16], for instances, have found that the decomposition fragments inside the particle have, on average, larger DP than the recovered condensed product indicating that these larger molecules have difficulty leaving the particle and crack further on the particle. These are all strong indications that mass transfer is playing an important role next to chemistry, but direct ex-

perimental proof for this hypothesis cannot be provided yet. However, we will show in the next paragraph a similar effect, caused by the final temperature of the screens, that we could predict by a simple model including chemical reactions and mass transfer.

We found it is impossible to explain the observed effect of pressure in the screen-heater on the product distribution solely by the rate of chemical reactions. Solid and liquid phase reactions are not effected by pressure. Reactions in the vapor phase are unlikely due to the fast quenching for both 5 mbar and 1 bar.

The total sugar yields (both sum of DP and after hydrolysis) at 1 bar in the screen-heater and fluidized bed were equal, while in the fluidized bed considerably more gas and glycol aldehyde was produced. It has been observed that levoglucosan is stable in the vapor phase [29] even at an extended hot vapor residence time of 12 seconds. This could imply that gases and other light products are formed from predominantly non-sugar compounds. These “unstable” non-sugar compounds are then formed already in the reacting cellulose particle.

4.3. Effect of T_{FS} on product yield and composition at 5 mbar

In Figure 8 the yields of residue and condensed product are plotted versus the final temperature of the screens. The presented experimental data was measured by 4 different experimenters. Note that experiments were performed with a holding time of 1 second and 5 seconds. Over the whole temperature range of $T_{FS} = 330\text{ °C} - 765\text{ °C}$, the gas yield was below 1 wt% (see S6.1). This absence of gas at temperatures as high as 750 °C further supports the conclusion that gases are formed mainly by cracking of decay products of cellulose in the vapor phase and that these reactions can be minimized in the screen-heater by fast quenching of these products.

FTIR analysis and visual inspection showed that the residue obtained below 400 °C is unconverted cellulose and not char (see Figure 24 in S6.6). This is in agreement with reported kinetic data [34] that indicate that, below 400 °C , char forming reactions are not significant at reaction times of 1 second to 5 seconds. Between 400 °C and 450 °C not enough solid residue was recovered for analysis. For conditions of 450 °C and higher, the yield of solid residue was very low ($<1\text{ wt\%}$) in both the fluidized bed and screen-heater (see Table 2 and Figure 8). The low yield of solid residue is in agreement with earlier published data on cellulose pyrolysis [14, 36]. In conclusion, the conversion of cellulose based on mass loss is higher than 99% by weight above 450 °C .

Figure 8A: Solid residue yield as function of T_{FS} and different holding time. The data of 4 experimenters are included. The pressure was 5 mbar.

Figure 8B: Condensed product yield as function of T_{FS} and different holding time. The data of 4 experimenters are included. The pressure was 5 mbar.

Model I including the kinetics of Shafizadeh predicts that the conversion is complete (> 99%) at 440 °C and 5 seconds holding time. In Figure 8A these model predictions are plotted. Below 450 °C the measured solid residue data appear more scattered and the measured effect of the holding time unexpectedly small. This is ascribed to the possible error in the measurement or the small difference in measured temperature between 1 second and 5 seconds experiments lead to the large drop in char yield in this very temperature sensitive regime. A better fit can be easily obtained by increasing the pre-exponential constant in the mode of the rate limiting mass loss reaction, k_2 (see Figure 8A: Shafizadeh $k_{2,0} = 3.2 \times 10^{14} \text{ s}^{-1}$ our fit $k_{2,0} = 2 \times 10^{15} \text{ s}^{-1}$). It is worthwhile to mention that the fitted k_2 and corresponding E_a are in agreement with the data as calculated by Burnham et al. using the Kissinger's method [24]. As input they used the results of the round-robin study of cellulose pyrolysis kinetics as reported by M. Gronli et al. [47]. An activation energy of $\sim 200 \text{ kJ mol}^{-1}$ of k_2 , as often experimentally determined [48] and recently supported by DFT calculation [24, 49], describes the measured increase in conversion from nearly zero to almost completion in a temperature range of 75 °C and reaction time of below 5 seconds. Lower activation energies result in a broader temperature range to achieve this. The measured yield of condensed product was constant after 450 °C.

Figure 9 shows the DP selectivity. Note that from 400 °C the cellulose conversion is (nearly) complete and accordingly selectivity equals yield. The data are quite scattered, which also caused by the uncertainty in the temperature measurement, though, due to large number of measurements, interesting trends do become clear. At $T_{FS} = 370 \text{ °C} - 450 \text{ °C}$ DP_1 is the dominant product together with DP_2 and DP_{1-2} , while at increasing temperature first DP_3 comes up followed by DP_4 & DP_5 and $DP_{>5}$ (See Figure 10) at the expense of predominantly DP_1 , and to a lesser extend DP_2 and DP_{1-2} . The decrease in DP_1 at increasing temperature cannot be explained solely by chemistry, as more cracking is expected at higher temperatures leading to more DP_1 . The scatter on $DP_{>5}$ was the largest. Obviously, compounds this large do not have a significant vapour pressure under our conditions studied. Therefore, it is likely that these compounds are ejected from the cellulose which seems to be quite a random process. As for the predictive mathematical models, these physical processes make exact predictions of the condensed product composition complicated.

Figure 9A: DP_1 selectivity as function of T_{FS} . The pressure was 5 mbar.

Figure 9B: DP_2 selectivity as function of T_{FS} . The pressure was 5 mbar.

Figure 9C: DP_3 selectivity as function of T_{FS} . The pressure was 5 mbar.

Figure 9D: DP_{4+5} selectivity as function of T_{FS} . The pressure was 5 mbar.

Figure 10: The $DP_{>5}$ selectivity as function of T_{FS} , the pressure was 5 mbar.

Figure 11: Recovery of glucose on carbon basis after hydrolysis of the condensed product. The pressure was 5 mbar.

The total yield of sugars, expressed as the recovery of glucose after hydrolysing the condensed product, remained constant in the range of 420 °C to 765 °C, see Figure 11. To the best of our knowledge, we are the first to report a constant yield of hydrolysable sugar as function of the pyrolysis temperature in such a broad range. The constant total sugar yield as function of temperature indicates that the newly developed screen-heater also minimizes the secondary reactions of sugars to non-sugar decay products.

Radlein et al. reported a strong effect of temperature on the DP_1 yield: in their measurements in an atmospheric fluidized bed the yield decreased monotonically from ~38 wt% at 400 °C to 15 wt% ~at 600 °C [39]. They reported a strong decrease of the yield of total sugars from ~60 wt% at 400 °C to 18 wt% at 600 °C [39]. Gong et al. reported decreasing yields (measured in an atmospheric screen-heater) of DP_1 , DP_2 and DP_3 in the range of 400 °C to 500 °C and constant yields thereafter from 500 °C to 700 °C [16]. Also in their case the yield of total sugars decreased significantly in the range of 400 °C to 700 °C (from ~60 wt% to 35 wt%) [16]. Shafizadeh et al. reported for the slow(er) pyrolysis of cellulose under vacuum a constant oil, levoglucosan and reducing sugar yield between 375 °C and 500 °C [9].

As stated before the decrease in DP_1 yield at increased temperature is unexpected when considering solely chemistry. The higher DP_1 yield at lower temperature is explained by the longer time available for cracking of higher DP's in the reacting sample (in the solid or liquid phase) due to their lower escape rate from the sample. At higher temperature, DP_3 and larger sugars have a higher escape rate from the sample and hence less time to crack leading to their increased presence in the condensed product. In an attempt to support this hypothesis, model II was developed. When including the cracking of oligomers on the reacting cellulose and giving the oligomers a lower escape rate than levoglucosan in the model (model II), the measured trend of decreasing DP_1 and increasing $DP_{>1}$ selectivity as function of increasing temperature is predicted by this model (see Figure 12). Note that, only the trend is predicted correctly. Quantitative agreement would need a model that includes independently measured or disentangled values for the rate constants of the chemical reactions on the particle and escape rates (velocity) of products from the sample.

The observations imply that pyrolysis kinetics, especially those based on the mass loss of cellulose or biomass particles, include both chemistry and mass transfer rates. For instance, at lower temperature only low DPs can evaporate as a result of which more bonds have to be broken of the original polymers as compared to higher temperatures at which also decay products of larger DP can escape. Hence, the definition of Pyle and Zaror of kinetically controlled pyrolysis, which is based on only the ratio of the reaction rate and heat transfer rate [13], needs to be reconsidered.

Upward of 550 °C - 600 °C the measured DP_1 , DP_3 , DP_{4+5} selectivity seem to be unaffected by the final screen temperature (see Figure 9). Analysis of the fits show that these measured DPs are better described by an equation leading to a plateau value at increased temperature as compared to a monotonic linear increasing or decreasing function (see S6.2). Model II also predicts that the DP yields / selectivity's above a final screen temperature of ca. 550 °C become constant, see Figure 12. This is because the actual reaction temperature becomes constant above this final screen temperature, as also argued by Piskorz et al. [15] and Lédé [50-52]. Figure 13 shows the average reaction temperature (defined as the average temperature of the sample between 10% and 90% conversion) versus the final temperature of the screens for several cases. Two extreme cases are: A) the screens heat with 5000 °C s⁻¹ and the heat transfer coefficient (screen to sample is 1000 W m⁻² K⁻¹); and B) the sample is heated with 10000 °C s⁻¹ (infinite heat transfer coefficient). The parity line represents kinetically controlled pyrolysis which was defined by Pyle & Zaror as pyrolysis at isothermal conditions [13]. The model predicts that the average reaction temperature is lower than the final temperature of the screens. For case A this happens at a lower T_{FS} in combination with a lower asymptotic reaction temperature as compared to case B. For both extreme cases, above $T_{FS} = 550$ °C, heat transfer cannot keep up with the reaction rate and consequently the conversion is complete within the heating trajectory. This was also observed experimentally by analysis of the pictures / movies taken during conversion. The blue LED in Figure 5, which was connected to the electrodes, lights up when current is passing through the screen (to heat the screen). The LED in this experiment (cellulose, 5 mbar $T_{FS} = 610$ °C) was continuously lighted during the first 121 ms, meaning that the experiment was still in the initial heating pulse. Note that all cellulose has reacted away before 121 ms. This show that the reaction was completed before the screen reached the final screen temperature.

Figure 12: Yield predictions using model II for DP_1 and $DP_{>1}$ as function of the final screen temperature (T_{FS}).

Figure 13: Predicted reaction temperature region using model I as function of the final screen temperature (T_{FS}). Kinetic constants used of Shafizadeh ($k=3.2 \times 10^{14}\ s^{-1}$ and $E_a=198\ kJ\ mol^{-1}$)

5. Conclusions

The fast pyrolysis of small Avicel cellulose particles (heating rate $\sim 5000\text{ }^{\circ}\text{C s}^{-1}$, 5 mbar vacuum and fast quenching at $\sim 100\text{ }^{\circ}\text{C}$) in a screen-heater has been studied while varying the temperature, the escape rate of products from the reacting cellulose particle and the hot vapour residence time. In addition, the obtained results are compared with pyrolysis in the same screen-heater at 1 bar pressure (lowering the escape rate) and pyrolysis in a common fluidized bed reactor (increasing the hot vapour residence time).

To the best of our knowledge, we are the first to observe experimentally that it is possible to convert cellulose in the broad temperature range of $370\text{ }^{\circ}\text{C}$ to $765\text{ }^{\circ}\text{C}$ into hydrolysable sugars with a high and constant yield (60% - 70% on carbon basis as a conservative estimate) while producing only a very limited amount of light oxygenates and gas. Below $450\text{ }^{\circ}\text{C}$ solid residue was found, though this turned out to be unconverted cellulose, not char. The results indicate that depolymerisation to anhydrosugars (DP_1 - DP_{11}) is a true primary reaction, gas formation not and that char formation can be, as was already known, avoided. It has been found that light oxygenated compounds and gases are formed predominantly in the vapour phase, most likely from non-sugar molecules. Evidence is accumulating that both the distribution of the polymerization degree of the produced sugars and the mass loss rate of cellulose is determined by the interplay between the chemistry and heat and mass transfer at cell wall level above $450\text{ }^{\circ}\text{C}$. Whereas, below $450\text{ }^{\circ}\text{C}$ and high heating rates, chemistry and mass transfer are the important processes. This leaves models aiming at quantitative prediction of the product distribution (bio-oil composition and yield) very challenging, if not impossible. However, the heating rate of particles, the rate at which decay products escape from the particle and the quenching rate of these escaped products can be steered. Thus it is possible to produce target products (e.g. fermentable sugar or oligo-sugars) in significant amounts from cellulose. In this way, the advantages of thermochemical processes in comparison to biotech concepts, such as high conversion rates & products not being heavily diluted with water, are combined with an increased value of the product slate. Translating the results obtained to real-world reactors and for the benefit of lignocellulosic biomass is subject of further research.

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Appendix A

The important effect of low concentrations of K_2CO_3 on the cellulose pyrolysis outcome

Abstract

In this appendix preliminary results on the effects of low concentration of K_2CO_3 in cellulose on the pyrolysis outcome are presented. Experiments were carried out at high heating rates ($5000\text{ }^\circ\text{C s}^{-1}$) combined with fast escape rate of products from the reacting cellulose particle and short hot vapor residence times (20 ms). It was found that the potassium concentration, typically found in untreated biomass, largely catalyzed the production of solid residue and non-condensable gases even under these “extreme” conditions. As a consequence, the glucose recovery was largely reduced. Adding 1000 mg kg^{-1} of potassium to levoglucosan already significantly reduced the levoglucosan recovery and led to the production of solid residue and non-condensable gases. The obtained results indicate that acid leaching or AAEM passivating is mandatory when anhydrosugars are targeted.

1. Introduction

It is commonly known that the presence of alkali and alkaline earth metals (AAEMs) in biomass and cellulose largely affect the pyrolysis outcome. The general reported observations are that these AAEMs lower the temperature at which the pyrolysis reactions start and catalyze the dehydration and ring fragmentation reactions of the anhydrosugar molecules [1-3]. Dehydration reactions yield mainly water and char [4], and the products of fragmentation reactions are non-condensable gases and light oxygenated compounds such as formic acid and glycolaldehyde [1, 5]. As a consequence, the production of anhydrosugars is largely reduced [1-3]. Patwardhan et al. showed that adding a low concentrations of KCl, only 500 mg kg^{-1} , to cellulose reduced the levoglucosan yield from 0.6 kg kg^{-1} to 0.3 kg kg^{-1} [5]. With respect to the levoglucosan reduction by the various cations the following order was found $Mg > Ca > Na > K$ [5]. Kuzhiyil et al showed the importance of the anion for various potassium salts [6]. The order reported in decreasing the levoglucosan yield was: $KHSO_4 > KH_2PO_4 > K_2SO_4 > KCl > K_3PO_4 > K_2HPO_4 > K_4P_2O_4 > KNO_3 > HCOOK > CH_3COOK$ [6].

In Chapter 2 the potential of producing anhydrosugars from very pure cellulose, containing only 1 mg kg^{-1} of AAEMs, under various process conditions was studied. It was found that 70% of hydrolyzeble sugar is obtained when high heating rates are combined with high escape and quenching rates of the volatile products. Reducing the escape rate of volatile products thereby increasing the time of the molecules on the pyrolyzing particle, obtained by increasing the pressure from 5 mbar to atmospheric, reduced the hydrolysable sugar yield to 50 wt%. Increasing the hot vapor residence time did not affect the sugar yield. It is well known that the presence of AAEMs reduces the anhydrosugars production in the particle and vapor phase [7, 8] under typical fast pyrolysis conditions. Methods exist to remove the AAEMs from biomass; however, complete removal of the AAEMs will not be realistic in practice. Currently it is unknown to which extent the effects of low concentration of AAEMs can be minimized by the means of process conditions, such as low pressure and short hot vapor residence times. Therefore, the goal of the work presented in this appendix is to investigate the effects of small amounts of AAEMs in cellulose under various pyrolysis process conditions.

Potassium carbonate was chosen as model compound for the AAEMs due to the high amount of potassium in biomass (see Table 3 in Chapter 3) and impregnating carbonate salts in acid leached biomass gave identical pyrolysis results as the native biomass (see Figure 1 Chapter 4). As shown in Chapter 3 not all AAEMs can be removed from biomass by acid leaching. Therefore the following concentrations were chosen: 100 mg kg^{-1} selected as lower boundary, 1000 mg kg^{-1} as rather easy to achieve concentration and 10000 mg kg^{-1} as concentration typical in untreated biomass. It is worth to mention that 100 mg kg^{-1} corresponds to a single potassium molecule per ~ 2500 sugar monomers and 1000 mg kg^{-1} to a single potassium mol-

ecule per ~250 sugar monomers.

The work reported in this appendix are preliminary results. Clearly further research is required to better understand the observed trends, therefore many recommendations for further research are made. The obtained trends are however used in the outlook of this thesis to help better understanding the results from the acid leached biomasses reported in the other chapters.

2. Experimental

2.1. Materials:

Cellulose (Avicel ph 101) was used as feedstock. The cellulose was dried for 24 h at 25 °C and 1 mbar before pyrolysis or K_2CO_3 impregnation. Potassium carbonate (Sigma Aldrich, purity >99.7%) and milli-Q water were used to impregnate the cellulose.

2.2. Experimental and methods.

K_2CO_3 impregnation: Pure cellulose was impregnated with 100 mg kg^{-1} , 1000 mg kg^{-1} and 10000 mg kg^{-1} of K_2CO_3 to study the effect of the AAEMs remaining in the biomasses after acid leaching on the pyrolysis outcome. The amount of K_2CO_3 used for impregnation was calculated based on the AAEM concentrations measured by XRF analysis before and after acid leaching. The desired amount of K_2CO_3 was dissolved in milli-Q water, the amount of water used was equal to 3.5 times the mass of the cellulose to completely wet the cellulose. After mixing the wet cellulose was vacuum dried in a rotary evaporator under continues stirring.

Pyrolysis: The cellulose samples were pyrolyzed in the screen heater at a temperature of 530 °C (± 15 °C). The screen heater setup and run procedure are explained in Appendix D.

2.3. Analytical techniques.

The produced gases and the hydrolysable sugars in the condensed product were determined identically to the method applied in Chapter 2. See appendix D for the procedure and yield calculations.

3. Results

The results presented in chapter 2 showed that hardly any gas ($<0.02 \text{ kg kg}^{-1}$) or solid residue ($<0.01 \text{ kg kg}^{-1}$) was produced from pure cellulose in the screen heater at both 5 mbar and 960 mbar. In Figure 1 the yields of produced gas and solid residue are plotted versus the logarithmic potassium content in the cellulose. The data in Figure 1 is rather scattered, though, due to multiple measurements and significant effects, trends become clear. When potassium is present during the pyrolysis of cellulose a significant amount of gas was formed in the screen heater both at 5 mbar and 960 mbar. This shows that the so-called prompt gas, gas produced on the reacting cellulose sample, as proposed in several mechanistic models is produced when potassium (expected also for other AAEMs) is present in the reacting cellulose particle. Figure 1 indicates a slight increase in the gas yield at 960 mbar compared to 5 mbar for potassium concentrations of 100 mg kg^{-1} and 1000 mg kg^{-1} . This can be explained by longer residence times of the produced products on the pyrolyzing particle resulting in more contact time with the potassium. The solid residue yield also largely increased at higher potassium concentrations. The data shows no effect of the pressure. It should be noted that the obtained solid residue is not unconverted cellulose as in chapter 2, but a black carbonic material. Based on the char yields, a dehydration product, it can be expected that significant amount of water was produced (order of magnitude ~ 0.75 times the char yield).

A drawback of the used screen heater setup is that very volatile products, including water, are (partially) lost during dismantling of the setup before weighing back the vessel. Based on the volume of the vessel (250 ml), the use of dry nitrogen to increase the pressure to atmospheric pressure (before the experiment or dismantling) and the temperature at disassembling ($\sim 20^\circ\text{C}$) it can be estimated that at least 4 mg ($\sim 0.08 \text{ kg kg}^{-1}$) of water should be produced before it is possible to weigh it back on the vessel wall. Based on the aforementioned and the increased char production at increased potassium concentration it can be expected that the total mass recovery will decrease at increased potassium concentration. Figure 2 shows the mass balance closure of the experiments. Again a large scatter in the values of the different experiments can be observed. In general, it seems that the mass balance closure decreased as function of the potassium content in cellulose. An interesting adaptation to the setup would be able to quantify the amount of water in the vapor phase.

Figure 1A: Solid residue yields as function of the potassium concentration and different pressures. Experiments performed at 530 °C (± 15 °C)

Figure 1B: Gas yields as function of the potassium concentration and different pressures. Experiments performed at 530 °C (± 15 °C)

In Figure 3 the yield of condensed product is plotted versus the potassium content in the cellulose. As expected, based on the solid residue and gas yield, the amount of condensed products largely decreased at increasing potassium concentration. Like for the gas yield there seems to be a difference at potassium concentration 100 mg kg⁻¹ between the 5 mbar and atmospheric experiments.

Figure 2: Mass balance closure as function of the potassium concentration and different pressures. Experiments performed at 530 °C (+15 °C)

Based on the results obtained at a potassium concentration of 10000 mg kg⁻¹, which corresponds to typical concentrations in untreated biomasses, it can be concluded that a significant amount of the solid residue and gas produced during conventional fast pyrolysis of biomass is formed due to the presence of AAEMs.

Based on the effects of AAEMs described in literature combined with the significant effects on the lumped products, as shown in Figure 1 and Figure 3, it can be expected that the presence of potassium in cellulose will lead to reduced sugar yields. Indeed, in Figure 4, a large decrease in the glucose recovery, defined as the ratio between the glucose in the oil after hydrolysis and the glucose in cellulose, at increased potassium concentration is shown. This figure shows that it is impossible to obtain high glucose recoveries from cellulose with 10000 mg kg⁻¹, which corresponds to typical AAEM concentrations in untreated biomass, even under the “extreme” conditions applied in the screen heater. This means that AAEM removal or passivation is required if high anhydrosugars yields are targeted. At lower potassium concentrations (<1000 mg kg⁻¹), low pressures can be used to increase the glucose recovery. It is expected that the difference in the glucose recovery at 5mbar compared to 960 mbar was caused by longer residence times of the produced products on the pyrolyzing particle resulting in more contact time with the potassium. However, as a minor effect secondary reactions due to contact between the relative cold aerosols, remaining within the vessel for long periods (see Figure 4 Chapter 2), and the hot screen containing the potassium cannot be excluded as a possible explanation for the observed results.

Figure 3: Condensed product yield as function of the potassium concentration and different pressures. Experiments performed at 530 °C (± 15 °C)

Figure 4: Glucose recovery as function of the potassium concentration and different pressures. Experiments performed at 530 °C (± 15 °C)

Comparing the hydrolysable sugar yield with the condensed product yield shows that condensed product produced at potassium concentrations of 1000 mg kg^{-1} and higher contains mainly compounds other than hydrolysable sugars. It would be very interesting to study the structure of these compounds. This might provide insight into the structure of the large “unknown” fraction in normal pyrolysis oil.

The large effects of the trace amounts of potassium is very interesting, especially if you notice that only one potassium molecule per 2500 sugar rings in the cellulose (in case of 100 mg kg^{-1}) reduces the glucose recovery from 0.7 kg kg^{-1} to 0.5 kg kg^{-1} at 5mbar. However, when the three-dimensional structure is taken into account one potassium molecule is located in a cube, with edges of ~ 14 glucose rings. Based on this it can be estimated that the distance between the potassium molecules will be in the range of 6.3 nm [9].

Additional tests with levoglucosan impregnated with 1000 mg kg^{-1} potassium were performed to obtain some insights in the AAEMs, i.e. does the AAEMs influence the initial decomposition to sugars or do they also influence the produced products, like levoglucosan. As reported in Chapter 2, pure levoglucosan just evaporates without reactions in the screen heater, both at 5 mbar and atmospheric pressure. Table 1 shows the gas, solid residue and condensed product yield and the levoglucosan recovery obtained from levoglucosan with 1000 mg kg^{-1} potassium. The presence of potassium resulted in the formation of both solid residue and gas from levoglucosan, even at 5 mbar and $5000 \text{ }^\circ\text{C s}^{-1}$. Interestingly, the solid residue yield from levoglucosan with 1000 mg kg^{-1} potassium seem to be comparable with that from cellulose with 1000 mg kg^{-1} potassium. Additional experiments should verify if these similar char yields are also obtained at other concentrations (e.g. 10000 mg kg^{-1} potassium). The levoglucosan recovery reduced from full recovery (Chapter 2) to 89 % at 5 mbar and 48 % at atmospheric pressure in the presence of 1000 mg kg^{-1} potassium. This shows that the AAEMs influence the formed products, if the AAEMs affect the initial decomposition to anhydrosugars cannot be excluded based on our results.

Table 1: Product yields of the levoglucosan with $1000 \text{ mg kg}^{-1} K_2CO_3$ experiments performed at $530 \text{ }^\circ\text{C}$. Both experiments were performed in duplicate, yields from the single measurements is presented between brackets. Levoglucosan recovery based on a single measurement.

	Levoglucosan + 1000 mg kg^{-1}	Levoglucosan + 1000 mg kg^{-1}
	K_2CO_3 at 5 mbar	K_2CO_3 at 980 mbar
Gas (kg kg^{-1})	0.006 (0.006 / 0.006)	0.056 (0.048/0.064)
Solid residue (kg kg^{-1})	0.027 (0.025/0.028)	0.053 (0.048/0.058)
Condensed product (kg kg^{-1})	0.94 (0.91/0.96)	0.077 (0.75/0.78)
Levoglucosan recovery (kg kg^{-1})	0.89	0.48

5. Conclusion

The fast pyrolysis of Avicel cellulose under high heating rates ($5000\text{ }^{\circ}\text{C s}^{-1}$) combined with fast evaporation of the volatile products (5 mbar) and quick quenching of the volatile products (20 ms) has been studied at $530\text{ }^{\circ}\text{C}$. In this study the K_2CO_3 concentration in cellulose and the escape rate of products from the pyrolyzing particle were varied.

It has been found that gases and char were formed when K_2CO_3 is present even under these “extreme” process conditions. As a result, lower condensed product yields were obtained. For low potassium concentrations ($<1000\text{ mg kg}^{-1}$) it was found that lower pressures can be used to reduce the char and gas formation. The hydrolysable sugar yield significantly reduced, even at 100 mg kg^{-1} and 5 mbar the hydrolysable sugar yield reduced from 0.7 kg kg^{-1} to 0.5 kg kg^{-1} . This shows that incomplete AAEM removal, by acid leaching, will always suppress the hydrolysable sugar yield. Moreover, the result from cellulose with 10000 mg kg^{-1} potassium indicate that it is impossible to obtain high anhydrosugar yields from untreated biomass, even under these “extreme” process conditions. Therefore, removing or passivation of the AAEMs is required when the production of anhydrosugars is targeted. At potassium concentrations of 1000 mg kg^{-1} and higher much more condensed products are formed than hydrolysable sugars. It would be interesting to investigate the composition of the products to obtain insights in the “unknown” fraction of pyrolysis oil from untreated biomasses. Experiments with levoglucosan, containing 1000 mg kg^{-1} , revealed that potassium affects the produced sugars, though it can be possible that the potassium also affects the initial decomposition reactions.

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Chapter 3

Fast pyrolysis of pyrolytic acid leached wood, straw, hay and bagasse: improved oil and sugar yields

Abstract

Pyrolytic acid leaching of pine wood, straw, bagasse and hay effectively reduced the amount of catalytically active alkali and alkaline earth metals (AAEMs). Using the (acetic) acid produced by pyrolysis as leaching agent, the AAEMs content could be reduced to 90 - 600 mg kg⁻¹. Tests with AAEMs impregnated Avicel cellulose (1 - 1000 mg kg⁻¹) showed that even at such low concentrations of AAEMs (100 mg kg⁻¹) the sugar yield was significantly suppressed. After leaching, single phase oils (condensed at 20 °C) were obtained even for straw and hay. A large increase in the yields of organic pyrolysis oil (e.g. straw: 37 to 58 wt%) and pyrolytic sugar (e.g. bagasse: 3 to 22 wt%) was observed for all acid leached biomasses. The increase in sugar yield can be ascribed to less intense dehydration and ring fragmentation reactions. A comparison of the sugar yields of the leached biomasses with those of AAEMs impregnated cellulose showed clearly that the concentration of AAEMs is not the only factor determining the sugar yield.

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1. Introduction

Fast pyrolysis of lignocellulosic biomass is a thermal depolymerization process aiming at the production of renewable bio-oil. This bio-oil is an intermediate for the production of transportation fuels and contains interesting chemicals like anhydrosugars (e.g. levoglucosan) and aromatics [1]. Anhydrosugars can be used as feedstock in fermentation processes to obtain e.g. bio-ethanol [2, 3] and in (catalytic) conversions to for example methyl levulinate [4].

Next to cellulose, hemicellulose, lignin and extractives, lignocellulosic biomass contains inorganic compounds including alkali and alkaline earth metals (AAEMs) [5, 6]. According to literature the presence of AAEMs during pyrolysis increases the char and water yield via dehydration reactions [7] and increases the yield of light oxygenates via ring-fragmentation reactions of carbohydrates [8]. These two AAEMs catalyzed reactions explain, at least partly, the low selectivity towards anhydrosugars and the presence of many small oxygenated molecules in the bio-oil. The increased water production is unwanted since a too high water content in bio-oil can easily lead to phase separation into an aqueous and an organic phase [9]. Phase separated bio-oil may cause serious problems during storage, transportation and in applications.

To minimize the catalytic effects of AAEMs during pyrolysis, three different approaches are reported in literature, namely:

- i) Mineral acid leaching, in which the AAEM salts react with the acid to water soluble compounds and the cations bound to the biomass structure are ion-exchanged by a proton [10]. Many papers on the fast pyrolysis of mineral acid leached biomass are available in literature [8, 11-13].
- ii) Reducing the catalytic effects of AAEMs on the sugar production by infusing strong acids into the biomass [14, 15], resulting in passivated (also called thermally stable) salts [14].
- iii) Acid leaching with organic acids, the principle is identical to mineral acid leaching.

In general all these papers report an increase in the anhydrosugar and oil yields. However there is less consensus in the reported yields of water and pyrolytic lignin. Piskorz et al. showed a large decrease in the produced water for poplar wood (12.2 wt% vs 1 wt% after acid leaching) [8] whereas Brown et al. measured an increase of 9.7 wt% vs 11.7 wt% for switchgrass and 2.6 wt% vs 10.6 wt% for cornstover [12]. Mourant et al. report doubling of the pyrolytic lignin yield for mallee wood pyrolysis [13] while Brown et al. showed that the yield

was approximately halved for both swithgrass and cornstover after acid leaching [12].

In our previous paper we utilized the organic acids produced in the pyrolysis process itself to reduce the AAEMs content [16]. These pyrolytic acids were concentrated, by applying fractional condensation of the pyrolysis vapors, and collected as a separated aqueous phase. This aqueous phase was successfully used to leach the AAEMs from pine wood (to 88 mg kg⁻¹) which resulted in high bio-oil and levoglucosan yields after pyrolysis [16]. The same concept is applied in this chapter for straw, hay and bagasse. These biomasses were analyzed for their extractives, sugar (xylose, mannose, arabinose and glucose), lignin (aromatics), ash and AAEMs (K, Na, Ca, Mg) content. Fast pyrolysis of these untreated and acid leached feed-stocks was carried out in a 150 g per run fluidized bed reactor operated at 530 °C.

The first aim of this chapter is to evaluate the effect of pyrolytic acid leaching on the chemical composition of biomass and the AAEMs removal efficiency for the broad selection of feed-stocks. The second aim is to produce high yields of single phase bio-oils containing a high amount of hydrolysable sugars by reducing the AAEMs content by the aforementioned procedure. Yields of organic oil, residue, gas, water, sugar and water insolubles of untreated and pretreated biomass are compared. These yields are also presented and analyzed as a function of AAEMs content. In our work, the importance of the AAEMs remaining in the biomass after leaching, is studied by comparing the yields of the selected biomasses with the pyrolysis results of Avicel cellulose (1 mg kg⁻¹, as received) and AAEMs (100 mg kg⁻¹ - 1000 mg kg⁻¹) impregnated Avicel cellulose.

2. Experimental Section

2.1. Materials

Pine wood (Lignocel 9, Rettenmaier & Söhne GmbH), wheat straw (Purchased from Praxis. Brand: Puik original, two different batches), hay (obtained from a local farm), bagasse (kindly supplied by Shell) and cellulose (Avicel ph 101 particle size $\sim 50 \mu\text{m}$) were used in this study. The synthetic leaching solution consisted out of 10 wt% of acetic acid (SAFC, purity 99.5 wt%), 3.75 wt% of acetone (Assink Chemie, purity $> 99.5 \text{ wt\%}$), 3.75 wt% of ethanol (Assink Chemie, purity 99.8 wt%), 1.5 wt% of guaiacol (SAFC, purity $> 98 \text{ wt\%}$), 1.5 wt% of propionic acid (SAFC, purity $> 99.9 \text{ wt\%}$) and 79.5 wt% of demineralized water (Milli-Q). The salt used for impregnating cellulose was potassium carbonate (Sigma Aldrich, purity 99.7%). In the fast pyrolysis experiments silica sand, sieve fraction $212 \mu\text{m} - 300 \mu\text{m}$ with a particle density of 2600 kg m^{-3} , was used as fluidized bed material.

2.2. Experimental and methods

2.2.1. Acid leaching:

The biomass samples were ground in a knife-mill and sieved to obtain a particle size fraction of $0.5 \text{ mm} - 2 \text{ mm}$. Half of the amount of biomass samples was leached with a synthetic acidic aqueous solution, mimicking the 2nd condenser liquid from the pyrolysis process. The use of this synthetic mixture instead of the real condenser stream has been validated in Appendix B. Below, the leaching method [16] is described briefly.

The biomass samples were leached in a 1 liter glass reactor. The reactor was filled with the leaching solution and preheated to $90 \text{ }^{\circ}\text{C}$. A water-cooled reflux condenser was used to condense the low boiling vapors. When the desired temperature was reached, biomass was added ($0.10 \text{ gram dry biomass per } 1 \text{ gram of leaching solution}$). The biomass slurry was mixed using a flat blade stirrer (660 rpm) combined with a baffle mounted on the reactor wall. After 2 hours the leaching liquid was drained from the reactor through a perforated plate (pore size 0.5 mm), leaving the solid biomass inside the reactor. The biomass remaining in the reactor was rinsed with Milli-Q water, to remove the leaching liquid remaining in the pores, until the pH of the effluent solution was higher than 6.0. Hereafter the biomass was dried for 24 hours in a hot air oven at $105 \text{ }^{\circ}\text{C}$.

2.2.2. Cellulose impregnation:

Cellulose was impregnated with 100 mg kg^{-1} and 1000 mg kg^{-1} of potassium (in the form

of K_2CO_3). The amount of K_2CO_3 used for impregnation was chosen based on the concentrations of AAEMs remaining in the biomass after acid leaching. Therefore, the pyrolysis outcome of cellulose can be compared with that of biomass after acid leaching. The cellulose samples were impregnated by dissolving the desired amount of K_2CO_3 in Milli-Q water. The dissolved K_2CO_3 solution was mixed with the cellulose (fully wetted). Hereafter the water was evaporated in a rotary evaporator (40 °C, 60 mbar and continuous stirring).

2.2.3. Fast pyrolysis:

The biomass samples were pyrolyzed in a fluidized bed reactor at a temperature of 530 °C. This setup is explained in more detail in our previous paper [16]. Short recap: preheated nitrogen was used as fluidization gas and silica sand was used as bed material. The process conditions are summarized in Table 1. Per experiment around 150 gram of biomass was fed manually in batches of 2 g – 5 g together with 4 g – 8 g sand, via a gas lock system consisting out of two valves, into the fluidized bed reactor during a period of 30 min – 40 min. After the experiment the bed was maintained at 530 °C for 15 min before cooling down to ensure full conversion of biomass. The particles were removed from the gas/vapor stream using two wire-mesh filters (pore size 9 µm and 5 µm). The vapors were condensed in two fractions using an electrostatic precipitator (ESP), operated at 80 °C (outgoing gas temperature), and a double walled glass condenser, operated at -5 °C (outgoing gas). Half of the liquids collected in the 1st and 2nd condenser were mixed to simulate liquid collected in a single condenser (operated at 20 °C). A gas filter (10 µm) was used to collect the remaining liquid (± 2 wt% of total oil) in order to complete the mass balance. The solid residue yield was determined by collecting the material remaining in the reactor and particle-filters and subtracting the initial weight of sand present at the start of the experiment and the amount of sand fed during the experiment. Since the solid residue after acid leaching has (partially) a different morphology than the “typical” char from untreated biomass, containing the original biomass structure, the organic fraction remaining in the reactor will be referred to as residue instead of char (see chapter 4). The residue yield was corrected for the amount of ash present in the pyrolyzed biomass.

$$Y_{residue} = \frac{\sum_{reactor, filter} (kg \text{ residue collected} - kg \text{ of ash in biomass})}{kg \text{ biomass fed} * (1 - \text{water fraction biomass} - \text{ash fraction biomass})}$$

The liquid production was measured by weighing both condensers and the gas filter before and after the experiment. The amount of produced gasses was calculated by difference.

For comparison between, pyrolysis of untreated or acid leached biomass, the yield is expressed on initial dry ash free (d.a.f.) biomass (intake of process, Y_f f=feed). When the effect of biomass composition on the lumped product classes and individual compounds is studied the yield is expressed on biomass fed to the pyrolysis reactor (Y_r r=reactor). For the hydro-

lysable sugars the recovery is defined as the ratio between the amount of individual sugar (e.g glucose, xylose) in the pyrolysis oil (after hydrolysis) and their corresponding concentration initially in the pyrolyzed biomass (after hydrolysis).

Table 1: Operational conditions of fast pyrolysis and acid leaching experiments.

Process condition	Value
Pyrolysis	
Run Time	45 min - 60 min
$M_{\text{sand,initial}}$	1.0 kg
$\Phi_{\text{v,N}_2} / \Phi_{\text{m,biomass}}$	1.5 Nl g ⁻¹
T_{reactor}	530 °C
τ_{vapors}	1.8 s
U / U_{mf}	2.5
$T_{\text{outgoing gas 1st condensor}}$	80 °C
$T_{\text{outgoing gas 2nd condensor}}$	-5 °C
Acid leaching	
Run Time	120 min
V_{vessel}	1 l
$V_{\text{leaching liquid}} / M_{\text{biomass}}$	10
Stirrer speed	660 RPM
$T_{\text{acid leaching}}$	90 °C

Table 2: Overview of analytical techniques applied.

Compounds / quality properties	Technique	Reference
Biomass feed		
Extractives	Soxhlet extraction with H ₂ O and EtOH	[18]
Lignin and sugar content	Acid hydrolysis + HPLC	[19]
Ash content	Dry oxidation @ 575 °C	[40]
Ash composition	XRF	
C/H/N content	Element analyser	
Bio oil		
C/H/N content	Element analyser	
Water	Karl Fischer	
Levogluconan and acetic acid.	GC/MS	
Hydrolysable sugars	Acid hydrolysis + HPLC	[20]
Water insolubles	Cold water precipitation	[21]
Gas		
Gas composition	Micro-GC	

2.3. Analytical techniques

The analytical techniques used to analyze the feedstocks and quantify the produced products are shown in Table 2. The extractives, structural carbohydrates and lignin content of the different biomasses were analyzed using the NREL LAP methods “Determination of Ethanol Extractives in Biomass” [18] and “Determination of Structural Carbohydrates and Lignin in Biomass” [19]. The ash content of the biomass was determined by quantifying the residue remaining after 24 hours of dry oxidation at 575 °C. The ash composition was determined with X-ray fluorescence (XRF) spectroscopy (Phillips PW 1480 spectrometer). The biomasses and produced oils were analyzed by elemental analysis (Thermo Scientific -FLASH 2000 CHN analyzer) for their C, H and N content. The oxygen content was calculated by difference ($O=100-C-H-N-Ash$). Duplicate measurements were performed, if the difference was larger than 1 wt% the measurement was repeated until satisfying results were obtained. The gases produced during pyrolysis were analyzed using a gas chromatograph (Varian CP 4900) equipped with two columns i) 10 m molsieve 5A operated at 70 °C, and ii) 10 m PPQ operated at 80 °C. Helium was used as carrier gas. The first column measured H_2 , O_2 , N_2 , CH_4 and CO and the second column CO_2 , C_2H_4 , C_2H_6 , C_3H_6 and C_3H_8 . The compounds were detected by two thermal conductivity detectors. The water content of the pyrolysis oil was measured by Karl Fischer titration (Metrohm 787 KF Titrino, titrant Hydranal Composite 5 and solvent 3/1 methanol dichloromethane). Duplicate titrations were carried out, if the difference was larger than 0.5 wt% the titration was repeated until satisfying results were obtained. The identification and quantification of levoglucosan and acetic acid was done by GC-MS analysis (GC 7890A MS 5975C Agilent Technologies) equipped with a capillary column (Agilent HP-5MS, HP19091S-433) and helium as carrier gas (inlet pressure programmed for constant 1st column flow of 2 ml min⁻¹). Samples were dissolved in acetone (50 mg g⁻¹ acetone) and filtered before analysis (Whatman 0.2 µm filter). The injection volume was 1 µl, injector temperature 250 °C, split ratio 20 : 1 (FID : MS), at injection the column was 4 minutes at 45 °C where after it was heated to 280 °C (by 3 °C min⁻¹) at which it was maintained for 20 min. The hydrolysable sugar content of the oil was quantified using NREL LAP method “Determination of sugars, byproducts, and degradation products in liquid fraction process samples” [20]. The oil was first separated using the cold water extraction method [21] (1 gram of 1st condenser oil per 100 ml cold water) followed by hydrolysis (3.5 vol% H_2SO_4 for 60 minutes at 120 °C) of the water soluble fraction. The samples were hereafter neutralized by adding $BaCO_3$ and filtered (Whatman 0.2 µm filter) before HPLC analysis (Agilent 1200 series, column Hi-Plex-pb operated at 70 °C, eluent milli-q water (0.6 ml min⁻¹)).

3. Results and Discussion

The reproducibility of the successive experiments (acid leaching followed by pyrolysis) was tested for pine wood ($n = 5$) and straw batch 2 ($n = 3$). The differences in the residue yield between the experiments with pine wood or the experiments with straw was smaller than 2 wt%, Similar differences were obtained for gas, water and organic oil, for both biomasses. Therefore it could be concluded that the reproducibility was good.

3.1. The effects of acid leaching on the biomass composition

Pine wood, hay, bagasse and two different wheat straw batches were selected as pyrolysis feedstocks relevant to practice. Table 3 shows the composition of these feedstocks before and after acid leaching and subsequent water rinsing. Acid leaching reduced the AAEM content of the tested biomasses by 97 wt%. Only for bagasse the removal efficiency was 91 wt%. Notice, bagasse was already washed with water during the sugar extraction process. The ash remaining in the biomass after acid leaching consisted for more than 85 wt% of silica. During the acid leaching step the AAEM salts dissolve in the water or react with the acid to form readily soluble salts. The fraction of AAEMs which are ionically bound to the biomass structure (i.e. to proteins [22] and carboxylic groups [23, 24]) are exchanged by protons [24]. Additional acid leaching and rinsing with excessive amounts of water did not further reduce the AAEM content. Comparable studies on acid leaching of biomass confirm this finding [25, 26]. An explanation for the incomplete removal of the AAEMs content might be that the AAEMs are partially located in inaccessible region for the rinsing liquid, like inside proteins. The oxygen and nitrogen content of the biomasses before and after acid leaching did not change much.

Next, the polysaccharide (hemicellulose and cellulose) and lignin content of the initial biomasses after water and ethanol extraction (between brackets) were compared to the acid leached biomasses. These data show that under our leaching conditions (pH 2.1 and 90 °C) hardly any loss of hydrolysable sugars or lignin to the leaching liquid did occurred due to the acidity of the acid leaching solution. Moreover, the mass loss of the biomass caused by the acid leaching was nearly identical to the sum of the AAEMs and water- and ethanol extractives in the biomass. The nitrogen content was hardly affected (in case of straw batch 1 and hay a slight increase due to removal of extractives) by acid leaching. Jiang et al. presented also a relative low (10 wt% - 20 wt%) decrease in the nitrogen content after water- and acid leaching (5 wt% CH_3COOH , HCL , HNO_3 or H_2SO_4) from rice straw [25]. Moreover experiments by Kootstra et al. showed that only 5 wt% of the proteins were extracted from *Jatropha* press cake by water- or acid leaching at 100 °C, increasing the leaching temperature resulted in higher protein removal (25 wt% at 140 °C) [27].

Table 3: Biomass composition before and after acid leaching.

	Pine		Straw (batch 1)		Straw (batch 2)		Hay		Bagasse	
	Initial	Acid leached	Initial	Acid leached	Initial	Acid leached	initial	Acid leached	Initial	Acid leached
Compositional Analysis on biomass d.a.f. (kg kg ⁻¹)										
H ₂ O Extractive	0.03	-	0.26	-	0.06	-	0.13	-	0.06	-
EtOH Extractive	0.01	-	0.02	-	0.02	-	0.02	-	0.02	-
Total extractives	0.04	0	0.27	0	0.08	0	0.16	0	0.08	0
Glucose	0.51 (0.53 ^a)	0.53	0.35 (0.49 ^a)	0.50	0.47 (0.51 ^a)	0.48	0.41 (0.48 ^a)	0.46	0.44 (0.48 ^a)	0.50
Xylose	0.05 (0.05 ^a)	0.04	0.16 (0.21 ^a)	0.23	0.24 (0.27 ^a)	0.25	0.18 (0.20 ^a)	0.19	0.20 (0.22 ^a)	0.24
Galactose	0.02 (0.02 ^a)	0.02	0.00 (0.01 ^a)	0.01	0.00 (0.01 ^a)	0.01	0.01 (0.01 ^a)	0.01	0.00 (0.00 ^a)	0.00
Arabinose	0.01 (0.01 ^a)	0.01	0.03 (0.04 ^a)	0.04	0.03 (0.04 ^a)	0.04	0.03 (0.04 ^a)	0.04	0.02 (0.03 ^a)	0.02
Mannose	0.12 (0.13 ^a)	0.13	0.00 (0.01 ^a)	0.00	0.01 (0.01 ^a)	0.01	0.00 (0.00 ^a)	0.00	0.00 (0.00 ^a)	0.01
total (poly)saccharides	0.70 (0.73 ^a)	0.73	0.54 (0.74 ^a)	0.78	0.78 (0.83 ^a)	0.79	0.64 (0.71 ^a)	0.68	0.66 (0.73 ^a)	0.77
acid soluble lignin	0.04 (0.04 ^a)	0.05	0.05 (0.07 ^a)	0.06	0.05 (0.05 ^a)	0.05	0.05 (0.06 ^a)	0.07	0.05 (0.05 ^a)	0.05
acid insoluble lignin	0.24 (0.25 ^a)	0.24	0.10 (0.14 ^a)	0.18	0.12 (0.13 ^a)	0.15	0.11 (0.14 ^a)	0.13	0.18 (0.20 ^a)	0.18
total lignin	0.28 (0.29 ^a)	0.29	0.15 (0.21 ^a)	0.25	0.17 (0.18 ^a)	0.20	0.17 (0.20 ^a)	0.20	0.23 (0.25 ^a)	0.23
Total Ash ^c	0.01	0.00	0.06	0.02	0.08	0.05	0.06	0.01	0.01	0.01
ultimate analysis on biomass d.a.f. basis (wt %)										
C	50.1	49.7	48.0	48.5	48.5	47.9	47.6	48.2	49.3	48.9
H	6.1	6.2	6.2	6.2	6.2	6.0	6.2	6.2	6.1	6.1
N	0.1	0.0	0.5	0.8	0.4	0.2	1.1	1.4	0.2	0.1
O ^b	43.7	44.1	45.3	44.5	44.9	45.8	45.1	44.2	44.4	44.9
Ash composition, cation on dry biomass basis (mg kg ⁻¹)										
Na ⁺	60	2	2365	62	117	22	737	26	24	18
K ⁺	398	9	11786	285	12595	55	28826	104	1792	123
Mg ²⁺	387	9	1093	30	427	15	1361	63	402	21
Ca ²⁺	1771	68	3037	218	2068	164	1795	207	700	56
Sum (AAEMs)	2626	88	18281	595	15208	256	32719	395	2558	218

[a] on dry ash and extractive free basis. [b] by difference. [c] including all non-organic material (metals, Si, etc)

From the results it is evident that the chemical composition of the biomass in terms of the hemicellulose, cellulose and lignin content is not affected by our pyrolytic acid leaching method. Contrary, mineral acid leaching, at pH below 1, changes the physical structure and chemical composition (removal of hemicellulose) of biomass significantly already at 25 °C [25].

Table 3 shows that both the water soluble and ethanol soluble extractives vanished after acid leaching. In light of producing sugars from biomass it was analyzed if sugars are lost as extractives. Therefore the water solution after extraction was hydrolyzed and analyzed by HPLC. The water soluble extractives from bagasse and straw (batch 2) showed the presence of roughly 15 wt% hydrolysable sugars (<2 wt% of original biomass), for pine, hay and straw (batch 1) this amount was less.

3.2. Pyrolysis experiments

3.2.1. Yields of residue, gas and oil

Figure 1 shows the pyrolysis yields of biomasses with and without acid leaching. The product yields are expressed on initial biomass input (Yf). The initial biomass input is defined as the dry ash free biomass before leaching and thus the product distribution includes the (losses of) extractives in the leaching step. Figure 2 shows the pyrolysis yields expressed on basis of the dry ash free biomass fed into the pyrolysis reactor during an experiment. The organic oil yield increases after acid leaching for all feedstocks (Figure 1 and Figure 2) despite of organic losses in the leaching step (Figure 2). A decrease in the water, residue and gas yield can be observed. Nevertheless, the gas yield is still quite high because of the high pyrolysis temperature (530 °C) chosen for the experiments. Our tests confirm [28-30] that pyrolysis of untreated straw, hay and bagasse results in lesser oil with a higher water content as compared to woody biomass. However, this was not the case after acid leaching of these biomasses. The pyrolysis yields (on reactor intake basis, see Figure 2) of the acid leached biomasses became more comparable. This is an advantage for pyrolysis plants processing various biomass feedstocks, also from an operational point of view (e.g. no large fluctuations in the amount of residue to the combustor and load of the condenser system).

Figure 1: Pyrolysis yields obtained from the different feedstocks with and without acid leaching. $T_{\text{reactor}} = 530^{\circ}\text{C}$. The yields are expressed on basis of initial biomass (before leaching).

Figure 2: Pyrolysis yields obtained from the different feedstocks with and without acid leaching. $T_{\text{reactor}} = 530^{\circ}\text{C}$. The yields are expressed on basis of biomass fed to the pyrolysis reactor.

Figure 3: Elemental composition of the organic oil obtained from the different feedstocks with and without acid leaching. $T_{\text{reactor}} = 530^{\circ}\text{C}$.

Figure 4: Fraction of carbon recovered in the oils from the different feedstocks with and without acid leaching. $T_{\text{reactor}} = 530^{\circ}\text{C}$. The recovery is expressed on basis of initial biomass (before leaching).

Figure 3 shows the elemental composition of the organic oils from the different biomasses with and without acid leaching. After acid leaching a decrease in the carbon content and an increase in the oxygen content was obtained. This can be explained by the less intense dehydration reactions after acid leaching. Figure 4 shows the carbon recovery, which is defined as the amount of carbon in the oil divided by the carbon initial in the feed (before leaching), for the different biomasses. This graph clearly shows that the carbon recovery increased after acid leaching, especially for biomasses with a high AAEM content and low amount of water and ethanol extractives.

Figure 5 shows the organic oil yield (on reactor intake basis) as function of the AAEMs content of the different biomasses. The data points of the initial and accompanying acid leached biomass are connected by a dashed line. The observed increase in organic oil yield as a result of lower AAEMs content is in line with the finding of other researchers for untreated biomasses [28, 31]. However, it appeared that a comparable AAEMs content doesn't result in the same yield of organic oil. For instance, the increase in the organic oil yield for bagasse is much higher as compared to pine wood while starting from the same AAEMs content and with even more remaining AAEMs after acid leaching. Therefore, the organic oil yield is strongly but not solely determined by the overall AAEMs content of the feedstock. By plotting the organic oil yield versus the moles of monovalent AAEMs ($K + Na$) or the divalent AAEMs ($Mg + Ca$) in the biomass (shown in Table 3) still no clear trend was obtained for both the untreated and acid leached biomasses (figures not shown here). The type of AAEMs, the feedstock composition, other feedstock characteristics, and/or physical/chemical processes during pyrolysis can have an impact as well. Figure 6 shows an overall trend of increasing residue, produced water and gas yield with increasing AAEM content for the 5 different feedstocks. These figures also show that a comparable AAEM content doesn't necessarily result in the comparable yields. The observations support that also other parameters influence the pyrolysis outcome than solely the AAEMs content. Reported data sets relating the oil yield to the total ash content (thus not solely on AAEMs basis) show indeed quite some scatter [28]. It should be noticed that the ash content of our biomasses after acid leaching still largely varies (pine 0.02 wt% while straw batch 2 had 4.5 wt% of ash). The remaining ash, mainly silica (not shown), doesn't seem to have a large influence on the pyrolysis results of acid leached biomass, since the organic and sugar production is quite constant (i.e. Figure 2 and Figure 10).

Figure 5: Organic oil yield as function of the AAEM content of the feed. The organic oil yield is expressed on basis of biomass fed to the pyrolysis reactor. Open symbols: acid leached before pyrolysis. AAEM content is expressed as mg of cation.

Figure 6A: Effect of AAEM content in pyrolysis feed on the residue yield. The yields are expressed on basis of biomass fed to the pyrolysis reactor. Open symbols: acid leached before pyrolysis. AAEM content is expressed as mg of cation.

Figure 6B: Effect of AAEM content in pyrolysis feed on the produced water yield. The yields are expressed on basis of biomass fed to the pyrolysis reactor. Open symbols: acid leached before pyrolysis. AAEM content is expressed as mg of cation.

Figure 6C: Effect of AAEM content in pyrolysis feed on the gas yield. The yields are expressed on basis of biomass fed to the pyrolysis reactor. Open symbols: acid leached before pyrolysis. AAEM content is expressed as mg of cation.

3.2.2. Light Oxygenates

In our concept fractional condensation of the pyrolysis vapors is applied [32]. The 1st condenser was operated at thermodynamic vapor-liquid equilibrium [32] and had a vapor/gas outflow temperature of 80 °C. This condenser collects the heavy compounds like anhydro-sugars and aromatics. It was previously shown that almost no light oxygenates (e.g. acetic acid, acetol, etc.) were collected in the 1st condenser [32]. The 2nd condenser was operated at -5 °C and collected all the light oxygenates and water. Figure 7 shows the amount of organic compounds (light oxygenates) collected in the 2nd condenser. As can be seen, pyrolysis of acid leached biomass produces slightly less light oxygenates compared to untreated biomass except for straw (batch 2). The overall trend is in line with mechanistic studies claiming that the presence of AAEMs enhance the formation of light compounds via ring scissoring [8, 33]. However, the decrease in light oxygenates was relatively small considering the large differences in AAEM content between untreated and acid leached biomass (see Table 3). Figure 8 shows the acetic acid yield and concentration in the 2nd condenser liquid. A decrease in the acetic acid yield was obtained after acid leaching for all biomasses. However the acetic acid concentration in the 2nd condenser liquid increased for all biomasses to 8-10 wt%, due to the large reduction in produced water after acid leaching. It should be noted that the acid concentration during acid leaching in practice will be lower than the 10 wt% applied in this work due to the amount of 2nd condenser liquid produced per kilogram feed (0.15 kg kg⁻¹- 0.20 kg kg⁻¹ pyrolyzed biomass d.a.f.) and the amount of liquid required to fully wet a biomass particle (2-3 times the dry biomass mass). However leaching tests with lower acid concentrations still showed successful AAEM removal. Calculations show that the pyrolysis of AAEMs lean biomasses still produce enough acetic acids to remove the AAEMs from the tested biomasses (in case of straw batch 1 and hay a first water wash step is required to dissolve a fraction of the potassium). In these calculations it was assumed that dissolving one mole of K or Na consumes 1 mol of acetic acid and that 1 mol of Ca or Mg consumes 2 moles of acetic acid. It should be noticed that only acetic acid was used in these calculations while also other acids are present in the 2nd condenser liquid like formic and propionic acid.

Figure 7: Amount of organic oil recovered in the 2nd condenser for the different untreated and acid leached biomasses. The gas outlet temperature was 80 °C for the 1st condenser and -5 °C for the 2nd condenser.

Figure 8: Acetic acid yield and concentration concentrated in the 2nd condenser for the different untreated and acid leached biomasses. The gas outlet temperature was 80 °C for the 1st condenser and -5 °C for the 2nd condenser.

3.2.3. Sugars

Figure 9 shows the sugar yield, determined after hydrolysis of the oils, obtained from the untreated and acid leached biomasses. This figure shows that the sugar yields increased for all 5 feedstocks after acid leaching. Besides for glucose, also an increase in the galactose, mannose and xylose yield after acid leaching was found. The latter three sugars originate from hemicellulose. Notice, the mannose content in pine wood is quite high and the xylose content low whereas for agricultural waste streams the opposite can be observed. The sugars were mainly recovered in the 1st condenser (> 95 wt% of the sugars). Besides sugars, the 1st condenser contains mainly aromatic oligomers, mono-aromatics and furans. The 1st condenser oil has a low water content (2 wt% -5 wt%) which could be beneficial for further processing, e.g. the recovery of the sugars from this mixture.

Figure 10 shows the recovery of glucose in pyrolysis oil versus the AAEMs content of the biomass and cellulose. Glucose was measured after hydrolysis of the pyrolysis oils. Figure 11 shows the hemicellulose derived sugars obtained after hydrolysis of the pyrolysis oils. Because further reduction of the AAEMs content of the biomasses was not possible, the glucose recovery of the tested biomasses was compared with the pyrolysis (identical setup and conditions) of Avicel cellulose with 1 mg kg⁻¹ AAEMs (as received) and Avicel cellulose impregnated with 100 and 1000 mg cation per kg of AAEMs salts (K₂CO₃). As discussed earlier the recovery of sugars increased after acid leaching (see Figure 10). When cellulose was used the glucose recovery steadily increased with decreasing AAEMs content (see Figure 10). For the leached biomasses there did not seem to be a clear relation between the AAEMs content (90 mg kg⁻¹ - 600 mg kg⁻¹) and the sugar yield. It is noteworthy that the glucose recovery of the leached biomasses was higher than that of cellulose at equal AAEMs content. Based on these results we conclude that the sugar recovery, like the organic oil yield, is strongly but not solely determined by the overall AAEMs content of the feedstock. Also here, chemical reactions such as lignin/cellulose/hemicellulose interactions [34, 35] and the characteristics of the biomass (e.g. composition or structure) may play a role as well. When the glucose recovery was plotted versus the moles of monovalent AAEMs (K+Na) or the divalent AAEMs (Mg+Ca) in the biomass (shown in Table 3) still no clear trend was obtained for the acid leached biomasses (figures not shown here). This means that the glucose recovery is not determined by the remaining of a specific AAEM. Additionally, the location of the AAEMs in the biomass could play an important role. In the cellulose experiments all the AAEMs were present in the cellulose whereas in the leached biomasses most of the AAEMs could be present in the hemicelluloses and proteins, like in natural materials [22-24]. The same observations and explanations hold for xylose, galactose and mannose, see Figure 11.

Figure 9: Effect of acid leaching on the sugar yield (after hydrolysis of the oil). The sugar yield is expressed on basis of initial biomass (before leaching).

Figure 11: Recovery of xylose, galactose and mannose in the oil versus the AAEM content of the feed. The recovery is defined as the amount of the sugar in the oil divided by the corresponding sugar in the feed. AAEM content is expressed as mg of cation per kg of dry biomass.

Figure 12: Effect of acid leaching on the levoglucosan concentration recovered in the 1st condenser. The 1st condenser temperature was 80 °C.

Figure 12 shows the levoglucosan concentration in the 1st condenser oil. The 1st condenser was operated at 80 °C. At this temperature light oxygenates and water remain in the vapor phase and are collected in a 2nd condenser at 20 °C. This figure shows that levoglucosan con-

centrations between 26 wt% - 38 wt% were obtained from acid leached biomasses while the concentration was between 3 wt% - 10 wt% without acid leaching. The high concentration of levoglucosan offers opportunities for chemicals production via biotechnological routes [2, 3] or acid catalyzed conversions [4, 36]. Plotting the levoglucosan yield per kilogram glucose in the feed versus the moles of monovalent AAEMs (K+Na) or the divalent AAEMs (Mg+Ca) in the biomass (shown in Table 3) gave no clear trend for both the untreated and acid leached biomasses (figures not shown here).

3.2.4. Water insolubles

Both the aromatics and sugars in the bio-oil are important products in the concept of chemicals production via pyrolysis. Analysis of the aromatic compounds in the pyrolysis oil was done by cold water precipitation (heavy fraction lumped as “water insolubles”).

Figure 13 shows the water insoluble yield for the different untreated and acid leached biomasses. Analysis of water insolubles from different feedstocks showed that these compounds mainly consist of aromatic structures derived from lignin [37, 38]. A decrease in the water insoluble yield was obtained after acid leaching whereas much more organic oil was produced (see Figure 2). It seems that the extent of the decrease depends on the feedstock: for pine the decrease was marginal while for hay and bagasse the decrease was more than a factor of 2. It turned out not to be possible to relate the decrease in water insoluble to the feedstock composition, including the AAEMs content nor the type of AAEMs.

Figure 13: Effect of acid leaching on the water insoluble yield. The water insoluble yield is expressed on basis of initial biomass (before leaching).

To study if the phase stability of pyrolysis oil was improved after acid leaching, the 1st and 2nd condenser oils were mixed to simulate an oil condensed as a single batch at 20 °C. It was found that all oils produced from acid leached biomasses were single phase liquids. This was not the case for the straws and hay without acid leaching. Too high concentration of water insoluble compounds and water are the cause of physical instability (phase separation) of the bio-oils [39]. Thus the improved stability can be explained by lower water (Figure 2) and water insoluble production for acid leached biomass and the resulting lower concentration of these compounds in the bio-oils.

4. Conclusions

The acidity of the pyrolytic leaching liquid ($\text{pH}=2.1$), resembling the liquid produced in the pyrolysis process, and the leaching temperature ($90\text{ }^{\circ}\text{C}$) did not affect the carbohydrate and lignin content of the biomass feedstocks tested. However, acid leaching did lead to a loss in organic matter (e.g. 27 wt% for straw batch 1) that turned out to be water and ethanol extractives. Pyrolytic acid leaching removed most of the AAEMs naturally present in biomass, though the AAEMs content could not be reduced below 90 mg kg^{-1} . After acid leaching, the organic oil yield was largely increased for all biomasses. The carbon to oil conversion increased after acid leaching, especially for high AAEMs content biomasses. Moreover, the residue, gas and oil yields, based on biomass fed to the reactor, became more comparable for the different biomasses after acid leaching. This may improve the operability of pyrolysis plants running on various types of biomasses. Only after acid leaching, pyrolysis of straw and hay resulted in production of single phase bio-oils (condensed at $20\text{ }^{\circ}\text{C}$) which makes them easier to handle. As a result of acid leaching the dehydration and ring fragmentation reactions of sugars are significantly suppressed. Consequently, 30 wt% - 40 wt% of the initial glucose and galactose in the biomass was recovered as hydrolysable sugar in the oil and 10 wt% - 22 wt% of the xylose and mannose. Unfortunately, even very small amounts of AAEMs ($\sim 100\text{ mg kg}^{-1}$) suppressed the production of sugars significantly. It turned out that the catalytic activity of AAEMs is a dominant factor with respect to sugar production. However, results of the leached biomasses and AAEMs impregnated avicel cellulose showed that, next to AAEMs, there are other factors (e.g. reactions, biomass structure/composition) of influence with respect to the sugar yield. Bagasse gave the highest total sugar yield (22.1 wt% of the feed) after hydrolysis. The acetic acid yield reduced after acid leaching, however calculations showed that still sufficient acid is produced to demineralize the tested biomasses. By applying staged condensation, levoglucosan, the most abundant sugar in our pyrolysis oils, could be concentrated up to 38 wt%.

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Appendix B

Validation of the use of a synthetic mixture instead of the 2nd condenser liquid for the leaching of AAEMs from biomass

Abstract

The use of a synthetic mixture instead of the real 2nd condenser liquid as leaching liquid was evaluated. The synthetic mixture and the real 2nd condenser liquid gave comparable AAEM removal efficiencies. Moreover the pyrolysis results obtained from pinewood leached with the synthetic mixture were similar to the pyrolysis results obtained from pinewood leached with real 2nd condenser liquid.

This appendix is based on:

Oudenhoven SRG, Westerhof RJM, Aldenkamp N, Brilman DWF, Kersten SRA. Demineralization of wood using wood-derived acid: Towards a selective pyrolysis process for fuel and chemicals production. *J Anal Appl Pyrolysis*. 2013;103:112-8.

In this set of experiments biomass leaching with real 2nd condenser liquid is compared to leaching with a synthetic mixture, representing the key compounds in the 2nd condenser liquid. The AAEM removal efficiency using both liquids as well as the pyrolysis products from pinewood leached with both liquids has been studied. Because relatively large amounts of leaching liquid are required for the leaching experiments, 10 times more on mass basis than the biomass, it will be beneficial for our experiments if a synthetic mixture can be used instead of the real 2nd condenser liquid. Table 1 shows the key compounds present in the 2nd condenser liquid, produced from untreated pinewood, and the selected composition of the synthetic mixture. This mixture represents approx. 50% of the organic compounds in the 2nd condenser liquid. Acetol was replaced by a combination of acetone and ethanol, which represent the functional groups (alcohol and ketone).

Pinewood batches were leached with one of the two leaching liquids (0.1 kg of biomass per kg of leaching solution) for 2 hours at 90 °C under continuous stirring. After acid leaching the drained pinewood was rinsed several times with milli-Q water to remove the remaining leaching liquid, containing dissolved AAEMs, from the pinewood pores. Rinsing with milli-Q water was repeated until the pH of the effluent solution was higher than 6.0. Before pyrolysis the pinewood was dried for 24 hours in a hot air oven at 105 °C.

Table 1: Chemical composition of the 2nd condenser liquid and the synthetic mixture used for acid leaching. The 2nd condenser liquid was produced from untreated pinewood at 530 °C. The temperature of vapors/gases leaving the 1st condenser and 2nd condenser were 81 °C and 20 °C, respectively.

Component	2 nd condenser solution	Synthetic mixture
Acetic acid (wt%)	9.5	10
Acetol (wt%)	7.6	-
Ethanol (wt%)	-	3.75
Acetone (wt%)	-	3.75
Propionic acid (wt%)	1.4	1.5
Guaiacol (wt%)	1.7	1.5
Other organics (wt%)	19.5	-
water (wt%)	60.5	79.5 (milli-Q)

Table 2 shows the ash content in pinewood before and after leaching. A large decrease in the ash content was obtained after leaching for both liquids. Comparable results were obtained for the removal of the individual AAEMs; i.e. Na, K, Mg, Ca and Si as shown in Figure 1. It can be concluded that leaching with the 2nd condenser liquid (real or synthetic) combined with additional rinsing is an efficient pre-treatment process to remove the AAEMs from biomass.

Table 2: Ash content of pinewood before and after acid leaching with real and synthetic 2nd condenser liquid. When duplicates of the experiments were performed, the ash contents of the single measurement are presented between brackets.

Acid solution	Temperature (°C)	Leaching time (min)	Ash content (wt%)
Untreated			0.53
Synthetic mixture	90	120	0.04 (0.02/0.05)
Real condenser 2 liquid	90	120	0.02

Figure 1: AAEM content in untreated pinewood and acid leached pinewood.

The reproducibility of pyrolyzing acid leached pinewood was checked by repetition of three sets of experiments. It should be noted that for each fast pyrolysis experiment with acid leached pinewood, two acid leaching experiments were carried out with different batches of 2nd condenser liquid. The product yields and oil composition obtained by pyrolysis of untreated and acid leached pinewood are shown in Table 3. First of all, it can be seen that the reproducibility is quite good, especially when considering the multiple process steps involved per experiment.

Table 3: Product yields and composition of the pyrolysis experiments with untreated and acid leached pinewood. $T_{\text{Reactor}} = 530$ °C. When duplicates of the experiments were performed the product yields of the single measurement are presented between brackets.

	Untreated	Synthetic mixture	2 nd condenser real
Organic yield (kg kg ⁻¹)	0.482 (0.497/0.467)	0.580 (0.559/0.601)	0.562 (0.550/0.573)
Water yield (kg kg ⁻¹)	0.119 (0.116/0.121)	0.086 (0.089/0.083)	0.065 (0.074/0.056)
Residue yield (kg kg ⁻¹)	0.102 (0.104/0.100)	0.086 (0.083/0.089)	0.087 (0.088/0.086)
Gas yield (kg kg ⁻¹)*	0.297 (0.282/0.312)	0.249 (0.269/0.229)	0.298 (0.291/0.305)
Levogluconan concentration 1 st condenser oil (wt%)	10.9 (10.9/10.0)	35.9 (35.4/36.4)	37 (41.4/32.5)
Levogluconan yields (kg kg ⁻¹)	0.034 (0.027/0.041)	0.176 (0.16.8/184)	0.170 (0.183/0.157)

* By difference

As can be seen from Table 2 the product yields were comparable for the pyrolysis of pine-wood leached with the real 2nd condenser liquid and the synthetic mixture. For levoglucosan, both the concentration and yield compare very well between the two different leaching liq-uids. From the results presented in this appendix it can be concluded that using a synthetic leaching liquid is a good alternative for the real 2nd condenser liquid. For more information on the rinsing process the reader is referred to our published paper [1].

[1] Oudenhoven SRG, Westerhof RJM, Aldenkamp N, Brilman DWF, Kersten SRA. Demin-eralization of wood using wood-derived acid: Towards a selective pyrolysis process for fuel and chemicals production. *J Anal Appl Pyrolysis*. 2013;103:112-8.

Chapter 4

Effect of temperature on the fast pyrolysis of pyrolytic acid leached pinewood; the potential of low temperature pyrolysis

Abstract

In this chapter, we have evaluated the potential of pyrolytic acid (mixture of acetic, formic and propionic acid) leaching of biomass and subsequent fast pyrolysis to increase the organic oil, anhydrosugars and monomeric phenolics yield by varying the fluidized bed temperature between 360 °C and 580 °C (360 °C, 430 °C, 480 °C, 530 °C, and 580 °C). The pyrolysis of acid leached pinewood resulted in more organic oil and less water and solid residue compared to untreated pinewood over the whole temperature range. Below 500 °C the difference was most profound; for acid leached pinewood at 360 °C the organic oil was already 0.65 kg kg⁻¹ pine, with a sugar yield of 0.23 kg kg⁻¹ pine. At this low pyrolysis temperature no bed agglomeration was observed for acid leached pine whereas at the higher temperatures agglomerates were found, which were identified to be clusters of fluidization sand glued together by sticky pyrolysis products (melt). Low reactor temperatures also favored the production of monomeric phenolics, though their absolute yields remained low for both untreated and leached pine (maximum: 0.023 kg kg⁻¹ pine, 0.08 kg kg⁻¹ lignin). GPC, GC/MS and UV-fluorescence spectroscopy showed that acid leaching did not influence significantly the yield and molecular size of the aromatic fraction in the produced pyrolysis oils. Back impregnation of the removed AAEMs into leached biomass revealed that the effects of the applied acid leaching, both with respect to the product yields and bed agglomeration, can be mainly assigned to the removal of AAEMs.

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1. Introduction

Fast pyrolysis is a promising rapid process (seconds) to decompose solid biomass into an oil that can be used directly for power production or further refined to liquid fuels [1, 2] and/or chemicals [3]. The oil composition depends largely on the biomass feedstock, process conditions and the oil recovery method. Since different oil applications require different specifications, control over the oil composition would be desirable.

Lignocellulosic biomass contains next to cellulose, hemicellulose, lignin and extractives, also inorganic compounds, including alkali and alkaline earth metals (AAEMs) [4, 5]. These AAEMs catalyze (ring) cracking [6] and dehydration reactions [7] of the initially formed anhydrosugars (e.g. levoglucosan) from hemicellulose and cellulose. Minimizing these catalytic effects of the AAEMs during pyrolysis can be achieved by removing them via organic acid (e.g. acetic acid) [8, 9] or mineral acid leaching [6, 10-12] or passivating via mineral acid infusion [13-16]. The anhydrosugars are then produced at higher yields making them an interesting feedstock for biological [17-19] and/or chemical conversion (see the review of Radlein [20]).

Recently, we have proposed a process concept in which the AAEM removal from the biomass is done via leaching with pyrolytic acids, produced and concentrated within the same process [8]. The products of interest are (fermentable) sugars, phenolics and light oxygenates. In the first paper the proof of principle of the proposed concept was presented. In Chapter 3 we applied the concept (fixed reactor temperature of 530 °C) to 5 different biomasses, including high AAEM content agricultural waste streams [21]. A large increase in the organic oil yield as well as sugar recovery (30 wt% to 40 wt% of the initial glucose) was obtained for all biomasses. However it has been found that it is impossible to remove all AAEMs from biomass via pyrolytic acid leaching, and that these remaining AAEMs (88 mg kg⁻¹ for pinewood) still suppress the hydrolysable sugar recovery considerably.

The pyrolysis temperature is undoubtedly an important parameter to steer the pyrolysis yield and product composition from untreated feedstocks [22-24]. So far all studies on pyrolysis of acid leached biomass have been carried out at temperatures between 450 °C to 530 °C (single temperature in each paper). Pernikis et al did study a temperature range (340 °C - 460 °C), however a hydrolyzed feedstock was used [25]. However it is generally found that hemicellulose and cellulose are already fully converted at 300 °C [26] and 360 °C [27] respectively. Therefore such high pyrolysis temperatures might not be necessary to obtain high organic oil and sugar yields from acid leached feeds.

Lignin pyrolysis yields a large variety of light organics and monomeric and oligomeric phenolics [28]. Especially the oligomeric phenolics are difficult to identify and quantify. This fraction is therefore often reported as the lumped group “water insolubles”, which is determined by the cold water precipitation method [29]. However, Garcia Perez et al. [23] showed that a significant fraction of the phenolic oligomers are overlooked when only the water insolubles are determined. The question whether AAEMs affect the lignin derived products has been studied in much lesser detail than the cellulose fraction and led to, sometimes, conflicting reports in the literature. Patwardhan et al. [30] claimed a negligible effect of impregnating AAEMs into lignin (no data were presented). Kleen and Gellersted [31] showed that sodium catalyzed the demethylation and dehydration of the monomeric phenolics while the total peak area of detected monomeric phenolics per gram of feed remained constant. Dalluge et al. obtained after acid infusion a reduction of 55 % and 49 % in the monomeric phenolics yield (0.028 kg kg^{-1} to 0.013 kg kg^{-1} and 0.024 kg kg^{-1} to 0.012 kg kg^{-1}) and 49 % and 14 % in the water insoluble yield (0.10 kg kg^{-1} to 0.05 kg kg^{-1} and 0.09 kg kg^{-1} to 0.08 kg kg^{-1}) for red oak and switch grass respectively [14]. Mourant et al. report a doubling of the pyrolytic lignin yield for mallee wood pyrolysis [11] while Brown et al. showed that the yield was approximately halved for both switchgrass and corn stover after acid leaching [12].

Many pyrolysis reactor concepts have been proposed (see Bridgwater [32]), though most operational and planned large scale processes are based on the fluid bed concept [32]. Radlein [20] and Dalluge et al. [14] reported that pyrolysis of mineral acid leached and acid infused biomass in fluidized bed setups both resulted in the formation of bed agglomerates leading to operational problems (blocking and defluidization). Radlein ascribed these agglomerates from acid leached biomass to the formation of a “sticky” melt, a mixture of high molecular weight polymer that decomposes very slowly, which coats the bed particles leading to agglomeration [20].

The main goal of this chapter is to investigate the effect of the fluidized bed temperature on the pyrolysis yields and oil composition using pyrolytic acid leached pinewood as feedstock. First, to get a better understanding of the acid leaching on the pyrolysis results it is investigated if the observed effects are mainly caused by the AAEM removal or that modification of the biomass induced by the acid leaching also play a role. Hereafter yields of organic oil, residue, gas, water, sugars, monomeric phenolics and water insolubles from untreated and acid leached pinewood pyrolyzed at various fluidized bed temperatures are compared. GC/MS, GPC and UV-fluorescence are used to shed light on the effects of AAEMs and reactor temperature on the lignin derived products. Finally, observations concerning the formation of bed agglomerates when pyrolyzing acid leached pinewood and ways to prevent this will be discussed.

2. Material and methods

2.1. Materials

Pinewood (Lignocel 9, Rettenmaier & Söhne GmbH, particle size fraction 0.5 mm to 2 mm) and wheat straw (Purchased from Praxis. Brand: Puik original, batch 2 in Chapter 3) were used as feedstock in this study. A fraction of the wood and straw was leached with a synthetic acidic aqueous mixture, mimicking the 2nd condenser liquid from the pyrolysis process. The use of this synthetic mixture instead of the real condenser stream has been validated in Appendix B and was found to lead to identical results. The synthetic leaching solution was made from (on mass fraction): 10 % of acetic acid (SAFC, 99.5 %), 3.75 % of acetone (Assink Chemie, purity > 99.5 %), 3.75 % of ethanol (Assink Chemie, purity 99.8 %), 1.5 % of guaiacol (SAFC, purity >98 %), 1.5 % of propionic acid (SAFC, purity >99.9 %) and 79.5 % of demineralized water (milli-Q). The composition of the pinewood and straw before and after acid leaching is shown in Table 1. Silica sand, sieve fraction (212 μm to 300 μm) with a particle density of 2600 kg m⁻³, was used as fluidized bed material during the pyrolysis experiments. The chemicals used for the hydrolysis and analysis of the oils were: sulfuric acid (Sigma Aldrich, purity 95.0-98.0 %), barium carbonate (Sigma Aldrich ACS reagent purity >99 %) methanol (Uvasol, purity >99.9 %), acetone (Chromasolv, purity >99.8 %) and tetrahydrofuran (Sigma-Aldrich, purity 99.9 %). The AAEM salts used for impregnating acid leached pinewood and straw were sodium carbonate (Riedel de Haen, purity 99.8 %), potassium carbonate (Sigma Aldrich, purity 99.7 %), magnesium carbonate (Taendos purity >99 %) and calcium carbonate (sigma Aldrich, purity >93 %).

2.2. Experimental and methods

2.2.1. Acid leaching

The leaching method was identical to the one described in Chapter 3. Briefly, the wood or straw particles were leached for 2 h at 90 °C in a 50 dm³ vessel (0.1 kg dry biomass per kg of leaching solution) under continuous stirring. After 2 h the leaching liquid was drained from the vessel through a perforated plate (pore size 0.5 mm), leaving the wood or straw particles inside the vessel. The wood or straw particles were rinsed with milli-Q water to remove the remaining leaching liquid containing dissolved minerals. The rinsing was continued until the pH of the effluent solution was higher than 6.0. Hereafter the pinewood particles were dried for 24 h in a hot air oven at 105 °C. After acid leaching a small amount (for pine 4 % mass fraction and straw 8 % mass fraction) of the initial biomass was lost which turned out to be water and ethanol extractives [21].

Table 1: Pinewood and straw* composition before and after acid leaching.

	Pine		Straw*	
	Untreated	Acid leached	Untreated	Acid leached
Compositional analysis, fraction in biomass da.f. (kg kg⁻¹)				
H ₂ O Extractive	0.03	0	0.06	0
EtOH extractive	0.01	0	0.02	0
Total extractives	0.04	0	0.08	0
Glucose	0.51	0.53	0.47	0.48
Xylose	0.05	0.04	0.24	0.25
Galactose	0.02	0.02	0	0.01
Arabinose	0.01	0.01	0.03	0.04
Mannose	0.12	0.13	0.01	0.01
Total sugars	0.70	0.73	0.78	0.79
Acid soluble lignin	0.04	0.05	0.05	0.05
Acid insoluble lignin	0.24	0.24	0.12	0.15
Total lignin	0.28	0.29	0.17	0.20
Ash composition, concentration in dry biomass (mg kg⁻¹)				
Na ⁺	60	2	117	22
K ⁺	398	9	12595	55
Mg ²⁺	387	9	427	15
Ca ²⁺	1771	68	2068	164
Total AAEMs	2616	88	15208	256
Total ash	0.01	0.00	0.08	0.05

* Batch 2 straw in Chapter 3

2.2.2. AAEM impregnation in acid leached biomass

The removed AAEMs were impregnated back into the acid leached wood or straw particles to study the effect of acid leaching on the pyrolysis products. Two different AAEM mixtures have been used namely i) impregnation with a synthetic mixture of CO₃ salts, and ii) impregnation of the leached minerals, which were recovered by evaporation of the leaching liquid followed by dry oxidation at 575 °C for 24 h to remove the organics. The amount of CO₃ salts used for impregnation was calculated based on the concentrations measured by XRF analysis before and after acid leaching. The desired amount of AAEM carbonates were dissolved in milli-Q water and mixed with the acid leached pinewood or straw. Hereafter the biomass was vacuum dried while stirring several times.

2.2.3. Fast pyrolysis

The wood and straw particles were pyrolyzed in the same fluidized-bed fast pyrolysis reactor as our other work on acid leached biomass pyrolysis. The most important features of the pyrolysis process and procedures are explained briefly here. In the fluidized bed reactor silica sand (sieve fraction 212 μm to 300 μm) was used as bed material. The sand was fluidized using pre-heated nitrogen. Per experiment around 150 g of biomass particles were fed manually at constant time intervals in batches of 2 g to 5 g together with 4 g to 8 g sand via a gas lock system consisting of two valves. The biomass particles were fed into the fluidized bed reactor during a period of 30 min to 40 min. To ensure maximal conversion of the pyrolyzing pinewood and straw the bed was maintained at the set reactor temperature for 30 min before cooling down. The vapors were condensed in an electrostatic precipitator (ESP), operated at 20 $^{\circ}\text{C}$ (outgoing gas temperature), and a double walled glass condenser, operated at -5 $^{\circ}\text{C}$ (outgoing gas). A gas filter (10 μm) was used to trap the last aerosols (± 2 % mass fraction of total oil) in order to complete the mass balance. The yields were calculated using the methods described in our previous paper [8]. Since the solid residue after acid leaching has (partially) a different morphology than the “typical” char from untreated biomass, containing the original biomass structure, the organic fraction remaining in the reactor will be referred to as residue instead of char.

Table 2: Pyrolysis process conditions.

Pyrolysis	Fluid bed
Biomass feeding time (min)	30-40
Run Time (min)	60-70
T_{reactor} ($^{\circ}\text{C}$)	530
τ_{vapors} (s)	1.8
P_{reactor} (mbar)	~ 1060
U / U_{mf}	2-3
$T_{\text{outgoing gas 1st condensor}}$ ($^{\circ}\text{C}$)	20
$T_{\text{outgoing gas 2nd condensor}}$ ($^{\circ}\text{C}$)	-5

2.3. Analysis

The gases produced during pyrolysis were analyzed for H_2 , CO, CO_2 , CH_4 , C_2H_4 , C_2H_6 , C_3H_6 and C_3H_8 using gas chromatography (Varian CP 4900). The water content of the pyrolysis oil was measured by Karl Fischer titration (Metrohm 787 KF Titrino, titrant Hydranal Composite 5 and solvent a mixture of methanol and dichloromethane in a 3 to 1 volumetric ratio). Titrations were performed in duplo, if the difference in the measured water content on mass fraction was larger than 0.5 % the titration was repeated until satisfying results were obtained.

The hydrolysable sugar content of the oils was quantified using NREL LAP method “Determination of sugars, byproducts, and degradation products in liquid fraction process samples” [33]. The oil was first separated using the cold water extraction method [29] (1 g oil per 100 cm^3 cold water) followed by hydrolysis (3.5 % volume fraction H_2SO_4 for 60 min at 120 °C) of the water soluble fraction. The samples were hereafter neutralized by adding $BaCO_3$ and filtered (Whatman 0.2 μm filter) before HPLC analysis (Agilent 1200 series, column Hi-Plex-Pb operated at 70 °C, eluent milli-q water, eluent flow 0.6 $cm^3 min^{-1}$).

To make a clear difference between the monomeric aromatics from lignin (containing a phenyl ring) and from carbohydrates (furanic) the monomeric structures with a phenyl ring will be referred to as monomeric phenolics. The quantification of monomeric phenolics was done by GC-MS analysis (GC 7890A MS 5975C Agilent Technologies) equipped with a capillary column (Agilent HP-5MS, HP19091S-433). Samples were dissolved in acetone (oil concentration in acetone was 50 $mg g^{-1}$) and filtered before analysis (Whatman 0.2 μm filter). The individual peaks were identified (NIST library) and integrated. Based on the average response factor of guaiacol ($1.31 \cdot 10^{10} g^{-1}$), eugenol ($1.63 \cdot 10^{10} g^{-1}$), vanillin ($1.99 \cdot 10^{10} g^{-1}$) and an 4-tert-butylphenol ($1.63 \cdot 10^{10} g^{-1}$) an estimation was made of the total amount of monomeric phenolics in the produced oils.

The water insoluble fraction was isolated from the pyrolysis oil by cold water precipitation as described by Scholze et al [29]. Briefly, 5 g of oil was dropwise added to 500 cm^3 intensively stirred cold Milli-Q water (<2.5 °C). Part of the oil will dissolve in the water and the rest will precipitate as a brown powder. The precipitated powder was recovered by filtration using a Buchner funnel (paper Whatman grade 42). The powder on the filter was rinsed multiple times with cold milli-Q water (<2.5 °C), till the eluent was colorless. The filter paper containing the water insolubles was dried in a vacuum oven at room temperature under 10 mbar for at least 24 h.

Gel permeation chromatography (GPC), also referred to as size exclusion chromatography (SEC), was used to obtain insights in the molecular weight distribution (MWD) of the pyrolysis oils. However, it should be noticed that the translation of the elution volume to exact

molar weight is affected by the shape and functional groups of a molecule as shown earlier by Hoekstra et al [34]. Nevertheless, GPC can be used to investigate relative changes between the spectra of oils produced under various conditions. The mole weight distribution of the oils was measured by a Agilent Technologies G1364C (3 columns in series Varian PLgel MIXED column E 7.5 mm × 300 mm operated at 40 °C, eluent THF, eluent flow 1 cm³ min⁻¹) equipped with both a refractive index detector (RID) and a variable wavelength detector (VWD, operated at 254 nm). The oils were diluted in tetrahydrofuran (THF), to a concentration of 10 mg g⁻¹, and filtered before analysis (Whatman 0.2 μm filter). The chromatograms measured at 254 nm have been integrated with respect to the elution volume (*v*, integrated from 14 cm³ to 32 cm³) to obtain a measure for the amount of compounds containing double bounds in the pyrolysis oils.

$$GPC\ area = \int_{v_1}^{v_2} f(v) dv$$

UV-fluorescence was used to study the sizes of aromatic clusters in the pyrolysis oils. This technique has been applied for pyrolysis oils from coal [35-38] and to a lesser extend from biomass pyrolysis [23, 39, 40]. The synchronous spectra were measured between 250 nm and 500 nm in a Perkin Elmer Lambda 850 UV-fluorescence spectrometer at a constant energy difference of 2800 cm⁻¹, as described in the paper of Garcia Perez et al. [23]. The samples were dissolved in methanol to obtain a 2 mg kg⁻¹ to 4 mg kg⁻¹ (wet basis) solution. The synchronous spectra are the average of two scans recorded with a slit of 2.5 nm and a scan speed of 200 nm min⁻¹.

The intensities measured by GPC and UV-Fluorescence for each oil are expressed on the intake of biomass basis (dry ash free (d.a.f.)). Thus, the measured intensity (*I*) was corrected for differences in dilution and multiplied by the product yields (*W* = weight in g). *X_{water}* is the water fraction in the sample.

$$\text{Corrected intensity} = \frac{W_{\text{solvent}} + W_{\text{sample}}}{W_{\text{sample}}} * \frac{\text{Intensity measured}}{(1 - X_{\text{water}})} * \left(\frac{W_{\text{organic PO}}}{W_{\text{organic biomass}}} \right)$$

The bed agglomeration was studied by a microscope (zoom 10-200x Conrad DP-M17) and scanning electron microscope (Zeiss Merlin). The samples were taken directly from the fluidized bed reactor and observed without any treatment.

3. Results

3.1. Reproducibility

The reproducibility of pyrolyzing acid leached pinewood at 530 °C (n=5) was tested. Yield and standard deviation of residue, water, organic oil and gas were: 0.087 ($\pm$ 0.004), 0.063 ($\pm$ 0.007) 0.583 ($\pm$ 0.023) and 0.271 ($\pm$ 0.025) respectively . This shows that the reproducibility is satisfactory and trends can be detected.

3.2. Influence of acid leaching on the pyrolysis outcome

Figure 1: Yield of residue, gas, organic oil and produced water from acid leached, acid leached impregnated with AAEMs and untreated pinewood and straw.

The results presented in the previous Chapter (3) show a clear effect of acid leaching of the feedstock on the yields of the lumped component classes and individual compounds. We showed that the pyrolytic acid leaching led to the (partial) removal of the AAEMs and the water and ethanol extractives but did not affect the carbohydrate and lignin content of the biomass feedstocks tested (Chapter 3). However, from these experiments it is not conclusive if the effects of acid leaching on the pyrolysis outcome were caused solely by the AAEM removal or if other changes to the biomass, such as structural modifications (e.g. reduced DP of cellulose or altered lignin-cellulose interaction), induced by the acid leaching also play a

role. To clarify this, AAEMs were impregnated back into acid leached pinewood and straw. Figure 1 shows the lumped products of these tests. The yields of untreated biomasses and acid leached biomasses back impregnated with AAEMs were quite similar. This was found for tests in which carbonate salts were used for the back impregnation of AAEMs as well as when real ashes were used.

Figure 2A: Molar weight distribution of the pyrolysis oil from untreated, acid leached and acid leached impregnated with AAEMs pinewood.

Figure 2B: Molar weight distribution of the pyrolysis oil from untreated, acid leached and acid leached impregnated with AAEMs straw.

Also the molar weight distribution (MWD) of the pyrolysis oils produced from acid leached biomasses back impregnated with AAEMs, as shown in Figure 2, were identical to the MWD of the untreated biomasses, while the MWD were significant different for pyrolysis oils from acid leached biomasses. From these results it can be concluded that the effect of pyrolytic acid leaching before pyrolysis on the pyrolysis yields and oil composition can be mainly attributed to the removal of AAEMs. If other changes to the biomass occur during the acid leaching these apparently do not have a significant influence on the yields and compositions of the lumped product classes. Interestingly, there is no significant difference in yields (see Figure 1) and oil composition (see Figure 2) between back impregnation with the original AAEMs and the synthetic mixture made from carbonate salts.

3.2. Lumped product yields as function of the fluidized bed reactor temperature.

Untreated and acid leached pinewood were pyrolyzed at reactor temperatures between 360 °C and 580 °C. This reactor temperature range can be divided in relatively two regimes:

- Temperatures below ~450 °C; at these temperatures the reaction kinetics are relative slow compared to the heat transfer, therefore the temperature of the pyrolysing particles will be close to that of the heat carrier. Moreover at these temperatures reactions in the vapor phase are of less importance as shown by Hoektra et al.[41], Hence, in this temperature range phenomena at particle level at the set temperature determine the yield and yield differences between untreated and pretreated biomass.
- Temperatures above ~480 °C, at these temperatures the heat transfer to the biomass particles is (much) slower than the chemical reactions. As a result, the effective pyrolysis temperature of the condensed phase (solid plus molten) is lower than the reactor temperature. Numerical simulations by Antal [42], Piskorz et al. [43] and Lede [44-46] reported maximum effective pyrolysis temperatures between 470 °C and 530 °C. On the other hand, the volatile compounds in vapor phase will reach the reactor temperature and at temperatures of 500 °C or higher significant vapor cracking will occur [22, 41]. So here the yields (differences) are the result of a combination of the pyrolyzing particles at ill-defined reaction temperature and vapor phase reactions.

Figure 3 shows the lumped product yields obtained from untreated and acid leached pinewood as function of the reactor temperature. In general, the gas yield increased and the residue yield decreased with increasing reactor temperature for both untreated and acid leached pinewood.

Figure 3A: Residue yield from untreated and acid leached pinewood versus the reactor temperature.

Figure 3B: Gas yield from untreated and acid leached pinewood versus the reactor temperature.

Figure 3C: Organic oil yield from untreated and acid leached pinewood versus the reactor temperature.

Figure 3D: Produced water yield from untreated and acid leached pinewood versus the reactor temperature.

Acid leached pinewood yielded more organic oil and less produced water and residue over the whole temperature range. At low reactor temperature less gas was produced from acid leached pinewood while above 480 °C comparable yields were obtained. Interestingly, pyrolysis of acid leached pinewood resulted in a relative high organic oil yield (0.65 kg kg⁻¹ pine d.a.f.) already at 360 °C. Remember that the used set-up facilitates long particle residence times (>30 min), which is expected to result in >99 % of the maximal achievable mass loss [47], even at 360 °C (based on kinetics from untreated biomass) [47]. The additional organic oil (0.15 kg kg⁻¹ pine d.a.f.) after acid leaching at 360 °C, 430 °C and 480 °C is the result of less produced water (~0.06 kg kg⁻¹ pine d.a.f.), residue (0.05 kg kg⁻¹ pine d.a.f.) and gas (0.05 kg kg⁻¹ pine d.a.f.) production. This shows that the dehydration reactions of the carbohydrates (see section 3.6) are suppressed after acid leaching. The organic oil yield showed an optimum around 480 °C, after which it decreased rather steeply for acid leached pinewood. It should be noted that untreated pinewood contains a relative low AAEM content (2616 mg kg⁻¹ dry pine) compared to other biomasses like straw or hay (typically > 10000 mg kg⁻¹ dry biomass). For these high AAEM content feedstocks a larger increase in the organic oil yield after acid leaching was obtained at 530 °C (Chapter 3).

The produced water yield was hardly affected by the reactor temperature for both untreated and acid leached pine. Water originates from dehydration reactions, which according to Mamleev et al. [48] occur inside the pyrolyzing particle (more specific, within the molten phase [48]). Their claim that water originates from reactions within the particle is supported by our experiments, showing no increase in the water production at higher temperatures while vapor cracking reactions took place (based on both oil and gas yield in Figure 3 and GPC analysis).

3.3. Sugar yields

The yield of glucose, xylose and mannose (all measured after acid hydrolysis of the oils) as function of the reactor temperatures is shown in Figure 4. The results of the acid leached pinewood are compared with the results of untreated pinewood. A large increase in the glucose, xylose and mannose yield was obtained for acid leached pinewood. Figure 5 shows the concentration of the sugars in the pyrolysis oil from acid leached pinewood. The oils condensed at 20 °C contained up to 49 % mass fraction of these sugars (Figure 5). The sugar concentration can be further increased by applying fractional condensation as proposed in our pyrolysis of acid leached biomass concept (see section 4.3 in Chapter 1). The maximum sugar yield was obtained around 480 °C which corresponds with the temperature producing the highest organic oil yield. Table 3 shows the sugar recovery based on the corresponding sugar initially present in the pinewood at a reactor temperature of 360 °C and 480 °C (maximum recovery). At 480 °C, the mannose, xylose and glucose recovery was 50 %, 54 % and 41 % mass fraction, respectively. Interestingly at 360 °C the sugar yields was already 0.23 kg

kg⁻¹ pine d.a.f.. Pyrolysis reactions at 360 °C are relatively slow [47] and therefore the heating rate of the particle is of less importance. Moreover, the sugar yield at 580 °C was still 0.20 kg kg⁻¹ pine d.a.f. showing that the sugars are quite stable at higher temperatures, which is in agreement with the work of Hoekstra et al. [41].

Figure 4: Sugar yield, after acid hydrolysis of the oils, for untreated and acid leached pinewood versus the reactor temperature.

Figure 5: Sugar concentration in the pyrolysis oil, condensed at 20 °C, for acid leached pinewood versus the reactor temperature. Glucose concentrations in untreated oils were in the range of 5 % mass fraction.

Table 3: Recovery of the individual sugars at 360 °C and 480 °C from acid leached pine. The sugar recovery is defined as the amount of the individual sugar in the oil divided by the corresponding sugar in the feed.

Reactor temperature (°C)	Glucose recovery (kg kg ⁻¹)	Xylose recovery (kg kg ⁻¹)	Mannose recovery (kg kg ⁻¹)
360	0.31	0.43	0.44
480	0.41	0.54	0.50

3.4. Monomeric phenolics

A rough estimation of the total monomeric phenolics (containing a single phenyl ring) concentration was made based by using the average response factor (see analysis 2.3). Figure 6 shows the yield of total monomeric phenolics. It can be seen that the highest monomeric phenolics yield was obtained at low reactor temperatures, though the maximal yield was low (0.023 kg kg⁻¹ pine d.a.f, 0.08 kg kg⁻¹ lignin). A maximum in the monomeric phenolics yield between 400 °C and 450 °C was also observed by Perez et al. [22]. Concluding, it has been observed quantitatively that acid leaching is not a method that increases the yield of monomeric phenolics (shown qualitatively by Kleen and Gellersted [31]).

Figure 6: Monomeric phenolics yield from untreated and acid leached pinewood pyrolysis versus the reactor temperature.

3.5. Water insolubles

The water insoluble compounds are considered to be relatively large molecules (heavies) originating mainly from lignin decomposition and represents an important part of pyrolysis oil [49]. Figure 7 shows that the water insoluble yield increased up to 480 °C, likely due to the increased lignin conversion. At higher reactor temperatures a small decrease was obtained which indicates that vapor cracking reactions of the water insoluble compounds start to play a role as shown by Zhou et al.[50] and Westerhof et al. [24]. Moreover, it can be seen that after acid leaching a decrease in the water insoluble yield is obtained above 360 °C compared to untreated pine. We also found a decrease in the water insolubles yield after acid leaching for hay, straw and bagasse (at 530 °C) (Chapter 3). Piskorz et al.[51], Brown et al.[12] and Dalluge et al. [14] reported also a significant decrease in the water insoluble yield while only Mourant et al.[11] found a doubling of the yield after acid leaching. It should be noted that after acid leaching a higher 1st condenser oil yield is obtained, therefore the concentration of water insolubles in the 1st condenser oil is decreased.

Figure 7: Water insoluble yield for untreated and acid leached biomass versus the fluidized bed reactor temperature.

3.6. Molecular weight distribution

The mole weight distribution (MWD) of the oils was measured by GPC analysis. The compounds leaving the column were recorded by both a refractive index detector (RID) and a variable wavelength detector (VWD operated at the ultraviolet wavelength of 254 nm). It is assumed that the RID detects the majority of organic oil compounds, whereas the VWD (at 254 nm) mostly detects compounds containing π electrons (like double bounds). The presented GPC spectra were multiplied with the organic oil yield to express the spectra on pine-wood intake basis (d.a.f.), allowing direct quantitative comparison of the spectra. For better readability and to make the data easier to understand the 580 °C experiments have been excluded from the graphs since vapor cracking reactions occurred resulting in decreased molecular weight of the oil.

Figures 8A and 8B show the MWD of the pyrolysis oils from untreated (Figure 8A) and acid leached pinewood (Figure 8B) detected by the RID as function of the reactor temperature. Both figures show that with increasing reactor temperature the pyrolysis oil became heavier, which is in agreement with the results of Westerhof et al. [24]. When comparing the MWD (RID) from untreated pine (Figure 8A) and acid leached pinewood (Figure 8B) it can be observed that the additional organic oil is mainly obtained between 100 g mol⁻¹ and 200 g mol⁻¹, which is the location of monomeric anhydrosugars. The other parts of the MWD spectra are quite comparable.

Figures 9A and 9B show the MWD of compounds detected at 254 nm as function of the reactor temperature. Both figures show that at higher pyrolysis temperatures more heavy compounds (MW > 200 g mol⁻¹) were produced. No significant difference in the integrated area of the UV spectra (Figure 9A and Figure 9B) from untreated and acid leached pinewood was obtained as shown in Figure S1 (Appendix E). Therefore it can be concluded that the increased organic oil yield after acid leaching originates from the hemicellulose and cellulose. Assuming that the majority of UV absorbing compounds are aromatics, the constant area of the UV spectra of the different oils indicates that the yield of aromatics did not increased after acid leaching. Interestingly, the MWD measured by both the RID (Figure 8) and VWD (Figure 9) indicates that the yield of heavies is not influenced significantly by leaching while this could be expected based on the water insolubles yield (Figure 7).

Figure 8: MWD spectra (RID) of the oils obtained from untreated (A) and acid leached (B) pine wood pyrolyzed at various fluidized bed reactor temperatures. Measured signals were multiplied by the organic yield to express the spectra on pine wood d.a.f. intake basis (see Experimental).

Figure 9: GPC-VWD spectra of the oils obtained from untreated (A) and acid leached pinewood (B) pyrolyzed at various fluidized bed reactor temperature. Measured signals were multiplied by the organic yield to express the spectra on pinewood d.a.f. intake basis.

3.7. UV-Fluorescence Spectroscopy

Figures 10A and 10B shows the synchronous spectra, measured by UV-fluorescence spectroscopy, of the pyrolysis oils produced from untreated (Figure 10A) and acid leached pine-wood (Figure 10B) at reactor temperatures between 360 °C and 530 °C. The detected aromatic systems by UV-fluorescence spectroscopy can be furans (furfural max intensity at 240 nm) or phenolics with various substituents (phenol, guaiacol and tert-butylphenol all max intensity at 275 nm.). Larger systems can be made of two or more membered aromatic ring structures connected by an oxygen or a double bond, which both can participate in the conjugated system (e.g. furoin 300 nm, stilbene 320 nm), or by fused rings (e.g. naphthalene 290 nm to 310 nm, phenantrene 315 nm to 345 nm). In essence, the size of the conjugated system dictate the wavelength of excitation (the larger the aromatic ring system, the higher the wavelength). See supplementary information (Figure S2, Appendix E) for the spectra of the model compounds described above. In this paragraph we only study the conjugated systems detected above 250 nm which correspond to monomeric phenolics and oligomeric aromatic structures (made of multiple phenolic and/or furanic rings).

Figures 10A and 10B show both that above 430 °C the reactor temperature had not a large effect on the amount and size of aromatic structures. When comparing the spectra of untreated pine oil with the acid leached pine oil it can be seen that both spectra are quite comparable. The only difference is that acid leached pinewood gave a slightly higher response between 320 nm and 350 nm (3-4 ring systems). In essence, the majority of aromatic structures are oligomeric structures, which is in agreement with the GPC-VWD measurements (Figure 9A and Figure 9B). More research is necessary to study the structure of these oligomeric compounds.

With respect to the effect of leaching on the production of aromatics we conclude that: i) the total amount of monomeric aromatic is not affected by acid leaching, ii) the MWD of the aromatic fraction measured by GPC as well as the aromatic cluster size determined by UV-fluorescence shows also no effect of acid leaching while the water insolubles yield decreased significantly. This latter discrepancy needs to be studied in more detail. A strategy to obtain more insights in the lignin derived products would be to use dedicated combinations of analytical techniques, such as (2D-) Nuclear magnetic resonance [52, 53], UV-fluorescence [22, 36] and (fractional) gel permeation chromatography [36, 54]).

Figure 10A: UV-Fluorescence spectra of the oils produced from untreated pinewood at various reactor temperatures. Measured signals were multiplied by the organic yield to express the spectra on pinewood d.a.f. basis (see Experimental).

Figure 10B: UV-Fluorescence spectra of the oils produced from acid leached pinewood (B) at various reactor temperatures. Measured signals were multiplied by the organic yield to express the spectra on pinewood d.a.f. basis (see Experimental).

3.8. Bed agglomeration

Figure 11 shows the reactor content (biomass residue-sand mixture) obtained after pyrolysis of acid leached pinewood. The pyrolysis of pyrolytic acid leached pinewood led to the formation of bed agglomerates at reactor temperatures of 430 °C and higher. No agglomerates were formed during the pyrolysis of the untreated biomasses between 360 °C and 580 °C. Agglomerates were also obtained from the other acid leached biomasses (straw, hay and bagasse) pyrolyzed at 530 °C (Chapter 3). These agglomerates lead to operational problems (blocking and defluidization) in our 1 kg h⁻¹ continuous fluidized bed setup (not presented here). Interestingly, no agglomerates were observed at 360 °C for leached biomass. At 360 °C still high organic oil (0.65 kg kg⁻¹ pine d.a.f.) and sugar yields were obtained (0.23 kg kg⁻¹ pine d.a.f.) and this might therefore be an interesting operation temperature. Previous studies on the pyrolysis of mineral acid leached [20] or mineral acid infused [14] biomass also reported on the formation of agglomerates inside the fluidized bed. To reduce the problems caused by the char agglomeration Kim suggested the partial oxidative pyrolysis of infused biomass. Kim showed that adding small amount of oxygen to the fluidization gas reduced the char agglomeration and improved the sugar yield while hardly affecting the carbon to oil yield. Other methods to reduce the formation of char agglomerates include the impregnating calcium hydroxide [55] or using phyllosilicate clay [56] as bed material as demonstrated for the pyrolysis of lignin.

Radlein ascribed the agglomerates from acid leached biomasses to the formation of a melt, a mixture of high molecular weight polymer that decomposes very slowly, which coats the bed particles leading to agglomeration [20]. Figure 13 shows SEM images of the residues from untreated (left) and acid leached pinewood (right) pyrolyzed at 480 °C. The SEM images show a clear difference in the morphology between residue from untreated and acid leached pinewood. The residue from untreated pinewood clearly shows the original biomass fibrous structure. The residue obtained from acid leached pinewood pyrolysis shows besides the biomass structure also bubbles likely formed by liquid boiling. In summary, there are typically two types of residues: one type that has the same structure as the biomass from which it originate and a second which apparently has gone through a melt phase. Figure 12 shows SEM images of the sand particles after pyrolysis of acid leached pinewood at 430 °C (left) and 480 °C (right). It can be seen that the sand particles were coated by (solidified) melt. This melt acted as a glue between the sand and residue particles and formed the observed agglomerates.

Interestingly the pyrolysis of acid leached pinewood back impregnated with AAEMs did not lead to the formation of bed agglomerates (as shown in Figure 15) and operational problems. The microscopic picture show that a fraction of the residue particles still were glued to sand particles but to a much lesser extend compared to the acid leached pinewood (Figure 11). These figures show that the effect of pyrolytic acid leaching before pyrolysis on the char ag-

glomeration can be attributed to a large extent to the removal of the AAEMs. Other possible changes to the biomass structure occurring during the pyrolytic acid leaching seems to contribute less to the bed agglomeration.

As discussed earlier, pyrolysis at 360 °C (Figure 11) of untreated as well as acid leached pine-wood did not result in bed agglomeration and accordingly their SEM images don't show signs of melting (Figure 14). It should be noticed that at 360 °C already a large increase in the organic oil and sugar yield after acid leaching is obtained compared to untreated pine. This trend continues at increasing temperatures despite of melting biomass. This indicates that the melting does not influence the outcome of the pyrolysis process considerably and that the removal of the catalytic effects of the AAEM is a more important factor.

Figure 11: Macroscopic (top) and microscopic (bottom) images of bed material after pyrolysis of acid leached pinewood. Sand particles are between 212 µm and 300 µm.

Figure 12: SEM images of sand covered with solidified melt after pyrolysis of acid leached pinewood at 430 °C (left) and 480 °C (right).

Figure 13: SEM images of residues from untreated (left) and acid leached (right) pinewood pyrolyzed at 480 °C.

Figure 14: SEM images of residues from untreated (left) and acid leached (right) pinewood pyrolyzed at 360 °C.

Figure 15: Macroscopic (top left) and microscopic (top right and bottom) images of bed material after pyrolysis at 530 °C of acid leached pinewood back impregnated with AAEMs. Sand particles are between 212 µm and 300 µm.

4. Summary of the most important observations

Fast pyrolysis of pyrolytic acid leached pinewood (AAEM content 88 mg kg^{-1} dry pine) at fluidized bed temperatures between 360°C and 580°C was studied and compared to untreated pinewood (AAEM content 2616 mg kg^{-1} dry pine). At all reactor temperatures the pyrolysis of acid leached pinewood yielded more organic oil and less water and residue than untreated pine. For both untreated and acid leached biomass, the water yield was constant over the temperature range investigated. Already at 360°C acid leached pinewood produced a high organic oil yield (0.65 kg kg^{-1} pine d.a.f.) containing a high sugar content (41 % mass fraction). At this temperature the mannose, xylose and glucose recovery was 44 %, 43 % and 31 % mass fraction, respectively. The highest production of monomeric aromatics was obtained at low reactor temperatures (360°C and 430°C), although the yield was relatively low (max 0.02 kg kg^{-1} pine d.a.f.). Based on GC-MS, GPC-VWD and UV-fluorescence analysis of the oils evidence accumulated that acid leaching did not influence largely the yield and molecular size of the aromatic products. Back impregnation of AAEMs in acid leached biomass revealed that the effects of acid leaching, on the pyrolysis outcome, are mainly caused by the AAEM removal under our acid leaching conditions. Pyrolyzing acid leached pinewood at 360°C did not lead to bed agglomeration while this was the case at higher reactor temperatures. SEM images of the bed material showed that the residue from untreated pinewood retained the original biomass fibrous structure. Contrary, the residue from acid leached pinewood ($\geq 430^\circ\text{C}$) has (partially) gone through a melt phase. This melt acts as a glue between the sand/residue particles causing bed agglomeration.

5. Conclusions

Evidence is accumulating that AAEMs have a strong effect on the yields of organic oil and sugars and the melting behavior of biomass during pyrolysis. Acid leaching has turned out to be not a suitable method to improve the yield of monomeric phenolics. Using mild pyrolytic acids (produced within the pyrolysis process) as leaching agent does not seem to effect the outcome of the pyrolysis process, other than the effects induced by the removal of AAEMs. Overall it can be concluded that pyrolyzing acid leached feedstocks at low temperatures can help to overcome operational problems caused by melted biomass, while still producing high organic oil and sugar yields. Because the reactions at 360°C are relatively slow, the heating rate is of less importance and reactors like augers and rotating kilns can be considered.

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Appendix C

Improved anhydrosugar production by fast pyrolysis of pinewood and straw: H_2SO_4 infusion in pyrolytic acid leached biomass

Abstract

Already in 1982 Shafizadeh and Stevenson showed that the impregnation of a small amount of H_2SO_4 into mineral acid leached wood can help to improve the levoglucosan production for slow pyrolysis under vacuum [1]. In this appendix it was studied if this method can be applied to further improve the anhydrosugars production from the pyrolysis of pyrolytic acid leached pinewood and straw. In addition to have a good comparison in the pyrolysis outcome from biomass treated by the pyrolytic acid leaching method and the acid infusion method, experiments were performed under identical pyrolysis conditions. It was found that acid infusion into untreated biomass can significantly increase the organic oil and anhydrosugars yield, however the yields were lower than obtained after pyrolytic acid leaching. Adding H_2SO_4 to pyrolytic acid leached biomass shows potential to improve the anhydrosugars yield even further and justifies therefore more research.

1. Introduction

The presence of alkali and alkaline earth metals (AAEMs) during fast pyrolysis largely reduces the anhydrosugars yield. In this thesis a process is designed to remove these AAEMs before pyrolysis via acid leaching using the organics acids produced in the pyrolysis process itself. Shafizadeh and Stevenson showed already in 1982 that adding a small amount of sulfuric acid to mineral acid leached wood can help to further increase the levoglucosan production for slow pyrolysis under vacuum [1]. It is important to highlight that too high sulfuric acid concentrations reduced the levoglucosan yield by acid catalyzed dehydration reaction forming additional char. In 2013 Zhou et al. [2] confirmed the findings reported by Shafizadeh and Stevenson. This was done by adding sulfuric acid to mineral acid leached Douglas fir and poplar. The experiments by Zhou et al. were carried out in a PY-GC\MS so consequently no oil yield and only the area of individual compounds per gram of sample were reported. The levoglucosan yield increased by an additional 50% when 0.1 wt% H_2SO_4 was added to acid leached Douglas fir. It was speculated by Zhou et al. that “adding sulfuric acid could mitigate undesirable poorly understood interactions between cellulose and the other constituents in lignocellulosic materials responsible for reductions in levoglucosan production” [3].

In addition, there has recently been several studies published in which biomass is infused (also referred to as passivated, impregnated or titrated) with mineral acids as alternative to removing them via acid leaching [2, 4-8]. In the acid infusion experiments biomass is soaked in diluted H_2SO_4 or H_3PO_4 , subsequently the water is removed via evaporation. The infused sulfuric or phosphoric acid will (partly) react with the AAEMs to (bi)sulfates or phosphates. The AAEM salts will precipitate in the biomass during the subsequent water evaporation. As a result of this titration it is claimed that the anion of the original AAEM salts is replaced by a less active one (i.e. (bi)sulfates or phosphates). Active as in influencing the pyrolysis reactions. Dalluge et al. [4] stated that the formed salts are thermally stable without specifying what is actually meant. If thermal stability is related to the thermal decomposition of the salt at higher temperatures (e.g. to oxides) the argumentation is questionable since carbonate salts are also thermally stable under the pyrolysis conditions [9] but largely affect the pyrolysis outcome as shown in this thesis (comparable effects as the original AAEMs, shown in chapter 4). The intended benefit of acid infusion compared to leaching is that the aqueous waste stream from drying the biomass contains no dissolved minerals (ash + acids) and organics (organic acids + extractives). Kuzhiyil et al. [5] showed that the highest sugar yield was obtained when the amount of infused sulfuric acid on molar basis is comparable to the amount of AAEMs in the biomass (amount of acid equal to $\text{K}+\text{Na}+2\text{Ca}+2\text{Mg}-\text{Cl}$). Consequently, the AAEM content of the feed should be known on forehand and cannot fluctuate too much during operation of the process.

In this appendix it will be studied whether H_2SO_4 infusion into pyrolytic acid leached biomass can further improve the organic oil and anhydrosugars yield. Furthermore, to get an idea how the pyrolysis yields and pyrolysis oil composition from acid infused biomass compares to our pyrolytic acid leaching process, experiments using the same biomass feedstock under identical process conditions were performed.

2. Experimental

2.1. Materials

Pinewood (Lignocel 9, Rettenmaier & Söhne GmbH) and wheat straw (Purchased from Praxis. Brand: Puik, batch 2 in Chapter 3) were used as feedstock. The biomass samples were ground in a knife-mill and sieved to obtain a particle size fraction of 0.5 mm - 2 mm. All biomasses were dried for 24 h at 105 °C. A fraction of the biomass samples was leached with the synthetic acetic aqueous mixture (as described in chapter 4). Sulphuric acid (sigma Aldrich, ACS reagent, concentration >95 wt%) and milli-Q water were used to impregnate the untreated and acid leached biomass. In the fast pyrolysis experiments silica sand, sieve fraction (212 μm - 300 μm) with a particle density of 2600 kg m⁻³ and bulk density of 1600 kg m⁻³, was used as fluidized bed material.

2.2. Experimental and methods.

Acid leaching: The leaching method is identical to the one described in Chapter 4

H₂SO₄ impregnation: H₂SO₄ was impregnated into untreated and acid leached biomass. The amount of H₂SO₄ impregnated in untreated pinewood to passivate the AAEMs during pyrolysis was determined (0.006 gram of H₂SO₄ per gram of biomass) based on the correlation published by Kuzhiyil et al.[5]. The used concentration of H₂SO₄ in acid leached pinewood and straw was chosen based on the results of Zhou et al.[3] (0.001 gram of H₂SO₄ per gram of biomass). The H₂SO₄ was diluted in Milli-q water, the amount of water used was equal to 3.5 times the mass of the biomass to completely wet the biomass. Hereafter the biomass was dried in a rotary evaporator (60 °C and 100 mbar).

Fast pyrolysis: The biomass samples were pyrolyzed in a fluidized-bed fast pyrolysis reactor at a temperature of 530 °C, the setup and procedure is explained in Chapter 4.

2.3. Analytical techniques

The ash content of the biomass was determined by quantifying the residue remaining after 24 h of dry oxidation at 575 °C. The ash composition was determined with X-ray fluorescence (XRF) spectroscopy (Phillips PW 1480 spectrometer). The water content of the pyrolysis oil was measured by Karl Fischer titration (Metrohm 787 KF Titrino, titrant Hydranal Composite 5 and solvent 3/1 methanol dichloromethane). Titrations were performed in duplo, if the difference was larger than 0.5 wt% the titration was repeated until satisfying results were obtained. The hydrolysable sugars content of the oil was quantified using NREL LAP method “Determination of sugars, byproducts, and degradation products in liquid fraction process samples” [10]. The oil was first separated using the cold water extraction method [11] (1 gram of 1st condenser oil per 100 ml cold water) followed by hydrolysis (3.5 vol% H₂SO₄ for 60 minutes at 120 °C) of the water soluble fraction. The samples were hereafter neutralized by adding BaCO₃ and filtered (Whatman 0.2 µm filter) before HPLC analysis (Agilent 1200 series, column Hi-Plex-pb operated at 70 °C, eluent milli-Q water (0.6 ml min⁻¹)).

3. Results

To compare our pyrolytic acid leaching method with acid infusion and to study the potential of further increasing the anhydrosugar yield via acid impregnation, sulfuric acid was impregnated into untreated (infusion) and pyrolytic acid leached pinewood and straw (batch 2). The pyrolysis product yields are shown in Figure 1 and the hydrolysable sugar yields in Figure 2. Figure 1 shows that infusing sulfuric acid into untreated pinewood led to increased organic oil yields but the yield was lower than obtained by pyrolytic acid leaching. Moreover, Figure 2 shows that acid infusion in untreated pinewood increased the hydrolysable sugar yield significantly compared to untreated pinewood but was clearly lower than obtained from pyrolytic acid leached pinewood. Impregnation of sulfuric acid into the pyrolytic acid leached biomasses increased the char and water yield. Moreover, the impregnation of sulfuric acid into pyrolytic acid leached pinewood and straw slightly reduced the organic oil yield, but increased the hydrolysable sugar yield. The glucose yield was 0.12 kg kg^{-1} and 0.20 kg kg^{-1} for the acid impregnated in untreated and acid leached pinewood, respectively (0.17 kg kg^{-1} for acid leached pinewood). This corresponds to a glucose recovery, defined as the ratio between the amount of glucose in the oil after hydrolysis and the glucose initially in the biomass, of 23 wt% and 40 wt% for the acid impregnated in untreated and acid leached pinewood, respectively (28 wt% for acid leached pinewood). By adding 0.1 wt% of sulfuric acid to pyrolytic acid leached pinewood the sugar concentration in the 1st condenser oil increased from 33 wt% for pyrolytic acid leached pinewood to 50 wt%. For straw the glucose recovery increased from 31 to 37 wt% after acid impregnation in acid leached straw. This shows that the presence of a low concentration of sulfuric acid in the biomass (0.1 wt%) increases the anhydrosugars production without promoting excessive dehydration reactions. Another important finding is that the hemicellulose derived sugars; mannose and xylose follow the same trend. Further research is required to better understand the full potential of acid addition on increasing the sugar yield. A recent publication by Pecha et al. showed that impregnating acetic acid instead of sulfuric acid into acid leached biomass also resulted in a relative increase in the levoglucosan yield [12]. Using acetic acid instead of mineral acids has as advantage that: i) no sulfur or phosphor is added which will end up in the char, gas and/or oil; ii) acetic acid is expected to be less corrosive to the used equipment; and iii) acetic acid turned out to be not strong enough to catalyze dehydration reactions, therefore this method is less sensitive to the exact amount of acid added and to fluctuations in the AAEM content in the biomass [12]. Further research is suggested to investigate if a fraction of the pyrolytic acids, which in an excess is produced in case of low AAEM content feedstocks (see Chapter 5), concentrated in the 2nd condenser liquid can be used for this purpose.

Figure 1: Pyrolysis product yields for untreated, pyrolytic acid leached, acid infused and acid leached biomass infused with H₂SO₄. Gas yield by difference. Acid leached + H₂SO₄: 0.1 wt% H₂SO₄ on dry biomass basis. Untreated + H₂SO₄: 0.6 wt% H₂SO₄ on dry biomass basis, based on equation published by Kuzhiyil et al.[5]. Pyrolysis temperature 530 °C.

Figure 2: Sugar yields for untreated, pyrolytic acid leached, acid infused and acid leached biomass infused with H₂SO₄. Acid leached + H₂SO₄: 0.1 wt% H₂SO₄ on dry biomass basis. Untreated + H₂SO₄: 0.6 wt% H₂SO₄ on dry biomass basis, based on equation published by Kuzhiyil et al.[5].

4. Conclusion

In this appendix it was studied if H_2SO_4 impregnation of pyrolytic acid leached biomass can further improve the organic oil and anhydrosugars yield. In addition, to make a good comparison between the pyrolytic acid leaching method with the acid infusion method on the pyrolysis outcome experiments were performed under identical pyrolysis conditions. Acid impregnation increased the organic oil yield and sugar recovery but the yields are significant lower than obtain by pyrolytic acid leaching. Impregnating H_2SO_4 into pyrolytic acid leached biomass further increased the sugar recovery from both hemicellulose and cellulose. Recent research by Pecha et al. showed that impregnating acetic acid can also be used, without the disadvantages of mineral acids, to increase the anhydrosugar production. Tests with impregnated pyrolytic acids, concentrated in the 2nd condenser, into acid leached biomass are recommended to investigate the feasibility of this stream to further increase the anhydrosugars recovery.

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Chapter 5

Using pyrolytic acid leaching as a pretreatment step in a biomass fast pyrolysis plant: process design and economic evaluation

Abstract

Removing alkali and alkaline earth metals (AAEMs) from biomass, with pyrolytic acids, before pyrolysis leads to increased organic oil and sugar yields. These pyrolytic acids are produced and concentrated within the pyrolysis process itself. The purpose of this chapter was to evaluate under which conditions acid leaching of pinewood, bagasse and straw can improve the technical and economic feasibility of a pyrolysis process. Therefore, a preliminary process design for the implementation of acid leaching at a pyrolysis plant, with a biomass capacity of 5 and 50 ton hr⁻¹, was made and compared with a pyrolysis plant using the untreated biomass. Target products were heating oil, additional pyrolytic sugars and phenolics.

It has been calculated that when including the leaching step the heat for pyrolysis and drying of the biomass can still be supplied by the combustion of the char and gases, but insufficient excess heat is available to produce electricity for the process. Critical for the economics of the acid leaching pyrolysis process are the amount of extractives in the biomass (waste water) but not its moisture content. Mechanical dewatering before thermal drying turns out to be very important. The economics of this approach turned out to be very sensitive to the plant scale, CAPEX and obviously to the biomass price. Under the current market scenario and state of proven techniques the production of sugars and heating oil from bagasse at 50 ton h⁻¹ is the most economic option (IRR 14.4%).

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1. Introduction

Fast pyrolysis of lignocellulosic biomass is a promising conversion process to depolymerize the biomass building blocks, hemi-cellulose, cellulose and lignin, into a liquid termed bio or pyrolysis oil. This oil, a mixture of oxygenates and water, can be used directly for heat and power production or further refined to liquid fuels [1-3] and/or chemicals [4]. In this process dry biomass particles are quickly heated to temperatures around 450 °C - 550 °C in the absence of oxygen causing the biomass to decompose into gases, vapors (condensed to obtain oil) and char. The oil yield and composition varies largely between different biomass feedstocks [5]. These differences are mainly caused by the varying alkali and alkaline earth metal (AAEM) contents [6], which have been reported to catalyze dehydration reactions leading to increased water and char production [7, 8]. The increased water production often leads to phase separation of the oil, which complicates further processing [9]. Moreover potassium and sodium reduce the melting temperature of ash leading to problems in the char combustor [10-12]. Typical AAEM concentrations of “clean” debarked wood are around 5000 mg kg⁻¹ while herbaceous and agricultural waste streams, like straw, contain around 15000 mg kg⁻¹ [13]. In the authors opinion, the lower organic oil yield and phase separation of the obtained oil from many biomass residue streams high in AAEMs makes these biomasses not suitable as feedstock for conventional pyrolysis.

In Chapter 1 (section 4.3) we proposed and validated (Chapter 3) that the majority of AAEMs can be removed from biomass via leaching with organic acids, produced and concentrated within the same pyrolysis process. The different functional blocks required for the proposed process are shown in Figure 1. Size reduction of the biomass is required to achieve reasonable AAEM removing rates during acid leaching (discussed in section 3.2). After acid leaching and rinsing the biomass will contain around 75% of moisture, which has to be removed before pyrolysis. The drying is done by a combination of mechanical and thermal treatment. The pyrolytic acids are separated from the majority of the oil (including anhydrosugars and phenolics) by applying fractional condensation of the pyrolysis vapor using at least two condensers operated at different temperatures [15]. The char and gases are combusted to provide the heat required for pyrolysis and drying.

Pyrolytic acid leaching of different biomasses (pine, straw, hay and bagasse) reduced the AAEM content to 90 mg kg⁻¹ – 600 mg kg⁻¹ (Chapter 3). Pyrolysis of these acid leached biomasses resulted in a large increase of the organic oil yield compared to the untreated biomasses (e.g. straw 0.37 kg kg⁻¹ to 0.58 kg kg⁻¹) (Chapter 3). In addition, the selectivity towards anhydrosugars (also referred to as pyrolytic sugars) was largely increased resulting in a high anhydrosugar content in the oils (e.g. bagasse, mass fraction anhydrosugar in 1st condenser 10 % to 48 %) (Chapter 3). These high anhydrosugar concentrations might allow the eco-

conomic fractionation of the oil into higher economic value products. The anhydrosugars can be separated from the oil (including phenolics and furanics) by water extraction followed by ethyl acetate extraction (further discussed in section 3.7). The isolated sugars, obtained from acid leached pinewood, were successfully fermented, after hydrolysis, to bio-ethanol with comparable yields as obtained from glucose [16]. The residue after sugar separation is rich in phenolics. Tests at laboratory scale showed that this fraction can be used for the production of transportation fuel via hydro deoxygenation (lower H₂ consumption and higher C to oil compared to normal pyrolysis oil) [17, 18]. To further improve the economic value of the pyrolysis oil, extraction of phenolics is proposed. The extracted phenolics (mainly oligomeric) can be used as feedstock for phenolic resins production [19] or cracked into mono phenolics [20], which would generate the highest value. The product slate including the purification steps, which are often overlooked, can be seen in Figure 2.

Figure 1: Function block diagram for the pyrolysis of pyrolytic acid leached biomass.

Several studies have evaluated the economics of pyrolysis oil production using untreated biomass [42,88]. Generally it is found that the biomass price has a large on the pyrolysis oil price (~50% for wood) [42,88]. The biomass prices vary a lot for different biomass types e.g. bagasse (~35 US\$ ton⁻¹), empty fruit bunches (15-35 US\$ ton⁻¹), mallee wood (~40 US\$ ton⁻¹) straw (~80 US\$ ton⁻¹) and pinewood (~80 US\$ ton⁻¹). It is worthwhile to mention that cheap biomasses often contains a high ash content. Techno economic studies involving acid leaching as pretreatment step to increase the oil yield and to improve the processability of the oil from high AAEM feedstocks have not been published so far. The economic potential of producing sugars (or ethanol) via pyrolysis has only been studied for two specific cases. In 1999 So and Brown showed that sugars (for fermentation to ethanol) produced from pre-hydrolysis, hydrolyzing the hemicellulose, followed by fast pyrolysis of the solid (cellulose and lignin) had a comparable production cost compared to sugars from dilute sulfuric acid hydrolysis or prehydrolysis combined with enzymatic saccharification [21]. In a later paper Brown compared the aforementioned methods for the production of ethanol also with syngas fermentation. It was found that the syngas fermentation route was the most promising [22]. However, it should be noted that in this study only ethanol was taken as product while in the case of pyrolysis a large fraction of the pyrolysis oil remained unused. The second case, the pyrolysis of acid infused biomass (with H₂SO₄) producing D-glucose (via hydrolysis) and

transportation fuels (via hydrogenation using hydrogen produced from the light organics), was evaluated by Zhang et al. in 2013 [23]. An IRR of 11.4 % was calculated. It should be noted that the selected method for the production of expensive glucose (600 US\$ ton⁻¹) is rather optimistic, since the sugar stream after hydrolysis will contain next to glucose also sugars produced from the hemicellulose. In addition, the effectiveness of the described acid impregnation method, using sulfuric acid with a concentration of 50% on mass basis, can be questioned because of: i) the low amount of liquid (acid) could lead to an uneven acid distribution and therefore not stabilizing all of the AAEMs; and ii) the low pH is expected to lead to dehydration of the biomass.

The objective of this chapter is to identify under which conditions acid leaching can improve the technical and economic feasibility of a pyrolysis process. Therefore a process design of a pyrolysis plant with and without acid leaching processing 5 or 50 ton dry biomass per hour was made. The feedstocks studied were: i) pinewood, which has a low AAEM and moisture content and a high feedstock price; ii) straw, which has a high AAEM content, low moisture content and a high feedstock price; and iii) bagasse, which has a low AAEM content, high moisture content and a low feedstock price. Four different cases, as depicted in Figure 2, were studied to evaluate the feasibility of producing multiple product streams, these were: i) pyrolysis of untreated biomass to produce heating oil (HO_U); ii) pyrolysis of acid leached biomass to produce heating oil (HO_{AL}); iii) pyrolysis of acid leached biomass to produce sugars and heating oil (S&HO_{AL}); and iv) pyrolysis of acid leached biomass to produce sugars, phenolics and heating oil (S&P&HO_{AL}). The mass and energy balances for these cases were calculated in Aspen Plus®, using our experimental data as input. Based on the obtained results the key factors which influence the economic feasibility for the different cases were identified. Additional benefits and disadvantages (e.g. processability, process conditions) of the different cases are discussed in the final outlook.

Figure 2: Overview of the different cases studied.

2. Methodology

Based on the functional units shown in Figure 1 a process design for a pyrolysis plant with and without acid leaching was made. Possible process options for each of the functional units are discussed. As input for the acid leaching process design the removal rate of AAEMs from pinewood and straw was experimentally determined (see section 3.2). The mass and energy balances of untreated and acid leached biomass pyrolysis were calculated using the process flowsheet software Aspen Plus® (V8.6). The input for the pyrolysis process was based on our experimental results obtained from the studied biomass feedstocks [6]. The heat and material balances combined with data from literature for the power consumption of specific equipment, i.e. grinding, pressing and leaching, were used to calculate the operating costs (OPEX). The capital cost (CAPEX) for the pyrolysis plant was based on published data of two commercial plants and a design study. The CAPEX of the acid leaching equipment was obtained from a commercial vendor (De Smet) who has experience with similar technologies. The CAPEX for the sugar separation train was calculated using Aspen Economics®. Since the layout of the phenolics purification was unknown the CAPEX was estimated to be identical to the CAPEX of the sugar separation. Based on the CAPEX and OPEX the economic potential was evaluated based on a net present value (NPV) calculation in Microsoft Excel®. A sensitivity analysis was performed to study the effect of the various parameters, such as feedstock price and product yields, on the economic performance. The methodology in this chapter is summarized in Figure 3.

Figure 3: Overview of the individual process steps and required data.

3. Process design

In this section the possible process options for each of the functional units, as shown in Figure 1, are discussed. Acid leaching is discussed before grinding since the leaching experiments will provide the optimal biomass particle size and sets thereby the requirements for the grinding. The design of the pyrolysis of acid leached bagasse at a scale of 50 ton h⁻¹ is presented in this section (selected as base case), however the pinewood and straw are also discussed. It should be noted that the process design will largely depend on the plant location (integration with other facilities available). In this chapter a new standalone plant was assumed, which is likely a worst case scenario. The system boundaries are defined as: i) the plant gate (feedstock at location); ii) products, i.e. pyrolysis oil or separated oil fractions (sugars and phenolics); iii) electricity, process water and cooling water are available at the plant location; and iv) waste water can be treated externally conform market price.

Table 1: Feedstock composition before acid leaching, Compositional and ultimate analysis are expressed on dry ash free basis (d.a.f.).

	Pine Untreated	Straw* untreated	Bagasse Untreated
Compositional analysis, mass fraction in biomass d.a.f. (kg kg⁻¹)			
H ₂ O Extractive	0.03	0.06	0
glucose	0.51	0.49	0.44
xylose	0.05	0.25	0.20
galactose	0.02	0.00	0.00
arabinose	0.01	0.03	0.02
mannose	0.12	0.01	0.00
lignin	0.28	0.17	0.23
Ultimate analysis, mass percentage in biomass d.a.f. (%)			
C	50.1	48.5	49.3
H	6.1	6.2	6.1
N	0.1	0.4	0.2
O*	43.7	44.9	44.4
Ash composition, mass concentration in dry biomass (mg kg⁻¹)			
Na ⁺	60	117	24
K ⁺	398	12595	1792
Mg ²⁺	387	427	402
Ca ²⁺	1771	2068	700
sum (AAEMs)	2616	15207	2918
Total ash	5260	78151	13387

* Batch 2 in Chapter 3.

3.1. Biomass feedstocks.

Fast pyrolysis is generally considered to be capable of processing most dry biomasses. However the feedstock type and composition will have impacts on the process and economics. For example the feedstock composition will influence the obtained pyrolysis products and the design of the pre-treatment process, e.g. the grinder type, particle size, the leaching apparatus and amount of process water required. The feedstocks studied in this work were pinewood, straw and bagasse. These biomasses are delivered as debarked wood chips (moisture mass fraction 15 %), straw bales (moisture mass fraction 15 %) and wet bagasse fibers (moisture mass fraction 75 %). The composition of the feedstocks were determined in our previous study [6] and are shown in Table 1. It can be seen that straw contains the highest AAEM and extractive content.

3.2. Acid leaching

The biomasses studied in this chapter are vascular plants containing pores (tracheid's); through which the water and nutrients were transported within a plant. The AAEMs exist partly as salts (e.g. oxide, carbonate, oxalate and chloride) deposited in cells or pores after drying [24, 25]. The other part of the AAEMs is ionically bound to the lignin or hemicellulose via the empty electron pair of the oxygen atoms in carboxyl groups and hydroxyl groups [25]. Aqueous acid-base reactions, involved in the leaching of the AAEMs, proceed almost instantly [26], therefore it can be expected that the removal of AAEMs is rate limited by mass transfer within the biomass. Therefore, the particle size is an important parameter. Small particles will allow fast leaching, resulting in smaller leaching equipment, but requires large amounts of electrical energy for the grinding. To obtain insights in the removal rate of AAEMs from straw and pinewood with various particle sizes, leaching experiments were performed. To minimize the energy requirement combined with the use of an air closed system it was tested if sufficient AAEM removal rates could be obtained at 30 °C and atmospheric pressure. The experiments and results are presented in supplementary information S1.

Summarizing; the leaching experiments with diluted acetic acid (10 wt%, identical to the 2nd condenser oil) at 30 °C showed that the removal of AAEMs from ball milled particles (<125 µm, containing no fibrous structure) was almost instantaneous (<2 min) whereas the AAEM removal from cylindrical rods (diameter 27 mm with length of 5 mm, 10 mm or 40 mm) took hours or even days. From these results it can be concluded that the AAEM removal rate is determined by mass transfer in the biomass pores, rather than mass transfer in the cell wall. Leaching with demineralized water at 30 °C removed most of the potassium and sodium (75% to 90% relative to washing with dilute acetic acid) but could remove only 20% of the calcium and magnesium. Although the AAEM content of untreated wheat straw is significantly higher compared to untreated pinewood, the rate of AAEM removal via both water and acid

leaching was approximately the same. Based on the experimental results and a 1D diffusion model the particle size for straw and wood was selected to be 2 mm (sieve size) in order to obtain leaching times of 10 minutes per stage. For bagasse it was assumed that no size reduction is required for the acid leaching since the size and structure has been altered before (and possible during) the sugar extraction to obtain good sugar leaching results.

The AAEM removal equipment should at least consist of an acid leaching step and a rinsing step [14]. The rinsing step is required since biomass retains around 3 times its own dry mass in (leaching or rinsing) liquid, containing dissolved minerals, after draining. To reduce the required amount of process water the rinsing should be performed in counter current operation. Figure 4 shows a schematic overview of the leaching and rinsing process. In this process the 2nd condenser oil, containing acids (see Figure 2), is added in the first stage to directly dissolve all AAEMs, the later stages are used for the rinsing. For some high AAEM biomasses, the amount of acetic acid produced in the pyrolysis process may not be sufficient to dissolve both the mono and divalent AAEMs [6]. Therefore, a pre-water wash in order to dissolve the water soluble monovalent AAEMs before acid leaching is required.

In practice there are two options for contacting the biomass with the (leaching or rinsing) liquid, these are: i) moving the liquid through the “fixed” particles, which is termed percolation; and ii) the biomass particles are added to the liquid for a desired time and subsequently recovered. Possible process equipment to carry out the leaching of biomass include; bollman-type extractors, rotocel extractors belt percolator (e.g. sugar cane diffuser from De Smet), kennedy extractors and bonotto extractor [27]. A diffuser, as applied to extract sugar from sugar cane, was selected because of its simple design, low energy consumption, adaptable to variations in feed capacity and little amount of damage to the fibers (leading to fines). If larger particles are used the AAEM removal rate can be increased by using ultrasonic mixing [28], mechanical pressing of the biomass [29] or increasing the leaching temperature (resulting in a closed system due to increased volatility of the acids).

Figure 4: Schematic overview of countercurrent leaching and rinsing.

The process shown in Figure 4 can be mathematically described as countercurrent liquid-liquid extraction. The washing liquid remaining in the biomass pores, containing the dissolved AAEMs, is regarded as the feed to the next stage. The free rinsing water, outside the biomass, is regarded as the solvent. Since the solubility of the AAEM acetate salts is much higher than the concentrations obtained during leaching the formation of salts can be neglected. If equilibrium between the water inside and outside of the biomass is assumed (sufficient contact time) this system can be described by the following equations

$$\text{Stage 1:} \quad \varphi_{2 \rightarrow 1} * C_2 - (\varphi_{1 \rightarrow 2} + \varphi_{1 \rightarrow \text{waste}}) * C_1 = -\varphi_{\text{biomass, dry}} * C_{\text{biomass, dry}}$$

$$\text{For 2 till } n-1 \quad \varphi_{i-1 \rightarrow i} * C_{i-1} + \varphi_{i+1 \rightarrow i} * C_{i+1} - (\varphi_{i \rightarrow i-1} + \varphi_{i \rightarrow i+1}) * C_i = 0$$

$$\text{Stage } n: \quad \varphi_{n-1 \rightarrow n} * C_{n-1} - (\varphi_{n \rightarrow n-1} + \varphi_{n \rightarrow \text{dryer}}) * C_n = -\varphi_{\text{fresh water}} * C_{\text{fresh water}}$$

In these equations φ is the mass flow of water (remaining in the biomass pores or free rinsing water) or dry biomass and C is the concentration of AAEMs in water or dry biomass. The mass flow of water (remaining in the biomass pores) to the next stage ($i \rightarrow i+1$) is equal to 3 times the mass flow of biomass. Using this set of equation together with a mass balance of the water for each stage, the required amount of rinsing water as function of the number of equilibrium stages required to reduce the AAEM content to a specific concentration given an AAEM concentration of the rinsing water can be calculated. The equations were written as a matrix and solved in Matlab®. The composition of process water largely depend on the location [30]. In this study we assume that the process water available at the location has an AAEM content of 50 mg kg⁻¹. Figure 5a shows the amount of equilibrium stages required to reduce the AAEM content of pinewood and bagasse to 200 mg kg⁻¹ using rinsing water containing an AAEM concentration of 50 mg kg⁻¹ water. Figure 5B shows the results for straw which requires a pre-water wash, in which the potassium and sodium content is reduced by 80 % (90% for straw was possible see Figure S5), and the acid leaching step, in which the AAEM concentration is reduced to 200 mg kg⁻¹. These figures shows that the amount of water required for acid leaching flattened out after 4 to 5 stages. For the straw water wash the amount of water required becomes quite stable after 3 to 4 stages. Therefore the amount of equilibrium stages required for acid leaching will be set to 5 and 3 for the pre-water wash, respectively. Moreover it can be seen that around 4, 7.5 (sum of water wash and acid leaching) and 3 kg of rinsing water will be requires per kg of dry biomass for pine, straw and bagasse, respectively. Note, the amount of “fresh” rinsing water required can be reduced by using the water from the biomass drying.

Figure 5A: Amount of rinsing water required versus the number of stages to reduce the AAEM content to 200 mg kg^{-1} biomass (assuming sufficient acid is present in the 1st stage). In the model pinewood contains 15 wt% moisture and bagasse 75 wt% moisture.

Figure 5B: Amount of rinsing water required versus the number of stages to reduce the AAEM content to 200 mg kg^{-1} biomass (assuming sufficient acid is present in the 1st stage). In model straw to water wash contains 15 wt% moisture and the straw to acid leaching 75 wt% moisture.

3.3. Grinding

As mentioned in the previous section (3.2) a biomass particle size of 2 mm was selected to achieve residence times of 10 min per equilibrium stage (resulting in a total residence time of 50 minutes in the diffuser). It is worthwhile to mention that several pyrolysis reactor types like (bubbling/circulating) fluidized bed require small particles. The selected particle sizes are also suitable for these types of pyrolysis reactors so no further size reduction is required. Therefore, this particle size is also selected for the untreated pinewood and straw case. The received straw bales first need to be broken up where after the straw is milled down to the required particle size. Literature is not clear what device (hammer or knife mill) is most favorable in terms of low amount of fines and low energy consumption [31, 32]. For the wood chips a hammer mill (screen size 6 mm) will be used (based on [33] and [34]). It is worth mentioning that the grinding energy for pinewood (50 kWh ton^{-1}) is significantly higher compared to straw (15 kWh ton^{-1}). Depending on the impurities, e.g. stones or metal nails, in the received feedstocks a (metal) separator can be installed before the grinder to prevent damage of the equipment. For the bagasse no size reduction is required, however it is assumed that the cane has been depithed, thereby removing the fines and majority of AAEMs.

3.4. Dewatering and drying

The biomass leaving the leaching process will contain a moisture content of $\sim 75 \text{ wt\%}$. Removing this amount of water via evaporation will consume a large fraction of the energy present in the biomass (only heat of evaporation per kg wet bagasse is 1.8 MJ kg^{-1} vs the HHV of dry bagasse 4.8 MJ kg^{-1}). Therefore mechanical dewatering, as applied industrial after the sugar cane diffuser, will be applied as a first step to remove the majority of water. The mechanical drying of bagasse is widely applied. Typical moisture contents $\sim 46 \text{ wt\%}$ after pressing are reported [35, 36]. Unfortunately, for straw and wood fibers (saw dust) less information is available. Nevertheless, comparable results are expected. Typical equipment used to mechanically dewater biomass include centrifuges, belt presses, screw presses and roller press [27].

Westerhof et al showed that an moisture content up to $20 \text{ wt\%}$ had no significant effect on the organic oil yield during fast pyrolysis in a fluidized bed [37]. Reducing (or completely removing) the moisture before pyrolysis will: i) reduce the required temperature of the used energy carrier since the reactor is operated at a higher temperature then the dryer; ii) reduce the volumetric vapor flow from the reactor, thereby decreasing the size of cyclones and condensers; and iii) increases the organics content of the 2nd condenser oil, which is beneficial for the acid concentration and its heating value (see section 3.8). Therefore it was decided to dry the biomass completely before pyrolysis.

The thermal energy required for drying can be supplied via hot gas (e.g. flue gas) or steam [38]. Because of: i) the low self-ignition temperature of dry biomass (fines), ii) the high moisture content of the feed (requiring large amounts of heat), and iii) possibility to utilize the condensation heat at higher temperatures a super-heated steam dryer has been selected. To reduce the energy requirement of the compressor in the steam cycle and the size of equipment (i.e. steam pipes in combustor and the dryer) the dryer will be operated at 3 bara and 140 °C. Note that higher pressures will increase the drying temperature. See Figure 6 for a schematic representation of the pretreatment section for 50 ton h⁻¹ bagasse. For the “dry” feedstocks (untreated pine and straw, containing 15 wt% moisture) significant less energy is required for drying. As a result, it is less important to recover the evaporation energy. Moreover the mass and energy balance showed that the flue gas from the combustor (after heating the recycle gas fed to the pyrolysis reactor) still contains enough energy to dry the biomasses (this is not the case for the wet and acid leached feedstocks). Therefore for untreated pine and untreated straw is was chosen to use flue gas drying instead of steam.

Figure 6: schematic overview of leaching and drying bagasse at 50 ton h⁻¹. Stream sizes and temperatures are based on mass and energy balance (discussed in section 4).

3.5. Fast pyrolysis and char combustor

Several pyrolysis reactor configurations have been studied and implemented in industry. These configurations include; bubbling fluidized bed (Dynamotive), circulating fluidized bed (Ensyn and Fortrum), rotating cone reactor (BTG), cyclone reactor (Latvian State Institute of Wood chemistry) and auger reactor (Lurgi together with Karlsruhe and Abritech) [39, 40]. The energy required for pyrolysis (heating the biomass, reaction enthalpy and heat loss of the reactor) per kg of dry biomass is estimated to be in the range of 1.2 to 2.5 MJ kg⁻¹ [41-43]. Based on typical yields and composition of the char and gases from untreated biomasses it

can be calculated that burning the char provides on biomass d.a.f. ($0.15 \text{ kg kg}^{-1} * 32 \text{ MJ kg}^{-1}$) $\sim 4.8 \text{ MJ kg}^{-1}$ and burning the produced gases produces on biomass d.a.f. ($0.3 \text{ kg kg}^{-1} * 8 \text{ MJ kg}^{-1}$) $\sim 2.4 \text{ MJ kg}^{-1}$. It should be noticed that after acid leaching the char yield largely decreases and becomes between 0.054 kg kg^{-1} and 0.086 kg kg^{-1} (see Table 2) [6], which corresponds to $1.8 \text{ MJ kg}^{-1} - 2.8 \text{ MJ kg}^{-1}$. Moreover in case of acid leaching a significant amount of heat is required to dry the wet biomass after leaching. Based on these numbers it can be concluded that for the pyrolysis of untreated biomass the produced gases and char contain significant more energy than the heat required for the pyrolysis process. Therefore the excess heat is often converted into electricity, which is partially used to provide the electricity consumption of the pyrolysis plant.

The heat to the reactor can be supplied via: i) a solid heat carrier (e.g. sand or steel beads), ii) hot gas, iii) superheated steam, iv) via the reactor wall, v) intermittent reactor concept (operation switching between pyrolysis and combustion mode) [44], or vi) via heating (fired) tubes. Pyrolysis reactions occur very fast (seconds) at high temperature ($> 500 \text{ }^{\circ}\text{C}$) [45] and are therefore often limited by the heat supply. Supplying the heat via heat (fired) tubes or the reactor wall will require a large heat exchange area. Therefore reactors heated via the wall will be limited in size. Pernikes et al. reported superheated steam to biomass ratios between 2 kg kg^{-1} and 7 kg kg^{-1} [46]. It can be calculated that the energy required for producing this amount of superheated steam is larger than the amount of energy in the produced char and gases. Supplying the process heat via recycling (fluidization) gases will result in large gas streams (heating recycle gas from $30 \text{ }^{\circ}\text{C}$ to $530 \text{ }^{\circ}\text{C}$ will cost $\sim 0.5 \text{ MJ kg}^{-1}$) and requires quite high gas temperatures. Moreover feeding steam or large gas streams to the reactor will result in larger cyclones and condensation equipment. The intermittent pyrolysis reactor concept as proposed by Siemons and Baaijens might be an interesting method [44], however this concept is still in its early stages. Therefore the use of a heat carrier was selected in this study.

The goal of this study was to evaluate under which conditions acid leaching can improve the technical and economic feasibility of the pyrolysis process. So far none of the pyrolysis reactor concepts is outperforming the others, so in this study we don't want to select a specific design (other than heating via a solid heat carrier). In this light, the input for the Aspen Plus® simulation was based on the results, summarized in Table 2, obtained from the studied biomass feedstocks in our fluidized bed setup. Therefore, the process conditions (pyrolysis temperature $530 \text{ }^{\circ}\text{C}$) were chosen identical to the experimental conditions used in [6]. We want to emphasize that these are not necessarily the optimal pyrolysis conditions. In the reactor the biomass is converted into a mixture of vapors, gases and char. A series of cyclones separates the particles from the gases and vapors. Part of the pyrolysis gases are recycled back to the pyrolysis reactor for fluidization or removing the pyrolysis vapors from the hot reactor (recycle gas flow on biomass d.a.f. 1 kg kg^{-1} , based on our setup). The char and surplus of pyrolysis gases are burned in the combustor to provide the heat for the circulating heat car-

rier. The combustor is operated at 580 °C, thus 50 °C above the reactor temperature. Steam is produced from the excess heat of the combustor and used for biomass drying and electricity production (in case of untreated pine and straw). Air is fed at an air to fuel ratio (λ) of 1.3 [ref]. See Figure 7 for a schematic representation of the combustor and pyrolysis reactor.

Table 2: Pyrolysis products in kg kg⁻¹ biomass d.a.f. from untreated and acid leached biomasses. Data based on the experiments reported in Chapter 3.

Compound	Pine		straw		bagasse	
	Untreated	acid leached	untreated	acid leached	untreated	acid leached
Produced water	0.117	0.085	0.113	0.077	0.104	0.044
Char	0.100	0.086	0.136	0.072	0.080	0.054
CO	0.140	0.130	0.149	0.132	0.162	0.120
CO ₂	0.116	0.088	0.200	0.070	0.247	0.125
CH ₄	0.020	0.020	0.020	0.015	0.038	0.020
C ₂₊	0.010	0.010	0.010	0.010	0.010	0.010
Levogluconan	0.044	0.155	0.007	0.157	0.020	0.200
Mannosan	0.012	0.030	0	0.001	0.002	0
Xylosan	0	0.010	0.002	0.030	0	0.043
Furanics	0.020	0.020	0.020	0.020	0.020	0.020
monomeric phenols	0.020	0.020	0.020	0.020	0.020	0.020
Water soluble phenolics	0.038	0.058	0.043	0.078	0.047	0.100
Water insoluble	0.122	0.102	0.054	0.043	0.093	0.041
Unknown cond 1	0.102	0.074	0.064	0.106	0.032	0.095
acetic acid	0.025	0.018	0.018	0.019	0.025	0.018
formic acid	0.010	0.010	0.010	0.010	0.010	0.010
Lights	0.104	0.084	0.134	0.140	0.090	0.080

3.6. Oil collection

Fractional condensation of the pyrolysis vapors is used as an inexpensive first downstream separation technique to separate the acids, required for acid leaching, from the sugars and phenolics (products). Pyrolysis oil collection systems described in the literature usually consist of a combination of several: i) spray condensers [37], ii) electrostatic precipitators (ESP) [47], or iii) (shell and tube) heat exchangers [48, 49]. Inside a condenser the vapor stream is quenched, causing the vapors to condense and thus forming aerosols. Spray condensers [37] and ESPs [47] have proven to be very efficient in collecting these aerosols. Therefore, the vapors and gases leaving the condenser are at vapor-liquid equilibrium, allowing controlled fractionation, as demonstrated by Westerhof et al. [37]. Based on the simplicity and better heat transfer of the spray condensers this type has been selected. A two stage condensation

system was selected in this study. Although, more condenser in series (high temperature condenser to collect the water insolubles) might be an option to improve the fractionation of the oil even further (as discussed in 3.7). The temperature of the condensers is controlled by the recirculated bio-oil. In the 1st condenser the temperature of the recirculated oil is controlled via indirect cooling (possibility to recover heat at temperatures below condenser temperature) while the oil in the 2nd condenser is cooled indirect with cooling water. The recovery of heat from the pyrolysis vapors, before entering the condensers, is not included due to the expected fouling caused by condensation inside the heat exchangers.

Figure 7: schematic overview of the pyrolysis, combustion and oil recovery section for the pyrolysis of acid leached bagasse. Stream sizes and temperatures based on mass and energy balance from Aspen Plus® (discussed in section 4)

3.7. Sugar and aromatic separation

The 1st condenser oil, rich in sugars and phenolic compounds, needs to be purified when applied as feedstock for fermentation (sugars) and monomeric phenolic or phenolic resins (phenolic fraction) production. Pyrolysis oil separates into an aqueous phase, containing oxygenates including the anhydrosugars, and a tarry organic phase, containing mainly phenolic oligomers [50, 51], when the water content reaches 30 %- 35 % on mass basis [52]. This principle is often applied as a first step in the separation of pyrolysis oil to remove the “sticky”

water insolubles [16-18, 20, 53, 54]. Rover et al. studied the phase separation of fractional condensed pyrolysis oil produced from acid infused red oak to recover a sugar-rich solution (for fermentation) and a phenolic oligomers stream [54]. It was shown that the sugars can be extracted effectively (> 93 % mass basis) by two water extractions using an oil to water ratio of 1:1 (mass basis). However, fermentation inhibitors, such as 5-hydroxymethylfurfural, guaiacol and phenol, were also extracted leading to suppressed growth of the used *E.coli* (biocatalyst for ethanol). Removal of the inhibitors was performed by overliming (with NaOH, Ca(OH)_2 and NH_4OH), however the concentration of the sugars in the fermentation broth was still limited to maximal 2 % mass fraction [54]. Moreover overliming leads to the formation of a solid waste stream which needs to be deposited. Other options to remove these inhibitors (mainly aromatics) is extraction with ethyl acetate. Luge et al. showed that the aqueous phase after ethyl acetate extraction and hydrolysis could be successfully fermented to ethanol [16]. However this method has several drawbacks including: i) the solubility of ethyl acetate in water is around 81 g dm^{-3} [55] requiring the recovery of ethyl acetate from the aqueous stream; ii) ethyl acetate and water form an azeotrope, however the recycled ethyl acetate is re-used for the extraction of the aqueous phase from the water separation therefore this azeotrope does not cause any practical problems; and iii) ethyl acetate is more volatile than the extracted aromatics which requires the evaporation of the solvent [55]. Another options for oil separation is by crystallization of the sugars in cold acetone as applied at the pyrolysis plant located at the Krasnodar hydrolysis plant (USSR) operated between 1958 and 1970 [56]. Unfortunately this method is quite sensitive to the pyrolysis oil composition; high water contents (< 10 % mass fraction [46]) and the presence of water insoluble compounds [46] results in poor separation results. Therefore, this method was only applied for the pyrolysis of hydrolyzed lignocellulose at mild temperature (< 420 °C using steam as heat carrier) combined with fractional condensation of the vapors (T 1st condenser < 100 °C [56]).

Because of the good fermentation results (at a high concentration) after ethyl acetate extraction combined with the presence of water insolubles in our oil the separation of sugars from the 1st condenser oil will be calculated based on the ethyl acetate extraction process, even though it is far from ideal. Figure 8 shows a schematic representation of the separation train for the 1st condenser oil from acid leached bagasse. In the process the 1st condenser oil is first extracted with water (water to feed ratio 1:1) in a countercurrent extractor with 3 stages. The aqueous stream is hereafter extracted with ethyl acetate (amount of ethyl acetate per aqueous phase 0.2 kg kg^{-1}) in a countercurrent extractor with 4 stages. The ethyl acetate extract is separated in a distillation column (6 stages). The ethyl acetate dissolved in the aqueous stream is recovered in a 2nd distillation column (8 stages). Note that the oil composition between the different acid leaching cases varies (e.g. water insoluble yield for bagasse 2 ton h^{-1} versus pinewood 5 ton h^{-1}). The stream sizes were estimated based on: i) our experimental experience for the phase separation of the 1st condenser oil; ii) the liquid-liquid equilibrium data determined by Li et al.[55] for the model mixture of ethyl-acetate, water, levoglucosan

and guaiacol [55]; and, Aspen Plus® simulation using the data Li et al.[55] for the CAPEX and OPEX of the distillation columns.

The aromatic fraction from the aforementioned separation (water insolubles together with ethyl acetate extract) still contains non phenolic compounds (furanics and lumped unknown compounds). So far no research has been performed to further purify/extract the phenolic compounds from this fraction. Therefore in the S&HO&P_{AL} cases this separation will be treated as a hypothetical separation. The CAPEX and OPEX are assumed to be identical to that of the sugar extraction from the 1st condenser oil. The remaining organics will be used as heating oil.

Figure 8: Schematic overview of the oil separation train used to purify the sugars in the 1st condenser oil from the pyrolysis of acid leached bagasse at 50 ton h⁻¹.

3.8. Waste water

The waste water from the leaching process (see Figure 4) will contain: i) dissolved light oxygenates (from the 2nd condenser liquid), ii) organic extractives (from the biomass), and iii) minerals (from the biomass). This stream needs to be treated before being discharged or reused. Several options to treat the dissolved organics have been studied, these include: i) aerobic bacterial treatment (rather costly), ii) reverse osmosis [57, 58], iii) anaerobic digestion to methane [59, 60], iv) fermentation to lipids [61], v), and v) microbial electrolysis to hydrogen [62]. Unfortunately, the aforementioned techniques are still in initial research scale except for aerobic bacterial treatment. Therefore, the costs (US\$ 330 per ton of organic material) for removing the organics via aerobic treatment (worst case) was used in the economic evaluation, however the potential of the other techniques will be discussed. To reduce the amount of organics in the waste water stream from the biomass leaching a fraction (depending on the required amount of acid required for leaching) of the 2nd condenser oil is fed to the combustor (see Figure 7). The dissolved minerals, mainly potassium and calcium, in the process water can be recovered via reverse osmosis combined with evaporation of the brine. However, since the sodium adsorption ratio of the leaching liquid is rather low the most favorable application would be to use it as irrigation water, to compensate for the nutrients taken from the soil to prevent soil depletion. The use as irrigation water, after organic treatment, is selected for the base case. Note that the sludge from the aerobic treatment will contain a fraction of the dissolved minerals.

4. Process evaluation: mass and energy balances

Based on the technologies discussed in the previous section, flowsheets for pyrolyzing untreated and acid leached bagasse were made. The flowsheet for the pyrolysis of acid leached bagasse is visualized in Figure 6 and Figure 7. The flowsheets for acid leached pinewood and straw have an almost identical layout; a grinder is required before leaching and the exact mass flows and temperatures of the streams differ slightly. The flowsheets for the pyrolysis of untreated pinewood and straw are shown in Figure S8 and Figure S9, and for untreated bagasse in Figure S10 and Figure S11. These flowsheets were translated into several Aspen Plus® models to calculate the mass, carbon and energy balances. The model input for the pyrolysis process was based on the pyrolysis yields, summarized in Table 2, obtained from the studied biomasses pyrolyzed in our fluidized bed reactor at 530 °C [6]. Other input to the model and assumptions are explained in section S10.3 (Appendix F). The solubility of AAEMs, as function of the amount of acetic acid added, and the product distribution over both condensers, as function of the condenser temperature, both calculated with Aspen Plus® were compared to experimental results to validate the used models (results presented in Appendix F section S10.4.4). The agreement was satisfactory.

4.1. Overall mass, carbon and energy balances

Table 3 summarizes the mass and energy balances for the HO_U and HO_{AL} cases for the different feedstocks. The mass conversion to oil only increased for bagasse after acid leaching. However the carbon and energy efficiency to oil also increased for straw after acid leaching. The decreased oil and carbon yield for pine can be explained by the rather small amount of additional oil after acid leaching (due to the low AAEM content in untreated) combined with the loss of the 2nd condenser oil. For all biomasses a large increase in the mass and carbon efficiency from biomass to sugar was obtained after acid leaching. As expected the outcome for the different feedstocks were quite comparable after acid leaching. The amount electricity added per amount of thermal energy in the biomass varied between 0.01 and 0.03 MJ_e MJ⁻¹. The differences in the amount of electricity required can be attributed to: i) the additional power consumption of the diffuser and press for acid leaching, and ii) the grinding of pinewood requires more power than straw. Based on the Aspen Plus® simulation it was quantified that for all biomass feeds the heat for both pyrolysis and biomass drying can be supplied by combustion of the char and gases. In case of the pyrolysis of untreated pine and straw large amount of excess heat are available which are converted to produce electricity (more than required by the process). All relevant mass and energy flows for the other cases are summarized in Tables S6 to S11 in supplementary information.

Table 3: Evaluation of mass and energy balances for the pyrolysis of untreated and acid leached feedstocks (HO_U and HO_{AL} cases). Yields on biomass dry ash free (d.a.f).

	Pine Untreated	Pine Acid Leached	Straw Untreated	Straw Acid Leached	Bagasse untreated	Bagasse Acid Leached
Mass to oil* ($kg\ kg^{-1}$)	0.61	0.48	0.44	0.44	0.46	0.54
C to oil* ($kg\ kg^{-1}$)	0.54	0.55	0.32	0.48	0.37	0.56
Energy to oil* ($kg\ kg^{-1}$)	0.54	0.52	0.33	0.51	0.40	0.57
Mass to sugar ($kg\ kg^{-1}$)	0.06	0.19	0.01	0.16	0.02	0.24
C to sugar ($kg\ kg^{-1}$)	0.05	0.17	0.01	0.15	0.02	0.22
Electricity added per energy in feed ($MJ_e\ MJ^{-1}$)	0.02	0.03	0.01	0.02	0.02	0.02

* oil in case of untreated is the whole oil and in case of acid leached only 1st condenser fraction.

4.2. Detailed mass, carbon and energy balance for the pyrolysis of acid leached bagasse

Figure 9 shows the mass flows for the pyrolysis of acid leached bagasse at a feed capacity of 50 ton h^{-1} dry mass. Note, the superheated steam stream from the combustor to the dryer and vice versa (red dotted arrow) is not displayed at the correct scale for better readability. It can be seen that the majority of the initial dry biomass leaves the process as 1st condenser oil (54 wt%) or flue gas (41 wt%). Only a small amount of the organic biomass leaves the process via the waste water stream. Because of the superheated steam drying, the moisture remaining after the dewatering press (44 ton h^{-1}) is converted into low pressure steam (140°C at 3bar). This steam can be (partly) used for: i) the distillation columns to separate the sugars from the 1st condenser oil, ii) to evaporate the brine obtained after reverse osmosis of the waste water if the inorganic containing water cannot be discharged, or iii) to crystallize sugar when the process is located at a sugar cane mill.

Figure 9: Mass balance for the pyrolysis of acid leached bagasse at 50 ton h^{-1} scale. Steam stream from combustor to dryer and back is not represented at correct scale for better readability.

Figure 10 shows the carbon mass balance (the recycle gas stream to the reactor was excluded for better readability). Bagasse consist for approximately 50% mass basis of carbon (Table 1). It can be seen that 56% (untreated bagasse 37%) of the carbon entering the process is recovered as product in the 1st condenser. The carbon balance shows that the majority of the unrecovered carbon is lost to the gas (20%) and char stream 10%). The char and gases are burned in the combustor to provide the heat for the pyrolysis reactor and biomass drying.

Figure 10: Carbon mass balance for the pyrolysis of acid leached bagasse at 50 ton h⁻¹ scale. The gas recycle to the reactor is excluded for better readability (this doesn't change the outcome). Note, elemental composition based on experimental determined product composition (see Table S5).

Figure 11 shows the energy flows for the pyrolysis of acid leached bagasse. The energy content of the organic streams was calculated using the Milne equation to obtain the higher heating values (HHV) of the streams. From this figure it can be seen that a part of the energy is lost during the condensation of the vapors (1st condenser 8% and 2nd condenser 1%), which can be recovered at the respective temperature of the condenser (90 °C and 25 °C). Moreover, the steam produced contains 12% of the energy in the feed. In the end 57% (untreated bagasse 40%) of the energy in the feed is recovered in the 1st condenser oil (product). Based on Figure 11 it can be concluded that the overall energy recovery (57%) in the final product for the pyrolysis of acid leached biomass cannot be increased much further without using an external heat sources (from wood, coal natural gas or fraction of produced oil). The simulation proved, as expected, that for the pyrolysis of untreated biomasses a larger fraction of the energy is recovered in the char and gases, which can be used for steam or electricity production. The total power requirement for the plant, including grinding, acid leaching pressing etc., is estimate at 5.8 MW (bagasse 50 ton h⁻¹ HO_{AL}), which in case of dry (15% moisture) untreated biomass can be produced from the excess heat produced in the combustor.

Figure 11: Energy flows for the pyrolysis of acid leached bagasse at 50 ton h⁻¹ scale . Energy content of the organic streams was based on HHV. Steam stream from combustor to dryer represents only the heat added to drying process.

4.3. Flows and composition of the waste water streams

The sizes and composition of the waste water streams for the different biomasses are summarized in Table 4. The amount of waste water per kg of dry biomass was 1.8, 5.9 and 3.7 kg kg⁻¹ for pinewood, straw and bagasse respectively. The large water stream for straw was caused by the mandatory separation of the two waste stream (see Figure 4), to prevent precipitation of the calcium in the prewash. The difference in the waste water stream flow between pinewood and bagasse was caused by the large amount of water in the bagasse feed, which is fed at the first stage. The differences in stream composition were mainly caused by both the higher extractive and AAEM content in straw. As a result more 2nd condenser oil is required for the acid leaching. The estimated Chemical oxygen demand (COD) of the waste water streams varied between 13 g kg⁻¹ and 70 g kg⁻¹. The biological oxygen demand (BOD), which can only be experimentally determined but often estimated as 70% of COD [63], is a good indicator for the potential to produce methane from water rich waste streams via anaerobic digestion. At BOD concentrations over 1 g kg⁻¹ anaerobic digestion before aerobic bacterial treatment is usually economic attractive [63]. It can be seen that all waste water streams have a higher COD. Therefore, it is expected that implementing anaerobic digestion before the aerobic bacterial treatment can reduce the costs associated with the waste water treatment (not done in this study). A good indication of the required waste water treatment layout and associate costs can be obtained from the design studies by Merrick & Company [63] and Brown & Caldwell [64], prepared for the biomass to ethanol process studied by NREL [65]. It should be noticed that the water streams from the ethanol process contains high ammonia concentrations which is not the case for waste water streams from the pyrolysis process.

Table 4: Amount and composition of the waste water streams for pyrolysis of acid leached biomass at a feedstock capacity of 50 ton h⁻¹.

	Pinewood	Straw	Bagasse
Waste water from prewash (ton h ⁻¹)	-	107	-
Organic content (% mass fraction)	-	2.4	-
Estimated COD (g kg ⁻¹)	-	40.5	-
Inorganic content (% mass fraction)	-	0.8	-
Waste water from acid leaching (ton h ⁻¹)	91	187	183
Organic content (% mass fraction)	2.5	2.7	0.4
Estimated COD (g kg ⁻¹)	58	70	13
Inorganic content (% mass fraction)	0.5	0.4	0.2

5. Economic assessment.

In this section the economic feasibility of the processes, as designed in the previous sections, is evaluated. The economic potential was evaluated using a net present value (NPV) calculation based on the CAPEX and OPEX.

5.1. CAPEX and OPEX

The capital cost (CAPEX) for the pyrolysis plant (including storage grinding pyrolysis and combustion) was based on published data for various pyrolysis systems. This data is summarized in Table S12 (Appendix F). Interestingly, the capital cost for the different reactor types, i.e. rotating cone, circulating fluidized bed and auger, did not differ much. An estimate of the CAPEX of the diffuser (for acid leaching) was supplied by De Smet, this data can be found in Table S13. The CAPEX for the separation train required to extract the sugars from the 1st condenser oil was estimated using Aspen Economics® (see Table S14). For the hypothetical purification of the aromatic fraction an identical CAPEX as the other separation train was assumed. Table 5 summarizes the total CAPEX for the different cases. Based on these numbers it can be calculated that implementing acid leaching at a new pyrolysis plant will increase the total CAPEX by 36% (HO_{AL}) 41% (S&HO_{AL}) and 47% (S&P&HO_{AL}).

Table 5: CAPEX for the different cases at 50 ton h⁻¹ feedstock capacity

Cases	Total CAPEX (million US\$)
HO _U	121
HO _{AL}	162
S&HO _{AL}	171
S&P&HO _{AL}	178

Tables 6 and 7 show the cost of materials and utilities and the prices for the different products respectively. Producing sugars for fermentation will increase the economic value of this oil fraction since sugar has a HHV of 17.5 MJ kg⁻¹, which corresponds to 210 US\$ ton⁻¹ (at 12 US\$ Gj⁻¹). The HHV of the phenolics (based on the elemental composition of the water insolubles) is around 28 MJ kg⁻¹, which corresponds to 330 US\$ ton⁻¹. The price for the phenolic fraction was estimated since no large batches of this fraction have been made and therefore no industrial applications currently exist.

Table 6: Material and utilities costs used in the economic evaluation.

Materials and utilities	Price	Source
Pinewood chips	80 US\$ ton ⁻¹	[66]
Straw bales	80 US\$ ton ⁻¹	
Bagasse	35 US\$ ton ⁻¹	[67]
Electricity	0.06 US\$ KWh ⁻¹	[68]
Process water	0.2 US\$ m ⁻³	[68]
Water treatment	330 US\$ per ton ⁻¹ (on organic basis)	[68]
Solid disposal (landfill)	170 US\$ ton ⁻¹ (on dry material basis)	[68]

Table 7: Product prices used in the economic evaluation.

Products	Price	Source
Heating oil	12 US\$ Gj ⁻¹ (on HHV basis)	Average (5 year) fuel oil #5
Sugars for fermentation	350 US\$ ton ⁻¹ (dry basis)	Based on sugar #11
Phenolics	400 US\$ ton ⁻¹ (dry basis)	Own estimate
Steam	6.6 US\$ ton ⁻¹	[68]

5.2. Economic feasibility of different cases and feedstocks

The annual operating costs and earnings for the different cases at 50 ton h⁻¹ are shown in Figure 12. From this figure it can be seen that:

- None of the cases using pinewood or straw as feedstock a profit is made while for bagasse in all cases a profit is obtained. This difference is mainly caused by the higher biomass costs for pinewood and straw.
- The waste water treatment, converting the dissolved organics, delivers a huge cost in case of straw, which is caused by both the higher extractive and AAEM content (requiring more 2nd condenser liquid for leaching) in straw.
- No increase in annual income is obtained after acid leaching when only heating oil is targeted. This was expected based on the energy to oil efficiency for pine (Table 3)
- The cases for the different feedstocks show mutual trends after acid leaching, the differences are mainly caused by: i) the larger amount of extractives in the straw, and ii) higher lignin content in pinewood yielding more phenolics.
- The production of sugars, phenolics and heating oil (S&P&HO_{AL}) from acid leached biomass generates the largest annual income, however compared to producing only sugars and heating oil (S&HO_{AL}) the increase in earnings was rather small. Recovering only sugars and phenolics (no heating oil) from the oil (see S&P&HO_{AL} case) generates a lower annual earning then recovering sugars and heating oil (S&HO_{AL}).

Figure 13 shows the annual cash flows for the different cases at a feedstock capacity of 5 ton h^{-1} . It can be seen that at this scale the capital, fixed (fraction of CAPEX) and labor cost are too large to obtain any profit even for bagasse. However, mismatch between the annual costs and the earnings is much less for the bagasse S&HO_{AL} and S&P&HO_{AL} cases compared to the HO_U and HO_{AL} cases.

Figure 12: Annual operating costs and earnings for the different cases at 50 ton h^{-1} scale. For each individual case the first column shows the operating costs and the second column the earnings.

Figure 13: Annual operating costs and earnings for the different cases at a feedstock capacity of 5 ton h^{-1} . For each individual case the first column shows the operating costs and the second column the earnings.

5.3. Sensitivity study

A sensitivity study was carried out to identify the key factors influencing the economic feasibility. The parameter varied were the biomass price, sugar price, sugar yield, aromatic price, aromatic yield, heating oil price, hours of operation, the CAPEX, labor price and electricity price. The results are shown in Figure 14. The project is economical feasible if the internal rate of return (IRR) is larger than the inflation and the interest or dividend paid to the project financiers. The IRR for the different bagasse cases at 50 ton h⁻¹ varied between 2.9 and 15.5%. The most important parameters for the production of only heating oil from untreated or acid leached bagasse were the biomass price, heating oil price and the CAPEX. The labor price (largely depending on location) and hours of operation had a moderate impact. The parameter with major influence for the production of sugars together with heating oil or aromatics was the CAPEX. Reducing the CAPEX by 20% would increase the IRR to 21.4% and 22.6% for the production of sugars with heating oil and sugars with aromatics respectively.

Figure 14: Sensitivity study for the different cases for bagasse pyrolysis at 50 ton h⁻¹ scale.

6. Discussion and outlook

In this study pine wood, bagasse and straw were used with varying moisture, ash and extractives content. Obviously, biomass price is one of the major cost drivers. For the S&HO_{AL} cases at 50 ton h⁻¹ scale the biomass cost was 44% (pinewood), 35% (straw) and 28% (bagasse) of the total annual costs. Obviously, this study showed that in case of acid leaching, processing biomass with a high moisture content does not lead to significant additional costs compared to dry feedstocks. Biomass with a high water extractives content will lead to large waste water treatment costs (straw 23% of total annual cost for S&HO_{AL} at 50 ton h⁻¹). Promising cheap biomasses next to bagasse might be; empty fruit bunches, mallee wood and rice husk.

Using organic acids, produced by pyrolysis itself, instead of mineral acids for the acid leaching of the biomass has several advantages; i) no sulfur (in case of H₂SO₄) is added which will end up in the char, gas and/or oil ii) the pyrolytic acids are expected to be less corrosive to the used equipment, especially at increased temperatures, iii) no hydrolysis reactions occur during leaching thus minimizing the organic loss to the waste water during the leaching process.

The energy balance showed that enough heat is produced from combustion of char and pyrolysis gases to provide the heat for pyrolysis and biomass drying. However, this only holds when the biomass is mechanically dried to approximately 50 wt% prior to thermal drying. This makes the dewatering press unequivocally one of the key operations in this concept.

Experiments performed on acid leaching of biomass gave a rough estimate of the leaching time, biomass moisture uptake, preferred biomass particle size and AAEM removal efficiency. Based on this information a diffuser (counter current moving bed extractor) was selected which is “readily” available. Further percolation tests and pilot testing, to optimize process parameters, are required. A key factor in minimizing the water usage in the leaching process and equipment cost is the multi-stage counter-current operation mode. Note, that the AAEM content in the rinsing water must be sufficiently low, in our case 100 mg kg⁻¹, to effectively remove the AAEM from the biomass.

The waste water treatment cost in this work was based on the typical price for aerobic bacterial treatment (330 US\$ ton⁻¹ organic material). As mentioned in section 4.3, the COD content of the waste water streams indicates that implementing anaerobic digestion (CH₄ production) before the aerobic bacterial treatment can reduce the costs. The removal of the inorganic, via e.g. reverse osmosis can reduce the fresh water consumption of the plant. However, the cost of rinsing water is only 0.5 % of the biomass feedstock cost (process water cost of 0.2 US\$ m⁻³). Nevertheless, new developments, like fermentation to lipids [61] or microbial elec-

trolysis to hydrogen [62] might increase the value of the organics in this stream even further.

In chapter 4 we showed that acid leached biomass has the tendency to melt during pyrolysis leading to char agglomerates in our fluidized bed reactor [69]. At 360 °C no operational problems caused by the melted biomass were observed, while still high organic oil and sugar yields were produced [69]. Since the pyrolysis reactions at 360 °C are relatively slow, the heating rate of the biomass particle is of less importance. Therefore reactors considered for slow or intermediate pyrolysis like augers and rotating kilns can be considered to produce high oil yields after acid leaching. However the slower reaction kinetics will require much longer residence times (min vs sec) of the biomass particles in the hot pyrolysis reactor which lead to increased CAPEX. The CAPEX and corresponding fixed costs (especially maintenance), were one of the major cost drivers of the process, e.g. for the S&HO_{AL} cases at 50 ton h⁻¹ scale the depreciation of the CAPEX plus fixed cost was 34% (pinewood), 29% (straw) and 52% (bagasse) of the total annual costs. The sensitivity study showed that reducing the CAPEX by 20% will increase the IRR from 14.4 % to 21.4% (S&HO_{AL}) and 15.4% to 22.6% (S&P&HO_{AL}). These results show the importance, and might challenge researchers and industry, to find cheap reactor concepts capable of dealing with melting biomass or long residence time. Moreover tests with existing reactor concepts, like the rotating cone reactor, auger reactor or circulating fluidized bed reactor, should be performed to study if the melting biomass leads to operational problems in these reactor types. Furthermore, the produced char contains far less AAEMs which reduces problems (slagging and corrosion) in the combustor.

The heating oil (1st condenser oil or its fractions) produced from acid leached biomass will have different physical properties than normal pyrolysis oil (untreated whole oil), e.g. a low water content, less volatiles and a much higher viscosity at room temperature [15]. This will require some preheating of the oil before usage (~60 °C) to reduce the viscosity [15].

Currently, ethanol is still mainly produced by fermentation of simple sugars from predominantly corn or sugar cane. Only recently a few lignocellulosic based processes have become commercial, which are based on pretreatment (e.g. acid hydrolysis, ammonia explosion) followed by enzymatic saccharification (using cellulase). The advantages of this process compared to sugar production via pyrolysis are a higher cellulose to glucose yield (90% vs 40%) [6, 65] and that a lower amount of inhibitors are formed. However the expensive cellulase (~0.1 US\$ dm⁻³ of ethanol) [65, 70], long residence time (~3 days) [65], and relative low sugar concentrations (11% mass basis) [65] of the enzymatic saccharification are major drawbacks. The sugar content of the aqueous fraction after water and ethyl acetate extraction in our concept will be around 25 % -30 % (see Figure 8), which is higher than the sugar content obtained from enzymatic hydrolysis (10-15 % [65]). The direct fermentation of anhydrosugars (without hydrolysis to glucose) would avoid the use of mineral acids and prevent large amounts of solid waste from neutralizing. However, currently higher yields and working concentrations

are obtained after hydrolysis of the anhydrosugars [71]. It should be noticed that this comparison is rather obscured since the biocatalyst for anhydrosugars are hardly studied [54, 71-74] whereas the biocatalyst for normal sugar fermentation are highly optimized. The IRR of 14.4% ($S\&HO_{AL}$) and 15.5% ($S\&P\&HO_{AL}$), based on a sugar price of 350 \$ ton^{-1} , shows that the production of sugars via pyrolysis has clearly an economic potential. Another conversion method for anhydrosugars next to fermentation is acid-catalyzed conversion to produced levoglucosenone [75], furanics [76] or levulinic acid [76].

In case new insights, potentially gained from the currently well-studied lignin depolymerization, lead to improved techniques to produce monomeric phenolics from the (mainly oligomeric) phenolic fraction in pyrolysis oil. This would largely increase the economic value of this product slate and thereby the IRR of the whole process (a phenolic fraction of 1000\$ ton^{-1} gives an IRR of 30.5 for bagasse $S\&P\&HO_{AL}$). Note that if the monomeric phenolic yield is improved still further research on the extraction of phenolic fraction from the 1st condenser oil is required.

Finally, process integration with for example a sugar cane mill or palm oil mill can significantly reduce the CAPEX and OPEX (e.g. less workers needed). For example the CAPEX largely reduces when the char and gases can be fed to an existing combustor. Note, the char combustor is typical one of the most expensive devices in the pyrolysis plant (heat carrier loop ~50 % of total CAPEX [42, 77]). Another example is co-feeding of waste water in an existing (on-site) waste water treatment plant.

7. Conclusions

In this work the feasibility of removing AAEMs from biomass, using leaching with pyrolytic acids, as a pretreatment step in a pyrolysis process (5 and 50 ton h⁻¹ scale) has been evaluated in terms of mass and energy balance, economics and overall performance. A preliminary process design for the pyrolysis of pinewood, straw and bagasse is presented and an economic comparison was made between the pyrolysis of the untreated and acid leached biomasses.

Process simulation quantified that the pyrolysis with acid leaching can still be self-providing in its heat, required for the pyrolysis process and biomass drying, but insufficient excess heat is available to produce the required electricity. The implementation of acid leaching will increase the total CAPEX of a new pyrolysis plant by 36% (only acid leaching) to 47% (including also product separation). For straw and bagasse an increase in the carbon to oil (straw 32% to 48%, bagasse 37% to 56%) and energy to oil (straw 33% to 51% bagasse 40% to 57% of the initial biomass energy) was obtained after acid leaching but not for pinewood. The increased production of anhydrosugars allows broadening of the product slate, which increases the product value (also for pinewood). Under the current market circumstances and comparison of the three feedstocks, the production of heating oil and sugars from bagasse at a biomass scale of 50 ton h⁻¹ is the most economic option (IRR 14.4%).

It is not surprising that the economic feasibility largely depends on the biomass cost and CAPEX (process scale). For the acid leaching concept biomass with a high moisture content does not lead to a large cost penalty. Biomasses with a high content of water soluble extractives will lead to significant water treatment costs. Crucial in the leaching concept is the mechanical dewatering step which significantly reduces the water content of the biomass before thermal drying. Additionally, selecting a multi-stage counter-current extractor reduces significantly the rinsing water consumption.

The economics of the acid leaching concept can be further improved by: utilization of the phenolic fraction, process integration (e.g. combustor, waste water treatment) with existing industry like the sugar cane and palm oil mills and carefully selection of cheap biomass waste streams. To summarize, acid leaching of biomass combined with pyrolysis and fractional condensation offers opportunities for cost effective production of pyrolytic sugars, next to heating oil.

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Chapter 6

Conclusion and outlook.

The work presented in this thesis deals with the design and evaluation of a pyrolysis process with improved selectivity towards anhydrosugars and monomeric phenolics next to bio-oil for energy applications. These compounds are interesting platform chemicals for the production of among others transportation fuels, plastics and pharmaceuticals. From literature it was understood that removing or passivating the AAEMs before pyrolysis is required to obtain high anhydrosugar yields. In literature this has been done by leaching or infusing the biomass with mineral acids (H_2SO_4 , H_3PO_4 or HNO_3) which usage leads to inorganic waste streams. In this thesis it was studied if the organic acids produced by pyrolysis and concentrated via fractional condensation of the vapors can be used instead. Studies were undertaken to reveal the chemical and transfer processes at the scale of particle and reactor. The concept of pyrolyzing acid leached biomass was studied using pinewood, straw, hay and bagasse at a scale of 150 gram per experiment. These experimental results were used as basis for a technological and economic evaluation. From the work described in this thesis the following conclusions can be drawn.

Pyrolytic acid leaching

Biomass leaching with pyrolytic acids concentrated in the 2nd condenser liquid proved to be an efficient method to remove the majority of AAEMs. It is worth to notice that the AAEM content could not be completely removed; even after excessive rinsing 90 mg kg⁻¹ – 600 mg kg⁻¹ of AAEMs remained in wood and agricultural waste streams. Ball milling of the pinewood fibers to <80 μm (cell wall) did not result in better AAEM removal efficiencies. A possible explanation is that the remaining AAEMs are located within the proteins, which are hardly removed by pyrolytic acid leaching. The acid leaching process is rate limited by diffusion within the tracheids, therefore relative small particle sizes (few mm) are required to achieve reasonable leaching times (minutes). Analysis of the biomasses showed that the applied acid leaching conditions did not affect the hemicellulose, cellulose and lignin content of the biomasses. However, the extractives were dissolved during leaching. Pyrolysis of acid leached biomass back impregnated with AAEMs revealed that the applied acid leaching method does not affect the biomass in such a way that it significantly influences the pyrolysis outcome, other than removing the AAEMs. In case of AAEM-rich biomasses, like straw and hay, insufficient acetic acid is produced by pyrolysis to dissolve all AAEMs during leaching. For these AAEM rich biomasses this shortage of produced acid can be resolved by applying first a water wash, to remove a fraction of the potassium and sodium, before acid leaching.

Anhydrosugars

The production of anhydrosugars from cellulose and biomass was studied under various conditions to obtain insights in the underlying chemistry and transport processes at all relevant scales, ranging from particle level to the process parameters at bench scale. It was found that

if pure cellulose is pyrolyzed at high heating rates ($5000\text{ }^{\circ}\text{C s}^{-1}$) with fast evaporation of the volatile products, obtained by low pressure (5 mbar), and quick quenching of the volatile products (20 ms) high anhydrosugar yield were obtained. Under these conditions the pyrolysis temperature affected the anhydrosugar DP distribution but the total anhydrosugar yield remained constant ($\sim 70\%$ on carbon basis as conservative estimate). Decreasing the product escape rate from the pyrolyzing particle, by increasing the pressure to 960 mbar, reduced the total anhydrosugar yield from 69 wt% to 50 wt% at $530\text{ }^{\circ}\text{C}$. Increasing the hot vapor residence time from 20 ms to 1.6 s, by pyrolyzing in the fluidized bed reactor, did not decrease the anhydrosugar yield. This indicates that anhydrosugars can significantly react to non anhydrosugars compounds on the pyrolyzing particle, expectedly in the molten phase as hypothesized by Mamleev [1], but are rather stable in the vapor phase at temperatures of $530\text{ }^{\circ}\text{C}$ in the absence of AAEMs. The AAEMs, naturally present in biomass, largely affected the pyrolysis outcome at particle level. The results presented in this thesis regarding the anhydrosugar recovery as function of the AAEM content are summarized in Figure 1. It can be concluded that it is impossible to obtain high anhydrosugar yields from untreated biomass under any process condition. When the AAEMs are largely removed ($<1000\text{ mg kg}^{-1}$) before pyrolysis, reduced pressure can be used to further increase the anhydrosugars yield. The glucose recovery from acid leached biomass were generally slightly higher than expected based on the results of cellulose with comparable AAEM content, indicating that the remaining AAEMs are not solely located within the cellulose micro fibrils (limited mobility).

Figure 1: Glucose recovery obtained at $\sim 530\text{ }^{\circ}\text{C}$ versus the AAEM ion content in cellulose or biomass.

The highest sugar recovery from acid leached biomass in the fluidized bed was obtained at 480 °C. It is worthwhile to mention that at 360 °C the sugar yield was already 0.23 kg kg⁻¹ compared to 0.29 kg kg⁻¹ obtained at 480 °C. Impregnating a small amount of sulfuric acid into acid leached biomass increased the glucose recovery as shown for pinewood (29% to 40%) and straw (32% to 37%). A similar trend for the sugars from hemicellulose was obtained. Pecha et al. indicated that impregnating acetic acid instead of mineral acids into acid leached biomass also improves the anhydrosugar recovery (only levoglucosan relative increase reported) [2]. Further research should reveal if increased sugar recoveries can be obtained by impregnating a small amount of 2nd condenser liquid in the biomass before pyrolysis but after leaching. Using the current insights and techniques it is possible to obtain sugar recoveries from real biomass in the range of 30% - 40%. It can be expected that further research will lead to an increased sugar recovery of 45% - 60% but likely not higher.

Monomeric phenolics

The production of monomeric phenolics, was only studied from biomass and not from isolated lignin. This was chosen as most extracted lignin underwent severe condensation reactions of the β -O-4 linkages during the isolation. Therefore the lignin derived products in the biomass derived pyrolysis oils had to be studied, which was done using a dedicated analytic strategy existing of a combination of GC-MS, GPC and UV-fluorescence analysis. Based on the results of the various analytical techniques evidence accumulated that the AAEMs did not largely influence the yield and molecular size of the phenolic products. Therefore, acid leaching turned out to be not a suitable method to improve the yield of monomeric phenolics. Low reactor temperatures (~430 °C) favored the production of monomeric phenolics, though their absolute yields remained low for both untreated and leached pinewood (maximum: 23 g kg⁻¹ pine, 80 g kg⁻¹ lignin). From the presented results and literature it did not become clear whether the production of monomeric phenolics via pyrolysis is suppressed by i) condensation reactions at particle level; ii) condensation reactions outside the particle, i.e. vapor phase or during oil recovery; or iii) the fact that the oligomeric structures are volatile enough to leave the pyrolysis reactor before they can crack to monomeric phenolics. A strategy to obtain more insights in the aforementioned would be to pyrolyze milled wood lignin, which is an extracted form of lignin with the least changes to the lignin structure, in the screen heater combined with dedicated analyses such as GC-MS, preparative fractionation GPC [3] and 2D NMR [4, 5]. A recent publication by Rahimi et al. showed that lignin can be converted with a high yield (51 wt%) in monomeric phenolics [6]. This was achieved by oxidation of the β -O-4 linkages followed by cleavage with formic acid. These new insights might lead to new pretreatment techniques that improve the monomeric phenolic production via pyrolysis without suppressing the anhydrosugars production.

Organic oil, produced water, residue and gas yield

Next to increasing the anhydrosugar yield, the mass-, energy- and carbon conversion to organic oil increased after acid leaching. However, when only the 1st condenser liquid is considered for acid leached biomasses a decrease in yield compared to whole oil from the untreated feedstock is obtained for pinewood. After acid leaching single phase bio-oils (condensed at 20 °C) were obtained also from straw and hay, which can simplify the further processing of the pyrolysis oil.

The pyrolysis of pure cellulose in the screen heater under vacuum produced only a very limited amount of light oxygenates and gas. A solid residue was found at pyrolysis temperatures below 450 °C and reaction times of 5 sec, though this residue turned out to be unconverted cellulose. It was found that the production of char from cellulose during fast pyrolysis (high heating rates) is caused by AAEM catalyzed dehydration reactions. Gases can be produced at particle level, only in the presence of AAEMs, and by cracking reactions in the hot vapor phase. The observed effects of AAEMs on the residue and gas yield obtained from cellulose are in agreement with the differences in products from untreated and acid leached biomass. Under the conditions applied in the fluidized bed, the otherwise obtained anhydrosugars in case of acid leaching, seem to react to predominately char, water and gases in case of untreated biomass. The light oxygenate yield, recovered in the 2nd condenser, varied only slightly after acid leaching. The char, gas and oil yields, based on biomass fed to the reactor, were more comparable after acid leaching for the tested biomasses. Therefore, the pyrolysis process is less sensitive to the feedstock composition after acid leaching.

The residue from acid leached biomass pyrolysis had a different morphology than that from untreated biomass. The residue from untreated biomass retained the original fibrous biomass structure whereas the residue from acid leached biomass has (partially) gone through a melt phase when pyrolyzed ≥ 430 °C. This melt acted as a glue between the sand/residue particles causing bed agglomeration. At 360 °C no operational problems caused by the melted biomass were observed, while still high organic oil and sugar yields were obtained. As a consequence of the melting behavior of acid leached biomass during pyrolysis, the following considerations can be made. On the one hand the pyrolysis process can be operated at low temperature (~ 360 °C). However, at these temperatures the pyrolysis reactions are relatively slow. This will require longer residence times (min vs sec) of the biomass particles in the hot pyrolysis reactor leading to increased CAPEX. Because of the slow pyrolysis reaction the heating rate of the biomass particle is of less importance, allowing reactors considered for slow or intermediate pyrolysis like augers and rotating kilns. On the other hand a reactor concept capable of dealing with melting biomass could be selected. For fluidized bed reactors it was found that the agglomeration leads to severe operation problems however, in other (existing) reactor concepts, like the rotating cone reactor or auger reactor, this doesn't have

to be the case. Therefore test should be performed to study if the melting biomass leads to operational problems in these types of reactors.

Pyrolysis fundamentals

With respect to the chemistry and heat/mass transfer process taking place during pyrolysis the following conclusions are drawn:

- i) The large amount of oligomeric anhydrosugars, ranging from DP_2 to DP_{11} , obtained in the screen heater reveal that random chain scission is the dominant mechanism during cellulose pyrolysis, though unzipping cannot be excluded completely based on the obtained results.
- ii) The cracking reactions become very fast (<100 ms for complete conversion) at temperatures above 500°C causing the conversion rate to be limited by the heat transfer, as a results the actual reaction temperature becomes constant at heat source temperatures above $\sim 530^\circ\text{C}$;
- iii) The presence of a single potassium molecule per 2500 glucose units (100 mg kg^{-1}) reduced the glucose recovery from 70% to 50%. This shows that a single potassium molecule has affected ~ 500 sugar molecules. The presence of potassium already affected the pyrolysis of levoglucosan, which without salts just evaporates. Further researchs is needed.
- iv) The insights obtained from the screen heater show that there is a clear interplay between chemistry and the heat and mass transfer. The obtained results could not be explained based on the kinetics and heat transfer only.

Because of the complexity of the chemistry, varying per state of matter, and mass transfer processes, evaporation as well as liquid ejection, it can be concluded that predicting the pyrolysis product yields and oil composition via modelling of a single lignocellulosic biomass particle or the total processes at reactor level will be extremely difficult, if not impossible.

Process design

The biomass leaching can be performed at room temperature. After pyrolytic leaching the biomass needs to be rinsed to remove the leaching liquid, containing the dissolved AAEMs, from the biomass pores ($\sim 3\text{ kg per kg dry biomass}$). Performing the acid leaching and rinsing in a multi-stage counter-current extractor reduces significantly the rinsing water consumption. Using the aforementioned combined with recycling the water from the dewatering press

and dryer the amount of rinsing water per kg of dry biomass required was 1.3, 5.5 and 0.6 kg kg⁻¹ for pinewood, straw and bagasse respectively. Possible process equipment for the acid leaching and rinsing is a “readily” available sugar cane diffuser. Only if mechanical dewatering before thermal drying is applied the heat for pyrolysis and drying of the biomass can still be supplied by the combustion of the residue and gases. However, insufficient excess heat is available to produce electricity for the process.

The large waste water streams from the acid leaching contains a mixture of organic and inorganic compounds. Aerobic bacterial treatment of this stream leads to large costs. Based on the COD content of the waste water streams it is expected that implementing anaerobic digestion (CH₄ production) before the aerobic bacterial treatment can reduce the costs and recover a fraction of the energy. It should be noted that for low AAEM content, requiring less 2nd condenser liquid for leaching, and water extractive content biomasses the amount of energy in the waste water stream is rather low compared to the energy recovered in the oil.

The sugars can be separated from the oil (including phenolics and furanics) by water extraction followed by ethyl acetate extraction. It is worth to mention that the separation using ethyl acetate is far from optimal because of the solubility of ethyl acetate in water. Further research on better separation techniques is required. In collaboration with the group of Lars Rehman it was demonstrated that the isolated anhydrosugars, obtained from acid leached pinewood, can be successfully fermented, after hydrolysis, to bio-ethanol with comparable yields as obtained from pure glucose [7]. Recent research has shown that anhydrosugars can be fermented directly, which eliminated the use of mineral acids and neutralization process. So far this research has mainly focused on the use of levoglucosan, it would be desirable to broaden this research to isolated sugar fractions including larger anhydrosugars, like cello-biosan, and hemicellulose derived anhydrosugars. In addition to fermentation, levoglucosan and the anhydrosugars, after purification, turned out to be an interesting feedstock for the production of levulinic esters via acid catalyzed reactions with alcohol [8]. The residue after sugar extraction (resembles something between heavy oil and water insolubles in [9]) can be hydrodeoxygenated to transportation fuel with higher carbon efficiency and lower hydrogen consumption compared to normal pyrolysis oil [8].

Economics

The economic evaluation showed that this process is very sensitive to the CAPEX and obviously to the biomass price. The different biomasses evaluated revealed that with respect to the biomass composition a low amount of extractives in the biomass, which end up in the waste water, is preferred but biomass with a high moisture content doesn't matter. This offers opportunities for processes in which the biomass is first treated to extract valuable products, like sugars or proteins. The implementation of acid leaching will increase the total CAPEX of

a new pyrolysis plant by 36% (only acid leaching) to 47% (including also product separation). Under the current market scenario and state of proven techniques the production of sugars and heating oil from bagasse at 50 ton h⁻¹ was the most economic option (IRR 14.4%).

A broader perspective

In this thesis, new insights and tools to increase the anhydrosugar and organic oil yield from lignocellulosic biomass are described. Options that might further improve the anhydrosugar recovery to a range of 45% - 60% have been identified. It should be noted that sugars for fermentation can also be produced from lignocellulosic biomass via several other processes. Amongst them enzymatic hydrolysis is the most studied and industrial applied. The advantages of this process compared to sugar production via pyrolysis are a higher cellulose to glucose yield (90% vs 40%) and a lower amount of inhibitors are formed. However, enzymatic hydrolysis is largely hindered by the lignin in biomass, therefore requiring pre-fractionation, which is not the case for pyrolysis. Moreover the expensive cellulase, long process time (days), and relative low sugar concentrations (~11% mass basis) of the enzymatic saccharification are major drawbacks. The work described in this thesis identified the advantages of the pyrolysis in comparison to enzymatic hydrolysis concepts, such as high conversion rates, more concentrated products, flexibility to various biomass sorts and producing other products next to sugars.

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Appendix D

Supporting information Chapter 2

S1. Materials

Avicel ph101 (Sigma-Aldrich, particle size $\sim 50\text{ }\mu\text{m}$, 60.5% crystallinity [1], ash content 0.005 wt%, AAEM content 1 mg kg⁻¹, degree of polymerization polymerization specified < 350 average 220 [2]), levoglucosan (1,6-Anhydro-b-D-glucopyranose, Carbosynth purity >98%) and cellobiosan (1,6-Anhydro-b-D-cellobiose, Carbosynth purity >95%) were used as a feed-stock for the pyrolysis experiments. The feedstocks were dried in a vacuum oven (Heraeus FVT420) at room temperature and 1 mbar for at least 24 h before usage.

The screens (2.5 cm by 5 cm) for the reactor were cut from a large metal wiremesh (Dinxperlo, Wire Weaving Co. Ltd, mesh 200 wire thickness 0.06 mm * 0.06 mm, twilled weave, AISI 316). The screens were cleaned with Milli-Q water followed by acetone (Sigma Aldrich, purity >99.5%) and dried before use (24 h at 105 °C). The reactor was rinsed with methanol (Sigma Aldrich, purity 99.9%) or Milli-Q water, to recover the condensed product, depending whether the GC/MS or HPLC, respectively, was used for analysis.

Sulfuric acid (Sigma Aldrich, purity 99.99%) was used for hydrolysis and barium carbonate (Sigma Aldrich, purity >99%) was used to neutralize the hydrolyzed samples before HPLC analysis.

Levoglucosan (1,6-Anhydro-b-D-glucopyranose, Carbosynth purity >98%) cellobiosan (1,6-Anhydro-b-D-cellobiose, Carbosynth purity >95%) cellotriosan (LC Scientific purity > 98%) celloterasan (LC Scientific purity > 98 wt%) and glucose (Sigma-Aldrich purity 99.5%) were used as standards for calibrating the HPLC.

S2. Detailed description of screen-heater

S2.1. Sample preparation

50-80 mg of feedstock (e.g. cellulose) was distributed evenly over a stainless steel screen (wiremesh). 0.5 cm of the screen was kept free of feedstock to be able to clamp the screen between the electrodes. A second screen was pressed on top of it with a hydraulic press (Rodac RQPPS30 30t, 450 kg cm^{-2}). The exact amount of feedstock between the screens was determined by weighing the pressed screens, including the feedstock, on an analytical balance (Mettler Toledo AX205, max 220 g, readability 0.01 mg) and subtracting the weight of the initial screens. Figure S1 shows the front view of the screens with the cellulose sample between. Figure 2 shows the side view of the screens.

Figure S1: Front view of the screens with cellulose in between. The left picture is a detailed picture of the right picture.

Figure S2: Side view of the screens with cellulose in between.

S2.2. Screen heater setup

The screen heater reactor consisted of a glass vessel (Duran 250 ml centrifuge tube, round bottom, D=5 cm #1). In this glass vessel, the pressed screens with in between the feedstock (#2) was clamped between two electrodes (#5). After installing, a vacuum was created of 5 mbar using a vane vacuum pump (10, Edwards E2M-1.5), see Figure S3. The reactor was filled with nitrogen gas to remove the remaining air. After this procedure a vacuum was created of 5 mbar. A liquid nitrogen bath (#4) was placed around the vessel to cool the wall of the vessel to approximately -100 °C. Nitrogen could be supplied to the vessel to control the pressure inside the vessel around 960 mbar in the case of the atmospheric pressure experiments. Note, during the atmospheric experiments a gas bag was connected to the reactor by a valve. After the experiment the valve was opened and the reactor was warmed to ambient temperature. The expanded gas flows inside the gas back. Therefore, the reactor vessel pressure never exceeded the maximum allowable reactor pressure of 1.1 bar. In addition, a 20 ml syringe was installed in all experiments. The 20 ml syringe was used to collect a gas sample (#9) after the experiments.

The pressure was precisely monitored during the experiment using an accurate and fast enough pressure gauge (Heise DXD3765) #8). A pyrometer (#12) was used to monitor the temperature. To prevent disturbance in measuring the thermal radiation emitted by the screens by the liquid nitrogen during the experiment, a glass tube (#13) with a silicone sealing (#14) was placed in the liquid nitrogen bath. During the experiment an electrical current was passed through the wires, which served as an electrical resistance heater. This method supplies the heat required for heating the sample and maintaining it at the set temperature, in this work termed final screen temperatuur (TFS), for a specified time called the holding time. The required power was supplied by two sets of two batteries connected in series. For the heating period these were two Varta Silver Dynamic batteries (12 V/100 Ah, 830 A) and for the supply of heat during the reaction two Varta Pro Motive batteries (12 V/225 Ah/1150 A) were used. The temperatures and pressures were recorded using a DAQ card (NI PCI-6281). The data was processed in a Labview program (running on a pc at 2000 Hz) which regulated the screen temperature via a PID controller. In an additional experiment a thermo-couple (unsheathed K-type, wire diameter 0.025 mm connected to a Weidmuller MAS K thermocouple signal conditioner) was installed on the screens or in the gas phase to check the temperature of the screens (comparison with the pyrometer) and to measure the temperature of the produced vapour/gas leaving the screens on their way towards the cooled vessel wall.

Figure S3: Schematic drawing of the screen heater setup. Top: front view.
 Bottom: side view.

S2.3. Run procedure

Before each experiment the screens & feedstocks (#2), copper clamps (#3), vessel (#1) and tape (#6) were weighed. Teflon tape was wrapped around the electrodes to be able to quantify the condensed products on this part. Hereafter, the different parts of the set-up were put together. Air was removed from the vessel by creating a vacuum (6 mbar). The reactor is than flushed with nitrogen. After 2 times flushing a vacuum was created of approximately 6 mbar. The bath (#4) surrounding the reactor vessel was filled with liquid nitrogen. In case of an experiment at atmospheric pressure (960 mbar) nitrogen was added to the vacuum vessel immersed in the liquid nitrogen bath. After everything was in position, the pyrolysis run was started following a pre-programmed procedure using the Labview program (with the set temperature, holding time and PID value). After the run, the set-up was removed from the liquid nitrogen bath and consequently warmed till ambient temperature.

S2.4. Sample recovery and mass balance

Once the set-up was at room temperature, in the case of the vacuum experiments, the pressure inside the vessel (#1) was increased to approximately 900 mbar by adding nitrogen gas (#11). Once this pressure was reached a gas sample was taken using the 20 ml syringe. In the case of experiments at atmospheric pressure the volume of the gas was determined as being the volume of the gas bag and the reactor vessel at ambient temperature and known pressure. The volume of the gas bag was determined by applying a water displacement method. Also in the atmospheric pressure experiments a gas sample was withdrawn from the reactor using a 20 ml syringe. The gas samples were analyzed using a Micro GC. (Varian MicroGC CP4900, 2 analytical columns, 10 m Molsieve 5A, 10 m PPQ. Carrier gas = He, calibrated for H₂, N₂, O₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈). The gas yield was calculated by:

$$Y_{gas} = \sum_{i=CO,CO_2} \frac{\frac{P_{gassample} \cdot Vol\%_i \cdot (V_{vessel} + V_{bag})}{R \cdot T_{room}} \cdot MW_i}{M_{screens+biomass} - M_{screens} - M_{EC}} \quad (1)$$

Note, the V_{bag} is zero in the case of vacuum experiments. The ejected cellulose (EC) in this formula is explained below. MW is the molecular weight of the gas component. Vol% is the volume concentration of a specific gas compound analyzed by gas chromatography. R is the gas constant (8.314 J K⁻¹ Mol⁻¹).

After the gas analysis, the reactor was dismantled and the screen (#2), vessel (#1), tape (#6) and clamps (#5) were weighted. The mass of condensed products (excluding residue between the screens and gas) was determined by subtracting the initial weight of the vessel, tape and clamps. The reactor was rinsed with approximately 6 ml (in batches of 2 ml) of solvent. Note, >90 wt% of these products were collected on the vessel wall and thus only < 10 wt% of these products was collected on the clamps and tape. The solvent was milli-Q water for HPLC analysis or methanol for GCMS analysis. It turned out that a very small amount of product on the vessel was insoluble, but still collected, in the rinsing solvent. The amount of these solvent insoluble compounds was determined as follow. A centrifuge tube was weighted empty and filled with the rinsing solvent (including insoluble compounds) and weighted again. After centrifugation the solvent insoluble compounds were precipitated and collected at the bottom. The solvent was then removed by decantation leaving the solids behind in the tube. After vacuum drying of the tube at 20 °C and 10 mbar the tube was weighted and the initial weight was subtracted. The weight difference represent these solids of which the mass did not exceeded (except for one experiment) the 6 wt% of the cellulose feedstock. The solids were analyzed by FTIR (see S6.5 Figure 23) and compare with the cellulose feedstock. It turned out that these solids have the same structure as the cellulose feedstock. In addition, the solids were completely white representing the original color of the cellulose feedstock. Therefore, this fraction is hereafter referred to as ejected cellulose (EC), see Formula 2. With known

amount of products (excluding residue and gas) and known amount of ejected cellulose the weight difference is hereafter called condensed product, see Formula 3. Note that the mass of ejected cellulose is excluded from the amount of cellulose feedstock.

$$M_{EC} = M_{tube+condensed\ product+EC} - M_{tube+condensed\ product} \quad (2)$$

$$Y_{condensed\ product} = \frac{M_{vessel+tape+clamps+product} - M_{vessel+tape+clamps} - M_{EC}}{M_{screens+cellulose} - M_{screens} - M_{EC}} \quad (3)$$

The vessel and screens were stored in the freezer at -24 °C before analysis. The residue was defined as the material remaining between the screens after an experiment. The solid residue yield was calculated by:

$$Y_{residue} = \frac{M_{screens+residue} - M_{screens}}{M_{screens+cellulose} - M_{screens} - M_{EC}} \quad (4)$$

S2.5. Temperature registration using a pyrometer

The temperature of the screen was measured with a Kleiber KGA 730 pyrometer. This pyrometer measures the radiation between a wavelength of 1.58 μm and the 2.20 μm . The output of the pyrometer is a 4 mA - 20 mA signal which was converted into a voltage signal by a resistor. The voltage was continuously recorded, using a DAQ card (NI PCI-6281), in a Labview program.

The measured temperature (radiation) by the pyrometer needs to be corrected for the emissivity (ϵ), the ratio between amount of radiation emitted by a real body and a blackbody, of the screen with cellulose and the transmittance (Tr) of the glass transitions. The following equation was used for this [3]:

$$\frac{1}{T_{screen\ \&\ cellulose}} = \frac{1}{T_{measured}} + \frac{\lambda}{C_2} \cdot \ln(\epsilon') \quad (5)$$

$$\epsilon' = Tr_{vessel} \cdot Tr_{tube} \cdot \epsilon_{screen\ \&\ cellulose} \quad (6)$$

$$C_2 = \frac{ch}{k} \quad (7)$$

In this equation, c is the speed of light ($3 \cdot 10^8\ \text{m s}^{-1}$), h Planck's constant ($6.63 \cdot 10^{-34}\ \text{J s}$), λ the wavelength (m), k the Boltzmann constant ($1.38 \cdot 10^{-23}\ \text{J K}^{-1}$) and T the temperature (K). An effective emissivity (ϵ') was used to lump the emissivity of the screen with cellulose and the transmittance of both glass parts. Since the majority of the radiation is detected at 2.2 μm this value is used as "effective wavelength" in equation 1.

The blackbody temperature calibration of the pyrometer was obtained by measuring a black copper cylinder (painted with Rust-oleum Heat Resistant 7778 BBQ Black) inside a tube oven at different temperatures (300 °C – 700 °C). The transmittance of both glass parts (vessel (#1) and tube (#13)) was determined by placing these glass parts separately between the black copper cylinder (3 different temperatures) and pyrometer. Using equation 1 the transmittance of the reactor vessel (#1) and the tube (#13) was determined to be 0.84 ± 0.01 and 0.77 ± 0.03 respectively. To verify these separate measured values, both glass objects were placed in series between the pyrometer and the black sample. The determined transmittance for the glass parts together was consistent with the separated determined transmittance. To determine the emissivity of the screens with cellulose the temperature of the screen with cellulose should be known. Therefore a K-type thermocouple (bare wire, diameter 0.025 mm connected to a Weidmuller MAS K thermocouple signal conditioner, reading every 16 ms) was attached to the screens to measure the temperature, see Figure S4. Due to the slower response of the thermocouple compared to the high heating rate of the screen heater it was only possible to measure the temperature accurate with the thermocouple during the stable holding time (see Figure 6). Moreover, the very fast pyrolysis reactions at temperatures above 450 °C (~200 ms) made it impossible to accurately measure the temperature of the screen with pyrolyzing cellulose using the thermocouple. Therefore the temperature of the screen with pyrolyzing cellulose was only measured for experiments below 420 °C. Additional measurements were performed to obtain an estimate of the boundary between which the emissivity of the screen with cellulose will be at higher temperatures. In these measurements a single screen was used as lower boundary (cellulose emits no radiation), whereas a double screen with black foil in between was used as upper boundary (cellulose emits radiation as a black body). The emissivity of the single screen, double screen with cellulose and double screen with black foil as function of temperature are shown in Figure S5. It can be observed that the emissivity at temperatures above 400 °C is quite constant around 0.65 ± 0.15 (for error calculation). Knowing this emissivity and transmittance (determined for the glass tube and vessel) the measured temperature by the pyrometer can be converted to the actual screen (plus cellulose) using Formula 5. From the uncertainties in the emissivity and transmittance the error on the temperature was calculated to be ± 20 °C at 330 °C increasing to ± 45 °C at 750 °C. A typical temperature profile measure by the pyrometer can be seen in Figure S6. The heating rate was around 5000 °C s⁻¹.

Figure S4: Microscopic picture of the thermocouple located on the screen.

Figure S5: Emissivity of a single screen, double screen with cellulose and double screen with black foil as function of temperature.

Figure S6: Typical temperature profile of the screen (5 mbar). The heating pulse is started at 0 s. The pyrometer doesn't detect temperatures lower than 190 °C therefore no temperature is shown between 0 and 36 ms.

S2.6. Visualization of pyrolysis using a high speed camera

Movies of the pyrolysis experiments were recorded using a high speed camera (Casio EX FH25, 240fps, 448 pxl x 336 pxl). A blue LED was connected to the electrodes outside of the reactor and lighted up when current was passed through the screens. The screen with cellulose between was lighted from the back with two white LED lights. The recorded videos were partitioned into separate frames using the freeware program IRfan view. Figure S7 shows some selected frames 0 ms and 346 ms. reaction time. In this experiment cellulose was pyrolyzed at 530 °C and at 1 bar. As can be seen, at 104 ms smoke is visible close to the screen which means very fast cooling. The smoke stays visible for a long time.

The evaporation time of levoglucosan and cellulose at 1 bar could not be determined on basis of the frames from the high speed recordings, because the aerosols blocked the view of the screen. To obtain an indication of the evaporation time of levoglucosan an experiment was performed without vessel, to improve the view on the screen. Figure S8 shows the frames of the test with levoglucosan without vessel. In this figure it can be seen that the produced vapors ignited after 350 ms. Since the produced vapors are directly cooled they can only ignite when they, together with oxygen, come into contact with the hot screen. Oxygen can only reach the hot screen if the levoglucosan has been evaporated, due to the mass flux going from the screen during evaporation. Therefore, at the time of ignition (350 ms) the majority of the levoglucosan should have been evaporated.

Figure S7: Frames from the recording of a screen heater experiment with cellulose performed at 530 °C and 1 bar.

Figure S8: Frames from the recording of a screen heater experiment with levoglucosan performed at 450 °C without vessel.

S3. Fast pyrolysis of cellulose in a bench-scale fluidized bed reactor

Cellulose was also pyrolyzed in a fluidized bed reactor at a temperature of 530 °C. This setup is explained in more detail in our previous paper [4]. Short recap: silica sand was used as bed material and preheated nitrogen was used to fluidize the sand. Per experiment around 100 g of cellulose was fed manually to the reactor in batches of 2 g – 5 g together with 4 g – 8 g sand, via a gas lock system consisting of two valves. The total experiment time was 25 min. The vapor residence time in the hot zone of the set-up (reactor + tubing) was ~1.6 s. In this calculation the flowrates of the nitrogen, produced vapors and gasses were considered. The char was separated from the gas/vapor stream using two wiremesh filters (pore size 9 µm and 5 µm). The pyrolysis vapors were condensed using an electrostatic precipitator (ESP) operated at 20 °C (outgoing gas temperature). A double walled glass condenser was placed in series to recover the remaining vapors and was operated at -5 °C (outgoing gas). The liquid bio-oil production, in the screenheater experiments termed condensed product, was measured by weighing both condensers before and after the experiment. The char yield, in the screenheater experiments termed solid residue, was determined by collecting the char/sand mixtures from the reactor and char-filters and subtracting the initial weight of sand present at the start of the experiment and the amount of sand fed during the experiment. The amount of produced gasses was calculated by difference.

The heating rate of a cellulose particle in the fluidized bed reactor was calculated using:

$$\frac{dT_c}{dt} = \frac{6\alpha}{\rho C_p d_p} (T_c - T^\infty) = \frac{6 \times 200}{1500 \times 1500 \times 50 \times 10^{-6}} \times 500 = \sim 5000 \frac{^\circ\text{C}}{\text{s}} \quad (8)$$

In this equation is, α the heat transfer coefficient (200 W m⁻² K⁻¹ from Prins [5]), ρ the density of cellulose (1500 kg m⁻³ [6]), C_p the heat capacity of the cellulose (1500 J kg⁻¹ K⁻¹ [7]), d_p the particle diameter, T_c the temperature of the cellulose particle and T^∞ the temperature of the fluidized bed. Note that this equation gives the initial heating rate, which decreases in the trajectory.

S4. Analysis techniques

ICP-OES: The ash content of Avicel ph101 was determined by quantifying the residue remaining after 24 hours of dry oxidation at 575 °C. The ash was dissolved in 2 wt% nitric acid and analyzed for its Na, K, Mg and Ca content using ICP. (Sequential ICP-OES with a radial plasma (Varian Liberty II)).

Gas Chromatography: The gas samples were analyzed for H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ using gas chromatography (Varian CP 4900, 2 analytical columns, 10 m Mol-sieve 5 A, 10 m PPQ. Carrier gas = He, calibrated for H₂, N₂, O₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈)

GC/MS: The identification and quantification of light oxygenates (glycolaldehyde, 5-hydroxymethyl furfural and acetol) was done by GC-MS analysis (GC 7890A MS 5975C Agilent Technologies) equipped with a capillary column (Agilent HP-5MS, HP19091S-433). Samples were dissolved in methanol (10 mg - 20 mg condensed product per gram of methanol) and filtered before analysis (Whatman 0.2 µm filter).

FTIR: The residue, remaining between the screens, and Ejected Cellulose was analyzed by FTIR (Bruker Tensor 27). The samples were scanned from wavenumber 650 cm⁻¹ to 4000 cm⁻¹ with a resolution of 1 cm⁻¹. Every sample was scanned 16 times. Baseline correction of the obtained IR spectra was applied.

HPLC and LC/MS analysis of the Anhydrosugars and Glucose: The anhydrosugars in the condensed product were analyzed by HPLC (Agilent 1200 series, column Hi-Plex-pb operated at 70 °C, eluent milli-Q water (0.6 ml min⁻¹)). The different peaks were identified by the available standards (DP₁ (levoglucosan) up to DP₄ (cellotetrasan)). DP₄ and DP₅ (for DP₅ the calibration of DP₄ was used) were quantified separately but due to a large overlap of those peaks they were lumped as DP₄₊₅. Large anhydrosugars with more than 5 units were quantified and summarized as DP_{>5}. As will be discussed later in more detail, these large compounds (DP_{>5}) and also the compounds between DP₁ and DP₂ (DP₁ - DP₂, see S6.4) were identified using LC/MS analysis. The position of the DP₁ - DP₄ standards were determined and a 4 point (different concentrations) calibration was performed (Figure S9). The peak wide, at the baseline, is a function of the peak height as can be observed from the calibration peaks. A typical HPLC chromatogram of a cellulose oil (T = 725 °C) can be seen in Figure S10. With known peak position, height and coupled peak wide (from the calibrations) and the height of the condensed product curve at these specific DP positions, the DP₁ - DP₄₊₅ and DP_{>5} integration borders are known for the condensed product spectra. With known surface area of the identified peak the concentration in the HPLC sample can be calculated from the

calibration using the standards. Thanks to the large temperature range studied and resulting large changes in DP distributions this method is found to be sufficient accurate to be used in this study. For the LC/MS analysis, 0.2 ml min^{-1} of the 0.6 ml min^{-1} flow was split and lead to a Thermo Scientific LCQ ion trap mass spectrometer equipped with an ESI source. Note, the retention times of the peaks has shifted compared to the measurements using only the HPLC column. The LCQ was operated using the LCQ Tune Plus interface and Xcalibur 2.0 software. The internal nominal pressure of the LCQ was maintained at about $0.798 \times 10^{-5} \text{ mbar}$, as read by an ion gauge. ESI experiments were carried out both in positive and in negative ion mode, for which a concentrated ammonium acetate solution was added post-column to a final concentration of 1.0 mM . ESI conditions were: 4.1 kV spray voltage, sheath and auxiliary gas (N_2) flow of 35 and 5 (arbitrary units), and a heated ion transfer capillary/mass spectrometer inlet temperature of 300°C . Unfortunately the Hi-Plex -PB column could not be placed in the oven of the LCMS, therefore the column was operated at room temperature. This resulted in an increase of residence time for the compounds.

Figure S9: HPLC chromatogram of DP_1 to DP_4 used for calibration.

Figure S10: HPLC chromatogram (Hi Plex PB column) for a typical condensed product. The integration (peak) areas (vertical dotted lines) for varies anhydrosugars are included in the figure.

Condensed product hydrolysis: The hydrolysable anhydrosugars in the condensed product were hydrolyzed to glucose using NREL LAP method “Determination of sugars, byproducts, and degradation products in liquid fraction process samples”. The glucose was quantified using the HPLC. Basically, 30 mg - 50 mg of condensed product was dissolved in 10 ml of Milli-q water. H_2SO_4 was added to the water solution to a final concentration of 3.5 vol%. The temperature of the mixture was kept at 120 °C for 60 min. After the experiment the mixture was neutralized by adding BaCO_3 and filtered (Whatman 0.2 μm filter) before HPLC analysis (Agilent 1200 series, column Hi-Plex-Pb, operated at 70 °C, eluent milli-Q water (0.6 ml min⁻¹)). The expression for the sugar recovery (equation 33) can be found in S6.3

S5. Interpretation models

S5.1. Evaporation model

The purpose of this model is to estimate the evaporation time of DP₃ (cellotriosan) from the screens, particularly the difference in evaporation time between an experiment at 5 mbar and 1 bar. A model was built that describes the evaporating of pure DP₃ from the screens. Evaporation is described by the film-model. The vapor pressure relation was determined from an estimated normal boiling point of 792 °C [8] taking the A value [9] of levoglucosan (DP₁) in the Antoine equation:

$$\ln(P^*) = 31.19 - \frac{20956}{T} \quad [Pa] \quad (9)$$

The mass flux from the screen was described by the film model assuming that the DP₃ concentration in the bulk is zero (0):

$$\Theta_m = -k_g C M_w \frac{P^*}{P} \left[\frac{kg}{m^2 s} \right] \quad (10)$$

C is the molar concentration (mol m⁻³) as calculated with the ideal gas law at P (bulk) and the sample temperature. M_w is the molecular weight (0.486 kg mol⁻¹ for cellotriosan). For k_g at ambient conditions (k_{g,0} at T₀, P₀) a conservative estimate of 0.01 m s⁻¹ was taken and it was scaled to the prevailing conditions by the dependency of the diffusion coefficient to T (sample) and P (vessel).

$$k_g = k_{g,0} \left(\frac{T}{T_0} \right)^{1.5} \left(\frac{P_0}{P} \right)^1 \left[\frac{m}{s} \right] \quad (11)$$

The evaporation was modelled by the following equations:

$$\frac{dL}{dt} = \frac{A_m \Theta_m}{\rho} \quad (12)$$

$$\frac{dT_c}{dt} = \frac{A_h \alpha (T_s - T_c) + \Theta_m \Delta H_v}{\rho C_p L} \quad (13)$$

$$\frac{dT_s}{dt} = 5000 \text{ if } T_s \leq T_{FS}, \text{ else } \frac{dT_s}{dt} = 0 \quad (14)$$

With initial conditions:

$$L = L_0, T_c = 298 \text{ K and } T_s = 298 \text{ K at } t = 0.$$

In these equations, L is (half) the thickness of the cellulose sample, A_m the fraction of the flat surface of the screens available for mass transfer, the flux, ρ the density of cellotriosan, T_c the temperature of the cellotriosan, A_h the fraction of the flat surface available for heat transfer, α the heat transfer coefficient, T_s the temperature of the screens, C_p the heat capacity of the cellulose and ΔH_v the enthalpy of evaporation. In Table 1 the numerical values used are listed. The model was solved using Matlab® (ode15s solver).

Table S1: Constants used for evaporation model.

parameter	Value	Comment
r	1500 kg m^{-3}	Particle density cellulose [6]
C_p	$1500 \text{ J kg}^{-1} \text{ K}^{-1}$	Specific heat capacity cellulose [7]
L_0	$25 \cdot 10^{-6} \text{ m}$	Half the thickness of the sample between the screens
A_m	0.5	Estimated based on the estimate of the porosity of the screens and the filling of the cellulose between the wires.
A_h	3	Estimated based on the porosity of the screens (~ 0.25), the diameter of the wires ($6 \cdot 10^{-5} \text{ m}$) and the filling of the cellulose between the wires.
a	$10^4 \text{ W m}^{-2} \text{ K}^{-1}$	Direct contact of wire to cellulose
ΔH_v	$0.7 \cdot 10^6 \text{ J kg}^{-1}$	Data of Suuberg [9] for cellulose realizing that on mass basis ΔH_v is reasonably constant in a homologous series.

The traveling time of a hot escaped molecule from screens to the cooled wall was estimated based on the random walk approximation:

$$t = \frac{L_v^2}{2D} = \frac{0.02^2}{2 \times 10^{-2}} = 20 \text{ ms} \quad (15)$$

In these equations, L_v is the distance from the screen to the vessel wall and D the diffusion coefficient scaled to 100 Pa (1 mbar). The order of magnitude of the calculated traveling time is in good agreement with the traveling time estimated based on analysis of the frames ~ 15 ms (Figure 5, Chapter 2).

S5.2. Pyrolysis models

Pyrolysis model I

To describe the weight loss and temperature of the cellulose sample we have used a modified version of the model as described by Lede and co-workers [10]. We used the reaction rate parameters as given by Shafizadeh [11]. In our model, contrary to Lede's, the sample has a spatially uniform temperature and the state of the intermediate/active cellulose is not defined (can liquid and/or solid). The purpose of this model is to predict the conversion (mass loss) as a function of the temperature (of the screens) and holding time for comparison with the measured data. Also the reaction temperature (T_r) defined as the mean temperature of the sample between 10 and 90% conversion as a function of the final temperature of the screens can be calculated. The following lumped reaction pathway scheme is used:

Figure S11: Schematic representation of interpretation model I.

In Figure S11 it is also indicated which reactions proceed on the particle. The vapors are recovered in the condensed product (on the cold wall of the vessel of the screen-heater, see Section S2). The reaction rate constant k_2 describes both chemical reactions and the escape rate of products from the reacting sample [11]. Both reaction 1 and 2 are described by first order rate equations and the Arrhenius temperature dependency. Mass balance equations are solved for C and AC. Symmetry is assumed as a result of which only one side of the sample is modelled.

$$\frac{dM_C}{dt} = -k_1(T_C)M_C \quad (16)$$

$$\frac{dM_{AC}}{dt} = k_1(T_C)M_C - k_2(T_C)M_{AC} \quad (17)$$

$$M_S = M_C + M_{AC} \quad (18)$$

$$X = 1 - \frac{M_S}{M_{S,0}} \quad (19)$$

In these equations, M_C and M_{AC} and M_s are the masses of cellulose, active cellulose and sample respectively, T_C the temperature of the sample (cellulose + active cellulose) and X the conversion on mass basis. The following energy balance is solved assuming that the heat of reaction 1 is negligible:

$$\frac{dT_C}{dt} = \frac{A\alpha(T_S - T_C) - k_2(T_C)M_{AC}\Delta H_2}{M_s C_p} \quad (20)$$

In this equation, C_p the heat capacity of the sample, A the area available for heat transfer, ΔH_2 the enthalpy of the reaction / evaporation and T_s the temperature of the screen. The temperature of the screens is modelled by:

$$\frac{dT_S}{dt} = B \text{ if } T_S < T_{set} \text{ \& } t \leq t_h \quad (21)$$

$$\frac{dT_S}{dt} = 0 \text{ if } T_S = T_{set} \text{ \& } 0 \leq t \leq t_h + \frac{T_{set}}{B} \quad (22)$$

$$\frac{dT_S}{dt} = -B' \text{ if } t > t_h + \frac{T_{set}}{B} \quad (23)$$

Here t_h is the holding time and T_{set} the set-point of the screen temperature. For the calculation of the solid residue yield (Figure S14) the cooling period was taken into account. For the calculation of the average reaction temperature, the cooling period is not taken into account; after heating the screen remains at the set-point temperature. The average reaction temperature is defined as:

$$T_r = \frac{\int_{x=0.1}^{x=0.9} T_s(x) dx}{\int_{x=0.1}^{x=0.9} dx} \quad (24)$$

The initial conditions are: $M_{s,0} (M_{c,0}) = 2.5 \cdot 10^{-5} \text{ kg}$, $M_{AC} = 0$,

$$T_{C,0} = 298 \text{ K}, T_{s,0} = 298 \text{ K}$$

In Table S2 the range of numerical values of the parameters used are listed. The model is solved using Matlab® (ode15s solver).

Table S2: Constants used for pyrolysis model I.

parameter	Value	Comment
B	5000 °C s ⁻¹ (10000 °C s ⁻¹)	Heating rate of the screens. 5000 °C s ⁻¹ was the experimentally determined value. In the sensitivity analysis also 10 ⁴ °C s ⁻¹ was used.
B'	60 °C s ⁻¹	Cooling rate (measured) of the screens after the holding time.
k _{1,0}	2.8*10 ¹⁹ s ⁻¹	Pre-exponential constant of reaction1 [11]
K _{2,0}	3.2*10 ¹⁴ s ⁻¹	Pre-exponential constant of reaction 2 [11]
E ₁	2.42*10 ⁵ J mol ⁻¹	Activation energy of reaction1 [11]
E ₂	1.98*10 ⁵ J mol ⁻¹	Activation energy of reaction 2 [11]
C _p	1500 J kg ⁻¹ K ⁻¹	Specific heat capacity cellulose [7]
A	0.003 m ²	Estimated based on the porosity of the screens (~0.25), the diameter of the wires (6*10 ⁻⁵ m) and the filling of the cellulose between the wires.
a	10 ³ to ∞ W m ⁻² K ⁻¹	A low estimate of the heat transfer coefficient and infinite.
ΔH ₂	-0.25*10 ⁶ to 0.7*10 ⁶ J kg ⁻¹	Slightly exothermic reaction till heat of evaporation of levoglucosan.

Pyrolysis model II

To predict the trend of the product distribution as function of the temperature model I has been extended by: i) an intermediate / active cellulose phase that consists of heavies (DP_{≥2}) and DP₁, ii) a reaction of heavies to compounds of lower DP that takes place on the sample and iii) a lower escape rates of heavies compared to lights. This is shown schematically in the figure below:

Figure S12: Schematic representation of interpretation model II.

In Figure S12 it is also indicated which reactions proceed on the particle. The vapors are recovered in the condensed product (on the cold wall of the vessel of the screen-heater, see S1). In this model the rate constants k_2 and k_4 only describe the escape rate of the products from the sample which is assumed to be a first order process. k_4 is chosen to be smaller than k_2 in order to describe that the larger sugars have a lower escape rate as compared to DP₁. k_3 is chosen/set arbitrary to 10% of the value of k_2 . k_1 and k_2 are the constants derived by Shafizadeh [11]. Note that the purpose of the model is to investigate if a model including chemical reac-

tions and mass transfer can predict the measured trends in DP-distribution of the condensed product as function of the temperature of the screens not for any quantitative prediction. The latter would need a model that includes independently measured or disentangled values for the rate constants of the chemical reactions on the particle and escape rates (velocity) of products from the sample. The mass balances are:

$$\frac{dM_C}{dt} = -k_1(T_C)M_C \quad (25)$$

$$\frac{dM_{DP_{\geq 2}}}{dt} = k_1(T_C)M_C - (k_3(T_C) + k_4(T_C))M_{DP_{\geq 2}} \quad (26)$$

$$\frac{dM_{DP_1}}{dt} = k_3(T_C)M_{DP_{\geq 2}} - k_2(T_C)M_{DP_1} \quad (27)$$

$$M_S = M_C + M_{DP_{\geq 2}} + M_{DP_1} \quad (28)$$

$$X = 1 - \frac{M_S}{M_{S,0}} \quad (29)$$

In these equations, M_C , $M_{DP_{\geq 2}}$, M_{DP_1} and M_S are the masses of cellulose, $DP_{\geq 2}$, DP_1 and sample respectively, T_C the temperature of the sample (cellulose + $DP_{\geq 2}$ + DP_1) and X the conversion on mass basis. The following energy balance is solved assuming that the heat of reaction 1 is negligible and that the heat effect involved with the escape of (evaporation of) DP_1 and $DP_{\geq 2}$ from the particle is equal on mass basis:

$$\frac{dT_S}{dt} = \frac{A\alpha(T_S - T_C) - (k_2(T_C)M_{DP_1} + k_4(T_C)M_{DP_{\geq 2}})\Delta H}{M_S C_p} \quad (30)$$

In this equation, C_p the heat capacity of the sample, A the area available for heat transfer, ΔH the enthalpy of the evaporation and T_S the temperature of the screen. The temperature of the screens is modelled as described under model 1.

The yields (Y) of DP_1 and $DP_{\geq 2}$ in the condensed product are calculated by:

$$Y_{DP_1} = \frac{\int_{t=0}^{t=\infty} k_2(T_C)M_{DP_1} dt}{M_{S,0}} \quad (31)$$

$$Y_{DP_{\geq 2}} = \frac{\int_{t=0}^{t=\infty} k_4(T_C)M_{DP_{\geq 2}} dt}{M_{S,0}} \quad (32)$$

The initial conditions are: $M_{S,0}$ ($M_{C,0}$) = $2.5 \cdot 10^{-5}$ kg, M_{DP_1} & $M_{DP_{\geq 2}} = 0$,

$$T_{C,0} = 298 \text{ K}, T_{S,0} = 298 \text{ K}$$

In Table S3 the numerical values of the parameters used are listed. The model is solved using Matlab[®] (ode15s solver).

Table S3: Constants used for pyrolysis model II.

parameter	Value	Comment
$k_{1,0}$	$2.8 \cdot 10^{19} \text{ s}^{-1}$	Pre-exponential constant of reaction1 [11]
$K_{2,0}$	$3.2 \cdot 10^{14} \text{ s}^{-1}$	Pre-exponential constant of reaction 2 [11]
E_1	$2.42 \cdot 10^5 \text{ J mol}^{-1}$	Activation energy of reaction1 [11]
E_2	$1.98 \cdot 10^5 \text{ J mol}^{-1}$	Activation energy of reaction 2 [11]
$K_{3,0}$	$3.2 \cdot 10^{13} \text{ s}^{-1}$	10% of $k_{2,0}$ (arbitrary choice)
E_3	$1.98 \cdot 10^5 \text{ J mol}^{-1}$	Equal to E_2 (arbitrary choice)
$K_{4,0}$	$10 \cdot 10^{20} \text{ s}^{-1}$	Overall k lower than k_2 (arbitrary choice)
E_4	$3.0 \cdot 10^5 \text{ J mol}^{-1}$	Overall k lower than k_2 (arbitrary choice)
C_p	$1500 \text{ J kg}^{-1} \text{ K}^{-1}$	Specific heat capacity cellulose [7]
A	0.003 m^2	Estimated based on the porosity of the screens (~ 0.25), the diameter of the wires ($6 \cdot 10^{-5} \text{ m}$) and the filling of the cellulose between the wires.
a	$10^4 \text{ W m}^{-2} \text{ K}^{-1}$	
ΔH	$0.7 \cdot 10^6 \text{ J kg}^{-1}$	Heat of evaporation of levoglucosan [9].

S6. Supporting experimental data

S6.1. Product yields including gas

The product yields as function of the final screen temperature (T_{FS}) can be seen in Figure S13, S14 and S15. The yields are expressed on cellulose basis. Figure S13 shows the condensed product yield as function of T_{FS} . Figure S14 shows the solid residue product left between the screens. Including in this figure are the modelling predictions. Details on the model can be found in S5.2. The gas yield as function of the temperature can be seen in Figure S15. The gas yield does not seem to be much higher than 0.01 kg kg^{-1} cellulose. Although, two points were somewhat higher; they seem to be out layers. Note, experiments were performed at 1 s or 5 s holding time. Four different experimenters we used in these sets of experiments.

Figure S13: Yield of condensed product at 5 mbar as function of temperature, experimenter and holding time.

Figure S14: Yield of solid residue at 5 mbar as function of temperature, experimenter and holding time.

Figure S15: The yield of gas at 5 mbar as function of temperature, experimenter and holding time.

S6.2. Sugars distribution

The DP_1 , DP_2 , DP_3 , DP_{4+5} and $DP_{>5}$ selectivity as function of the temperature are plotted in Figure S16 and S17. The difference between the two figures are the type of trend lines. In Figure S16 the linear fit trend line is shown and in Figure S17 the best-fit trend line. Note, that only in the case of DP_2 the linear fit is the best describing our data and is therefore not depicted in Figure S17. For illustration the linear fit for all DP's are shown. The R^2 for the linear trend lines and the best fit trend lines are shown in Table S4. Again, for DP_1 , DP_3 , DP_{4+5} and $DP_{>5}$ the highest R^2 is for the best model fit option. These trend lines together with the linear fit trend line for DP_2 are used in chapter 2.

Figure S16A: DP_1 selectivity as function of T_{FS} . Dotted line shows trendline for the linear fit. The pressure was 5 mbar.

Figure S16B: DP₂ selectivity as function of T_{FS} . Dotted line shows trendline for the linear fit. The pressure was 5 mbar.

Figure S16C: DP₃ selectivity as function of T_{FS} . Dotted line shows trendline for the linear fit. The pressure was 5 mbar.

Figure S16D: DP_{4+5} selectivity as function of T_{FS} . Dotted line shows trendline for the linear fit. The pressure was 5 mbar.

Figure S16E: $DP_{>5}$ selectivity as function of T_{FS} . Dotted line shows trendline for the linear fit. The pressure was 5 mbar.

Figure S17A: DP_1 selectivity as function of T_{FS} . Dotted line shows trendline for the best fit (exponential model ($a \cdot \exp(-b \cdot x) + c$)). The pressure was 5 mbar.

Figure S17B: DP_3 selectivity as function of T_{FS} . Dotted line shows trendline for the best fit (exponential model ($a / (1 + \exp(-b \cdot (x - c)))$)). The pressure was 5 mbar.

Figure S17C: DP_{4+5} selectivity as function of T_{FS} . Dotted line shows trendline for the best fit (exponential model ($a/(1+\exp(-b*(x-c)))$)). The pressure was 5 mbar.

Figure S17D: $DP_{>5}$ selectivity as function of T_{FS} . Dotted line shows trendline for the best fit (exponential model ($a/(1+\exp(-b*(x-c)))$)). The pressure was 5 mbar.

Table S4: Curve fitting summary, linear fit vs exponential fit .

	DP ₁	DP ₂	DP ₃	DP ₄₊₅	DP ₄	DP ₅	DP _{>5}
Linear model							
SSE	0.063	0.015	0.016	0.015	0.007	0.003	0.008
R ²	0.744	0.561	0.495	0.900	0.833	0.907	0.794
Exponential model							
SSE	0.028	-	0.008	0.011	0.005	0.003	0.008
R ²	0.887	-	0.751	0.927	0.882	0.924	0.798

S6.3. Hydrolysis results

The condensed product contains a wide range of DP's. A rough estimation of the total amount of anhydrosugars in the oil can be obtained by hydrolysis of the condensed product to produce glucose. These sugars are often referred to as hydrolysable sugars. The hydrolysis efficiency, in other words the glucose recovery, of the condensed product was estimated by hydrolyzing glucose, levoglucosan and cellobiosan. The result are presented in Table S5. As can be observed, the glucose recovery decreases significantly for cellobiosan compared to levoglucosan. Therefore, it is decided that the glucose recovery of the condensed product should be corrected for the obtained efficiencies, see Formula 33. The R is the glucose recovery from DP₁ or DP₂, S_{DP1} is the selectivity of DP₁. The selectivity is defined as the specific sugar concentration divided by the total sugar concentration detected. The glucose recovery is expressed as the amount of carbon recovered in glucose divided by the amount of carbon originally in the cellulose.

Table S5: Recovery of glucose, levoglucosan and cellobiosan after hydrolysis at 120 °C, 3.5 vol% H₂SO₄ and 1 h.

Glucose		Levoglucosan		Cellobiosan	
Sample concentration (mg ml ⁻¹)	Glucose recovery (wt% sample)	Sample concentration (mg ml ⁻¹)	R _{DP1} : Glucose recovery (wt% sample)	Sample concentration (mg ml ⁻¹)	R _{DP2} : Glucose recovery (wt% sample)
5	95.8	5	92.2	5	83.3
10	95.3	10	91.7	10	85.1
15	92.4	15	95.2	15	84.5
average	94.5	average	93.1	average	84.3

$$\frac{C_{Glucose}}{C_{Cellulose}} \left[\frac{g}{g} \right] = \frac{\frac{M_{Glucose}}{M_{Cellulose}} * \frac{162}{180}}{(1 - Cellulose_{ejected}) * (S_{DP1} * R_{DP1} + (1 - S_{DP1}) * R_{DP2})} \quad (33)$$

S6.4. LCMS results

Figure S18 shows the spectra of a typical oil produced at 725 °C. The peak at 8.83 min represents the compounds, in our work, lumped as DP_{>5}. The mass spectra measured at 8.83 min is presented in Figure S19. As can be seen this fraction contains indeed many large compounds up to DP₁₁. The smaller compounds like DP₂ etc. are fragmentation products produced during ionization of the large sugars, a well-known feature of the MS. Note, the peak intensities around 191 and 391 are background noise.

Figure S18: Full LC/MS chromatogram of the condensed product. 725 °C and 5 mbar.

Figure S19: peak intensities (mass spectra) at a retention time of ~8.8 min.

In all HPLC and LC/MS spectra's typically 3 peaks can be observed between DP_1 and DP_2 . No standards were found that could be used to identify these peaks. Therefore, LC/MS analysis was used to get a rough idea about the composition of these compounds. In Figure S20 a spectra of the oil produced at 524 °C is shown. The levoglucosan (DP_1) and cellobiosan (DP_2) peaks are highlighted as well as the peaks between, numbered 1, 2 and 3. The mass spectra of these compounds can be seen in Figure S21. The numbers in the mass spectra correspond to the numbers in Figure 20. As can be seen a clear peak appears around 342 in all spectra's representing the same mass as cellobiosan. Therefore, it is likely that these peaks between DP_1 and DP_2 represent isomers of cellobiosan. Note, the peaks 191 and 390 are background noise.

Figure S20: LC/MS spectra of a condensed product produced at 524 °C. The reactor pressure was 5 mbar. Highlighted are Levoglucosan, cellobiosan and the peaks termed; between DP_1 - DP_2 (3 peaks).

S6.5. FTIR

FTIR analysis have been performed on levoglucosan, cellobiosan, cellotriosan, cellotetrasan and cellulose. The FTIR spectra of the anhydrosugars are compared with the FTIR spectra of cellulose to identify the mean peak differences. The results can be seen in Figure S22. The biggest difference between cellulose and the anhydrosugars (DP_1 - DP_4) is highlighted with an arrow (solid line). Some additional peaks appear for the DP_1 - DP_4 sugars which were absent in the spectra of cellulose and vice versa. This information will be used to find out whether the ejected cellulose spectra compares to cellulose or the anhydrosugars.

Figure S21: Mass spectra of Peak 1, 2, 3 and cellobiosan.

Figure S22: FTIR spectra of Levoglucosan (top), cellobiosan, cellotriosan, cellotetrasan and cellulose (bottom).

Figure S23: FTIR spectra of water soluble condensed product, cellotetrasan, cellulose and ejected cellulose. The arrows highlight the differences between the spectra's. The two spectra at the bottom are cellulose and ejected cellulose. The two spectra at the top are cellotetrasan and condensed product.

Figure S24: FTIR spectra of avicel cellulose and char obtained from avicel cellulose. The residues between the screens were obtained after pyrolysis at 331 °C, 371 °C, and 390 °C under 5 mbar.

Figure S23 shows the spectra of a water soluble condensed product, cellotetrasan, cellulose and ejected cellulose. The two spectras at the bottom are cellulose and ejected cellulose. The two spectras at the top are cellotetrasan and condensed product. As can be seen the spectra of ejected cellulose looks similar to the initial cellulose whereas the spectra of the water soluble condensable product is comparable with the spectra of cellotetrasan.

The FTIR spectra of avicel cellulose, char obtained from avicel cellulose and the residues between the screens after the screen heater experiments can be seen in Figure S24. The screen heater experiments were performed at 331 °C, 371 °C and 390 °C. The char was obtained from a pyrolysis experiment performed with avicel cellulose at 530 °C in an oven in a nitrogen environment. As can be seen the residue between the screens show a similar spectra as the cellulose. Moreover, the spectra of the char is clearly different as the rest.

S6.6. Pyrolysis experiments with levoglucosan (DP₁) and cellobiosan (DP₂)

Levoglucosan was pyrolyzed at various temperatures and pressures, see Table S6. The results of these levoglucosan experiments are almost the same for all temperatures and pressures (1mbar – 889 mbar): there is no residue or gas fraction found after the experiment, the entire sample is converted to condensed product. HPLC analysis shows that for both temperatures the condensed product consists of only levoglucosan. This is supported by the observation that the condensed product present on the vessel wall still has the original white colour of levoglucosan.

Table S6: Product yields (kg kg⁻¹ levoglucosan) for levoglucosan feedstock at varied temperatures and pressures

Temp (°C)	Pressure (mbar)	Holding Time (s)	Condensed product (kg kg ⁻¹)	Gas (kg kg ⁻¹)	Residue (kg kg ⁻¹)	DP ₁ (kg kg ⁻¹)	DP ₂ (kg kg ⁻¹)
270	5	1	0.96	<0.01	<0.01	0.96	N.D.
585	5	1	0.97	<0.01	<0.01	0.97	N.D.
484	479	1	0.90	<0.01	<0.01	0.90	N.D.
488	889	1	0.88	<0.01	<0.01	0.88	N.D.

N.D. not detected

Table 7: Product yields (kg kg⁻¹ cellobiosan) for cellobiosan experiments at different temperatures and pressures

Temp (°C)	Pressure (mbar)	Holding Time (s)	Condensed product (kg kg ⁻¹)	Gas (kg kg ⁻¹)	Residue (kg kg ⁻¹)	DP ₁ (kg kg ⁻¹)	DP ₂ (kg kg ⁻¹)
333	1	5	0.43	<0.01	0.53	0.02	0.40
345	1	5	0.75	<0.01	0.15	0.04	0.71
603	1	1	0.94	<0.01	0.06*	0.00	0.94
500	93	5	0.97	0.01	0.03*	0.05	0.80
500	946	5	0.68	0.03	0.18*	0.28	0.37

* Residue was located between the clamps which remain colder during the experiments. The residue was still white which indicates unreacted cellobiosan.

Cellobiosan was pyrolyzed at various temperatures and pressures, see Table S7. The results for the cellobiosan experiments show that besides evaporation also some cracking to levoglucosan has occurred, especially at low temperatures and increased pressures, see Figure S25. No polymerization products were observed. Due to the high hygroscopicity of cellobiosan the standard method of applying an equal thin layer with a sieve was not possible. Therefore a concentrated mixture of cellobiosan with water was smeared as a thin layer on a screen.

This method is less precise and therefore a small amount of sample was located between the electrodes, this was also the location where the residue was found after pyrolysis at 610 °C and 5 mbar. FTIR analysis of the residue at low temperature and low pressure shows that the residue is unreacted cellobiosan (not shown).

Figure S25: HPLC spectra of condensed product from cellobiosan pyrolysis. The temperature was 500 °C and pressure 5 mbar.

S6.7. Summary of all screen heater experimental data

Table S8: Overview of yields (g g⁻¹ cellobiosan) for cellobiosan experiments at different temperatures and pressures

General Information				Sample (cellulose) weight based				Sample (cellulose) weight based corrected for ejected cellulose				Oil composition (measured by HPLC), wt fraction in oil								
Experimenter	T _{PS}	Pressure	Holding Time	Condensed product yield			Sample (cellulose) weight based		Sample (cellulose) weight based corrected for ejected cellulose		DP ₁	DP ₂	DP ₁ - DP ₂	DP ₃	DP ₄	DP ₅	DP _{>5}	Total		
				Gas Yield	Residue Yield	Ejected cellulose Yield	CP Yield	Gas Yield	Residue Yield	(kg kg ⁻¹ condensed product)										
(-)	(°C)	(mbar)	(s)	(kg kg ⁻¹ Cellulose)			(kg kg ⁻¹ Cellulose)							(kg kg ⁻¹ condensed product)						
1	331	≤ 5	5	0.04	≤ 0.01	0.91	≤ 0.01	0.04	≤ 0.01	0.91	0.41	0.04	0.17	0.08	0.03	0.02	0.05	0.80		
1	371	≤ 5	5	0.61	≤ 0.01	0.29	0.04	0.59	≤ 0.01	0.30	0.46	0.19	0.20	0.07	0.01	0.00	0.00	0.93		
1	390	≤ 5	5	0.87	≤ 0.01	0.04	0.06	0.87	≤ 0.01	0.05	0.37	0.24	0.20	0.12	0.06	0.01	0.00	1.00		
1	400	≤ 5	5	0.92	≤ 0.01	0.03	0.01	0.92	≤ 0.01	0.03	0.33	0.23	0.15	0.10	0.04	0.01	0.01	0.88		
2	411	≤ 5	5	0.88	ND	0.03	0.01	0.88	ND	0.03	0.38	0.24	0.17	0.10	0.03	0.01	0.01	0.95		
3	415	≤ 5	5	0.88	0.01	0.06	0.01	0.88	0.01	0.06	0.30	0.16	0.07	0.09	0.03	0.00	0.00	0.66		
2	421	≤ 5	5	0.88	ND	0.04	0.01	0.88	ND	0.04	0.31	0.20	0.15	0.09	0.03	0.01	0.01	0.79		
2	443	≤ 5	5	0.99	ND	≤ 0.01	0.09	0.99	ND	0.01	0.30	0.29	0.17	0.15	0.07	0.03	0.03	1.04		
2	447	≤ 5	5	0.85	ND	0.06	0.01	0.85	ND	0.06	0.37	0.28	0.18	0.11	0.04	0.01	0.01	1.00		
2	456	≤ 5	5	0.95	ND	≤ 0.01	0.02	0.95	ND	≤ 0.01	0.28	0.29	0.16	0.14	0.06	0.03	0.03	0.99		
2	468	≤ 5	5	0.95	ND	0.01	0.02	0.95	ND	0.01	0.21	0.24	0.19	0.16	0.08	0.03	0.02	0.92		
2	469	≤ 5	5	0.97	ND	≤ 0.01	0.01	0.97	ND	≤ 0.01	0.33	0.26	0.16	0.12	0.04	0.01	0.01	0.93		
1	479	≤ 5	1	0.98	0.02	≤ 0.01	0.01	0.98	0.02	≤ 0.01	0.24	0.25	0.16	0.16	0.07	0.02	0.01	0.92		

2	482	≤ 5	5	0.93	ND	0.01	≤ 0.01	0.93	ND	0.01	0.30	0.25	0.18	0.11	0.04	0.01	0.01	0.91
2	485	≤ 5	5	0.97	ND	≤ 0.01	0.01	0.97	ND	≤ 0.01	0.28	0.25	0.17	0.15	0.07	0.03	0.02	0.97
3	513	≤ 5	5	0.85	0.01	0.01	≤ 0.01	0.85	0.01	0.01	0.26	0.24	0.22	0.20	0.12	0.04	0.02	1.10
3	520	≤ 5	5	0.89	0.01	≤ 0.01	≤ 0.01	0.89	0.01	≤ 0.01	0.25	0.25	0.20	0.19	0.09	0.03	0.02	1.02
4	526	≤ 5	5	0.98	0.01	0.01	0.01	0.98	0.01	0.01	0.20	0.24	0.18	0.19	0.11	0.06	0.04	1.01
4	535	≤ 5	5	0.94	0.01	0.01	0.04	0.94	0.01	0.01	0.20	0.24	0.23	0.22	0.13	0.07	0.03	1.12
4	536	≤ 5	5	0.96	0.01	0.01	0.03	0.96	0.01	0.01	0.20	0.23	0.18	0.19	0.12	0.06	0.05	1.02
2	537	≤ 5	5	0.94	ND	0.01	0.01	0.94	ND	0.01	0.21	0.24	0.16	0.17	0.09	0.04	0.04	0.94
2	555	≤ 5	5	0.96	ND	≤ 0.01	0.02	0.96	ND	≤ 0.01	0.18	0.21	0.16	0.15	0.08	0.04	0.06	0.88
2	610	≤ 5	5	0.94	ND	≤ 0.01	0.01	0.94	ND	≤ 0.01	0.15	0.21	0.16	0.19	0.12	0.07	0.09	0.99
3	641	≤ 5	5	0.91	0.01	≤ 0.01	0.03	0.91	0.01	≤ 0.01	0.26	0.19	0.14	0.13	0.08	0.06	0.06	0.92
2	648	≤ 5	5	1.00	ND	0.01	0.06	1.00	ND	0.01	0.12	0.16	0.15	0.17	0.13	0.09	0.05	0.87
3	707	≤ 5	5	0.97	0.01	≤ 0.01	0.03	0.97	0.01	≤ 0.01	0.11	0.15	0.13	0.16	0.12	0.10	0.10	0.86
1	725	≤ 5	1	0.95	0.01	≤ 0.01	≤ 0.01	0.95	0.01	≤ 0.01	0.15	0.15	0.15	0.17	-	-	-	-
1	726	≤ 5	1	0.94	0.01	≤ 0.01	≤ 0.01	0.94	0.01	≤ 0.01	0.17	0.18	0.09	0.16	0.15	0.09	0.07	0.91
1	755	≤ 5	1	0.94	0.01	≤ 0.01	0.04	0.94	0.01	≤ 0.01	0.14	0.18	0.14	0.17	0.13	0.10	0.06	0.93
3	765	≤ 5	5	0.95	0.01	≤ 0.01	0.04	0.94	0.01	≤ 0.01	0.11	0.15	0.12	0.16	0.13	0.11	0.13	0.91

ND: Not detected

NM: Not measured

General Information			Sample (cellulose) weight based				Sample (cellulose) weight based corrected for ejected cellulose			Oil composition (measured by HPLC), wt fraction in oil								
Experimenter	T _{FS}	Pressure	Holding Time	Condensed Product yield	Gas Yield	Residue Yield	Ejected cellulose	CP Yield	Gas Yield	Residue Yield	DP ₁	DP ₂	DP ₁ - DP ₂	DP ₃	DP ₄	DP ₅	DP _{>5}	Total
(-)	(°C)	(mbar)	(s)	(kg kg ⁻¹ Cellulose)			(kg kg ⁻¹ condensed product)											
Cellulose (Screen Heater; Vacuum; without HPLC Analysis)																		
2	338	≤ 5	1	0.07	≤ 0.01	0.89	≤ 0.01	0.07	≤ 0.01	0.89	ND	ND	ND	ND	ND	ND	ND	ND
2	388	≤ 5	1	0.80	≤ 0.01	0.19	≤ 0.01	0.80	≤ 0.01	0.19	ND	ND	ND	ND	ND	ND	ND	ND
2	460	≤ 5	1	0.93	≤ 0.01	-0.03	≤ 0.01	0.93	≤ 0.01	-0.03	ND	ND	ND	ND	ND	ND	ND	ND
2	527	≤ 5	1	0.96	≤ 0.01	≤ 0.01	0.01	0.96	≤ 0.01	≤ 0.01	ND	ND	ND	ND	ND	ND	ND	ND
2	539	≤ 5	1	0.93	≤ 0.01	≤ 0.01	0.01	0.93	≤ 0.01	≤ 0.01	ND	ND	ND	ND	ND	ND	ND	ND
2	540	≤ 5	1	0.93	≤ 0.01	≤ 0.01	0.06	0.93	≤ 0.01	≤ 0.01	ND	ND	ND	ND	ND	ND	ND	ND
2	551	≤ 5	1	1.03	≤ 0.01	≤ 0.01	≤ 0.01	1.03	≤ 0.01	≤ 0.01	ND	ND	ND	ND	ND	ND	ND	ND
Cellulose (Screen Heater & Fluidized Bed Reactor; Atmospheric)																		
3	530	1000	5	0.83	0.01	0.01	0.02	0.83	0.01	0.01	0.38	0.13	0.20	0.04	0.01	0.01	0.01	0.78
5	530	1000	-	0.84	0.01	0.01	≤ 0.01	0.84	0.01	0.01	0.47	0.06	0.22	0.04	0.01	0.00	0.01	0.80
3	545	1000	5	0.83	0.02	0.01	≤ 0.01	0.83	0.02	0.01	0.41	0.08	0.18	0.06	0.02	0.01	0.01	0.77
Levoglucosan and Cellobiosan (Screen Heater; Vacuum)																		
2	535	1000	5	0.88	ND	≤ 0.01	≤ 0.01	0.88	ND	≤ 0.01	0.89	0.00	0.01	0.00	0.00	0.00	0.00	0.90
2	536	450	5	0.90	ND	≤ 0.01	≤ 0.01	0.90	ND	≤ 0.01	0.86	0.00	0.00	0.00	0.00	0.00	0.00	0.86

2	415	1000	5	0.68	ND	0.18	≤ 0.01	0.68	ND	0.18	0.29	0.42	0.09	0.06	0.02	0.02	0.01	0.90
2	765	100	5	0.97	ND	0.03	≤ 0.01	0.97	ND	0.03	0.05	0.83	0.03	0.02	0.02	0.00	0.00	0.96
Experiment with gold sputtered screen (Screen Heater; Vacuum)																		
2	526	≤ 5	1	0.98	≤ 0.01	≤ 0.01	≤ 0.01	0.98	≤ 0.01	≤ 0.01	0.22	0.20	0.12	0.13	0.04	0.05	0.00	0.76

ND: Not detected
NM: Not measured

General Information				Product yield (cellulose basis, corrected for the ejected cellulose)									
Experimenter	T _{FS}	Pressure	Holding Time	DP ₁	DP ₂	DP ₁ - DP ₂	DP ₃	DP ₄	DP ₅	DP _{>5}	DP ₄ + DP ₅	Total by HPLC	CP minus sugar by HPLC
(-)	(°C)	(mbar)	(s)	(kg kg ⁻¹ cellulose)									
				Cellulose (Screen Heater; Vacuum)									
1	331	≤ 5	5	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.04	-0.01
1	371	≤ 5	5	0.27	0.11	0.12	0.04	0.01	0.00	0.00	0.01	0.55	-0.04
1	390	≤ 5	5	0.32	0.21	0.17	0.10	0.05	0.00	0.00	0.06	0.87	0.00
1	400	≤ 5	5	0.30	0.21	0.14	0.09	0.03	0.01	0.01	0.05	0.80	-0.11
2	411	≤ 5	5	0.33	0.21	0.15	0.09	0.03	0.01	0.01	0.04	0.83	-0.05
3	415	≤ 5	5	0.26	0.15	0.06	0.08	0.03	0.00	0.00	0.03	0.58	-0.30
2	421	≤ 5	5	0.27	0.17	0.13	0.08	0.03	0.01	0.01	0.04	0.70	-0.18
2	443	≤ 5	5	0.30	0.29	0.17	0.15	0.07	0.03	0.03	0.10	1.04	0.04
2	447	≤ 5	5	0.31	0.24	0.16	0.10	0.03	0.01	0.01	0.04	0.84	0.00
2	456	≤ 5	5	0.27	0.27	0.15	0.13	0.05	0.03	0.03	0.08	0.94	-0.01
2	468	≤ 5	5	0.20	0.22	0.18	0.15	0.07	0.02	0.02	0.10	0.87	-0.07
2	469	≤ 5	5	0.32	0.25	0.16	0.11	0.04	0.01	0.01	0.05	0.91	-0.06
1	479	≤ 5	1	0.23	0.24	0.16	0.15	0.07	0.02	0.01	0.10	0.90	-0.08
2	482	≤ 5	5	0.28	0.23	0.16	0.10	0.04	0.01	0.01	0.05	0.85	-0.09
2	485	≤ 5	5	0.28	0.25	0.16	0.15	0.07	0.03	0.02	0.09	0.95	-0.02

3	513	≤ 5	5	0.22	0.21	0.19	0.17	0.10	0.03	0.02	0.13	0.93	0.08
3	520	≤ 5	5	0.22	0.22	0.18	0.17	0.08	0.02	0.02	0.11	0.91	0.02
4	526	≤ 5	5	0.20	0.23	0.17	0.19	0.11	0.06	0.04	0.16	0.99	0.01
4	535	≤ 5	5	0.19	0.23	0.21	0.20	0.12	0.07	0.03	0.19	1.06	0.11
4	536	≤ 5	5	0.19	0.22	0.17	0.18	0.11	0.05	0.04	0.17	0.97	0.02
2	537	≤ 5	5	0.20	0.22	0.15	0.16	0.08	0.04	0.04	0.12	0.88	-0.06
2	555	≤ 5	5	0.18	0.20	0.16	0.14	0.07	0.04	0.06	0.11	0.85	-0.11
2	610	≤ 5	5	0.14	0.20	0.15	0.18	0.11	0.06	0.08	0.17	0.93	-0.01
3	641	≤ 5	5	0.23	0.17	0.13	0.12	0.07	0.05	0.06	0.12	0.83	-0.07
2	648	≤ 5	5	0.12	0.16	0.15	0.17	0.13	0.09	0.05	0.22	0.87	-0.13
3	707	≤ 5	5	0.11	0.15	0.12	0.16	0.11	0.09	0.10	0.21	0.84	-0.14
1	725	≤ 5	1	0.14	0.14	0.14	0.16	-	-	-	-	0.59	-0.36
1	726	≤ 5	1	0.16	0.13	0.09	0.13	0.14	0.09	0.05	0.19	0.79	-0.15
1	755	≤ 5	1	0.13	0.17	0.13	0.16	0.12	0.09	0.06	0.21	0.87	-0.06
3	765	≤ 5	5	0.10	0.14	0.11	0.15	0.12	0.11	0.12	0.22	0.86	-0.09

ND: Not detected
NM: Not measured

General Information				Product yield (cellulose basis, corrected for the ejected cellulose)									
Experimenter	Final Mesh Temperature	Pressure	Holding Time	DP ₁	DP ₂	DP ₁ - DP ₂	DP ₃	DP ₄	DP ₅	DP _{>5}	DP ₄ + DP ₅	Total by HPLC	CP minus sugar by HPLC
[-]	[°C]	[mbar]	[s]	(kg kg ⁻¹ cellulose)									
2	338	≤ 5	1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	388	≤ 5	1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	460	≤ 5	1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	527	≤ 5	1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	539	≤ 5	1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	540	≤ 5	1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	551	≤ 5	1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cellulose (Screen Heater & Fluidized Bed Reactor; Atmospheric)													
3	530	1000	5	0.32	0.10	0.17	0.04	0.01	0.01	0.01	0.02	0.65	-0.18
5	530	1000	-	0.39	0.05	0.19	0.03	0.01	0.00	0.01	0.01	0.68	-0.17
3	545	1000	5	0.34	0.07	0.15	0.05	0.01	0.01	0.01	0.02	0.64	-0.19
Levoglucosan and Cellobiosan (Screen Heater; Vacuum)													
2	535	1000	5	0.78	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.79	-0.08
2	536	450	5	0.77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.77	-0.12
2	415	1000	5	0.20	0.28	0.06	0.04	0.02	0.01	0.00	0.03	0.62	-0.07

2	765	100	5	0.05	0.81	0.03	0.02	0.02	0.00	0.00	0.02	0.93	-0.04
				Experiment with gold sputtered screen (Screen Heater; Vacuum)									
2	526	≤ 5	1	0.21	0.20	0.11	0.13	0.04	0.05	0.00	0.09	0.75	-0.23

ND: Not detected
NM: Not measured

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Appendix E

Supporting information Chapter 4

Figure S1: Area of the GPC spectra measured at 254 nm. The spectra were integrated with respect to the eluent volume.

Figure S2A: UV-fluorescence spectra of model compounds.

Figure S2B: UV-fluorescence spectra of model compounds.

Figure S2C: UV-fluorescence spectra of model compounds.

Figure S2D: UV-fluorescence spectra of model compounds.

Figure S3: Model compounds used in UV- fluorescence spectrometer.

Appendix F

Supporting information Chapter 5

S1. Acid leaching experiments

S1.1. Materials and methods

Materials

Pinewood fibers (Lignocel 9) were purchased from Rettenmaier & Söhne GmbH. The fibers were used after sieving (sieve fraction 0.5 mm -2 mm) or after ball milling (ceramic balls for 24 h). Ball milling was applied to destroy the fibrous structure ($<125\text{ }\mu\text{m}$, referred to as cell wall material) [78], thereby minimizing the mass transfer of ions (via diffusion) within the pores to the bulk liquid. Cylindrical pinewood rods (diameter 27 mm) were purchased from Koninklijke Jongeneel B.V. and cut to the desired length (0.5, 1 and 4 cm). Wheat straw was purchased from Praxis (brand Puik) and chopped to obtain a sieve fraction of 0.5 mm -1 mm (batch 2 in chapter 3). All biomasses were dried in an oven at $105\text{ }^{\circ}\text{C}$ for 24 h prior to the experiments. Acetic acid (Assink Chemie 70 wt%, diluted further with Milli-Q water) and demineralized water (Milli-Q) were used as leaching solutions. Table S1 shows the specific AAEM concentrations in the biomasses used for the leaching tests.

Table S1: AAEM content of the biomass used for the leaching experiments

	Pinewood fibres	Straw fibres	Pinewood rods
Na^{+}	60	117	50
K^{+}	398	12595	190
Mg^{2+}	387	427	150
Ca^{2+}	1771	2068	740
sum (AAEMs)	2616	15207	1130

Biomass leaching method

Pinewood (particles and rods) and straw (particles) were leached in a 1 liter vessel (0.1 kg dry biomass per kg of leaching solution) under continuous stirring (see Figure S1). In case of pinewood rods the mixer was replaced by a pump, to circulate the washing liquid, and a screen was added on top to fix the biomass rods under the liquid level (see Figure S2). The temperature of the double walled vessel was controlled using a thermostatic water bath at $30\text{ }^{\circ}\text{C}$. Samples of the liquid phase were taken and analyzed for their Na, K, Mg and Ca content using ICP. (Sequential ICP-OES with a radial plasma (Varian Liberty II)). After the leaching experiments the ash remaining in the particles was analyzed after dry oxidation at $575\text{ }^{\circ}\text{C}$ for 24 h. The obtained ash was dissolved in 2 % mass fraction nitric acid and analyzed by ICP.

Figure S1: Setup used for leaching experiments of pinewood cell wall and pinewood/straw fibers.

Figure S2: Setup used for leaching experiments of pinewood rods

S1.2. Results

Pinewood fibers (sieve fraction 0.5 mm – 2 mm) were ball milled to destroy the fibrous structure of the pinewood [78]. The obtained material (sieve fraction $<125\text{ }\mu\text{m}$), referred to as cell wall, was leached with diluted acetic acid (mass fraction 10 %) at 30 °C to determine whether the AAEM removal rate is limited by mass transfer within the solid structure. The removal of potassium and calcium from the cell wall material and original pinewood fibers (sieve fraction 0.5 mm – 2 mm) as function of the leaching time are presented in Figure S3A. Due to the heterogeneous biomass micro structure it is difficult to relate the particle size to the AAEM removal rate, however it can be expected that the main mass transfer limitation is within the pores in longitudinal direction. Therefore cylindrical pinewood rods, with a “pore” length of 5, 10 and 40 mm (cut in tangential direction) and a diameter of 27 mm, were leached with 10% acetic acid at 30 °C. The removal of potassium from the cylindrical rods as function of the leaching time is shown in Figure S3B. As can be seen from the graphs, the removal of calcium and potassium from the cell wall material was almost instantaneous whereas the removal from the cylindrical rods took hours or days. Sodium (not shown) showed a comparable behavior as potassium and magnesium (not shown) a comparable behavior as calcium. The results show that the AAEM removal rate is determined by mass transfer in the biomass pores, rather than mass transfer in the cell wall. Analysis of the ashes from the leached pinewood fibers and cell wall material (see Figure S4) showed that the remaining ash had a comparable AAEM composition, this shows that the incomplete removal of AAEMs from wood fibers (as found for all biomasses tested in [6]) was not improved by intensive milling.

Figure S3A: Removal of potassium and calcium from cell wall material (pinewood < 125 μm).

Figure S3B: Removal of potassium and calcium from cylindrical pinewood rods with a diameter of 27 mm.

Figure S4: Ash composition before and after acid leaching for pinewood fibers (sieve fraction 0.5mm - 2mm) and cell wall material (<125 µm).

Previous pyrolysis experiments showed that in case of high AAEM content biomass the amount of (acetic) acids produced was not sufficient to dissolve both the mono and divalent AAEMs [5]. Based on the water leaching results of Jenkins et al. [12] and Turn et al. [10] it can be expected that a large fraction of the monovalent AAEMs, i.e. potassium and sodium, can already be removed by leaching with water. To validate this, pinewood fibers (sieve fraction 0.5 mm – 2 mm) and wheat straw fibers (sieve fraction 0.5 mm - 1 mm) were leached with demineralized water at 30 °C. The removal of potassium and calcium from the biomass particles versus the leaching time is shown in Figure S5. It can be seen that most of the potassium could be removed from the biomass by water leaching, i.e. 75% to 90% relative to washing with dilute acetic acid. Water leaching also removed 20% of the calcium. Note, this result is influenced by the fact that the solubility in water is not entirely zero. Although the AAEM content of untreated wheat straw is significantly higher compared to untreated pinewood, the rate of AAEM removal via both water and acid leaching was approximately the same. Identically to the acid leaching results, sodium (not shown) showed comparable behavior as potassium and the results of magnesium (not shown) were comparable to calcium. It can be seen that potassium and calcium reach a stable concentration within 10 minutes.

Figure S5A: Removal of potassium and calcium from pinewood fibers (0.5 mm - 2 mm) using water and 10 % mass fraction acetic acid.

Figure S5B: Removal of potassium and calcium from straw (0.5 mm - 2 mm) using water and 10 % mass fraction acetic acid.

Attempts have been made to model the leaching of AAEM ions from softwood particles. Saltberg et al found that the leaching of calcium from well-defined sawn wood particles (40 mm x 25 mm x 7 mm) could be described by a diffusion model with 2 different diffusion coefficients (longitudinal and radial direction) [79]. The determined diffusion coefficients were $5.9 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ in the longitudinal direction and $0.41 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ in the radial direction of the wood particle at 60 °C [79], which are in the same range of the diffusivity of calcium in water (Ca^{+} in water, $7.9 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ at 25 °C [80]). It was found that increasing the leaching temperature matched with the rule of thumb that the diffusion coefficient increases by a factor 1.3 for a 10 °C temperature increase [79]. The model was extended to deal with heterogeneities (e.g. cracks, rough surface and particle size distribution) from industrial cut wood chips based on fitting [79]. Another model describing the diffusion of dissolved ions through wood was developed by Behr et al in 1952 [81]. This model includes many biomass parameters, such as wood cell characteristics (e.g. fractional void volume and cross sectional area of fiber cavities of swollen wood) and information on the bordered pits (e.g. number of pit membranes and average pit membrane thickness) [81].

To get an idea of the required leaching time for various pore lengths a simple 1D 2nd order diffusion model with the diffusivities of potassium and sodium was solved. The used boundary conditions are shown below. The partial differential equation was solved numerically using Matlab®. These results are represented by the dashed lines in Figure S6 and Figure S7. These figure includes also the experimental determined AAEM content in the pinewood fibers and ball milled fibers versus the acid leaching time at 30 °C. It was found that the AAEM were removed from the fibers (sieve fraction 0.5 mm – 2 mm, average size of 1 mm) faster than expected based on the diffusion model whereas the pinewood rods were slower. The later can be explained by the slow transport of water into the particle pores (which were still floating to the screen in the leaching reactor after several hours). It should be noticed that the sieve size doesn't have to correspond with the pore length. This shows that the leaching rate largely depends on the particle geometry caused by the grinding technique and wetting rate. Both of the aforementioned models are not capable to solve these problems without performing detailed analysis of the grinded feedstock. Therefore it is expected that a leaching experiment with a grinded feed will cost less time than characterizing the heterogeneities caused by industrial chipping. For this design study particle sizes in the range of 2 mm (sieve fraction) for straw and wood were selected. For bagasse it was assumed that no size reduction is required since the size and structure has been altered before and during sugar extraction.

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

With initial condition ($t=0$) $c=1$, and boundary conditions

$$x = 0 \rightarrow \frac{\partial c}{\partial x} = 0 \quad x = L \rightarrow c = 0.1$$

Figure S6A: Effect of particle size on the potassium removal as function of time. Symbols are experimental data, lines are the results of the 1D diffusion model. Diffusion coefficient for potassium ($D=19.6 \cdot 10^{-10} \text{ m s}^{-1}$) in water from [80].

Figure S6B: Effect of particle size on the potassium removal as function of time. Symbols are experimental data, lines are the results of the 1D diffusion model. Diffusion coefficient for potassium ($D=19.6 \cdot 10^{-10} \text{ m s}^{-1}$) in water from [80].

Figure S7A: Effect of particle size on the calcium removal as function of time. Symbols are experimental data, lines are the results of the 1d diffusion model. Diffusion coefficient for calcium ($D=7.9 \cdot 10^{-10} \text{ m s}^{-1}$) in water from [80].

Figure S7B: Effect of particle size on the calcium removal as function of time. Symbols are experimental data, lines are the results of the 1d diffusion model. Diffusion coefficient for calcium ($D=7.9 \cdot 10^{-10} \text{ m s}^{-1}$) in water from [80].

S2. Process flow sheets

Figure S8: Schematic overview of the pretreatment section for untreated pinewood and straw cases.

Figure S9: Schematic overview of the pyrolysis and combustion and oil recovery section for untreated pinewood and straw cases.

Figure S10: Schematic overview of the pretreatment section for untreated bagasse case.

Figure S11: Schematic overview of the pyrolysis, combustion and oil recovery section for untreated bagasse case.

S3. Aspen Plus® model and assumptions

The flowsheets made for pyrolyzing untreated and acid leached bagasse were translated into three different Aspen Plus® (V8.6) models. The model based on the flowsheet for the pyrolysis of acid leached biomass (Figure 6 and Figure 7) is visualized in Figure S12. The model for the pyrolysis of untreated bagasse (Figure S10 and Figure S11) is shown in Figure S13, whereas the model for the pyrolysis of untreated pinewood and straw (Figure S8 and Figure S9) is shown in Figure S14. The models were divided in three different sections (hierarchy blocks), i.e. pretreatment, pyrolysis and utilities. The use of hierarchy blocks allows the use of different physical property methods for the different sections (only electrolyte method for pretreatment). For the pyrolysis of acid leached biomass the pretreatment section corresponds with the flowsheet in Figure 6 and the pyrolysis and utilities block with the flowsheet shown in Figure 7. First the general model is discussed where after each of the different sections are discussed in more detail.

The 3 biomasses were modeled as non-conventional solids. The property models HCOAL-GEN and DCOALIGT were used to estimate the biomass enthalpy of formation, specific heat capacity and density based on the ultimate (presented in Table 1) and proximate analyses (moisture 0%, fixed carbon(FC) 19.5 %, volatile mater calculated as 100%-ash-FC) of the dry biomasses. The moisture was treated separately as a MIXED stream. The inorganic compounds in the biomass were specified as K_2CO_3 , $CaCO_3$ and SiO (remaining ash). The H_2O extractives were specified as glucose.

Figure S12: Flow diagram of the overall process for the pyrolysis of acid leached biomass. Water-ww is the rinsing water for the water wash (0 for pine and bagasse) and water-al is the rinsing water for the acid leaching.

The physical properties of levoglucosan, mannosan and xylosan (non-databank components) were estimated in Aspen Plus® using the group contribution model. Next to the molecular structure the vapor pressure and standard molar enthalpies were provided for levoglucosan and mannosan (assumed to be identical to levoglucosan) to the simulator [82]

Figure S13: Flow diagram of the overall process for the pyrolysis of untreated bagasse.

Figure S14: Flow diagram of the overall process for the pyrolysis of untreated pinewood and straw.

S3.1. Pretreatment

In the pretreatment section the biomass is grinded, leached, mechanically dewatered and dried using superheated steam. The Aspen Plus® simulation was used to obtain the mass balances for the leaching, pressing and drying together with the energy balance for the drying. The energy consumptions of grinding, leaching and pressing were taken from literature, these numbers are summarized in Table S2.

Table S2: Power consumption of specific equipment.

Equipment	Energy requirement (kwh ton ⁻¹)	Source
Grinding pinewood (Hammer mill, screen size 6 mm)	50	[83]
Grinding straw (knife or hammer mill)	15	Average of [84] and [31]
Diffuser	52 (5 ton h ⁻¹) 18 (50 ton h ⁻¹)	De Smet
Pressing biomass to 46 wt% moisture	10	[36]

The acid leaching process modeled in the block pretreatment uses the property package EN-RTL-RK, due to the ions in the acid leaching process. In the model sodium is lumped in potassium and magnesium in calcium. Therefore the relevant compounds for the leaching step are acetic acid, formic acid, potassium carbonate, calcium carbonate and water. The ions and reactions between the aforementioned compounds were looked up using the electronic wizard database (the formation of bicarbonate salts was excluded). Because Aspen Plus® did not display all equilibrium constants all constant were overwritten. The reactions, used to describe the acid leaching, and corresponding equilibrium constants (at 25 °C) are summarized in Table S3.

Table S3: Ionic reactions and equilibrium constants (defined as $\ln(K_{eq})=A$).

Reaction	A
$\text{CH}_3\text{COOH} \leftrightarrow \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$	-14.9779
$\text{HCOOH} \leftrightarrow \text{CHOO}^- + \text{H}_3\text{O}^+$	-12.2396
$\text{H}_2\text{O} + \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+$	-27.8108
$2 \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+$	-18.6607
$\text{K}_2\text{CO}_3 (\text{S}) \leftrightarrow \text{CO}_3^{2-} + 2 \text{K}^+$	7.1667
$\text{CaCO}_3 (\text{S}) \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$	-23.5159

A diffuser was selected for the acid leaching, as explained in section 3.2. The diffuser is modeled as multiple SSPLIT blocks in series. The SSPLIT block separates all solids stream plus a fraction of the MIXED stream (3 times the weight of dry biomass) from the ingoing stream. This stream is fed to the next SSPLIT block while the remaining MIXED stream is fed to the previous SSPLIT block. Before the first acid leaching SSPLIT block a flash vessel is located to remove the CO_2 produced from the reaction between acid and carbonates. The biomass leaving stage 5 is fed to a press where the moisture content (MIXED stream) is reduced to 46 % on mass basis. After pressing the biomass is dried with steam in a flash vessel at 3 bar. The excess steam, produced from the biomass moisture, is removed using a split. In the Aspen Plus® model the additional steam is condensed, mimicking an application in which the steam is used for its condensation heat. Finally, the relatively clean condensate is fed back to the rinsing process. The pretreatment section for acid leached bagasse or pinewood is shown in Figure S15 (see Figure 7 for design flowsheet). For acid leached straw the Aspen Plus® flow diagram was extended with 3 SSPLIT blocks for the pre-water wash (see Figure 4). The Aspen Plus® flow diagram for pretreatment of untreated bagasse contained only a press and a steam dryer (see Figure S10). The Aspen Plus® flow diagram for pretreatment of untreated pinewood and straw is shown in Figure S14.

The following assumptions were used:

- The Ca and K present in the biomass are modeled as carbonate salts.
- Process water used for rinsing contains $50 \text{ mg kg}^{-1} \text{ CaCO}_3$ and K_2CO_3 .
- All H_2O soluble extractives are dissolved during leaching.
- Bagasse doesn't contain H_2O soluble extractives since it has been thoroughly washed with water during sugar extraction. The H_2O soluble extractives content of straw and pinewood is shown in Table 1.
- The diffuser can be described by several equilibrium stages (5 stages for acid leaching and rinsing, 3 stages for pre water wash).
- The biomass retains 3 times its own dry mass in (leaching or rinsing) liquid, containing dissolved minerals, after draining. This amount is based on our practical experience.
- All Ca and K present in the biomass can dissolve when enough acid is present.
- The AAEM (cation) content after acid leaching (BIO-DRY Figure S12) is reduced to 200 mg kg^{-1} on dry biomass basis.
- CO_2 concentration in the atmosphere above the leaching liquid is 1 vol% (see 10.4.3).

following assumptions were used:

- The heat needed for pyrolysis was specified as 1.5 MJ kg⁻¹ on dry biomass basis
- The anhydrosugar yield was based on the sugar yields after hydrolysis of the oils (see [6])
- C₂H₄, C₂H₆, C₃H₆ and C₃H₈ were lumped as C₂H₆
- Water soluble phenols = 0.7*lignin in biomass feed – monomeric phenols – Water insolubles
- The produced char had an elemental composition of C₈H₈O [85].
- The HHV of the 1st condenser oil was calculated based on measured elemental composition. After sugar extraction the HHV was calculated as $\text{HHV}_{\text{cond1}} - X_{\text{sugar}} * 17.5$. For the residue after sugar and phenolic extraction the HHV was calculated as $\text{HHV}_{\text{cond1}} - X_{\text{sugar}} * 17.5 - X_{\text{phenolics}} * 28$. In these equation X is the mass fractions

Table S4: Pyrolysis products from untreated and acid leached biomasses.

Compound	Compound	Pine		Straw		Bagasse	
	in Aspen	Acid		Acid		Acid	
Compound	Plus®	Untreated	leached	Untreated	leached	Untreated	leached
Produced water	Water	0.117	0.085	0.113	0.077	0.104	0.044
Char	C ₈ H ₈ O	0.100	0.086	0.136	0.072	0.080	0.054
CO	CO	0.140	0.130	0.149	0.132	0.162	0.120
CO ₂	CO ₂	0.116	0.088	0.200	0.070	0.247	0.125
CH ₄	CH ₄	0.020	0.020	0.020	0.015	0.038	0.020
C ₂₊	C ₂ H ₆	0.010	0.010	0.010	0.010	0.010	0.010
Levogluconan	Levogluconan*	0.044	0.155	0.007	0.157	0.020	0.200
Mannosan	Mannosan*	0.012	0.030	0	0.001	0.002	0
Xylosan	Xylosan*	0	0.010	0.002	0.030	0	0.043
	Furfuryl						
Furanics	alcohol	0.020	0.020	0.020	0.020	0.020	0.020
monomeric phenols	Guaiacol	0.020	0.020	0.020	0.020	0.020	0.020
Water soluble							
phenolics	Bisphenol A	0.038	0.058	0.043	0.078	0.047	0.100
Water insoluble	Bisphenol A	0.122	0.102	0.054	0.043	0.093	0.041
Unknown cond 1	Bisphenol A	0.102	0.074	0.064	0.106	0.032	0.095
acetic acid	acetic acid	0.025	0.018	0.018	0.019	0.025	0.018
formic acid	formic acid	0.010	0.010	0.010	0.010	0.010	0.010
Lights	acetol	0.104	0.084	0.134	0.140	0.090	0.080

* The physical properties of Levoglucosan, Mannosan and Xylosan were calculated by Aspen Plus®.

The condensers were modeled as flash vessel assuming vapor liquid equilibrium. The 1st condenser was operated at 90 °C (10 °C higher than in [15] due to lower gas velocity per kg biomass) and 1.3 bar, the 2nd condenser was operated at 25 °C 1.2 bar. The compressor increases the pressure by 1 bar to compensate for the pressure losses over the different process equipment. The split after the compressor recycles 1 kg of gas to the reactor per kg of dry biomass fed.

Figure S17: Flow diagram of the pyrolysis hierarchy block for the pyrolysis of acid leached biomass (untreated contains a single condenser).

Table S5: Elemental composition of the different pyrolysis oils obtained from untreated biomass and the composition of the 1st condenser oils obtained from acid leached biomass.

	Pine untreated	Pine acid leached	Straw untreated	Straw acid leached	Bagasse untreated	Bagasse acid leached
	Whole oil	Condenser 1	Whole oil	Condenser 1	Whole oil	Condenser 1
C (% mass basis)	44.2	53.5	34.9	51.9	39.7	50.7
H (% mass basis)	6.9	6.0	7.2	6.1	7.9	6.1
O (% mass basis)	48.7	40.4	57.0	41.7	51.1	42.6
Water content (% mass basis)	21.1	5.2	36.0	1.5	27.5	0.2
HHV (MJ kg ⁻¹)*	17.5	21.1	13.1	20.7	16.8	20.3

* Calculated using Milne equation.

S3.3. Utilities

Figure S18 shows the flow diagram of the hierarchy block “utility” for the pyrolysis of acid leached biomass and untreated bagasse. In case of pyrolysis of untreated pinewood and untreated straw the flow diagram was identical to Figure S18 except that the steam cycle was not included. The physical property method used for this hierarchy block was NRTL. The combustor was modelled as an stoichiometric reactor (RStoic) in which all organics were oxidized. The amount of heat produced by the oxidation reactions was calculated by Aspen Plus®. The combustor is operated at 580 °C and air is fed at an air to fuel ratio (λ) of 1.3. A fraction of the heat produced in the combustor is used for the pyrolysis reactor. From the remaining energy steam is produced, which is used for biomass drying (acid leached biomasses and untreated bagasse) and electricity production (in case of untreated pine and straw). The heat to the steam cycle was added via the heater “STEAM-PR” (using a calculator $Q_STEAM = Q_COMBUST - Q_SAND$). For some cases the temperature of the steam was higher than the maximal (530 °C) set temperature, in this case some water was added to the cycle to reduce the temperature (WAT-STM). This additional steam is purged later together with the steam produced from the biomass moisture. In case of untreated pine wood and straw, in which no steam is required for drying, the steam is converted into electricity with an thermal efficiency of 30%. The compressors for the air and the steam cycle both increases the pressure by 0.5 bar to compensate for the pressure losses over the different process equipment.

Figure S18: Flow diagram of the utility hierarchy block for the pyrolysis of acid leached biomass (untreated contains a single condenser).

S3.4. Validation of Aspen Plus[®] model

Fractional condensation of pyrolysis oil

The fractional condensation experiments reported by Westerhof et al. [15] were simulated in Aspen Plus[®] to validate the outcome of the simulator. Figure S19 shows the water, acetol, acetic acid, levoglucosan and water insoluble's concentration in the 1st condenser oil. The figure shows that the model works well for all compounds except acetic acid, for which Aspen Plus[®] overestimates the volatility. Since the 1st condenser is operated around 81 °C this difference has no large effect on the mass balance outcome.

Figure S19A: Concentration of water in the oils obtain in the 1st condenser, as function of the 1st condenser temperature as calculated by Aspen Plus[®] and experimental determined.

Figure S19B: Concentration of acetic acid in the oils obtain in the 1st condenser, as function of the 1st condenser temperature as calculated by Aspen Plus® and experimental determined.

Figure S19C: Concentration of acetol in the oils obtain in the 1st condenser, as function of the 1st condenser temperature as calculated by Aspen Plus® and experimental determined.

Figure S19D: Concentration of levoglucosan in the oils obtain in the 1st condenser, as function of the 1st condenser temperature as calculated by Aspen Plus® and experimental determined.

Figure S19E: Concentration of water insoluble's in the oils obtain in the 1st condenser, as function of the 1st condenser temperature as calculated by Aspen Plus® and experimental determined.

Acid leaching

In order to obtain a better understanding of the aqueous solubility of the AAEMs and validate the calculations performed in Aspen Plus®, an experiment was carried out to determine the combined solubility of potassium carbonate (0.3455 g) and calcium carbonate (0.6207 g) in water (500 cm³) as function of the added amount of acetic acid (added in steps of 0.1 cm³ up to 0.8 cm³). The concentration of potassium and calcium in the aqueous phase, analyzed by ICP, as function of the amount of acetic acid added to the aqueous solution is shown in Figure S20.

As expected potassium carbonate, based on its solubility of 1.11 kg kg⁻¹ water [86], dissolved immediately without requiring acetic acid. This was also calculated by Aspen Plus® (not shown). According to the solubility product of calcium carbonate, calcium can only dissolve when the carbonate anion concentration in the aqueous solution is sufficiently low. Figure S20 shows that hardly any calcium dissolved at low amounts of acetic acid added, since still carbonate anions originating from potassium carbonate were present in the aqueous phase. The added acetic acid reacts with the carbonate anions to water and CO₂, which is released from the solution to the air in case of an open system. When no gas phase is taken into consideration in the Aspen Plus® simulation the amount of calcium dissolving is overestimated. Based on the results it can be seen that around two moles of acetic acid are required to dissolve one mole of calcium carbonate.

Overall, it can be concluded that the Aspen Plus® solubility model is in good agreement with the experimental data. Hence, the reactions taking place in the leaching system are understood and can be described using this solubility model.

Figure S20: Potassium and calcium concentration as function of the amount of acetic acid added determined experimentally and calculated by Aspen Plus®. Potassium concentrations calculated by Aspen Plus® are not shown since these were identical to experimental results.

S3.5. Detailed Mass and energy balances

The detailed mass and energy balances shown in Table S6 up to and including Table S11 can be found in the supplementary information of the publication on the biomass and bioenergy website

S4. Methodology for the economic assessment

The economic feasibility of pyrolyzing untreated or acid leached biomass was evaluated based on the net present value (NPV) of the project. The NPV of each project was based on a discounted cash flow calculation in which all (ingoing and outgoing) cash flows were estimated and corrected for time (discounting) by using the cost of money (inflation and interest).

S4.1. Capital expenses (CAPEX)

CAPEX pyrolysis plant

The capital costs of the pyrolysis plant was based on published data for various pyrolysis systems. The prices were adjusted for time, to 2014 basis, using the Chemical Engineering Plant Cost Index (CEPCI), and to the desired scale, using a 0.7 scaling term. The € prices were converted to US\$ using the yearly average exchange rate of the specific year. Table S12 summarizes the available data and shows the corrected costs for a 50 ton h⁻¹ in 2014. It should be noticed that the reported BTG-BTL (empyro) plant is for a complete constructed plant whereas the cost for the Ensym pyrolysis plant excluded front-end material handling, utilities, offsite requirements, product storage, foundations, site preparation, buildings, spares, safety containment, fire water systems, wastewater system, startup fuel systems, emissions control, and installation [66]. Therefore the CAPEX of the complete ENSYN plant will be somewhat higher. This shows that the capital expenses does not largely depends on the selected pyrolysis system. Each of the reactor types has their own advantages and disadvantages. The final selection is expected to be largely depending on the planned feedstock, application of the oil and plant location (available utilities).

$$\text{Cost in 2014} = \text{cost in year } X * \left(\frac{\text{CEPCI 2014} = 580}{\text{CEPCI year } X} \right)$$

$$\text{cost} = \text{cost at original capacity} * \left(\frac{\text{new capacity}}{\text{original capacity}} \right)^{0.7}$$

Table S12: Published CAPEX for various pyrolysis systems.

	type	Capacity (Ton h ⁻¹)	Year	Price	Source	Corrected price (2014 50 ton hr ⁻¹)
BTG-BTL	Rotating cone	5	2014	19 M€	[87]	121 M US\$
Ensyn	Circulating fluidized bed	18	2009	38 M\$*	[66]	84 M US\$
Kahlsruhe	Auger	25	2010	40 M€-47 M€**	[42]	114 M US\$

*Excluding front-end material handling, utilities, offsite requirements, product storage, foundations, site preparation, buildings, spares, safety containment, fire water systems, wastewater system, startup fuel systems, emissions control, and installation.

** depending on different configurations like sand or steel beats heat carrier loop.

CAPEX acid leaching

An estimate of the capital cost of the diffuser was supplied by DeSmet based on the calculated stream sizes, the results are summarized in Table S13. When sugar for fermentation is produced an additional purification section is required.

Table S13: Estimate of OPEX and CAPEX for the biomass leaching equipment as supplied by De Smet

PLANT CAPACITY (ton h ⁻¹)	5	50
Overall Dimensions (estimated):		
Width (m)	3.0	9.5
Length (m)	31.5	65.0
Height (m)	8.0	10.0
Material of Construction (MOC):		
Casing	Stainless Steel 316L	
Conveyor	Stainless Steel 316L	
Drive Elements	Carbon Steel	
Supporting structure	Carbon Steel	
Installed Power		
TOTAL (KW)	+/-260	+/- 890
Budget (estimated)		
Total Installed Cost (EUR)	5,600,000	40,500,000

CAPEX separation of sugars from 1st condenser oil

The considered separation system for the 1st condenser oil is shown in Figure S21. The 1st condenser oil is extracted with water (water to feed ratio 1:1) in a countercurrent extractor with 3 stages. The aqueous stream is hereafter extracted with ethyl acetate (amount of ethyl acetate per aqueous phase 0.2 kg kg⁻¹) in a countercurrent extractor with 4 stages. The ethyl acetate extract is separated in a distillation column (6 stages). The ethyl acetate dissolved in the aqueous stream is recovered in a 2nd distillation column (8 stages).

The cost of the separation train was estimated using Aspen Economics Evaluation® V8.4. An installed cost of 6.7 million US\$ was obtained (see Table S14).

Figure S21: Schematic overview of the considered separation train to extract the sugars from the 1st condenser oil.

Table S14: CAPEX for the considered separation train to extract the sugars from the 1st condenser oil.

Unit	Equipment Cost [US\$]*10 ³	Installed Cost [US\$]*10 ³
distillation 1	1,000	4,202
distillation 2	447	1,452
Heat exchanger 1	12	71
Heat exchanger 2	66	176
Extraction column (water)	75	376
Extraction column (ethyl acetate)	80	402
total	1.7 M US\$	6.7 M US\$

S4.2. Operating expenses (OPEX)

The fixed costs of the pyrolysis plant, which include maintenance, miscellaneous materials, plant insurance, labor, license and fee, were estimated as a percentage of the CAPEX. These percentages are shown in Table S15. The labor demand was estimated to be 5 shifts of 4 operators (5 ton h⁻¹) or 16 (5 ton h⁻¹) with an average cost per employee and year of 60000 US\$. The costs associated with the consumed materials and utilities were estimated based on the mass and energy balances. The material and utility costs are summarized in Table 6 (main text). The product prices are listed in Table 7 (main text).

Table S15: Assumptions for annual fixed costs of the pyrolysis plant.

Parameter	Assumption
Annual maintenance	5% of CAPEX
Miscellaneous materials	10% of maintenance
Labour	US\$60000 per person per year [68]
Number of personnel	20 (5 ton h ⁻¹) or 80 (50 ton h ⁻¹)
Plant Insurance	2% of Capex
License and fee	2% of sales

S4.3. Net present value (NPV)

Due to inflation and the interest/dividend rate at which you are able to borrow money (the cost of money), the value of money is decreasing. Therefore future cash streams have a lower value then current money. To compensate for the factor time, cash streams were corrected (discounted), which results in the net present value (NPV). The discount factor includes the inflation and the cost of money (interest (loan)/dividend (shares)). If the NPV of a project is positive it indicates that the projected earnings exceeds the anticipated costs and therefore may be accepted. The cash stream to the government (taxes) was calculated using the differences between costs, sales and the depreciation of the equipment (over the project period of 15 years). The NPV was calculated Based on the CAPEX and cash flow (OPEX and sales) at each successive year using the following formula:

$$NPV = I_0 + \frac{CF_1}{(1 + IRR)^1} + \frac{CF_2}{(1 + IRR)^2} + \dots + \frac{CF_n}{(1 + IRR)^n}$$

In this equation I_0 represents the CAPEX at the start of the project, n the project duration (15 years), CF the cash flow after tax for each year. The internal rate of return (IRR) includes both inflation and the interest rate and was assumed to be constant in the future (i.e., till n years). For the sensitivity study the IRR resulting in a $NPV=0$ was calculated. It was assumed that the costs and sales are increased each year to correct for the inflation (only investment not).

Table S16: Assumption for the NPV calculation.

Parameter	Assumption
Inflation	3% per year
Taxes	30% of profit
Project duration	15 years
Operating hours per year	7500

Samenvatting

Het grootschalig gebruik van fossiele brandstoffen sinds de 18^e eeuw heeft een belangrijke rol in onze hoge levensstandaard, door o.a. verhoging van de productiviteit en betere mobiliteit. Het nadeel van het gebruik van fossiele bronnen is dat ze eindigend zijn en dat het gebruik ervan leidt tot verhoogde atmosferische CO₂-concentraties, en daarmee verantwoordelijk is voor de opwarming van de aarde. Voor de productie van warmte en elektriciteit zijn er verscheidene duurzame opties (o.a. wind, zon en waterkracht), echter voor de productie van transportbrandstoffen en chemicaliën is koolstof nodig. De enige duurzame geconcentreerde koolstofbron is biomassa. Een van de grootste potentiële biomassastromen is lignocellulose biomassa zoals ongebruikte afvalstromen van de landbouw (bijv. de niet-eetbare delen van een maisplant, suikerriet of graan) of de industrie (zaagsel of lignine van de papierindustrie). De uitdaging in het gebruik van lignocellulose biomassa als grondstof voor het produceren van chemicaliën en transportbrandstoffen is dat de bouwstenen, cellulose, hemicellulose en lignine, waaruit biomassa is opgebouwd, afgebroken dienen te worden in kleinere moleculen. Een interessant proces hiervoor is snelle pyrolyse, door de extreem korte reactietijd en robuustheid (geschikt voor alle droge biomassa). Echter heeft de conventionele snelle pyrolysetechnologie als nadeel dat er honderden verschillende componenten, elk met een lage concentratie, gevormd worden, waardoor verdere verwerking naar chemicaliën erg lastig is.

Het doel van het onderzoek, beschreven in dit proefschrift, was daarom het ontwerpen en evalueren van een pyrolyseproces met een verbeterde selectiviteit naar de productie van anhydrosuikers en monofenolen (de bouwstenen van de polysachariden en lignine), naast de “gebruikelijke” bio-olie voor energietoepassingen. Deze verbindingen zijn interessante platformchemicaliën voor de productie van o.a. transportbrandstoffen, kunststoffen en farmaceutica.

In **Hoofdstuk 2** is allereerst de productie van anhydrosuikers vanuit pure cellulose onderzocht om inzicht te krijgen in de onderliggende chemische- en transportprocessen die plaatsvinden op alle relevante schalen, variërend van deeltjesniveau tot op bench-schaal. Experimenten toonden aan dat als pure cellulose gepyrolyseerd wordt onder hoge opwarmingsnelheden (5000 °C s⁻¹) gecombineerd met een snelle verdamping van de geproduceerde vluchtige producten, verkregen door een lage reactor druk (5 mbar), en snelle afkoeling van deze vluchtige producten (20 ms), een hoge anhydrosuikeropbrengst verkregen wordt. Onder deze omstandigheden heeft de pyrolysetemperatuur een invloed op de distributie van de anhydrosuikerketenlengte maar niet op de totale anhydrosuikeropbrengst. Deze bleef constant rond de 70 % op koolstofbasis (een voorzichtige schatting). Het reduceren van de verdampingssnelheid van de vluchtige producten vanaf het pyrolyserende deeltje, door de

druk te verhogen naar 960 mbar, verminderde de totale anhydrosuikeropbrengst van 69 % naar 50 % (bij 530 °C). Het verlengen van de hete damp verblijftijd van 20 ms naar 1.6 s, door te pyrolyseren in een wervelbedreactor bij 530 °C, beïnvloedt de anhydrosuikeropbrengst niet. Dit toont aan dat de anhydrosuikers op het pyrolyserende deeltje weg kunnen reageren tot niet anhydrosuikercomponenten, dat verondersteld wordt te gebeuren in de smeltfase zoals geclaimd wordt door Mamleev [1], maar stabiel zijn in de dampfase bij een temperatuur van 530 °C (en verwacht lager) in de afwezigheid van alkali en aardalkalimetalen (AAEMs). De hoge productie van oligomere anhydrosuikers, van DP₂ tot DP₁₁, in de screen-heater toont aan dat willekeurige ketenkraking het dominante mechanisme is tijdens cellulose pyrolyse, echter het selectiever kraken van eindgroepen kan niet volledig worden uitgesloten op basis van de verkregen resultaten. Bij temperaturen boven 500 °C is de reactiesnelheid van de kraakreacties erg hoog (<100 ms voor volledige omzetting) waardoor de conversie gelimiteerd wordt door de warmteoverdracht. Hierdoor wordt de temperatuur van het biomassadeeltje (werkelijke reactietemperatuur) constant voor warmtebrontemperaturen boven ~ 530 °C. De resultaten tonen duidelijk aan dat er interactie is tussen de chemie en de warmte- en massaoverdracht. Vanwege de complexiteit van de chemie, variërend per aggregatietoestand, en massaoverdracht, zowel verdamping als aerosol-ejectie, kan er worden geconcludeerd dat het voorspellen van de pyrolyse productopbrengsten of oliesamenstelling via wiskundige modellen uiterst moeilijk zal zijn, zo niet onmogelijk.

Het is bekend dat de AAEMs, die van nature aanwezig zijn in biomassa, de anhydrosuiker productie onderdrukken. Echter is het onbekend in welke mate de effecten van de AAEMs geminimaliseerd kunnen worden door de procesomstandigheden, zoals lage druk en korte hete damp verblijftijden. In **Appendix A** is daarom cellulose, geïmpregneerd met verschillende AAEM concentraties, gepyrolyseerd in de screen-heater onder verschillende procesomstandigheden. De resultaten tonen aan dat de AAEMs al grote invloed hebben op de reacties die plaatsvinden in het pyrolyserende deeltje. Gebaseerd op deze testen kan er geconcludeerd worden dat het onder geen van de procesomstandigheden mogelijk is om een hoge anhydrosuikeropbrengst te verkrijgen uit cellulose met een AAEM-concentratie gelijk aan die van onbehandelde biomassa. Hieruit volgt dat het verwijderen of het pacificeren van de AAEMs voor pyrolyse vereist is om een hoge anhydrosuikeropbrengst te krijgen. Indien de AAEMs grotendeels verwijderd (<1000 mg kg⁻¹) zijn voor de pyrolyse kan de druk gebruikt worden voor het verder verhogen van de anhydrosuikeropbrengst.

Het verwijderen van AAEMs uit biomassa is voorheen gedaan door middel van uitloging of het impregneren van de biomassa met minerale zuren (H₂SO₄, H₃PO₄ of HNO₃), wat resulteert in grote anorganische afvalstromen. In **Hoofdstuk 3** is onderzocht of de organische zuren geproduceerd uit de biomassa zelf tijdens pyrolyse en geconcentreerd via gefractioneerde condensatie van de pyrolysedampen als alternatief gebruikt kunnen worden voor het uitloggen van de AAEMs. De organische zuren, geconcentreerd in de 2^{de} condensorvloeistof, bleek een

efficiënte uitloogvloeistof om het merendeel van de AAEMs uit de biomassa te verwijderen. De pyrolyse van verschillende onbehandelde en zuur geloogde biomassa (grenen hout, stro, hooi en bagasse) is bestudeerd om inzicht te krijgen in het effect van de biomassasamenstelling op de productopbrengsten en productsamenstelling. Uit de uitloog testen van de verschillende biomassa bleek dat volledige AAEM verwijdering niet mogelijk is; zelfs na intensief uitloggen en naspoelen met demiwater blijft er tussen de 90 mg kg^{-1} - 600 mg kg^{-1} van de AAEMs achter in de biomassa. De toegepaste condities van het zuur uitloggen leidden niet tot een verlies van hemicellulose, cellulose en lignine uit de biomassa. Het zuur uitloggen van de biomassa voor pyrolyse resulteert in een verhoogde massa-, energie- en koolstofconversie naar de pyrolyse-olie. Echter, indien de 1^{ste} condensorvloeistof als enige product wordt beschouwd voor het uitloogproces (2^e condensorvloeistof wordt gebruikt voor het uitloggen) dan resulteert het loggen in een afname in het geval van grenenhout (relatief laag initieel AAEM-gehalte) ten opzichte van de complete pyrolyse-olie uit de onbehandelde grondstof. De anhydrosuiker productie nam fors toe na het zuur loggen. Alleen na het loggen met zuur was de pyrolyse-olie geproduceerd uit stro en hooi een een-fase vloeistof (gecondenseerd bij 20°C), wat verdere verwerking van de olie vereenvoudigd.

In **Appendix B** is gevalideerd dat de 2^{de} condensorvloeistof vervangen kan worden door een synthetisch mengsel voor het uitloggen van de AAEMs uit biomassa.

In **Hoofdstuk 4** is het effect van de pyrolysetemperatuur op de pyrolyseproducten bestudeerd voor grenenhout. De hoogste olie- en anhydrosuikeropbrengst vanuit zuur geloogd grenenhout in de wervelbedreactor werd verkregen bij 480°C . Interessant is dat bij 360°C de suikeropbrengst al $0,23 \text{ kg kg}^{-1}$ was in vergelijking tot de $0,29 \text{ kg kg}^{-1}$ verkregen bij 480°C . Dit laat zien dat hoge temperaturen niet per se nodig zijn om hoge anhydrosuikeropbrengsten te krijgen.

De productie van mono-fenolverbindingen is alleen onderzocht vanuit biomassa en niet vanuit geïsoleerde lignine (in tegenstelling tot de anhydrosuikers uit cellulose). Deze keuze was gemaakt omdat tijdens het merendeel van de isolatiemethoden de β -O-4 bindingen in lignine wegreageren (condensatiereacties), en hierdoor niet representatief zijn. De lignine-gerelateerde producten zijn daarom in pyrolyse-olie geproduceerd uit biomassa bestudeerd door een combinatie van GC-MS, GPC en UV-fluorescentie. Op basis van deze resultaten is er bewijs opgebouwd dat de AAEMs geen grote invloed hebben op de opbrengst en de molecuulgrootte van de fenolverbindingen. Hieruit kan geconcludeerd worden dat het loggen met zuur geen geschikte methode is om de opbrengst van mono-fenolverbindingen te verhogen. De maximale mono-fenolopbrengst was verkregen op relatief lage reactortemperaturen ($\sim 430^\circ\text{C}$), echter de absolute opbrengst is erg laag voor zowel onbehandeld als geloogd grenen (maximum: 23 g kg^{-1} grenen, 80 g kg^{-1} lignine).

Het residu verkregen door pyrolyse van zuur geloogde biomassa had een andere morfologie dan die vanuit onbehandelde biomassa. Waar het residu van onbehandelde biomassa de oorspronkelijke vezelachtige structuur van de biomassa behield, is te zien dat het residu van zuur geloogde biomassa (gedeeltelijk) door een smeltfase is gegaan bij pyrolysetemperaturen van 430 °C of hoger. Deze smelt fungeerde als lijm tussen de zand- en residueeltjes, wat leidde tot bed-agglomeratie. Het residu van geloogde biomassa verkregen op 360 °C laat geen sporen van smelt zien, terwijl wel een verhoogde pyrolyse-olie- en anhydrosuikeropbrengst verkregen is. Als gevolg van de smelteigenschappen van zuur geloogde biomassa dient de volgende overweging gemaakt te worden: Enerzijds kan het pyrolyseproces worden geopereerd bij een lage temperatuur (~ 360 °C). Echter, bij deze temperaturen zijn de pyrolysereacties relatief langzaam. Als resultaat hiervan is een langere verblijftijd (min vs s) van de biomassadeeltjes in de hete pyrolyse reactor nodig wat leidt tot een hogere kapitaalinvestering. Vanwege de langzame reactiesnelheid is de opwarmsnelheid van de biomassadeeltjes minder belangrijk, waardoor andere reactortypes toegepast kunnen worden, zoals de schroefreactor en roterende ovens die normaal alleen overwogen worden voor langzame(re) pyrolyse. Anderzijds kan een reactorconcept opgewassen tegen het smelten van de biomassa worden geselecteerd.

In **Appendix C** is het pacificeren van de AAEMs door middel van zuur impregnatie vergeleken met het ontwikkelde uitloogproces. Daarnaast is er gekeken of het impregneren van een kleine hoeveelheid zwavelzuur in zuur geloogde biomassa de anhydrosuikeropbrengst verder kan verhogen. Het verwijderen van de AAEMs via logen was effectiever om een hoge anhydrosuikeropbrengst te krijgen dan het pacificeren via zuurimpregnatie. Het toevoegen van 0.01 % zwavelzuur verhoogde de glucoseterugwinning, zoals getoond voor grenen (van 29% naar 40 %) en stro (van 32% naar 37%).

De experimentele resultaten zijn gebruikt als input voor een technologische en economische evaluatie beschreven in **Hoofdstuk 5**. Allereerst zijn er testen gedaan om de snelheid van het uitlogingsproces te bepalen. Testen toonden aan dat dit proces gelimiteerd is door de diffusie van ionen in de tracheïden, hierdoor zijn relatief kleine deeltjes (enkele mm) nodig om reële procestijden (minuten) te behalen. Het logen van de biomassa kan uitgevoerd worden bij kamertemperatuur. Na het logen dient de biomassa nagespoeld te worden om de uitloogvloei stof te verwijderen die de opgeloste AAEMs bevat die zijn achtergebleven in de biomassa poriën (~ 3 kg per kg droge biomassa). Het uitvoeren van dit logen en naspoelen in een meertraps-tegenstroomextractor beperkt het naspoelwaterverbruik. Een mogelijke apparaat voor dit logen en naspoelen is een “standaard” suikerrietdiffuser. Indien mechanische ontwatering voor het verdere thermische drogen wordt toegepast kan de warmte voor het proces (pyrolyse en drogen) geproduceerd worden door de verbranding van het residu en de gasen. Echter is er onvoldoende overtollige warmte beschikbaar om elektriciteit te produceren voor het proces.

Uit de economische evaluatie bleek dat het beschreven proces zeer gevoelig is voor de CAPEX en uiteraard de biomassaprijs. Uit de testen met verschillende biomassa kwam naar voren dat een lage hoeveelheid extractieven in de biomassa, die eindigen in het afvalwater, de voorkeur heeft. Echter een hoog vochtgehalte in de biomassa maakt niet veel uit. Dit biedt mogelijkheden voor processen waarbij de biomassa eerst behandeld dient te worden om waardevolle producten, zoals suikers of eiwitten, te extraheren. De implementatie van zuur logen van de biomassa verhoogd de totale CAPEX van een nieuwe pyrolysefabriek met 36% (alleen zuur uitloging) tot 47% (inclusief productscheiding). Onder het huidige marktscenario en de stand van bewezen technieken is de productie van suikers samen met stookolie uit bagasse op een schaal van 50 ton per uur een economische interessante optie (IRR 15,4%).

Suikers voor fermentatie kunnen ook uit lignocellulose biomassa geproduceerd worden via verschillende andere processen. Hiervan is enzymatische hydrolyse het meest bestudeerd en industrieel toegepast. De voordelen van dit proces ten opzichte van suikerproductie via pyrolyse is een hogere suikerterugwinning (90% vs 40%) en dat er een lagere hoeveelheid schadelijke stoffen gevormd worden. Echter de dure cellulase, lange procestijden (dagen), en de relatieve lage suikerconcentraties (~ 11% massabasis) van de enzymatische hydrolyse zijn grote nadelen. Het pyrolyseproces beschreven in dit proefschrift is een interessant alternatief en dient daarom verder onderzocht te worden.

About the author

Stijn Oudenhoven was born on the 17th of July 1987 in Zevenaar. After passing his HAVO he started studying Chemical Engineering at the Saxion Hogescholen in Enschede. He did his traineeship at the research and development department of the business unit Ecosystems of AkzoNobel in Deventer.

In July 2009 he graduated under the supervision of Roel Westerhof on the topic “effects of temperature on the fluidized bed fast pyrolysis of pine wood” at the Thermo-Chemical Conversion of Biomass (TCCB) group. In this project Stijn looked at the influence of the fluidized bed temperature, condenser temperature, stepwise pyrolysis and the char/minerals content in the reactor on the bio-oil yield and composition.

After his HBO he started with the master chemical engineering (process technology). During this period he worked as a student assistant at the TCCB group working on the PhD project (biomass pyrolysis) of Roel Westerhof.

He graduated in November 2011 on the topic ‘Utilization of process conditions and concepts during wood pyrolysis to obtain fractionated oils to steer the production of transportation fuels and chemicals by HDO and HPTT’. the project was under the supervision of ir. R.J.M. Westerhof, dr. ir. Kees Hogendoorn and Prof. Dr. S.R.A. Kersten.

Following his master degree graduation he started in february 2012 as a PhD student at the University of Twente on the CatchBio project “Catalytic steps in the conversion of lignocellulosic biomass via pyrolysis to fuel precursors”. The work performed during his PhD is written down in this thesis.

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- [3] S.R.G. Oudenhoven, R.J.M. Westerhof, D.W.F. Brilman and S.R.A. Kersten Fractional condensation of biomass fast pyrolysis vapors: An important process step in a pyrolysis based bio-refinery. European Biomass Conference 2012, Milan, Italy.

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