The Interplay Between Chemistry and Transport Phenomena During the Fast Pyrolysis of Cellulose, Lignin and Biomass

Pushkar Satish Marathe

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TRANSPORT PHENOMENA DURING THE FAST
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BIOMASS

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Dedicated to my father

... If I have seen further it is by standing on the shoulders of Giants.

- Sir Isaac Newton (5th February 1676)

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Summary

Depleting fossil energy resources and the changes in climatic conditions have propelled humanity to find alternative sustainable resources to satisfy the increasing demand. Lignocellulosic biomass is one of the carbon-based renewable resources which can be used to produce fuels and chemicals. Fast pyrolysis is one of the promising technologies in which lignocellulosic biomass is decomposed at ~ 500 °C and in the absence of oxygen, to produce oil ($\sim 75\%$), char ($\sim 12\%$) and gas ($\sim 13\%$). Pyrolysis oil can be upgraded to fuel or platform chemicals via downstream processing.

Literature suggests that the yields of products and their composition obtained during the pyrolysis are affected by the competition between transport phenomena and chemistry. The research described in this thesis aims at advancing the current understanding of the three simultaneously occurring processes, viz. chemical reactions (decomposition, cracking, polymerisation), heat transfer and mass transfer (evaporation, sublimation, random ejection), and their interplay during the fast pyrolysis of cellulose, lignin and lignocellulosic biomass.

For that, a dedicated screen-heater reactor was used, which was designed: 1) to minimise non-isothermality (heating rate: ~ 5000 °C s^{-1}), 2) to control the reaction time inside the reacting particle by the escape rate of compounds from the reaction zone by variation of the pressure, and 3) to minimise reactions outside the reacting particle by minimising hot vapour residence time (~ 20 ms) and fast quenching of the products (~ 180 °C). Experiments were also carried out in a bench-scale 1 kg h^{-1} fluidised bed unit equipped with a fractional condensation system to investigate the effect of hot vapour residence time (~ 2 s).

Qualitative and quantitative characterisation of pyrolysis products was done using various analytical tools. In order to understand the reaction mechanisms, quantitative analysis of species present in pyrolysis oil is necessary. The suitability of gas chromatography (GC) and liquid chromatography (LC) for the quantification of levoglucosan (LG) and hydroxyacetaldehyde (HA) was evaluated. It was found that both GC and LC can principally determine LG quantitatively in pyrolysis oils. However, depolymerisation of oligo-anhydrosugars in GC owns a risk of overestimation of the LG yields. HA can only be determined quantitatively by LC because of its reactions during the high temperature (~ 250 °C) injection in GC.

It was found that in the absence of potassium salts, cellulose could almost entirely be converted to anhydrosugars while producing hardly any gas ($<1\%$) and char ($<1\%$) in

a wide temperature range of 450 to 765 °C. Depolymerisation of cellulose to anhydrosugars was identified to be a true primary reaction; gas and char formation secondary. Mathematical models were developed, including the interaction between chemistry, heat transfer and mass transfer. The escape rate of products from the hot reacting particle was identified as a crucial process affecting the DP distribution of anhydrosugars.

The potassium concentration in cellulose was varied to mimic the mineral-rich and pre-treated feedstock and subsequently pyrolysed at 530 °C in screen-heater and fluidised bed. Potassium was found to be catalytically active even when the escape rate of the product away from the reaction front was extremely high (milliseconds). The yields of oil and anhydrosugars decreased significantly as a function of potassium concentration, while the production of other products (water, gases, light oxygenated compounds) was enhanced. The production of char was found to be independent of the escape rate of products at any given potassium concentration. It could be concluded that pyrolysis at reduced pressure, i.e. by fast removal of products from the hot reaction zone, can improve the oil and sugar yields, but only for low alkali and alkaline earth metals content feedstock.

The effect of molecular weight on the competing physio-chemical processes was investigated by pyrolysing 14 lignins (350 – 1900 Da) in the screen-heater at 0.5 kPa and 100 kPa. A population balance model was developed, which includes simultaneously occurring cracking reactions, polymerisation reactions and mass transport away from the reaction zone. The model was able to predict all experimentally observed trends after parametrisation. The molecular weight distribution was found to be one of the crucial characteristics of the lignin feedstock, which has a significant influence on the pyrolysis product distribution. Upwards 530 °C, the temperature turned out to have only a minor influence on the yields and composition of the oils produced, whereas the system pressure was identified as the main steering wheel to manipulate the product yields and the molecular weight of the oils. HSQC NMR analysis of lignins and its oils showed that the yields of oil and char and the number average molecular weight of oils were found to be independent of the number of ether linkages in the lignin feedstock.

Fast pyrolysis of acid-leached bagasse was carried out in the pressure range of 0.005 to 100 kPa in screen-heater. At the lowest pressure, the total yield of C₆-anhydrosugars (sum of DP₁ to DP₆) was as high as 73% of the poly-C₆-sugars in the feedstock. A mathematical model, including again reaction and mass transfer away from the reaction zone, was able to predict the measured decrease in a total yield of C₆-anhydrosugars and the shift to lighter C₆-anhydrosugars as a function of increasing pressure. At identical pressure and temperature, the total yield of C₆-anhydrosugars obtained from acid-leached

pinewood was the same for the screen-heater and fluidised bed. As a result of the longer hot vapour residence time in the fluidised bed, $DP_{\geq 2}$ C₆-anhydrosugars depolymerised towards DP_1 .

In nutshell, besides the heating rate of sample, hot vapour residence time of products and the temperature during the pyrolysis, the system pressure is the key parameter, which alters the residence time of products in/on the hot reacting particle, thereby, providing a means to steer the yields and composition of the products of pyrolysis.

Samenvatting

Het uitputten van fossiele energiebronnen en de klimaatveranderingen hebben de mensheid ertoe aangezet om alternatieve duurzame bronnen te vinden om aan de toenemende vraag te voldoen. Lignocellulose biomassa is een van de hernieuwbare bronnen op basis van koolstof die kunnen worden gebruikt om brandstoffen en chemicaliën te produceren. Snelle pyrolyse is een van de veelbelovende technologieën waarbij lignocellulosische biomassa wordt afgebroken bij ~ 500 °C en in afwezigheid van zuurstof, om olie ($\sim 75\%$), kool ($\sim 12\%$) en gas ($\sim 13\%$) te produceren. Pyrolyse-olie kan worden opgewaarderd tot brandstof of platformchemicaliën via vervolgstappen in het proces.

In de literatuur wordt gesuggereerd dat de opbrengsten en de samenstelling van producten verkregen tijdens de pyrolyse, worden beïnvloed door een samenhang van transportverschijnselen en chemie. Het onderzoek dat in dit proefschrift beschreven wordt, is gericht op het bevorderen van het huidige begrip van de drie gelijktijdig optredende processen. Deze drie processen zijn: chemische reacties (ontleding, kraken en polymerisatie), warmte- en massaoverdracht (verdamping, sublimatie en willekeurige uitstoot) en hun wisselwerking tijdens de snelle pyrolyse van cellulose, lignine en lignocellulose biomassa.

Voor het onderzoek werd een speciale screen-heater reactor gebruikt, die ontworpen was om: 1) niet-isotherm gedrag te minimaliseren (verwarmingssnelheid: ~ 5000 °C s^{-1}), 2) de reactietijd in het reagerende deeltje door de ontsnappingsnelheid van componenten uit de reactiezone te controleren door variatie van de druk, en 3) reacties buiten het reagerende deeltje te minimaliseren door de verblijftijd van hete damp te minimaliseren (~ 20 ms) en de producten snel af te koelen (~ 180 °C). Er werden ook experimenten uitgevoerd in een 1 kg h^{-1} wervelbed opstelling uitgerust met een fractioneel condensatiesysteem om het effect van de verblijftijd (~ 2 s) van de hete damp te onderzoeken.

Kwalitatieve en kwantitatieve karakterisering van pyrolyseproducten werd uitgevoerd met behulp van verschillende analytische hulpmiddelen. Om de reactiemechanismen te begrijpen, is kwantitatieve analyse van de in pyrolyse-olie aanwezige componenten noodzakelijk. De geschiktheid van gaschromatografie (GC) en vloeistofchromatografie (LC) voor de kwantificering van levoglucosaan (LG) en hydroxyacetaldehyde (HA) werd geëvalueerd. Zowel GC als LC kunnen in principe LG kwantitatief bepalen in pyrolyse-oliën. Echter, depolymerisatie van oligo-anhydrosuikers in GC kan resulteren in een overschatting van de LG opbrengsten. HA kan alleen kwantitatief worden bepaald door middel van LC vanwege reacties tijdens de injectie op hoge temperatuur (~ 250 °C) in GC.

Cellulose kon bij afwezigheid van kaliumzouten vrijwel volledig worden omgezet in anhydrosuikers, terwijl er nauwelijks gas ($<1\%$) en kool ($<1\%$) werd geproduceerd over een breed temperatuurbereik van 450 tot 765 °C. Depolymerisatie van cellulose naar anhydrosuikers werd geïdentificeerd als een primaire reactie; gas- en koolvorming als secundaire reacties. Wiskundige modellen werden ontwikkeld, inclusief de interactie tussen chemie, warmte- t en massaoverdracht. De ontsnappingssnelheid van producten uit het verwarmde reagerende deeltje werd geïdentificeerd als een cruciaal proces dat de *DP*-verdeling van anhydrosuikers beïnvloedde.

De kaliumconcentratie in cellulose werd gevarieerd om de mineraalrijke en voorbehandelde biomassa na te bootsen en vervolgens werd de cellulose bij 530 °C in de screen-heater en wervelbedreactor gepyrolyseerd. Kalium bleek katalytisch actief te zijn, zelfs wanneer de ontsnappingssnelheid van het product van de reactie zone af extreem hoog was (milliseconden). De opbrengsten van olie en anhydrosuikers namen aanzienlijk af als functie van de kaliumconcentratie, terwijl de productie van andere producten (water, gassen en kleine geoxygeneerde verbindingen) was toegenomen. De productie van kool bleek onafhankelijk te zijn van de ontsnappingssnelheid van producten bij elke gegeven kaliumconcentratie. Er zou kunnen worden geconcludeerd dat pyrolyse bij verlaagde druk, d.w.z. door snelle verwijdering van producten uit de hete reactiezone, de olie- en suikeropbrengsten kan verbeteren, maar alleen voor biomassa met een laag gehalte alkali- en aardalkalimetaal.

Het effect van het molecuulgewicht op de competitie tussen fysisch-chemische processen werd onderzocht d.m.v. het pyrolyseren van 14 lignines (350 - 1900 Da) in de screen-heater bij 0.5 kPa en 100 kPa. Er is een populatiebalansmodel ontwikkeld dat gelijktijdig optredende kraakreacties, polymerisatiereacties en massatransport uit de reactiezone omvat. Het model was in staat om, na parametrisatie, alle experimenteel waargenomen trends te voorspellen. De molecuulgewichtsverdeling bleek een van de cruciale kenmerken van de lignine-grondstof te zijn, en heeft een significante invloed op de distributie van pyrolyseproducten. Een temperatuur groter dan 530 °C bleek slechts een geringe invloed te hebben op de opbrengsten en samenstelling van de geproduceerde oliën, terwijl de systeemdruk werd geïdentificeerd als de belangrijkste variabele om de productopbrengsten en het molecuulgewicht van de oliën te manipuleren. HSQC NMR-analyse van lignines en bijbehorende oliën toonde aan dat de opbrengsten van olie en kool en de getalgemiddelde molecuulmassa van oliën onafhankelijk zijn van het aantal etherbindingen in de lignine-grondstof.

Snelle pyrolyse van zuur-uitgeleogde bagasse werd uitgevoerd in het drukbereik van 0.005 tot 100 kPa in de screen-heater. Bij de laagste druk was de totale opbrengst

aan C6-anhydrosuikers (som van DP_1 tot DP_6) maximaal 73% van de poly-C6-suikers in de voeding. Een wiskundig model, dat opnieuw reactie en massaoverdracht van de reactiezone af omvat, was in staat om de gemeten afname in een totale opbrengst aan C6-anhydrosuikers en de verschuiving naar lichtere C6-anhydrosuikers als een functie van toenemende druk te voorspellen. Bij identieke druk en temperatuur was de totale opbrengst aan C6-anhydrosuikers, verkregen uit met zuur uitgeloozd dennenhout, hetzelfde voor de screen-heater en de wervelbedreactor. Als gevolg van de langere verblijftijd van hete damp in het wervelbed werden $DP_{\geq 2}$ C₆-anhydrosuikers gedepolymeriseerd naar DP_1 .

Kortom de systeemdruk is de belangrijkste parameter die de verblijftijd van producten in/op het heet reagerende deeltje verandert, waardoor de opbrengsten en samenstelling van de producten van pyrolyse gestuurd kunnen worden. Andere parameters zijn de verwarmingssnelheid van het sample, de verblijftijd van warme dampen van producten en de temperatuur tijdens de pyrolyse.

सारांश

जीवाश्म उर्जा संसाधनांतील सततची होणारी घट आणि हवामानात होणारी स्थित्यंतरे या बाबींमुळे मानवाला, उर्जेचे पर्यायी स्रोत शोधण्याची गरज निर्माण झाली आहे. या पार्श्वभूमीवर लिग्नेसेल्युलोसिक बायोमास (उदा. उसाची चिपाडे, वाळलेले गवत) हा एक कार्बन आधारित उर्जेचा स्रोत आहे ज्याचा उपयोग इंधन तसेच रसायने तयार करण्यासाठी होऊ शकतो. फास्ट पायारोलीसीस (Fast Pyrolysis) हे एक असामान्य तंत्रज्ञान आहे ज्याद्वारे लिग्नेसेल्युलोसिक बायोमासचे रुपांतर, ५०० डी. से.ला आणि प्राणवायूच्या अनुपस्थितीत, तेल (७५%), कोळसा (१२%) व इंधन-वायूत (१३%) असे करता येते.

पायारोलीसीस तंत्रज्ञाना दरम्यान तयार होणारी उत्पादने आणि त्यांची घटक रचना ही उष्णता हस्तांतरण, वस्तुमान हस्तांतरण व रसायन शास्त्र ह्यांच्या मधील स्पर्धेने प्रभावित होते. प्रस्तुत प्रबंधात केलेले व मांडलेले संशोधन एकाच वेळी होणऱ्या रासायनिक अभिक्रिया, वस्तुमान हस्तांतरण आणि उष्णता हस्तांतरण यावर प्रकाश टाकते. सेल्युलोस, लिग्निन आणि लिग्नेसेल्युलोसिक बायोमास यांच्या पायारोलीसीस मध्ये असलेल्या स्पर्धेचा अभ्यास या प्रबंधात सादर केला आहे.

या संशोधनामध्ये स्क्रीन-हिटर रीअक्टरचा वापर केला गेला आहे. त्याची प्रमुख वैशिष्ट्ये पुढील प्रमाणे आहेत. (१) उष्णता हस्तांतरण दर ५००० डी.से. प्रति सेकंद (२) रीअक्टर मधील दाबात बदल करून लिग्नेसेल्युलोसिक बायोमास अंतर्गत व बाह्य अश्या दोन्ही रासायनिक अभिक्रियांना लागणारा वेळ नियंत्रित करता येतो. (३) रासायनिक अभिक्रियांमधून तयार झालेली उत्पादने द्रावित नायट्रोजन (-१९६ डी.से.) वापरून थंड केली जातात.

सेल्युलोस, लिग्निन आणि लिग्नेसेल्युलोसिक बायोमास चा फास्ट पायारोलीसीस निःसन्देहपणे एकाच वेळी होणऱ्या रासायनिक अभिक्रिया, वस्तुमान हस्तांतरण आणि उष्णता हस्तांतरण यांच्यातील आंतरक्रियेद्वारा नियंत्रित होतो. आधीपासूनच माहित असल्याप्रमाणे, उच्च उष्णता हस्तांतरण दर तेलाचे उत्पादन वाढविण्यासाठी आवश्यक आहे. बायोमास बाहेरील घडणाऱ्या रासायनिक अभिक्रियांच्या वेळेचा (१ - २सेकंद) साखर उत्पादनावारती नाममात्र परिणाम घडतो. लिग्निनचे आण्विक वजन (वितरण) हा एक महत्त्वाचा गुणधर्म असून त्याचा पायारोलीसीसच्या उत्पादनांच्या वितरणावर महत्त्वपूर्ण प्रभाव पडतो. पायारोलीसीसचे तापमान ५०० डी. से. पेक्षा कमी असल्यास तेल उत्पादनावर लक्षणीय प्रभाव पडतो. ५५० डी.से. च्यावर पायारोलीसीसचे तापमान गेल्यास रासायनिक अभिक्रियांचा दर हा उष्मा हस्तांतरण दरापेक्षा जास्त होतो ज्या परतवे पायारोलीसीसचे तापमान न वाढता स्थिर रहाते. या सर्वव्यतिरिक्त पायारोलीसीस दरम्यान असलेला वायूचा दाब हा महत्त्वाचे परिमाण असून त्याचा उपयोग तेलाचे उत्पादन आणि त्यातील घटकांची संरचना नियंत्रित करण्यासाठी करता येऊ शकतो.

C_1

General introduction

1.1 Motivation

The world population is estimated to reach 9.15 billion by the end of 2040, and with that, the energy demand is expected to grow annually at a rate of 1%^[1]. Currently, fossil fuels are the primary energy sources, and their extensive use has resulted in the emission of greenhouse gases and particulate matter, causing air pollution and global warming. Uneven distribution of fossil energy resources across the globe and geopolitics dictates the supply and price of energy. Climatic change and energy security, primarily, have stimulated the search for the alternative, CO₂ neutral (or negative), energy sources to meet the growing energy demand and to mitigate the carbon footprint.

Solar energy, wind energy, hydropower, geothermal and biomass have been identified as renewable resources. Among these, the availability of the first four energy sources is very much dependent on the geographical locations^[2,3]. Biomass, being the only renewable carbon source ($\sim 45\%$ C on dry ash free basis^[4]), may fit into the existing fossil infrastructure^[5], and could partially replace crude oil derived fuels and materials. Also, biomass energy is essentially CO₂ neutral, if none or little fossil energy is used for its production and processing since it is based on a short carbon cycle^[5]. Currently, 12 – 13% of the total world energy demand is satisfied by biomass^[5]. However, biomass is often available as low bulk density solids, especially agricultural/forestry waste, and it needs a processing step before it can be transported and used.

1.2 Lignocellulosic biomass

The 1st generation biofuels (bio-diesel, bio-ethanol), produced from food crops, have been commercialised to mature technologies. In the EU alone, the production of biofuels has increased from 625 (2000) to 35311 kTon y⁻¹ (2017)^[6]. However, growing concern about the competition between the increasing demand for food and fuel has shifted the focus towards the 2nd generation biomass feedstock, i.e. lignocellulosic biomass. It can be subdivided into three types namely; softwood (e.g. pine, spruce, cedar), hardwoods (e.g. oak, beech, maple.) and grasses (e.g. miscanthus, switchgrass, reed canary). Lignocellulosic biomass is composed of cellulose, hemicellulose, lignin, extractives and inorganics. They are discussed briefly hereafter since next to biomass their pyrolysis behaviour is investigated in this thesis.

Cellulose: Cellulose, an essential structural component of the primary cell wall, accounts for 35 to 50 wt. % of dry lignocellulosic biomass. It is the most abundant, naturally occurring polymer in the biosphere^[7]. It is a linear polymer composed of anhydroglucopyranose units connected by β -(1-4) glycosidic bond^[8]. The degree of polymerisation

of native cellulose is between 10000 to 14000, whereas it is much lower (200 – 3000) in microcrystalline cellulose (isolated via a pulping process)^[7].

Hemicellulose: A second major component of lignocellulosic biomass is hemicellulose. It accounts for ~28% and ~35% of dry lignocellulosic biomass in softwoods and hardwoods, respectively^[9]. Hemicellulose is composed of three hexoses (glucose, mannose and galactose) and two pentoses (xylose and arabinose), together with some uronic acids^[8], which makes it a hetero-polysaccharide. Softwood hemicelluloses are rich in galacto-glucomannan, and hardwood hemicelluloses are rich in xylans^[9]. Unlike cellulose, it is a branched polymer and has a degree of polymerisation in the range 50 to 200^[7,9].

Lignin: Lignin is a three dimensional, highly cross-linked, hydrophobic, heteropolymer^[10]. It is the most abundant naturally occurring aromatic polymer and accounts for up to ~35% of dry lignocellulosic biomass. Coumaryl-, coniferyl- and sinapyl alcohols, the precursors of lignin, are interconnected by various linkages, which are broadly classified as ether linkages and carbon linkages^[11–13]. During the isolation process (e.g. kraft, organosolv^[14,15]), native lignin undergoes structural changes, and the extent to which the structure of native lignin is preserved is controlled by the severity of the isolation method^[15,16]. Note that milled wood lignin, obtained by Björkman's method, is considered to represent native lignin most accurately^[17].

Extractives: In addition to the above three main constituents, extractives are present in the biomass (~5% on dry mass). They are low molecular weight species, including fats, waxes, alkaloids, proteins, phenolics and essential oils^[7,9]. Extractives act as intermediates in plant metabolism, energy reserves, and defences against microbial threats^[9]. These can be extracted by using polar (e.g. water, alcohols) or non-polar (e.g. toluene, hexane) solvents^[7,9].

Inorganics: The content of inorganic species (also known as ash) in biomass varies significantly as a result of soil and climate conditions^[18]. In woody biomass, it is typically in the range between 0.1 to 7.1 wt. %, while in grasses, it can be as high as 42 wt. %^[18]. Following are commonly found elements in woody biomass: calcium (Ca), potassium (K), sodium (Na), silicon (Si), magnesium (Mg), aluminium (Al), sulphur (S), iron (Fe), phosphorous (P), manganese (Mn)^[18,19]. These minerals are attached to the biomass matrix by an ionic or a covalent bond^[19]. The content of alkali and alkaline earth metals (AAEMs), i.e. Na, K, Ca, Mg, in biomass is especially of importance for thermo-chemical conversion process^[20].

1.3 Biomass conversion routes

Figure 1.1 shows an overview of different conversion processes to convert ligno-cellulosic biomass to fuels and chemicals. Direct combustion of biomass to produce energy has been the first step in the history of human civilisation. Worldwide, in large scale plants, direct combustion of biomass is carried out in a fixed bed reactor or grate furnace^[21–24]. The main processes and routes depicted in Figure 1.1 are briefly discussed here. In gasification, biomass is converted to CO, CO₂, H₂, and CH₄ at high temperatures (>900°C) in the presence of air, oxygen or steam. Depending on the relative composition of these gasses, they are referred to as synthesis gas or producer gas^[25]. In the liquefaction process, biomass is converted in a temperature range of 150 – 360 °C and at elevated pressures (90 – 250 bar) to yield two main products, liquid (organic + aqueous) and gas^[26,27]. The organic fraction is considered as the targeted product of liquefaction and has a significantly lower oxygen content than the feedstock (10 – 25 wt. % in organic phase vs 45 wt. % in feed)^[28]. The organic part of the liquid can be upgraded into diesel/gasoline range fuels by catalytic hydrocracking in the presence of a solvent^[27]. In the following section, pyrolysis technology, being the focus of this thesis, is elaborated in detail.

Figure 1.1: Biomass conversion routes for the production of fuels and chemicals [24]

1.4 Pyrolysis

The word *pyrolysis* is based on Greek-derived elements; *Pyr* ($\pi\upsilon\rho$) implies *fire* and *Lysi* ($\lambda\upsilon\sigma\eta$) implies *releasing*, meaning releasing by fire. In pyrolysis lignocellulosic biomass is converted in the absence of oxygen, to form char, gas, and oil. The yields of these lumped products are affected by the type of feedstock, its ash content, reactor type, heating rate, operating conditions, (hot) vapour residence time of the products^[4]. Various pyrolysis modes are available to selectively maximise the yield of the product(s) of interest, i.e. char (charcoal), oil or gas^[29,30]. These modes are differentiated based on the size of particles, temperature, heating rate and, most importantly, the vapour residence time of products, as shown in Table 1.1.

Table 1.1: Typical product yields (dry wood basis) obtained by different modes of pyrolysis^[29,30]

Mode	Temperature	RT ^a	HVRT ^b	Oil	Char	Gas
Torrefaction	~290 °C	~10 – 60 min	–	0 – 5%	80%	15 – 20%
Intermediate	~500 °C	~20 min	10 – 30 s	50%	25%	25%
Fast	~500 °C	~10 s	1 – 2 s	75%	12%	13%
Gasification	750 – 900 °C	seconds	~5 s	5%	10%	85%

^a Reaction time

^b Hot vapour residence time

The char, black carbonaceous material rich in minerals, is widely used for the combined heat and power (CHP) generation or as an additive to soil as a fertiliser and carbon sequestration agent^[31]. The gas produced during pyrolysis is mainly composed of CO, CO₂ and light hydrocarbons, and can be burned to produce process heat. Oil (or bio-oil or pyrolysis oil) is a complex mixture of organic compounds of different chemical classes such as acids, aldehydes, ketones and anhydrosugars, which are generally present in low concentrations. As an example, typical properties and composition of the fast pyrolysis oil derived from wood are presented in Table 1.2. Compared to crude oil, the composition of pyrolysis oil differs significantly. The relatively high oxygen content in pyrolysis oil makes it thermally unstable, making its direct use as a fuel in CHP systems, burners/engines difficult^[32,33]. However, significant efforts have been made to upgrade pyrolysis oil (catalytically) to transportation fuel^[34–37] and use as a source for the production of chemicals^[38–40].

Table 1.2: Typical composition of pinewood derived pyrolysis oil and its properties^[32,41]

Chemical class	Unit	Value
Water	wt. %	24
Acids	wt. %	4
Alcohols	wt. %	2
Aldehydes and ketones	wt. %	15
Sugars	wt. %	34
LMM lignin	wt. %	13
HMM lignin	wt. %	2
Extractives	wt. %	4
Property	Unit	Value
pH		2.5
Specific gravity		1.2
Elemental composition	wt. %	
C		54 – 58
H		5.5 – 7
O		35 – 40
N		0 – 0.2
Ash		0 – 0.2
HHV	MJ kg ⁻¹	16 – 19
Viscosity (at 42°C)	cP	25 – 1000
Solids	wt. %	0.2 – 1
Distillation residue	wt. %	up to 50

1.4.1 Pyrolysis reactors

The historical developments in the fields of pyrolysis reactors have been summarised by Garcia-Nunez et al.^[42]. Reviews of Butler et al.^[43] and Venderbosch et al.^[41] have summarised the commercial scale efforts in the fast pyrolysis of biomass. Different fast pyrolysis reactor configurations have been implemented on commercial scale: bubbling fluidised bed reactor (Dynamotive (Canada) 200 tpd, Biomass Engineering Ltd. (UK) 4.8 tpd, Agri-Therm (Canada) 1 – 10 tpd), circulating fluidised bed reactor (Ensyn (Canada) 100 tpd, Metso Consortium (Finland) 7.2 tpd), rotating cone reactor (BTG (Netherlands) 120 tpd, Bio-oil Holding NV. (Belgium/Netherlands) 12 tpd), auger reactor (KIT-Lurgi (Germany) 12 tpd, ARBI-Tech (Canada) 50 tpd, Renewable Oil International LLC (USA) 4.8 tpd), ablative reactor (PyTec (Germany) 6 tpd). At the time of writing this thesis, a consortium of TechnipFMC, BTG-BTL and Green Fuel Nordic Oy has decided to build four 120 tpd pyrolysis units in Finland^[44]. Although fast pyrolysis technology is close to commercialisation, the following are the main chal-

lenges: 1) scale-up of the technology from laboratory scale concepts/setup to commercial plants, 2) design and operational difficulties, 3) flexibility to accommodate different feedstock (wet/dry, high ash content), and 4) production of quality product to find suitable applications^[41,43].

Table 1.3: Characteristics of various laboratory-scale setups used for pyrolysis

Reactor	Heating rate	Temperature	Pressure	HVRT ^a	Analysis ^b
–	°C s ⁻¹	°C	kPa	–	–
TGA	~3	30 – 900	100	seconds	Online
Tubular	10	200 – 900	100	milliseconds	Online/ offline
Micro-pyrolyser	~200	400 – 600	100	seconds	Online
PHASR ^c	11800	400 – 500	–	~10 ms	Online
Screen-heater	5000	320 – 800	0.005 – 100	~20 ms	Offline

^a Hot vapour residence time of products

^b Possibility of analysing pyrolysis products

^c Pulse heated analysis of solid reactions

In laboratories, mainly, thermogravimetric analyser (TGA), tubular reactor, micro-pyrolyser, PHASR reactor and screen-heater reactor (also called wiremesh) are used: 1) to study the yield of lumped products (gas, char, oil) and their composition of varies types of biomass, 2) to measure (lumped) reaction kinetics, and 3) to investigate ongoing physio-chemical processes and primary/early stage reactions of biomass pyrolysis^[45]. The main characteristics of various reactors types used in laboratories are as follows; sample heating rate, operating conditions, (hot) vapour residence time of products and the possibility of analysing formed pyrolysis products, see Table 1.3. For further reading on these reactors, the reader is referred to the review of Sribala et al.^[45]. It is important to note that, especially in TGA and micropyrolysers, the actual heating rate of the sample can be significantly different from the one claimed by the machine manufacturer^[46–49].

In the screen-heater, nearly isothermal operation is achieved by applying a high heating rate (5000 °C s⁻¹). Other important characteristics of the screen-heater are: 1) the escape rate of products, away from the hot reacting particle, can be controlled by manipulating pressure during the pyrolysis, 2) rapid quenching of products is achieved by a liquid nitrogen bath to minimize outside the reacting particle, and 3) importantly, not only light but also heavy species in the oil are collected and can subsequently be analysed. For example, compounds having a molecular weight up to 30000 Da and anhydrosugars with a degree of polymerisation up to 11 can be analysed by using GPC and

LC/MS, respectively. The combination of these characteristics can be achieved using the screen-heater, making it suitable for studying primary reaction products.

1.4.2 Chemical and physical processes during pyrolysis

Figure 1.2: Schematic representation of chemical and physical processes occurring during pyrolysis

Léde^[47] suggested that the pyrolysis of biomass and its building blocks is governed by the competition between physical and chemical processes. During pyrolysis, a fraction of lignocellulosic biomass passes through a liquid intermediate (Figure 1.2), also called a melt, which has a lower degree of polymerisation compared to that of the original polymers. In the case of cellulose, this intermediate liquid is termed the active cellulose^[50]. At the reacting particle and/or within this liquid intermediate^[51], a large number of chemical reactions take place, which are broadly classified into cracking reactions to form volatiles and gases, and polymerisation reactions to produce char.

Volatile products are transported away from the hot reaction front not only by evaporation but also by random ejection in the form of aerosols^[52–55] or by sublimation^[56]. The mass transport rate of products depends on two factors, i.e. the molecular weight of species and the operating conditions during the pyrolysis. At a constant pyrolysis temperature, smaller molecules have higher vapour pressure due to which they can escape the hot reaction front easily. On the contrary, because of the lower mass transport rates, bigger molecules spend a longer time at the hot reaction front, where they consequently undergo cracking as well as polymerisation reactions. Once escaped from the hot reaction front, products may undergo secondary reactions in/on the surface of

nascent char (containing AAEMs) or in the hot vapour phase before condensation. Secondary reactions of the vapours facilitate the formation of gasses and light oxygenated compounds. The extent of secondary reactions depends on the hot vapour residence time^[57,58], temperature^[58] and the presence of AAEMs^[58].

Next to the mass transport of species, the supply of energy to drive the pyrolysis reactions is of equal importance. The heat transfer is strongly influenced by the size of the biomass particle, surrounding temperature and the transfer mechanism^[59]. Pyle et al. have identified the following three regimes, based on Biot number (Bi) and Pyrolysis (Py₁ and Py₂) numbers^[60], in which pyrolysis reactions are controlled by: 1) kinetics (reactions taking place at the surrounding temperature), 2) External heat transfer (absence of heat carrier from the heat source to the particle), and 3) Internal heat transfer (big particles). In essence, the heating rate of the lignocellulosic biomass predominantly affects the set of pyrolysis reactions it will undergo, resulting in a different outcome.

Collectively, the yields and the distribution of pyrolysis products are influenced by the interplay between reaction rates, the heating rate of the particle and the rate of mass transport of species/products away from the hot reaction front.

1.4.3 Role of AAEMs during pyrolysis

The AAEMs, present in the biomass matrix, reportedly affect the carbohydrate fraction (cellulose and hemicellulose) of the biomass by catalysing ring-fragmentation and dehydration reactions^[61,62]. As a result of that, the yields of anhydrosugars and organics decrease while facilitating the production of light oxygenated compounds, water and gaseous species (e.g. CO, CO₂, CH₄). The yields of organics and anhydrosugars can be improved by: 1) minimising AAEMs content by pre-treating the lignocellulosic biomass with (hot) water^[63] or by acid-water mixture (mineral acid^[61,64,65] or organic acid^[62,66,67]), and 2) by ceasing the catalytic activity of AAEMs by passivating them by strong acids (H₂SO₄, H₃PO₄) to form stable salts which are catalytically less active^[68–70]. However, it is unknown to what extent the destructive effects of AAEMs on sugar production can be minimised by maximising the product removal rate.

In the literature, Oudenhoven et al.^[71] have reported the maximum sugar yields of 30% on acid-leached pinewood basis in a fluidised bed, whereas others have reported the sugar yields in the range between 8% and 22%^[61,64,72–75]. Pyrolytic sugars can be up-graded to monosaccharides (e.g. glucose, xylose, mannose) via hydrolysis followed by fermentation and catalytic processing to produce bio-ethanol and platform chemicals^[76], respectively.

1.4.4 Analytical techniques

A combined use of qualitative and quantitative analysis of pyrolysis oil is needed: 1) in understanding its composition, 2) for proposing reaction mechanisms, 3) for optimising process conditions to maximise the production of the targeted product(s), and 4) for determining its physical properties for downstream applications such as catalytic upgrading. Reviews^[77–79] available in the literature, provide a detailed overview of analytical techniques and strategies used for the characterisation of pyrolysis oils. Gas chromatography (GC) with mass spectrometry (MS) is used to analyse the volatile fraction ($T_{\text{boiling}} \sim 320$ °C) of pyrolysis oil. In principle, whole pyrolysis oil, i.e. water-soluble (e.g. sugars, acids, aldehydes) and water-insoluble (e.g. mono-, oligo-phenolics), can be characterised by liquid chromatography (LC) with MS. Gel permeation chromatography (GPC) or size exclusion chromatography (SEC) provides a molecular weight distribution of pyrolysis oil. Additionally, different spectroscopic (e.g. NMR, ESR) and spectrometric (e.g. mass, UV-vis, FTIR) techniques are used extensively to characterise pyrolysis oil.

1.4.5 Modelling

Figure 1.3: Multi-scale modelling for the pyrolysis of biomass

Mathematical modelling proves to be a useful tool for process design, development and optimisation, and predicting reactor performance and product yields^[4]. In a few extensive reviews^[4,59,80–82], efforts of biomass pyrolysis modelling have been summarised. Pyrolysis of biomass is a multi-scale modelling problem (Figure 1.3), encompassing reactions at the molecular level to the hydrodynamics in the reactor. One/multi component (lumped) kinetic models are based on the weight loss profiles of biomass (or its building blocks) measured under slow pyrolysis conditions^[83–91]. In transport models, the physical processes (mass, heat and momentum transfer) are taken into account across the biomass particle where volume and the physical properties vary with the degree of conversion and temperature^[92–100]. Next, reactor models, a combination of previous two models and hydrodynamics, are available in the literature for fixed bed reactor^[101,102], rotating cone reactor^[103], fluidised bed reactor^[104,105]. More recently, density functional

theory (DFT) based calculation methods have been exploited to understand and describe the pyrolysis reaction mechanisms of cellulose^[106–108], hemicellulose^[109,110] and lignin pyrolysis^[111–113].

Independently developed lumped reaction kinetics models and transport models, when combined, can be used to predict the trends of the yields of oil, char and gas^[4]. However, they possess limited prediction power due to the wide variation in the reported kinetics^[114]. Also, these combined models, except those of Solomon et al.^[115,116], do not take into account the effect of molecular weight on the mass transport rate of species. The macroscopic structures of microcrystalline cellulose^[117] and lignin^[118] are significantly different from that of lignocellulosic biomass^[7], hence, restricting the applicability of transport models to biomass. Most importantly, as described in Section 1.4.2 of this introduction, the mass transport rate dependent likelihood of chemical reactions occurring at the hot reaction front, is not included in the combined lumped reaction kinetics-transport models. Therefore, in the author's point of view, a unified mechanistic model (yellow shaded area in Figure 1.3) incorporating a simultaneous competition/interaction between chemistry (cracking and polymerisation reactions), heat transfer (sample heating rate) and mass transport of products (by sublimation, evaporation and random ejection) away from the hot reaction front is needed to describe the pyrolysis of biomass and/or its building blocks more accurately.

1.5 Outline of the thesis

As mentioned in preceding sections, the yields of products and their distribution obtained during pyrolysis are affected by the relative rates of reactions (cracking and polymerisation), heat transfer and mass transfer. The work presented in this thesis aims at advancing the current understanding of these chemical and physical processes and their interplay during fast pyrolysis of biomass, cellulose and lignin. For that, a significant part of the experimental work was done using a previously developed^[119] and characterised^[120] screen-heater. It is designed to obtain insights into primary (or early stage) reactions of pyrolysis by minimising non-isothermality by employing high heating rates ($\sim 5000\text{ }^{\circ}\text{C s}^{-1}$). In addition, mass transfer limitations of products were minimised (hot vapour residence time $\sim 20\text{ ms}$) by reducing pressure during pyrolysis in combination with rapid quenching of products ($\sim 180\text{ }^{\circ}\text{C}$), thereby, minimising secondary reactions outside the reacting particle. The work presented in the subsequent chapters is as follows.

Chapter 2. A detailed overview of materials, experimental procedures, experimental setups, and analytical techniques that are used in this thesis is provided in this chapter. Product definitions, yield calculations and mass balances are also described.

Chapter 3. This chapter evaluates the pitfalls of using gas chromatography and liquid chromatography in the quantification of levoglucosan (LG) and hydroxyacetaldehyde (HA) in biomass and cellulose derived pyrolysis oils. For that, pyrolysis oil samples infused with known amounts of LG and HA were analysed using both techniques.

Chapter 4. This chapter deals with fast pyrolysis of microcrystalline cellulose (Avicel PH 101) in the dedicated screen-heater to study the primary pyrolysis reactions and products. Under these conditions, the effect of temperature on the product yields and the distribution of anhydrosugars in oil is studied. Two mathematical models are developed to interpret and predict experimentally observed trends and to investigate if the pyrolysis is kinetically controlled or if there is an interplay between heat, mass transfer and chemistry. Based on the experimental observations and modelling results, the most prevailing parameters influencing the *DP* distribution of anhydrosugars are identified.

It is widely accepted that the AAEMs have a destructive effect on the production of anhydrosugars. However, it is unknown to what extent this effect can be minimised by maximising the product removal rate from the reacting particle. For that, potassium infused cellulose (concentration: 1 to 10000 mg kg^{-1}) samples were pyrolysed, and the effect of potassium on the yields of oil, char, gas and sugars is investigated. The conditions applied in the screen-heater (0.5 kPa and $\sim 20\text{ ms}$ hot vapour residence time)

are challenging to replicate in an industrial scale reactor. Hence, results obtained from screen-heater are compared with a bench scale fluidised bed.

Chapter 5. In this chapter, the interplay of chemistry and mass transfer will be studied using 14 lignins having number average molecular weights between 350 Da and 1900 Da. These lignins were characterised and subsequently pyrolysed in a wide range of operating conditions (Temperature: 425 to 793 °C; Pressure: 0.5 kPa and 100 kPa). Experimentally obtained oil and char yields and the molecular weight (distribution) of oils are interpreted as a function of molecular weight of the feedstock. A population balance model, including three concurrently occurring processes, viz. cracking reactions, polymerisation reactions and mass transport (molecular weight dependent) from the hot reacting particle, was developed. Based on the experimental observations and the modelling results, the most crucial process parameter to steer the yields of oil and char, and the molecular weight of the oil was identified.

Chapter 6. Next to the molecular weight of the feedstock lignin, its chemical structure may influence the pyrolysis outcome as well. Five lignins, isolated via three different methods, and their oils (Temperature: 530 °C; Pressure: 0.5 kPa and 100 kPa) are characterised by HSQC NMR to elucidate structural changes. Three main ether linkages, namely, β -aryl ether (β -O-4), phenylcoumaran (β -5') and resinol (β - β'), were detected and quantified. In this appendix, the influence of these ether linkages on the yields of oil and char, and the molecular weight of products is studied.

Chapter 7. Finally, fast pyrolysis of acid-leached biomass is studied by varying the system pressure (0.005 to 100 kPa) in order to investigate the relative effects between the reaction rate and the escape rate of products. The total yield of anhydrosugars and their DP distribution is obtained as a function of pressure. A mathematical model, including the competition between (depolymerisation and decomposition) reactions and mass transport of anhydrosugars, is used to interpret and predict experimentally observed trends. Additionally, the effect of hot vapour residence time on the DP distribution of anhydrosugars is investigated by pyrolysing acid-leached biomass in a fluidised bed reactor. Additionally, a mathematical model is developed to interpret experimentally observed influence of hot vapour residence time on the DP distribution of anhydrosugars.

Chapter 8. The main conclusions of this thesis with the outlook are presented in this chapter.

Appendix A. Supporting information for chapter 3. **Appendix B.** Supporting information for chapter 4. **Appendix C.** Supporting information for chapter 5. **Appendix D.** Supporting information for chapter 7.

Nomenclature

Bi	Biot number	$\frac{hR}{\lambda} = \frac{\text{External heat transfer rate}}{\text{Internal heat transfer rate}}$
Py ₁	Pyrolysis number 1	$\frac{\lambda}{k\rho c_p R^2} = \frac{\text{Internal heat transfer rate}}{\text{Reaction rate}}$
Py ₂	Pyrolysis number 2	$\frac{h}{k\rho c_p R} = \frac{\text{External heat transfer rate}}{\text{Reaction rate}}$

C₂

C_2

Materials and methods

Abstract

This chapter provides an overview of the materials, experimental procedures and setups, and analytical techniques used in this thesis. Short, but adequate, descriptions are given and for details the reader is directed to relevant publications.

2.1 Chemicals and Materials

All chemicals and materials used in the experiments performed in this thesis are listed in Table 2.1 and Table 2.2, respectively.

Table 2.1: Chemicals used in the experiment

Compound	Purity %	Supplier
Acetol (1-Hydroxy-2-propanone)	>89	Sigma Aldrich
Barium carbonate (BaCO ₃)	>99	Sigma-Aldrich
Cellobiosan (1,6-Anhydro- β -cellobiose)	>95	Carbosynth Ltd.
Cellotriosan (1,6-Anhydro- β -D-cellotriose)	>98	LC Scientific
Cellotetrasan (1,6-Anhydro- β -D-cellotetrose)	>98	LC Scientific
Dichloromethane (DCM)	≥ 99.8	Merck
Glucose	>99.99	Sigma-Aldrich
Hydroxyacetaldehyde (as glycolaldehyde dimer)	>99	Sigma-Aldrich
Levogluconan (1,6-Anhydro- β -D-glucopyranose)	>98	Carbosynth Ltd.
Levogluconone (1,6-anhydro-3,4-dideoxyhex-3-enopyran-2-ulose)	>95	Carbosynth Ltd.
Potassium carbonate (K ₂ CO ₃)	>99	Sigma-Aldrich
Potassium chloride (KCl)	>99	Sigma-Aldrich
Potassium hydroxide (KOH)	>98	Sigma-Aldrich
Sulfuric acid (H ₂ SO ₄)	>99.99	Sigma-Aldrich

Table 2.2: Materials used in the experiment

Materials	Supplier	Comment
Avicel PH 101 cellulose	Sigma-Aldrich	$\sim 50 \mu\text{m}$, 60.5% crystallinity ^[121] , 5 mg kg ⁻¹ ash, 1 mg kg ⁻¹ AAEMs, average DP 220 ^[122]
Bagasse	Shell	Particle size: $< 150 \mu\text{m}$
Milled wood lignin (MWL)	Prepared in house	Isolated by Björkman's method ^[15]
Pinewood (lignocel 9)	Rettenmaier & Söhne GmbH	Particle size: 1) 0.5 to 2 mm, 2) $< 150 \mu\text{m}$
Pyrolytic lignin (PL)	Prepared in house	Isolated by cold water precipitation (Section 2.2.5)
Sigma organosolv lignin (SOL)	Sigma-Aldrich	Prepared from a mixture of three hardwoods (50% Maple, 35% Birch, 15% Poplar)
Silica sand		Particle size: 212 to 300 μm , particle density: 2600 kg m ⁻³
Spruce organosolv lignin (SL)	Energy Research Centre of the Netherlands (ECN)	Isolated by water-ethanol organosolv process ^[16]
Wheat straw organosolv lignin (WSL)	Energy Research Centre of the Netherlands (ECN)	Isolated by water-ethanol organosolv process ^[16]

The chemicals used for the characterisation are listed in Table 2.3.

Table 2.3: Chemicals used in the characterisation

Compound	Purity %	Supplier	Analysis
Acetone	>99.9	Merck	GC-FID/MS
Acetonitrile		Merck	HPLC
Ammonium acetate ($\text{NH}_4\text{CH}_3\text{CO}_2$)	≥ 99.98	Sigma Aldrich	Direct infusion MS
Deionised water	>99.9		HPLC
Deuterated methanol (CD_3OD)	99.9 atom	Cambridge Isotope Laboratories Inc.	^1H NMR
Deuterium oxide (D_2O)	99.9 atom	Sigma Aldrich	^1H NMR
Dimethyl sulfoxide (DMSO)	≥ 99.9	Sigma Aldrich	Q-CAHSQC NMR
Methanol	>99.9	Merck	GC-FID/MS
Tetrahydrofuran (THF)	≥ 99.8	Merck	GPC

2.2 Methods

2.2.1 Impregnation of salts in cellulose and levoglucosan

K_2CO_3 , KCl or KOH was dissolved in deionised water, and then dry cellulose was added to the mixture. The potassium (source: K_2CO_3) concentration in cellulose was varied between 100 mg kg^{-1} and 10000 mg kg^{-1} . For KCl and KOH, the concentration of potassium was 1000 mg kg^{-1} . The water-salt-cellulose mixtures were thoroughly mixed ($T = 20 \text{ }^\circ\text{C}$) in a round bottom flasks for 1 h. After mixing, deionised water was removed using a rotary evaporator (BÜCHI Rotavapor R-200, $T = 65 \text{ }^\circ\text{C}$, $P = 10 \text{ kPa}$, $\sim 1 \text{ h}$), and wet cellulose samples were dried for 24 h using a vacuum oven (Heraeus FVT420, $T = 20 \text{ }^\circ\text{C}$, $P = 0.5 \text{ kPa}$).

Potassium (source: K_2CO_3) was impregnated in levoglucosan to have a concentration of 1000 mg kg^{-1} . Unlike cellulose, levoglucosan readily dissolved in a water- K_2CO_3 mixture. Deionised water was slowly removed using the same method as for cellulose, while the mixture is continuously stirred to ensure uniform distribution of potassium. Gradual precipitation of sugar and salt, from the saturated aqueous solution, ensured a homogeneous distribution of potassium in levoglucosan.

2.2.2 Acid Leaching

The acid leaching of biomass samples was carried out in a 1 L round bottom glass reactor. For acid leaching of biomass, a synthetic mixture mimicking 2nd condenser liquid (aqueous acidic solution) from the pyrolysis process was used, of which the composition is presented in Table 2.4. For details, readers are kindly referred to the literature^[62,66,71]. The glass reactor, filled with the leaching solution, was preheated to $90 \text{ }^\circ\text{C}$. A water-cooled condenser was used to condense the volatile compounds. Biomass was added to the reactor, once the desired temperature was reached, in a mass ratio of 0.1 g of dry biomass to 1 g of the leaching solution. The mixture was thoroughly mixed by a magnetic stirrer (Magneetroerder X-1250) at 600 rpm for 2 h. After that, biomass slurry was vacuum filtered through a $6 \text{ }\mu\text{m}$ filter (Whatman quantitative filter paper, ashless, grade 42). The biomass was rinsed with the deionised water, to remove the leaching solution from the pores of the particle, until the pH of the effluent liquid was higher than 6. Acid pre-treated biomass was dried in a vacuum oven (Heraeus FVT420, $P < 0.5 \text{ kPa}$) at room temperature for 24 h.

Table 2.4: Chemical composition of synthetic mixture mimicking 2nd condenser liquid

Component	Mass percentage
-	%
Acetic acid	10
Ethanol	3.75
Acetone	3.75
Propionic acid	1.5
Guaiaicol	1.5
Deionised water	79.5

2.2.3 Ash content determination

The ash content of a sample was determined by using a dry oxidation method^[123]. A crucible was rinsed with deionised water followed by dilute nitric acid (0.1 M). The crucible was dried at 105 °C and stored in a desiccator at room temperature. The weight of the crucible was measured three times with and without sample on a weighing balance (Mettler Toledo AX205, max 220 g, precision 0.01 mg) and the average weight was recorded. Next, the crucible containing the sample was kept in a muffle furnace at 575 ± 5 °C for 24 h. After that, it was cooled down to room temperature in a desiccator and weighted again using the same balance. The ash content of the sample was determined by subtracting the weight of the empty crucible from the crucible including ash, and the weight difference is divided by the sample weight (Eq. 2.1).

$$Y_{Ash} = \frac{M_{crucible+ash} - M_{crucible}}{M_{crucible+sample} - M_{crucible}} \times 100 \quad (\text{Eq. 2.1})$$

2.2.4 Acid hydrolysis

The total amount of anhydrosugars present in pyrolysis oils were determined by acid hydrolysis. For that, the NREL LAP method “Determination of sugars, by-products, and degradation products in liquid fraction process samples” was used^[124]. Approximately 40 mg of pyrolysis oil was dissolved in 10 g of deionised water. 350 µL of concentrated H₂SO₄ (72 wt.%) was added to the diluted oil sample. The mixture was heated in an autoclave at 120 °C for 1 h and was allowed to reach the room temperature. The mixture was transferred to a centrifuge tube, and BaCO₃ was added to the mixture to neutralise H₂SO₄. Precipitated barium sulphate (BaSO₄) was separated by centrifuge (Eppendorf centrifuge 5804, 9000 rpm, 5 min).

2.2.5 Cold Water Precipitation

Pyrolytic lignin was produced by cold water precipitation as described in the literature^[125,126]. Pinewood-derived pyrolysis oils were added dropwise to ice-cold water while being stirred continuously. The precipitated powder was recovered by vacuum filtration followed by drying in a vacuum oven (Heraeus FVT420, $P < 0.5$ kPa) at room temperature for 24 h. Dry pyrolytic lignin was stored in a freezer maintained at -25 °C.

2.2.6 Lignin fractionation

Lignins were fractionated into low and high molecular weight fractions by solvent extraction^[127,128]. A lignin sample was added to DCM in a weight ratio of 1 to 10. The DCM insoluble fraction, referred to as the heavy fraction (H), was separated from the soluble fraction by filtration. The DCM soluble fraction, referred to as the light fraction (L), was recovered by evaporating DCM. See Figure 2.1 for the schematics.

Figure 2.1: Lignin fractionation procedure

2.3 Fast pyrolysis setups

2.3.1 Screen-heater

Fast pyrolysis of cellulose, lignin and biomass was carried out in the screen-heater setup. The schematic representation of screen-heater is shown in Figure 2.2. The screen-heater setup and its main characteristics, sample preparation, and the operating procedure is described here.

Figure 2.2: Schematics of the screen-heater setup

Sample preparation and setup

A uniformly distributed sample (~ 50 mg) was pressed between the two catalytically inactive^[120] screens (#2, thickness: $\sim 45 \mu\text{m}$ ^[119]) using a 16-tonne hydraulic press. The pressed screens were clamped between two copper electrodes with bolts (#5). The electrodes, clamps and bolts (#5) were covered with tape (#6). A glass vessel (#1, Duran 250 mL centrifuge tube, round bottom, 147 mm x 56 mm) was installed around the copper electrodes (#5) and screens (#2) as shown in Figure 2.2. The reactor with the glass

vessel was placed in the liquid nitrogen ($-196\text{ }^{\circ}\text{C}$) bath (#4) to achieve quick quenching of the produced vapours/aerosols.

The glass vessel was purged with the dry nitrogen gas (#11) to remove air from the vessel before each experiment. Vacuum ($\leq 0.5\text{ kPa}$) was achieved by an inline vacuum pump (#10). In case of atmospheric pressure experiments (referred to as 100 kPa experiment), a nitrogen atmosphere of $\sim 100\text{ kPa}$ was maintained in the glass vessel after flushing the air out. The pressure inside the glass vessel was 0.5 kPa or 100 kPa and was monitored by two high-speed pressure sensors (#9, Heise DXD3765 and Druck PTX 520). The vapour phase temperature was recorded by using a K-type thermocouple (diameter 0.025 mm connected to a Weidmuller MAS K-type thermocouple signal conditioner, recording every 16 ms), introduced from #7, placed at 15 mm distance from the screens. The temperature of screens was measured with a pyrometer (#12, Kleiber KGA 730). The detailed calibration procedure of the pyrometer is described elsewhere^[120]. The optical beam of pyrometer was focused at the centre of the screens (#3) via a glass tube (#13) and silicon sealing (#14) to avoid the disturbance of the temperature measurement by the liquid nitrogen.

The temperature measured at the pyrometer spot was termed as the final temperature of the screens (T_{FS}), and to reach T_{FS} the screens were heated at a rate of $5000\text{ }^{\circ}\text{C s}^{-1}$ approaching as close as possible to isothermal measurements^[119,120]. The temperature of the screens was measured and regulated by a calibrated pyrometer^[120] and a PID control routine programmed in LabVIEW, respectively. The holding time of the screens at a given T_{FS} was set at 5 s unless otherwise mentioned, and after that, they were cooled at a rate of $\sim 60\text{ }^{\circ}\text{C s}^{-1}$. Experiments were performed at 0.5 kPa and 100 kPa unless otherwise mentioned. It was estimated that for both pressures the quenching rate of the formed products was very fast (hot vapour residence time in order of 20 ms), which ruled out a significant effect of reactions outside the reacting sample (minimised vapour phase reactions)^[120].

Product recovery and mass balance determination

At the end of each experiment, the reactor was allowed to reach room temperature. In reduced pressure experiments, the reactor was filled with dry nitrogen gas before taking a gas sample from the glass vessel (#8), and for 100 kPa experiments, a sample was taken from a gas bag. The composition of gases, determined by using gas chromatography, was used to calculate the gas yield ($\text{kg gas kg}^{-1}\text{ feedstock}$), as given by Eq. 2.2. The char yield ($\text{kg char kg}^{-1}\text{ feedstock}$) was estimated from the difference between the weights of the screens before (with feedstock), and after (with char) the experiment (Eq.

2.3).

$$Y_{Gas} = \frac{\frac{P_{sample} f_{v,i} (V_{vessel} + V_{bag}) M_{w,i}}{RT_{ambient}}}{M_{feedstock} (1 - f_w - f_{ash})} \quad (\text{Eq. 2.2})$$

$$Y_{Char} = \frac{M_{screens+char} - M_{screens}}{M_{feedstock} (1 - f_w - f_{ash})} \quad (\text{Eq. 2.3})$$

Oil was condensed primarily on the interiors of the glass vessel and to a minor extent on the electrodes, clamps and bolts. The weights of the tape, wrapped around the electrodes, clamps and bolts, and the glass vessel were recorded before and after the experiment and used to calculate the oil yield (kg oil kg⁻¹ feedstock), see Eq. 2.4. Independently determined oil, char, and gas yields were summed together to determine the overall mass balance closure of the experiment (Eq. 2.5).

$$Y_{Oil} = \frac{(M_{vessel+oil} - M_{vessel}) + (M_{c+b+t+oil} - M_{c+b+t})}{M_{feedstock} (1 - f_w - f_{ash})} \quad (\text{Eq. 2.4})$$

$$Mass\ balance = Y_{Gas} + Y_{Char} + Y_{Oil} \quad (\text{Eq. 2.5})$$

2.3.2 Fluidised bed

Bench-scale fluidised bed

Cellulose samples (pure, 100 mg kg⁻¹ and 1000 mg kg⁻¹ potassium impregnated) were pyrolysed in a bench scale fluidised bed reactor at a temperature of 530 °C. Silica sand was used as bed material and preheated nitrogen as the fluidisation gas. During each experiment, ~100 g of cellulose was fed manually to the reactor in batches of 2 to 5 g together with 4 to 8 g of sand. The feeding system consisted of two valves which functioned as a gas lock. The experimental time was 25 min. Produced char was separated from the outgoing gas/vapour stream leaving the reactor by using a wire-mesh filter (opening size 9 μm). Almost all char, including potassium, was collected on the filter. This filter cake, with varying amounts of potassium, was used as a tool to study the secondary vapour phase reactions. The estimated vapour residence time of products in the hot zone of the setup, including reactor and tubing, was always kept around 1.6 s. About 95% of the produced vapours were condensed by an electrostatic precipitator

(ESP) operated at 20 °C (outgoing gas temperature). The remaining vapours were condensed in a double-walled glass condenser operated at -5 °C (outgoing gas temperature). Both fractions were considered for the mass balance. The char yield was determined by weighing the char/sand mixture and char/filter after the experiment and subtracting the initial weight of the sand and filter plus the sand fed during the experiment. The gas yield was determined by difference.

Pilot plant - continuous fluidised bed

Fast pyrolysis of (untreated and acid-leached) pinewood, under atmospheric and reduced pressure, was carried out in the continuous fluidised bed, with a capacity of 1 kg h⁻¹ biomass. The schematic representation of the setup is shown in Figure 2.3. All experiments were carried out in a nitrogen atmosphere. The pilot plant included two hoppers each with 4 kg capacity, of which one is used for storing pinewood (#1) and second for the sand (#5). The feeding rates of pinewood and sand screws were calibrated and controlled by two different systems. A mixture of pinewood and sand was fed to the fluidised bed reactor by using a third screw (#3). The temperatures of two hot zones, i.e. fluidised bed reactor (#6) and char separation section, were controlled independently. In all experiments, the temperature of the fluidised bed reactor was maintained at ~485 °C. The operational conditions are summarised in Table 2.5.

An overflow vessel (#7), connected at the bottom of the reactor, was used to collect sand and char particles from the reaction zone. Solid particles, entrained with gas/vapours, were removed by a knocked out vessel (#8) and cyclones (#9). The outlet of cyclones was connected to the jacketed electrostatic precipitator (ESP, #10), where the temperature of the ESP condenser was maintained at 20 °C (outgoing gas temperature). The products, which could not be condensed in ESP, were sent to a second condenser,

Table 2.5: Summary of the experimental conditions of reactor and condenser

Parameter	Unit	Normal operation	Reduced pressure operation
Run time	min		90
M _{sand,initial}	kg		~2
U/U _{mf}	-	~2	~4
T _{ESP}	°C		20
T _{IC}	°C		-10
P _{Reactor}	kPa	100	55
τ _{vapors}	s	1.9	1

Figure 2.3: Schematic representation of pilot plant – continuous fluidised bed

1) Biomass hopper, 2) Stirrer, 3) Feeding screw, 4) Cooling jacket of feeding screw, 5) Sand storage/feeding system, 6) Fluidized bed reactor, 7) Overflow, 8) Knock-out vessel, 9) Cyclones, 10) Electrostatic precipitator (ESP), 11) Intensive cooler (IC), 12) Gas filter, 13) Vacuum pump

also called as an intensive cooler (IC, #11), operated at -10 °C. The permanent gases passed through a gas filter (#12) to collect the remaining liquid. The vacuum in the pilot plant was achieved by using a vacuum pump (#13) connected at the outlet of the gas filter (#12). A needle valve was used at the inlet of the vacuum pump to control the pressure in the pilot plant. The volumetric flow rate of the outgoing gas was measured by using a dry gas meter. At every 10 min, a gas sample was taken from the outgoing gas stream.

Mass balance determination

After each experiment, oil, char and gas yields were individually determined as follows. The char present in the reactor, the overflow vessel, the knock out vessel and the cyclones was collected to determine the char yield (Eq. 2.6). Based on the gas composition and the flowrate of nitrogen gas fed to the fluidised bed, the gas yield (Eq. 2.7) was calculated. The mass of oil collected in ESP and IC were added together to determine the total yield of (wet) pyrolysis oil (Eq. 2.8). The yields of oil, char and gas were summed together to determine the overall mass balance of the experiment (Eq. 2.5).

$$Y_{Char} = \frac{M_{C,R} + M_{C,O} + M_{C,KD} + M_{C,C}}{M_{biomass}(1 - f_w - f_{ash})} \quad (\text{Eq. 2.6})$$

$$Y_{Gas} = \frac{\int_{t=0}^{t=t_{end}} \left\{ \frac{\phi_{out} P_{sample}}{RT_{ambient}} - \frac{\phi_{in} P_{sample}}{RT_{ambient}} \right\} \sum_{i=1}^n f_{v,i} M_{w,i} dt}{M_{biomass}(1 - f_w - f_{ash})} \quad (\text{Eq. 2.7})$$

$$Y_{Oil} = \frac{M_{O,ESP} + M_{O,IC}}{M_{biomass}(1 - f_w - f_{ash})} \quad (\text{Eq. 2.8})$$

2.4 Analytical techniques

2.4.1 Gas Chromatography (GC)

Micro-GC

A gas chromatograph (Varian MicroGC CP4900, 2 analytical columns: 10 m Molsieve 5A, 10 m PPQ, carrier gas: He) was used for analysing gas samples of screen-heater experiments for N₂, O₂, CO, CO₂, CH₄, C₂H₆, C₂H₄, C₃H₆ and C₃H₈. The samples were analysed twice to ensure the reproducibility.

Refinery GC

The gas composition of the samples, collected during the pilot plant experiments, was determined using gas chromatography (Varian 450-RGA). The GC was equipped with three channels. Channel 1 equipped with two columns (Hayesep Q - Agilent CP1305 and Molsieve 5A - Agilent CP1306) detected H₂ using thermal conductivity detector (TCD) with N₂ as a carrier gas. N₂, O₂, CO and CO₂ were separated by three columns (Hayesep Q - Varian CP1308, Hayesep N - Varian CP1307, Molsieve 13X - Varian CP1309), and were detected by channel 2 using TCD with He as a carrier gas. In channel 3, equipped with two columns (CP-Sil 5CB - Varian CP1310 and Al₂O₃/MAPD - Varian CP7433), hydrocarbons (CH₄, C₂H₆, C₂H₄, C₃H₆, C₃H₈) were detected using a flame ionisation detector (FID) with He as a carrier gas.

2.4.2 Gas Chromatography-Mass Spectrometry

Pyrolysis oils were diluted with a solvent in a mass ratio of 1:20 and were filtered with a 0.45 μm Whatman RC Agilent filter, and subsequently analysed by using GC-FID/MS (GC - 7890A, MS - 5975C Agilent Technologies system) equipped with a Agilent HP-5Ms HP19091S-433 capillary column (60 m, ID 0.25 mm, Film thickness: 0.25 μm). The column is packed with (5%-Phenyl)-methylpolysiloxane. Helium was used as carrier gas with a constant flow of 1.95 mL min⁻¹. The oven temperature was programmed from 45 °C (4 min) to 280 °C (20 min) at a heating rate of 3 °C min⁻¹. The injector and the column to MS interface were maintained at a constant temperature of 250 °C and 280 °C, respectively. A sample of 1 μL was injected into the GC. The deactivated inlet liner (Agilent part no: 5183-4711) was regularly replaced to eliminate the influence of non-volatile (inorganic) species deposited on the glass wool. The MS was operated in electron ionisation mode, and ions were scanned in a m/z range from 15 to 500. The identification of the peaks was made by matching its mass spectra with the NIST and Wood library or on the retention times of standards of known compounds

injected in the column. The limit of detection for a given species was 0.008 wt. %, while 0.01 wt. % was the limit of quantification. The quantification was performed based on the FID.

2.4.3 Ion chromatography

The content of AAEMs (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) present in a sample was determined by using ion chromatography (IC). The water-soluble fraction of the sample was dissolved in 8 g of deionised water. The samples were filtered (Whatman RC Agilent 0.2 μm filter) before the IC analysis. The IC (Metrosep 850 Professional IC) was equipped with a cation column (Metrosep C6 - 150/4.0) and Metrohm 732 IC detector coupled to an IC Separation Centre. The analysis was performed at room temperature and with eluent (1.7 mM nitric acid + 1.7 mM dipicolinic acid) flow rate of 1 mL min⁻¹. The quantification was done based on four point calibration of each cation.

2.4.4 High-pressure liquid chromatography

Liquid phase analysis of pyrolysis oils was performed by using HPLC (Agilent 1200 series). The system was equipped with Hi-Plex Pb column (7.7 x 300 mm, 8 μm), and refractive index detector (RID, T = 55 °C) and variable wavelength detector (VWD, λ = 254 nm). The column was packed with a strong cation-exchange resin consisting of sulfonated crosslinked styrene/divinylbenzene copolymer in lead (Pb) form. Deionised water was used as a mobile phase at a flowrate of 0.6 mL min⁻¹. Pyrolysis oils (water-soluble fraction) were diluted in deionised water in a mass ratio of 1:20 and were filtered with 0.2 μm Whatman RC Agilent filter. During analysis temperature of the column was maintained at 70 °C and 10 μL of sample volume was injected into the system at room temperature. The limit of detection for a given species is 0.002 wt. %, while 0.008 wt. % is the limit of quantification. Quantification was performed based on the RID.

Analysis of model compound pyrolysis oils was performed on LC-UV (UHPLC 3000 Thermo Fisher Scientific) system, equipped with Kinetex F5 core-shell LC column by phenomenex operated at 35 °C. A mixture of acetonitrile and water was used as eluent (0.2 mL min⁻¹), where the concentration of acetonitrile was gradually increased from 10 vol. % to 90 vol. % over 60 min. During the analysis, VWD was set at 254 nm and it was used for the quantification.

2.4.5 Direct infusion mass spectrometry

The pyrolysis oils (water-soluble fraction) were diluted with deionised water to a concentration of ~ 150 mg kg⁻¹. Ammonium acetate was added to the diluted oil-

water mixture as an ionisation agent^[129,130]. A 1 mL Hamilton syringe loaded onto a syringe pump was used to infuse diluted samples directly into the ESI chamber at a rate of 0.01 mL min⁻¹. The instrument used was an ESI Ion-Trap mass spectrometer (Bruker amaZON SL, Germany). The ESI MS analysis was accomplished in manual mode using drying temperature of 200 °C, N₂ flowrate and nebulizer pressure of 6 L min⁻¹ and 10 psi, respectively. Full scan mass spectra were acquired over the m/z range of 50 - 2000. For MS² experiments, helium gas was used as a collision gas with a fragmentation amplitude voltage of 1 V and a mass window was 1.5 Da.

2.4.6 Gel permeation chromatography (GPC)

The molecular weight distribution (M_wD) of lignin and pyrolysis oils was determined by using GPC (Agilent Technologies 1200) equipped with three columns (7.5 mm x 300 mm, particle size 3 μm) placed in series packed with highly cross-linked polystyrene-divinylbenzene copolymer gel (Varian PLgelMIXED E). The column temperature was maintained at 40 °C during analysis. Samples were dissolved in tetrahydrofuran (THF) in a 1:100 mass ratio and were filtered through a 0.45 μm Whatman RC Agilent filter. THF was used as a mobile phase at a flowrate of 1 mL min⁻¹. A RID and VWD (λ = 254 nm) were installed. The calibration line was made with 10 polystyrene standards with molecular weights ranging from 162 Da to 29510 Da, which was used for the conversion of elution volume to molecular weight.

2.4.7 Nuclear magnetic resonance (NMR)

1D NMR: ¹H

¹H NMR spectra were recorded on a Bruker Avance II 600 MHz NMR spectrometer (14.1 T), using a 5 mm triple nucleus TXI ¹H-¹³C/¹⁵N/²H probe and Avance III 400 MHz NMR spectrometer (9.4 T) provided with a broadband BBFO probe. Both spectrometers are equipped with a z gradient coil producing a maximum gradient strength of 50 gauss cm⁻¹.

2D NMR: Q-CAHSQC

2D Q-CAHSQC NMR spectra were acquired on a Bruker Avance II 600 MHz spectrometer (14.1 T), using a 5 mm triple nucleus TXI ¹H-¹³C/¹⁵N/²H probe, equipped at 25 °C without sample spinning using the Q-CAHSQC pulse program^[131]. Matrices of 2048 data points for the 1H-dimension and 256 data points for the 13C-dimension were collected with a relaxation delay of 6 s and spectral widths from 14 to -1 ppm and from

200 to 0 ppm for the ^1H and ^{13}C dimensions, respectively. The samples were dissolved in DMSO- d_6 (Concentration: $0.1 \text{ mg } \mu\text{L}^{-1}$), and chemical shifts were referenced to the solvent signal (2.5/39.5 ppm). The spectra were processed using MestReNova.

2.4.8 Karl-Fischer Titration (KFT)

The water content of pyrolysis oils was determined by Karl-Fischer titration using a Metrohm 787 KF Titrino. Hydranal Composite 5 was used as a titrant and a solution of methanol : dichloromethane (3:1 in volume) was used as a solvent.

2.4.9 Elemental analysis

A Perkin-Elmer elemental analyser (Thermo scientific Flash 2000) was used for the ultimate analysis (C, H, N) of the samples. The analyser was equipped with a column of two reactive beds, i.e. copper oxide and electrolyte copper. The column temperature was maintained at 900°C . Argon (140 mL min^{-1}) and O_2 (250 mL min^{-1}) were used as a carrier and reactive gases, respectively. TCD was used for the detection of 29 gases. Tin cups loaded with the sample ($\sim 3 \text{ mg}$) were inserted into the column by an auto-sampler. The weight fraction of C, H and N were calculated based on the amount of H_2O , CO_2 and N_2 evolved from the decomposition of the samples. The oxygen fraction was calculated by difference.

Nomenclature

i	-	Number of components detected in the gas sample
$M_{feedstock}$	kg	Dry mass of feedstock
$M_{screens}$	kg	Mass of the screens before experiment
$M_{screens+residue}$	kg	Mass of the screens with char
M_{vessel}	kg	Mass of the vessel before experiment
$M_{vessel+oil}$	kg	Mass of the vessel with oil
M_{c+b+t}	kg	Mass of the clamps (c), bolts (b) and tape (t) before experiment
$M_{c+b+t+oil}$	kg	Mass of the clamps (c), bolts (b) and tape (t) with oil
$M_{crucible}$	kg	Mass of the empty crucible
$M_{crucible+sample}$	kg	Mass of the empty crucible and sample
$M_{crucible+ash}$	kg	Mass of the empty crucible and ash
$M_{biomass}$	kg	Mass of biomass pyrolysed in fluidised bed
$M_{C,R}$	kg	Mass of char collected from the fluidised bed reactor
$M_{C,O}$	kg	Mass of char collected from the overflow vessel
$M_{C,KD}$	kg	Mass of char collected from the knock out vessel
$M_{C,C}$	kg	Mass of char collected from the cyclones
MW_i	$kg\ mole^{-1}$	Molecular weight of component i
P_{sample}	Pa	Pressure at which the gas sample was taken
R	$J\ mole^{-1}K^{-1}$	Universal gas constant
$T_{ambient}$	K	Temperature at which the gas sample was taken
$f_{v,i}$	-	Volume fraction of component i in the gas sample
f_w	-	Mass fraction of moisture in feedstock
f_{ash}	-	Mass fraction of ash in feedstock
V_{vessel}	m^3	Volume of the vessel
V_{bag}	m^3	Volume of the gas bag; for vacuum experiment V_{bag} was zero
Y_{Ash}	$kg\ kg^{-1}$	Ash yield
Y_{Gas}	$kg\ kg^{-1}$	Gas yield, dry ash free basis
Y_{Char}	$kg\ kg^{-1}$	Char yield, dry ash free basis
Y_{Oil}	$kg\ kg^{-1}$	Oil yield, dry ash free basis
ϕ_{out}	$m^3\ s^{-1}$	Total flowrate of gas measured by the gas meter
ϕ_{in}	$m^3\ s^{-1}$	Total flowrate of nitrogen added to the fluidised bed reactor

C₃

Evaluating quantitative
determination of levoglucosan and
hydroxyacetaldehyde in bio-oils by
gas and liquid chromatography

Abstract

C₃

This chapter evaluates the suitability of gas and liquid chromatography for the quantification of levoglucosan and hydroxyacetaldehyde in bio-oils. It was found that both techniques can principally determine levoglucosan quantitatively in cellulose/biomass derived bio-oils. However, it is also shown that oligo-anhydrosugars present in the bio-oils undergo depolymerisation to levoglucosan during gas chromatography, resulting in an overestimation of the concentration of levoglucosan. Hydroxyacetaldehyde can only be determined quantitatively by liquid chromatography. Presented experimental evidence shows that the high temperature (200-320 °C) of injection in gas chromatography is a key factor causing oligo-anhydrosugars and hydroxyacetaldehyde to react during analysis, which may lead to flawed results.

This chapter is based on:

P.S. Marathe, A. Juan, X. Hu, R.J.M. Westerhof, S.R.A. Kersten, Evaluating quantitative determination of levoglucosan and hydroxyacetaldehyde in bio-oils by gas and liquid chromatography, *J. Anal. Appl. Pyrolysis* (2019).

3.1 Introduction

This chapter deals with the quantitative determination of levoglucosan (LG) and hydroxyacetaldehyde (HA) in bio-oils by gas (GC) and liquid (LC) chromatography, being the most frequently used analytical techniques. In the literature, a limited number of studies deal with the GC analysis of silylated of bio-oils (e.g.^[132–138]), whereas >100 research articles report GC analysis of non-silylated bio-oils. Therefore, in this work, GC analysis of only non-silylated bio-oils is considered.

The motivation for this work is our observation that analysing the same oil on our GC and LC instrument resulted in different concentrations of LG and HA in the samples. In order to rule out the artefacts of our equipment and methods, LG and HA yields reported in the literature were examined. 65 papers^[48,49,61,64,66,72–75,107,130,136,139–191], including 6^[66,130,154,174,181,185] of our own, reporting on different biomasses, reactors, operating conditions and analytical techniques were evaluated. All data used are listed in Table A.1 to A.4 in Appendix A. Aligning the LG (or HA) yields obtained under different conditions and by different measurement techniques is rather difficult. However, the statistical analysis of these data shows that the influence of measurement (analytical) technique used on the reported yields of LG is significant and for HA yields cannot be excluded. This statement is substantiated below in more detail. Table 3.1 shows the range and average of LG and HA yields reported, for cellulose and lignocellulosic biomass pyrolysis, in the temperature range between 300 and 650 °C. This table also lists standard deviations, *p*-values and the results of the principal component analysis (PCA).

The *p*-values indicate that for LG there is a difference between the population means of the sets with a different analytical technique, i.e. reported yields by GC and LC are statistically different. This is not the case for HA, although PCA indicates that for HA the analytical technique is the 3rd (biomass) and the 4th (cellulose) principle component out of six. This suggests that there may be an effect of the analytical technique. Wang et al.^[174] reported the LG yields determined by GC and LC, in which they report higher LG yields by GC than by LC for cellulose-derived oils, and vice-versa for pyrolysis oils obtained from biomass. No study in the literature reports HA yields measured by both GC and LC.

Based on our observations and analysis of literature data, we decided to investigate the suitability of GC and LC for the quantification of LG and HA in bio-oils systematically. To the best of our knowledge, no such study is available in literature. Conducting such a study would be of significant importance for obtaining the correct information about the true yields of LG and HA. These are two important compounds derived from

Table 3.1: Reported yields of levoglucosan (LG) and hydroxyacetaldehyde (HA): minimum, maximum, mean (μ), standard deviation (σ), number of data points, number of papers, p -values (Welch test), and principal components

Compound Unit Analytical technique Feedstock	LG				HA			
	wt. % on cellulose/biomass				wt. % on cellulose/biomass			
	GC	LC	GC	LC	GC	LC	GC	LC
	Cellulose		Biomass		Cellulose		Biomass	
nr of data points	21	26	97	32	16	6	55	22
nr of papers	12	9	33	12	9	3	19	8
minimum	0.1	0.5	0.0	0.0	1.6	0.0	0.0	0.0
maximum	63.5	48.0	23.5	22.1	16.0	15.3	12.7	17.1
μ	36.7	19.9	3.6	5.3	6.8	9.8	4.5	5.7
σ	20.4	13.1	4.3	5.7	4.0	5.2	3.6	4.6
AT being PC nr. ^a	2 ^b		2		4		3	
p -value	0.003		0.037		0.278		0.302	

^a The following 6 principal components (PC) were used: Y: yield; A: ash content; R: reactor type; T: temperature; P: pressure; AT: analytical technique. In Section A.3 of Appendix A, the complete output of the PCA is presented.

^b For example, AT being PC number means analytical technique is 2nd principal component

cellulose via pyrolysis, which is a prerequisite for understanding the composition of bio-oil and for understanding the mechanism for pyrolysis cellulose or biomass.

3.2 Bio-oils

Bio-oils used in this chapter were derived from cellulose and pinewood. Cellulose samples (pure and 1000 mg kg⁻¹ potassium infused) were pyrolysed in a screen-heater (0.5 kPa) and fluidised bed reactor (100 kPa) at 530 °C. Pinewood was pyrolysed in a continuous fluidised bed reactor, (two separate experiments) at 530 °C. For the details of pyrolysis experiments and the discussion about experimentally observed trends, refer to Chapter 4 and the work of Oudenhoven et al.^[62]. The oil yields observed for pure cellulose in screen-heater (0.96 kg kg⁻¹) and fluidised bed (0.73 kg kg⁻¹) were higher compared to the oil yields obtained for 1000 mg kg⁻¹ potassium infused cellulose (screen-heater: 0.52 kg kg⁻¹ and fluidised bed: 0.6 kg kg⁻¹) (see Chapter 4). For pinewood, 0.55 kg kg⁻¹ oil yields, excluding water, were obtained in the work of Oudenhoven et al.^[62]. All bio-oils were stored at -25 °C in the absence of light before analysis.

Note that, because of the limited quantity (~30 mg) of oil collected from a single

screen-heater experiment, it was not possible to analyse the same oil by GC and LC. Therefore, both cellulose samples were pyrolysed, in the screen-heater eight times, under identical experimental conditions, of these four oils were analysed individually by either GC or LC. The error bars in Figure 3.1 and 3.3 represent the standard deviations on the mean. Contrary, the quantity of oil obtained from a single fluidised bed experiment was sufficient for both analysis techniques. Thus, for each fluidised bed oil, three separate samples (for each analysis technique) were prepared and were subsequently analysed. The LG (and HA) yield values are averages of three separate analyses. The standard deviation on the mean, for the LG (and HA) yields obtained (in GC and LC) from three injections (per oil) was <1% for LG (and HA). Hence, to avoid the confusion between LG (and HA) yields from four experiments (in screen-heater) and three separate samples (of a single fluidised oil), the error bars for latter were not included in Figure 3.1 and 3.3.

3.3 A note on GC and LC settings reported in literature

GC: Table A.5 in the Appendix A presents the summary of GC settings, i.e. solvent, injection temperature, column, oven temperature program, reported in the literature. Methanol and acetone are the commonly used solvents for diluting bio-oils before GC analysis. Diluted oils are subsequently introduced into GC via an injection port/section, of which temperature ranges between 200 to 320 °C. It is important to note that during (high temperature) injection, solvent and species present in the pyrolysis oil matrix are present together. In the literature, 20 different chromatographic columns varying in polarity are reported. Typically, the GC oven temperature increases with a low heating rate of 3 to 5 °C min⁻¹.

LC: Table A.6 in the Appendix A presents the summary of LC settings, i.e. mobile phase and its flowrate, column, and the temperature at which the separation takes place, reported in the literature. Different mobile phases, from acidic to basic in nature, are used to separate the species present in the pyrolysis oil, and its flowrate ranges from 0.4 min⁻¹ to 2 min⁻¹. In literature, 8 different LC columns are reported, and their operation temperature lies in between 25 to 85 °C.

It is worth mentioning that the GC and LC settings used in this work do not deviate from the ones reported in the literature.

3.4 Results and discussion

3.4.1 Levoglucosan

Figure 3.1 shows that LG yields determined by GC were consistently higher than that by LC. The difference was most noticeable for the pyrolysis oil obtained from pure cellulose and was smaller for oils obtained from 1000 mg kg⁻¹ potassium infused cellulose. Note, the effect of potassium on cellulose pyrolysis has been elaborated in Chapter 4, and hence it is not discussed here.

Literature shows that the pyrolysis of oligo-anhydrosugars (e.g. cellobiosan) results in the production of LG^[130,174]. Based on these findings, it has been proposed, by us, that the oligo-anhydrosugars present in the pyrolysis oil partially depolymerise to LG at the injection temperature of 250 °C of a GC. To validate this hypothesis, a cellobiosan solution (of known concentration) diluted in methanol was injected into the GC and it was confirmed that the only observed peak in the chromatogram of cellobiosan was of LG (RT = 55.5 min), see Figure A.3 in Appendix A. Based on the recovery of LG calculated from the chromatogram, the estimated conversion, based on the assumption that cellobiosan only reacts to levoglucosan, was 28%. On the other hand, cellobiosan analysed by LC showed no evidence of decomposition. Accordingly, it can be concluded that the oligo-anhydrosugars partially depolymerise to smaller anhydrosugar(s) at the temperatures as low as 250 °C during GC analysis.

It has been shown in literature that pyrolysis oil obtained from pure cellulose is comprised of oligo-anhydrosugars with a degree of polymerisation up to 11^[130,178,187,192,193]. Therefore, it is argued that the higher LG yields (by GC) observed (in Figure 3.1), in the case of pure cellulose oils, is a result of the partial depolymerisation of oligo-anhydrosugars taking place in GC. In the case of 1000 mg kg⁻¹ potassium impregnated cellulose pyrolysis, the majority of oligo-anhydrosugars were destroyed during pyrolysis (Chapter 4); consequently, the difference in the LG yields determined by the two analytical techniques was smaller.

Figure 3.2 shows the LG yields, obtained from unspiked and spiked cellulose oils (fluidised bed), determined by GC and LC. The oils were spiked with 0.07 kg kg⁻¹ LG (on cellulose basis). Hereafter, original bio-oils and bio-oils doped with extra LG (or HA in Section 3.4.2) are referred to as unspiked and spiked oils, respectively. The additional LG was recovered completely by both analytical techniques. These findings suggest that quantification of LG is not affected by the analytical techniques self, even when present in the matrix of other chemical species. In conclusion, to avoid the over-estimation of the LG yield caused by depolymerisation of oligo-anhydrosugars and for precise quan-

Figure 3.1: LG yield measured by GC and LC

Figure 3.2: LG yield, obtained from unspiked and spiked cellulose bio-oils (fluidised bed), determined by GC and LC

tification of LG yield, liquid chromatography is recommended. If in case, a GC system is used for the quantification of LG, careful interpretation of the LG yield is essential.

3.4.2 Hydroxyacetaldehyde

Figure 3.3: HA yield measured by GC and LC

Figure 3.3 compares the HA yield determined by GC and LC. It can be seen that the yield of HA measured by GC is lower than by LC. This observed trend is independent of feedstock and the experimental setup. Note, for the details about the isolation, identification and quantification of the HA, Section A.6 of Appendix A can be referred.

In order to understand the discrepancy in HA yields, bio-oils spiked with 0.07 kg kg⁻¹ HA (on cellulose basis) were analysed by GC and LC. Figure 3.4A and 3.4B present the HA yields, obtained from unspiked and spiked cellulose oils determined by GC and LC. The difference between the HA yields obtained from unspiked and spiked oils, determined by GC analysis, was smaller than the spiked amount, while it was 0.07 kg kg⁻¹ for both oils when determined by LC. This observed trend is independent of the solvent used for dilution of oils prior to GC analysis, see Figure 3.4A (methanol) and 3.4B (acetone).

These results suggest that HA undergoes reactions during GC analysis, while it does not react during LC analysis. One of the decomposition products, glycolaldehyde dimethyl acetal, was detected in the GC chromatograms. Glycolaldehyde dimethyl ac-

Figure 3.4A: HA yield, obtained from unsiked and spiked cellulose bio-oils (fluidised bed), determined by GC and LC; solvent: Methanol

Figure 3.4B: HA yield, obtained from unsiked and spiked cellulose bio-oils (fluidised bed), determined by GC and LC; solvent: Acetone

etal is a product of the reaction between HA and methanol. A similar decomposition product, namely glycolaldehyde methyl acetal, was observed by Stassinopoulou et al.^[194] in deuterated methanol, which was used for dilution. Shen et al.^[195] have proposed that HA can decompose thermally to form permeant gases (e.g. CO, CH₄, H₂) and other species (e.g. methanol, acetic acid, pyruvaldehyde). Diebold^[196] has identified the reactions between saturated aldehydes, present in pyrolysis oil, with methanol at low temperatures. Similarly, Patwardhan et al.^[148] have reported interactions between methanol and aldehydes during the GC analysis. Interestingly, for pure cellulose (spiked and unspiked) oils (diluted in methanol), the difference in the HA yield is 0.055 kg kg⁻¹, while it is only 0.019 kg kg⁻¹ for oils (spiked and unspiked) obtained from potassium infused cellulose. Although, Stassinopoulou et al.^[194] found no decomposition products of glycolaldehyde in acetone at room temperature, incomplete recovery of the spiked HA was observed by us, when acetone was used as a diluent. Hence, in the view of these results, the possibility of thermal degradation of HA, and reactions between HA and other species present in the bio-oils cannot be neglected. Nevertheless, further experimental investigation is needed to understand the reactions of HA at the GC injection temperature.

In summary: during injection of the sample in GC, HA – 1) might react with the solvent in which oil is diluted, 2) decomposes, and 3) might undergo reactions with other species present in the pyrolysis oil, on the other hand, during liquid chromatography it does not react. Therefore, liquid chromatography is recommended for determining the yield of HA present in the bio-oils.

3.5 Conclusions

In this chapter, the suitability of gas chromatography and liquid chromatography for the quantification of levoglucosan and hydroxyacetaldehyde was investigated. Levoglucosan can be quantified with gas chromatography, but there is a risk of overestimation due to its production out of oligo-anhydrosugars. For ash rich feedstock (>0.1 wt %), this effect is minor. Hydroxyacetaldehyde can decompose, and react with compounds in the matrix and solvent used during gas chromatography. Liquid chromatography does not suffer from these shortcomings and allows for the quantitative determination of levoglucosan and hydroxyacetaldehyde in bio-oils. Generalising, the high injection temperature of gas chromatography analysis leads to a flawed quantitative analysis of reactive components.

C_4

C₄

Fast pyrolysis of cellulose:
interaction between chemistry and
transport phenomena in the absence
and presence of potassium

Abstract

C₄

The interplay between chemistry and transport processes in the pyrolysis of cellulose has been investigated in the presence and absence of potassium salts. For this, a dedicated screen-heater set-up has been used that combines a high heating rate of the sample with fast removal and quenching of reaction products. In the absence of potassium salts, cellulose can almost entirely be converted to anhydrosugars while producing hardly any gas (<1%) and char (<1%) in a wide temperature range of 450 to 765 °C. The obtained product yields and the degree of polymerisation (*DP*) distribution of anhydrosugars as a function of process and pyrolysis conditions are presented and interpreted, also using two mathematical models, on the level of chemistry, heat transfer, mass transfer and their interplay. In addition to the heating rate of sample and the hot vapour residence time, the escape rate of products from the hot reacting particle has been identified as a crucial process determining the mass loss rate and the *DP* distribution of anhydrosugars. Next, the potassium concentration in cellulose is varied to mimic the mineral-rich and pre-treated feedstock. Potassium has been found to be catalytically active even when the escape rate (milliseconds) of the product from the reaction front is extremely high. The yields of oil and anhydrosugars decrease significantly as a function of potassium concentration, while the production of other products (water, gases, light oxygenated compounds) is enhanced as a result of potassium catalysed dehydration and ring opening reactions. The production of char is found to be independent of escape rate of products at a given potassium concentration. Pyrolysis at reduced pressure, i.e. by fast removal of products from the hot reaction zone, can improve the oil and sugar yields, especially for low alkali and alkaline earth metals (AAEMs) content feedstock.

This chapter is based on:

R.J.M. Westerhof, S.R.G. Oudenhoven, P.S. Marathe, M. Engelen, M. Garcia-Perez, Z. Wang, S.R.A. Kersten, The interplay between chemistry and heat/mass transfer during the fast pyrolysis of cellulose, *Reaction Chemistry & Engineering* 1 (2016) 555-566

P.S. Marathe, S.R.G. Oudenhoven, P.W. Heerspink, S.R.A. Kersten, R.J.M. Westerhof, Fast pyrolysis of cellulose in vacuum: The effect of potassium salts on the primary reactions, *Chem. Eng. J. (Lausanne)* 329 (2017) 187-197

4.1 Introduction

Pyrolysis oil is a complex mixture of organic compounds, with different chemical classes^[77,197,198]. Nowadays, the majority of the research focuses on the production of targeted compounds (e.g. mono-phenols, sugars) at high yields. Especially the production of anhydrosugars from lignocellulosic biomass seems to be a promising route. These pyrolytic sugars can be converted to monosaccharides (e.g. glucose, xylose, mannose) via acid hydrolysis, and subsequently upgraded to bio-ethanol^[199,200] by fermentation or catalytically to platform chemicals^[32,201–204]. In literature, sugar yields up to 30 wt. % have been reported^[62,71]. Pyrolysis of cellulose, being one of the major building blocks of lignocellulosic biomass, has been studied, over a century^[205]. Recent reviews of L have summarised the primary reactions of cellulose pyrolysis^[50,206], and others have identified the gaps in the knowledge and challenges^[9,207,208]. 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) lack at molecular, cell, particle and reactor level.

The first part of this chapter aims at advancing the understanding of reactions and transport phenomena by pyrolysing cellulose, under the conditions that are nearly isothermal, maximise the escape rate of volatile products from the reacting cellulose particles and maximise the rate of the subsequent quenching of these products. High escape rates will minimise, on/in the hot reacting particle, the secondary reactions of the volatile products. Rapid quenching ensures minimal reactions in the vapour phase and the ejected fragments (e.g. aerosols). In order to be able to draw conclusions without being hindered by uncontrollable and poorly understood phenomena, such as the effects of AAEMs^[140,209,210] and interactions between the biomass' building blocks^[211,212], it was decided to start with Avicel PH 101 (very pure) cellulose. Additionally, two mathematical models, which include reactions and heat transfer, were developed to - 1) interpret and predict experimentally observed trends, and 2) to investigate if the pyrolysis is kinetically controlled^[60] or if there is an interplay between heat, mass transfer and chemistry.

The second part of the chapter is dedicated to understanding the effects of AAEMs on the early stage products of cellulose pyrolysis. It is well known that the presence of AAEMs has an adverse effect on the production of anhydrosugars. Although, several methods exist to remove (or passivate) the AAEMs from (or in) biomass, complete removal of the AAEMs is impossible in practice. Moreover, it is unknown to what extent the destructive effects of AAEMs (in low concentration), on sugar production, can be minimised by manipulating - 1) operating conditions, 2) short hot vapour residence time, and 3) rapid quenching. Therefore, potassium, being naturally present in the

biomass^[18,19], was selected as a model cation representing other AAEMs and was infused in Avicel PH 101 cellulose. The following concentrations were chosen: 1 mg kg⁻¹ was selected as a lower boundary, 100 and 1000 mg kg⁻¹ because it is typically achievable after acid leaching^[61,62], and 10000 mg kg⁻¹ representing untreated biomass^[19]. It is worth mentioning that 100 mg kg⁻¹ corresponds to a single potassium molecule per ~2500 glucose units (in cellulose) and 1000 mg kg⁻¹ to a single potassium molecule per ~250 glucose units (in cellulose). Additionally, the catalytic effect of different anions (CO₃²⁻, Cl⁻, OH⁻) on pyrolysis products was studied by infusing different potassium salts in cellulose.

The experiments were carried out in a screen-heater and a bench scale fluidised bed reactor. The screen-heater is designed to combine the high heating rate of the sample with fast removal and rapid quenching of reaction products^[119]. The effect of vapour residence time on the pyrolysis products was studied by comparing the results from the screen-heater experiments (~20 ms) with fluidised bed experiments (~1.6 s). Oils were analysed to identify and quantify light oxygenated compounds (e.g. levoglucosenone, acetol, hydroxyacetaldehyde) and levoglucosan as well as the yield of bigger anhydro-sugars ($DP_{>1}$), lumped as glucose after acid hydrolysis.

4.2 Interpretation models

Figure 4.1: Schematic representation of the mass and heat transport processes

To support the analysis of the experimental data, two interpretation models were used. The models are schematically visualised in Figure 4.1. Heat is transferred via direct contact with the wires to the sample. The wires have a heating rate of approx. $5000\text{ }^{\circ}\text{C s}^{-1}$ ^[120]. At elevated temperatures, chemical reactions will start to proceed in the solid cellulose 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 locally inside the solid matrix. Such liquids have been observed in pyrolysing biomass^[213]. 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 vapour pressure can be much higher than the prevailing pressure in the vessel. The work of Teixeira et al.^[54] has shown that it is also possible that aerosols are ejected from reacting cellulose samples. Summarising, products can escape from the pyrolysing particle via sublimation, evaporation and aerosol ejection.

Model I

To describe the weight loss and temperature of the cellulose sample, a modified version of the model as described by Boutin et al.^[214] was used, in combination with the reaction rate parameters given by Bradbury et al.^[83]. In our model, contrary to Boutin et al.'s, the sample has a spatially uniform temperature, and the state of the intermediate/active cellulose is not defined (can be 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 average 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 pathways shown in Figure 4.2 are used.

Figure 4.2: Schematic representation of interpretation model I

The vapours were recovered on the cold glass vessel as oil. The reaction rate constant k_2 describes both chemical reactions and the escape rate of products from the reacting sample^[83]. Both reactions, i.e. 1 (Cellulose to intermediates) and 2 (Intermediates to vapours), are described by first order rate equations and the Arrhenius temperature dependency. Mass balance equations are solved for cellulose (C) and active/intermediate cellulose (AC). Symmetry is assumed, thus, only one side of the sample is modelled.

$$\frac{dM_C}{dt} = -k_1(T_C)M_C \quad (\text{Eq. 4.1})$$

$$\frac{dM_{AC}}{dt} = k_1(T_C)M_C - k_2(T_C)M_{AC} \quad (\text{Eq. 4.2})$$

$$M_S = M_C + M_{AC} \quad (\text{Eq. 4.3})$$

$$X = 1 - \frac{M_S}{M_{S,0}} \quad (\text{Eq. 4.4})$$

The following energy balance is solved assuming that the heat of reaction of the 1st reaction is negligible:

$$\frac{dT_C}{dt} = \frac{A\alpha(T_S - T_C) - k_2(T_C)M_{AC}\Delta H_2}{M_S C_p} \quad (\text{Eq. 4.5})$$

The temperature of the screens is modelled by:

$$\frac{dT_S}{dt} = \begin{cases} B & \text{if } T_S < T_{set} \wedge t \leq t_h; \\ 0 & \text{if } T_S = T_{set} \wedge 0 \leq t \leq t_h + \frac{T_{set}}{B}; \\ -B' & \text{if } t > t_h + \frac{T_{set}}{B}. \end{cases} \quad (\text{Eq. 4.6})$$

For the calculation of the char yield (Figure 4.5A) the cooling period was taken into account. For the calculation of T_r , given by Eq. 4.7, the cooling period was not taken into account; after heating, the screens remain at the set-point temperature.

$$T_r = \frac{\int_{X=0.1}^{X=0.9} T_S(X) dX}{\int_{X=0.1}^{X=0.9} dX} \quad (\text{Eq. 4.7})$$

The initial conditions are:

$$M_{S,0}(M_{C,0}) = 2.5 \times 10^{-5} kg$$

$$M_{AC,0} = 0$$

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

Model II

To predict the trend of the product distribution as a function of the temperature, model I has been extended by – 1) an intermediate / active cellulose phase that consists of heavies ($DP_{\geq 2}$) and DP_1 , 2) a reaction of heavies to compounds of lower DP that takes place on the sample and 3) lower escape rates of heavies compared to lights. This is shown schematically in Figure 4.3.

Figure 4.3: Schematic representation of interpretation model II

The vapours were recovered on the cold glass vessel as oil. 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 show that the larger sugars have a lower escape rate compared to DP_1 . k_3 is chosen/set arbitrary to be 10 % of the value of k_2 . k_1 and k_2 are the constants derived by Bradbury et al.^[83]. Note, the purpose of the model is to investigate if a model, including chemical reactions and mass transfer, can predict the experimentally observed trends, i.e. the DP -distribution in the oil as a function of the temperature of the screens, and 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:

$$\frac{dM_C}{dt} = -k_1(T_C)M_C \quad (\text{Eq. 4.8})$$

$$\frac{dM_{DP_{\geq 2}}}{dt} = k_1(T_C)M_C - (k_3(T_C) + k_4(T_C))M_{DP_{\geq 2}} \quad (\text{Eq. 4.9})$$

$$\frac{dM_{DP_1}}{dt} = k_3(T_C)M_{DP_{\geq 2}} - k_2(T_C)M_{DP_1} \quad (\text{Eq. 4.10})$$

$$M_S = M_C + M_{DP_1} + M_{DP_{\geq 2}} \quad (\text{Eq. 4.11})$$

$$X = 1 - \frac{M_S}{M_{S,0}} \quad (\text{Eq. 4.12})$$

The following energy balance is solved assuming that the heat of reaction of the 1st reaction (cellulose to intermediates) 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 a mass basis:

$$\frac{dT_C}{dt} = \frac{A\alpha(T_S - T_C) - (k_2(T_C)M_{DP_1} + k_4(T_C)M_{DP_{\geq 2}})\Delta H}{M_S C_p} \quad (\text{Eq. 4.13})$$

The temperature of the screens is modelled using the same procedure as for Model I (Eq. 4.6). The yields of DP_1 and $DP_{\geq 2}$ in the condensed product are calculated by:

$$Y_{DP_1} = \frac{\int_{t=0}^{t=\infty} k_2(T_C)M_{DP_1} dt}{M_{S,0}} \quad (\text{Eq. 4.14})$$

$$Y_{DP_{\geq 2}} = \frac{\int_{t=0}^{t=\infty} k_4(T_C)M_{DP_{\geq 2}} dt}{M_{S,0}} \quad (\text{Eq. 4.15})$$

The initial conditions are:

$$M_{S,0}(M_{C,0}) = 2.5 \times 10^{-5} kg$$

$$M_{DP_1,0} = M_{DP_{\geq 2},0} = 0$$

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

Numerical method

Model I and Model II equations were solved in the coding environment of Matlab®2016a. The numerical integration was carried out with a built-in ode15s solver, especially suited for a system of differential algebraic equations (DAE). In Table 4.1 the numerical values of the parameters used in model I and model II are listed.

Table 4.1: Constants used for pyrolysis model I and model II

Parameter	Unit	Value	Comment
B	$^{\circ}\text{C } s^{-1}$	5000 (10000)	The heating rate of the screens. $5000 ^{\circ}\text{C } s^{-1}$ was the experimentally determined value. In the sensitivity analysis also $10000 ^{\circ}\text{C } s^{-1}$ was used.
B'	$^{\circ}\text{C } s^{-1}$	60	Cooling rate (measured) of the screens after the holding time.
$k_{1,0}$	s^{-1}	2.8×10^{19}	Pre-exponential constant of reaction 1 ^[83]
E_1	$J mol^{-1}$	2.42×10^5	Activation energy of reaction 1 ^[83]
$k_{2,0}$	s^{-1}	3.2×10^{14}	Pre-exponential constant of reaction 2 ^[83]
E_2	$J mol^{-1}$	1.98×10^5	Activation energy of reaction 2 ^[83]
$k_{3,0}$	s^{-1}	3.2×10^{13}	10 % of $k_{2,0}$ (arbitrary choice)
E_3	$J mol^{-1}$	1.98×10^5	Equal to E_2 (arbitrary choice)
$k_{4,0}$	s^{-1}	10×10^{20}	Overall k lower than k_2 (arbitrary choice)
E_4	$J mol^{-1}$	3.0×10^5	Overall k lower than k_2 (arbitrary choice)
Cp	$J kg^{-1} K^{-1}$	1500	Specific heat capacity cellulose ^[215]
A	m^2	0.003	Area, 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.
α	$W m^{-2} K^{-1}$	1000 to ∞	A low estimate of the heat transfer coefficient and infinite. (Model I)
α	$W m^{-2} K^{-1}$	1×10^4	Good contact between sample and wires (Model II)
ΔH_2	$J kg^{-1}$	-0.25×10^6 to 0.7×10^6	Slightly exothermic reaction till the heat of evaporation of levoglucosan.
ΔH	$J kg^{-1}$	0.7×10^6	Heat of evaporation of levoglucosan ^[216] .

4.3 Results and discussion

4.3.1 Screen-heater and fluidised bed characteristics

The characteristics of the screen-heater have been discussed in detail by Hoekstra et al.^[119] and Oudenhoven^[120]. Here, the characteristics are briefly discussed and summarised in Table 4.2. The cellulose sample is distributed evenly between the two screens to achieve nearly uniform heating. The heating rate of the screens is $\sim 5000\text{ }^{\circ}\text{C s}^{-1}$. The temperature difference over the screen was $\pm 15\text{ }^{\circ}\text{C}$. The screens were held at the T_{FS} for 5 s. The cooling rate of the screens was $\sim 60\text{ }^{\circ}\text{C s}^{-1}$. A detailed validation of the temperature profiles and measurements can be found elsewhere^[120]. It has been shown that the pyrolysis time, i.e. the time to reach full conversion, at $610\text{ }^{\circ}\text{C}$ and 0.5 kPa is around 121 ms for pure cellulose^[120]. The pyrolysis time was also checked for cellulose impregnated with potassium (10000 mg kg^{-1}) at $530\text{ }^{\circ}\text{C}$ and 0.5 kPa , see Figure 4.4. This figure shows screenshots of a movie recorded with a high-speed camera. It can be seen that the first products were condensed on the cold glass vessel after 63 ms. After that, no change in the shape of the black material present between the screens and the appearance of the oil on the glass vessel (see red arrows), between 79 ms and 304 ms, implied that the pyrolysis reactions were finished.

The time difference between the escape of vapours or aerosols from the reacting particle until quenching is defined as the hot vapour residence time. At 0.5 kPa , the vapours/aerosols are rapidly quenched at the glass vessel, which was surrounded by the liquid nitrogen ($-196\text{ }^{\circ}\text{C}$) bath, equilibrated at $-180\text{ }^{\circ}\text{C}$. It was estimated that for both pressures (0.5 and 100 kPa) hot vapour residence time is in order of $\sim 20\text{ ms}$, which ruled out a significant effect of reactions outside the reacting cellulose particle^[120]. The most significant difference between the screen-heater and the bench-scale fluidised bed is the hot vapour residence time ($\sim 20\text{ ms}$ ^[120] vs 1.6 s ^[66]), see Table 4.2. In the screen-heater at 0.5 kPa , the escape rate of the DP_1 anhydrosugar (levoglucosan) is a factor 10 higher compared to 100 kPa , see Table 4.2. As a consequence, the residence time of the products on the hot reacting particle was considerably lower in the case of vacuum.

Figure 4.4: Screenshots extracted from a high-speed camera movie of potassium impregnated cellulose (10000 mg kg^{-1}) pyrolysis. Pressure 0.5 kPa , $T_{\text{FS}} = 530 \text{ }^{\circ}\text{C}$

Table 4.2: Summary of experimental conditions in screen-heater and fluidised bed

	Screen-heater	Screen-heater	Fluidised bed
Temperature, °C	530	530	530
Pressure, kPa	0.5	100	100
Heating rate, °C s ⁻¹	5000	5000	5000
Hot vapour residence time, s	0.02	~0.02	1.6
Vapour Temperature, °C	N.A.	80 ^a	530
Levoglucosan evaporation time, s	0.03	<0.3	<0.3

^a Temperature measured 1.5 cm away from the screens

4.3.2 Identification and hydrolysis of anhydrosugars

The anhydrosugars 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 $DP_{>5}$ were analyzed using HPLC (see Section 2.4.4 of Chapter 2) and obtained chromatograms were integrated by following the procedure described by Oudenhoven^[120]. LC/MS analysis was used to identify the degree of polymerization of compounds referred to as $DP_{>5}$ and to obtain information on the composition of compounds termed DP_{1-2} ^[120]. Hydrolysis of anhydrosugars to glucose was done by the procedure described in Section 2.2.4 of Chapter 2. Oudenhoven^[120] has shown that the hydrolysis efficiency decreases with an increase in the degree of polymerisation of anhydrosugars; DP_1 (~93%) and DP_2 (~84%). Therefore, the glucose yields reported in this chapter were corrected as described by Oudenhoven^[120].

4.3.3 Effect of T_{FS} on the pyrolysis of pure cellulose

Mass balance closure

The mass balance closure of the 37 reported cellulose screen-heater experiments at the level of gas, oil and char was in the range of 0.87 kg kg⁻¹ to 1.01 kg kg⁻¹ with a median of 0.94 kg kg⁻¹. Reproducibility was checked by taking into account 5 measurements in the range of 520 to 540 °C (a single constant temperature was not possible due to control issues). The standard deviation in the yields of oil, gas and char 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 DP_1 to $DP_{>5}$ was 0.02 kg kg⁻¹ (average value of the standard deviations of the individual DP s). Taking into account the small amount of sample, the tedious recovery and the analysis procedure these numbers were considered quite satisfactory.

Lumped product yields

In Figure 4.5A and 4.5B, the yields of char and oil are plotted versus the final temperature of the screens (T_{FS}). The presented experimental data was measured by four different experimenters. Note that experiments were performed with a holding time of 1 s and 5 s. Over the whole temperature range of T_{FS} (330 to 765 °C), the gas yield was below 0.01 kg kg⁻¹^[120]. This absence of gas at temperatures as high as 750 °C further supports the conclusion that gases were formed mainly by cracking of decay products of cellulose in the vapour phase and that these reactions can be minimised in the screen-heater by fast quenching of these products.

Fourier-transform infrared spectroscopy (FTIR) analysis and visual inspection indicated that the residue obtained below 400 °C was unconverted cellulose and not char^[120]. This is in agreement with reported kinetic data^[83] which indicate that, below 400 °C, char forming reactions are not significant at reaction times of 1 s to 5 s. Between 400 and 450 °C, not enough char was recovered for analysis. For conditions of 450 °C and higher, the yield of char was very low (<0.01 kg kg⁻¹) in both the fluidised bed (Figure 4.12) and screen-heater (Figure 4.5A). The low yield of char is in agreement with earlier published data on cellulose pyrolysis^[64,193]. In conclusion, the conversion of cellulose based on the mass loss was higher than 99 % by weight above 450 °C.

The model I, including the kinetics of Shafizadeh, predicts that the conversion is complete (>99 %) at 440 °C and 5 s holding time. In Figure 4.5A these model predictions are plotted. A better fit can be easily obtained by increasing the pre-exponential constant of the rate-limiting mass loss reaction, k_2 (see Figure 4.5A: Shafizadeh $k_{2,0} = 3.2 \times 10^{14} \text{ s}^{-1}$ Vs. fit $k_{2,0} = 2 \times 10^{15} \text{ s}^{-1}$). It is worthwhile to mention that the fitted k_2 and corresponding E_2 are in agreement with the data calculated by Burnham et al.^[217] using the Kissinger's method. As an input, they used the results of the round-robin study of cellulose pyrolysis kinetics as reported by M. Gronli et al.^[218]. An activation energy of $\sim 200 \text{ kJ mol}^{-1}$ of k_2 , as often experimentally determined^[219] and recently supported by density functional theory (DFT) calculation^[106,217], describes the measured increase in conversion from nearly zero to almost completion in a temperature range of 75 °C and reaction time of <5 s. Lower activation energies result in a broader temperature range to achieve this. The measured yield of oil was constant after 450 °C.

Figure 4.6A to 4.6D show 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 is caused by the uncertainty in the temperature measurement. However, due to a large number of measurements, interesting trends do become clear. For the T_{FS} between 370 °C and 450 °C, DP_1 (levoglucosan) is the dominant product

Figure 4.5A: Char yield as a function of T_{FS} and different holding time. The data of 4 experimenters are included. The pressure was 0.5 kPa

Figure 4.5B: Oil yield as a function of T_{FS} and different holding time. The data of 4 experimenters are included. The pressure was 0.5 kPa

together with DP_2 and DP_{1-2} (not shown), while at increasing temperature first DP_3 became dominant followed by DP_4 (Figure 4.6D), DP_5 (Figure 4.6D) and $DP_{>5}$ (Figure 4.7) at the expense of DP_1 , DP_2 and DP_{1-2} , which decreased slightly. The decrease in DP_1 selectivity 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 $DP_{>5}$, especially above 530 °C, was the largest. Obviously, compounds this large do not have a significant vapour pressure under the studied conditions. Therefore, it is likely that these compounds were ejected from the reacting cellulose which seems to be quite a random process. As for the predictive mathematical models, these physical processes make exact predictions of the oil composition complicated.

Figure 4.6A: DP_1 selectivity as a function of T_{FS} . The pressure was 0.5 kPa

Figure 4.6B: DP_2 selectivity as a function of T_{FS} . The pressure was 0.5 kPa

Figure 4.6C: DP_3 selectivity as a function of T_{FS} . The pressure was 0.5 kPa

Figure 4.6D: DP_{4+5} selectivity as a function of T_{FS} . The pressure was 0.5 kPa

The total yield of sugars, expressed as the recovery of glucose after acid hydrolysis of the oil, remained constant in the temperature range of 420 to 765 °C, see Figure 4.8. To the best of our knowledge, we are the first to report a constant yield of hydrolysable sugar as a function of the pyrolysis temperature in such a broad range. The constant total sugar yield as a function of temperature indicates that the newly developed screen-heater also minimises the secondary reactions of sugars to non-sugar decay products.

Radlein et al.^[220] also reported a strong effect of temperature on the DP_1 yield; in their measurements, in an atmospheric fluidised bed, the yield decreased monotonically from $\sim 0.38 \text{ kg kg}^{-1}$ at 400 °C to $\sim 0.15 \text{ kg kg}^{-1}$ at 600 °C. They reported a strong decrease in the yield of total sugars from $\sim 0.60 \text{ kg kg}^{-1}$ at 400 °C to $\sim 0.18 \text{ kg kg}^{-1}$ at 600 °C^[220]. Gong et al.^[178] reported decreasing yields (measured in an atmospheric screen-heater) of DP_1 , DP_2 and DP_3 in the range of 400 to 500 °C and constant yields between 500 to 700 °C. Also in their case, the yield of total sugars decreased significantly in the range of 400 to 700 °C (from $\sim 0.6 \text{ kg kg}^{-1}$ to 0.35 kg kg^{-1})^[178]. Shafizadeh et al.^[140] reported for the slow(er) pyrolysis of cellulose under vacuum a constant oil, levoglucosan and reducing sugar yield between 375 and 500 °C.

As stated before the decrease in DP_1 yield at increased temperature is unexpected when considering chemistry solely. The higher DP_1 yield at a lower temperature is explained by the longer time available for cracking of higher DP sugars in/on 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 oil. 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 $DP_{\geq 2}$ selectivity as a function of increasing temperature is predicted (see Figure 4.9) by this model. Note that, only the trend is predicted correctly. The quantitative agreement would need a model that includes independently measured or disentangled values for the rate constants of the chemical reactions in/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 a lower temperature, only low DP s can evaporate as a result of which more bonds have to be broken in 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 the reaction

rate and heat transfer rate^[60], needs to be reconsidered.

For temperatures of 550 to 600 °C the measured DP_1 , DP_3 , DP_{4+5} selectivity seem to be unaffected by the final screen temperature (see Figure 4.6A to 4.6D). Analysis of the fits shows that these measured DPs are better described by an equation leading to a plateau value at an increased temperature as compared to a monotonic linear increasing or decreasing function. Model II also predicts that the DP yields/selectivity's above a final screen temperature of ca. 550 °C become constant, as shown in Figure 4.9. This is because the actual reaction temperature becomes constant above this final screen temperature, as also argued by Piskorz et al.^[192] and Lde^[47,221,222]. Figure 4.10 shows the average reaction temperature calculated by model I (defined as the average temperature of the sample between 10 % and 90 % conversion, see Eq. 4.7) versus the final temperature of the screens for several cases. Two extreme cases were: A) the screens were heated at a rate of 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 et al.^[60] as pyrolysis at isothermal conditions. 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 a T_{FS} of 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, which was connected to the electrodes, lights up when current is passing through the screen (to heat the screen)^[120]. The LED in this experiment (cellulose, 0.5 kPa, T_{FS} = 610 °C) was continuously lighted during the first 121 ms, meaning that the experiment was still in the initial heating pulse^[120]. 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 4.7: $DP_{>5}$ selectivity as a function of T_{FS} . The pressure was 0.5 kPa

Figure 4.8: Recovery of glucose on a carbon basis after hydrolysis of oils. The pressure was 0.5 kPa

Figure 4.9: Yield predictions using model II for DP_1 and $DP_{>1}$ as a function of the final screen temperature (T_{FS})

Figure 4.10: Predicted reaction temperature region using the model I as a function of the final screen temperature (T_{FS}). Kinetic constants used of Shafizadeh ($k = 3.2 \times 10^{14} \text{ s}^{-1}$ and $E_A = 198 \text{ kJ mol}^{-1}$)

4.3.4 Effect of potassium on pyrolysis products

Potassium impregnation efficiency

In this part of the work, the concentration of potassium (K_2CO_3) in cellulose was varied between 1 mg kg^{-1} and 10000 mg kg^{-1} . Note, 1 mg kg^{-1} potassium concentration in cellulose, called in the text below, refers to the pure Avicel PH 101 cellulose. The total amount of potassium added to the cellulose, and the actual amount of potassium retained in cellulose after impregnation are presented in Table 4.3. The total amount of potassium retained in cellulose was measured by ion chromatography (IC). The error represents the standard deviations on the mean for three different IC measurements. As can be seen, these values nicely match one another for all three concentrations.

Table 4.3: Potassium content added and detected by IC

Added potassium mg kg^{-1}	Potassium impregnated in cellulose mg kg^{-1}	Error %
100	98	2.5
1000	962	3.8
10000	9982	0.3

Mass balance closure

The obtained mass balance closure of experiments was between 0.77 kg kg^{-1} and 0.96 kg kg^{-1} . The reason for the lower mass balance closure is that water and other light oxygenates were lost during dismantling of the set-up. The mass balance closure was the lowest for the high potassium concentrations. For pyrolysis experiments with a higher concentration of potassium, higher production of water can be expected^[62]. The fluidised bed experiments showed that water production increased from 0.11 kg kg^{-1} to 0.14 kg kg^{-1} when potassium concentration increased from 1 mg kg^{-1} to 1000 mg kg^{-1} , respectively. The number of experiments in the screen-heater performed, for each potassium concentration, was at least 6 at 0.5 kPa and 2 at 100 kPa . As can be seen, the reproducibility of the experiments was satisfactory, see Figure 4.11 to 4.13.

Lumped product yields

Figure 4.11: Oil yield as a function of potassium concentration in cellulose, in screen-heater and fluidised bed, at the T_{FS} of 530 °C

Figure 4.11 (Table B.1 and B.2 in Appendix B) shows the oil yield as a function of the potassium concentration (on a logarithmic scale) at 0.5 kPa and 100 kPa. The figure includes the data from the screen-heater and fluidised bed experiments. It can be seen that, as an effect of increasing potassium concentration, the oil yield decreased from 0.86 kg kg⁻¹ to 0.57 kg kg⁻¹ at 100 kPa. At 0.5 kPa the oil yield decreased from 0.96 to 0.52 kg kg⁻¹.

A clear difference in oil yield was observed between vacuum and atmospheric pressure experiments at a low concentration of potassium, i.e. up to 1000 mg kg⁻¹. In this range, the oil yield was higher at 0.5 kPa compared to that of 100 kPa experiments. A plausible explanation is that under vacuum the escape rate of pyrolysis products from the hot reacting particle is faster resulting in shorter contact time, or even no contact at all, between the hot products and the potassium. The pyrolysis time at 0.5 kPa is ~79 ms (see Figure 4.4), which implies a very high product escape rates from the hot reacting particle. Moreover, even in this short pyrolysis time, potassium causes the oil yield to decrease dramatically. When the potassium concentration was further increased to 10000 mg kg⁻¹ the yield of oil became almost equal at both pressures. It is worthwhile to mention that during pyrolysis in the screen-heater some water insoluble compounds (<0.12 kg kg⁻¹ of the cellulose) were ejected from the screens. In the case of cellulose with 1 mg kg⁻¹ AAEMs, the insoluble fraction turned out to be unconverted white cellulose^[120],

whereas in the presence of potassium the ejected material had a dark brown colour, indicating that it has been (partially) converted.

For the fluidised bed experiments, a comparable reduction in oil yield was observed with an increase in the potassium concentration in cellulose. The oil yields in the fluidised bed were always lower compared to the screen-heater due to significant vapour phase cracking reactions. Concluding, a significantly higher yield of oil could be obtained as long as – 1) vacuum is applied, and 2) the concentration of potassium (K_2CO_3) in cellulose is low. At higher AAEMs concentrations, partial removal or passivation of the AAEMs before pyrolysis is mandatory to prevent AAEMs catalysed reactions that lead to low oil and sugar yields.

The effect of potassium (K_2CO_3) concentration on the gas yield, at two different pressures in the screen-heater and fluidised bed experiments is shown in Figure 4.12 (Table B.1 and B.2 in Appendix B). It can be seen that in the case of the screen-heater more non-condensable gas is formed at higher potassium concentration. However, at both pressures until a potassium concentration of 1000 mg kg^{-1} the gas yield remained below 0.05 kg kg^{-1} and was even close to zero when the potassium concentration was 1 mg kg^{-1} . At higher potassium concentration (10000 mg kg^{-1}) the gas yield increased to 0.1 kg kg^{-1} and 0.15 kg kg^{-1} at 0.5 kPa and 100 kPa , respectively. Reactions at the particle level, catalysed by potassium, are responsible for the gas production here since the vapour phase reactions were largely suppressed in the screen-heater. The gas produced during screen-heater experiments was mainly composed of CO and CO_2 , and their yields are presented in Table B.1 of Appendix B.

The fluidised bed experiments revealed that a large amount of the gas was already produced at low potassium concentration (1 mg kg^{-1}), which was produced by vapour phase reactions induced by the long hot vapour residence time ($\sim 1.6 \text{ s}$). Even at very low potassium concentration (1 mg kg^{-1}) most of the gas is already produced in the vapour phase. At higher concentrations of potassium (K_2CO_3), the additional amount of gas produced is small.

Figure 4.13 (Table B.1 and B.2 in Appendix B) shows the char yield as a function of potassium (K_2CO_3) concentration in cellulose, at 0.5 kPa and 100 kPa . It was found that for cellulose with 1 mg kg^{-1} AAEMs, virtually no char was observed on the mesh at both pressures. At 100 mg kg^{-1} potassium in cellulose, the char yield was still very low. A general trend shows that with an increase in potassium concentration, char yield increased. This observed trend was comparable to the trend observed for the gas yield. The char yield remained below 0.05 kg kg^{-1} until 1000 mg kg^{-1} potassium concentration at both pressures (0.5 kPa and 100 kPa) and increased steeply to 0.15 kg kg^{-1} for 10000

Figure 4.12: Gas yield as a function of potassium concentration in cellulose, in screen-heater and fluidised bed, at the T_{FS} of 530 °C

Figure 4.13: Char yield as a function of potassium concentration in cellulose, in screen-heater and fluidised bed, at the T_{FS} of 530 °C

mg kg⁻¹ potassium concentration. At the high potassium concentration (10000 mg kg⁻¹), black coloured carbonaceous material was found between the meshes at the end of the experiment. No significant differences were observed between the fluidised bed and screen-heater experiments. Thus, in conclusion, it can be said that the char formation reactions are independent of the escape rate of other components.

Oil Composition

Figure 4.14A (Table B.3 in Appendix B) shows the levoglucosan yield and Figure 4.14B (Table B.3 in Appendix B) shows the glucose recovery as a function of the potassium (K₂CO₃) concentration in cellulose. Glucose was obtained after the acid hydrolysis of anhydrosugars, varying in the degree of polymerisation, present in the oil. The glucose recovery is expressed as the ratio between the carbon in glucose and carbon in cellulose, see Figure 4.14B. The following observations can be made from the data – 1) Levoglucosan (Figure 4.14A) was found to be the major product in fluidised bed experiments and for the screen-heater experiments performed at 100 kPa for a potassium concentration below 1000 mg kg⁻¹. When the potassium concentration was 1000 mg kg⁻¹ or higher no differences in levoglucosan yield was found at 0.5 kPa and 100 kPa, for experiments carried out in the screen-heater. Moreover, with an increase in the potassium concentration in cellulose, levoglucosan production decreased, 2) When the vacuum was applied, in the screen-heater experiments, the glucose recovery was highest due to the production of higher *DP* anhydrosugars (cellobiosan, cellotriosan, etc.). The presence of the bigger anhydrosugars in the oil can be explained by their higher escape rate, at 0.5 kPa, away from the hot zone than at 100 kPa, which resulted into less time for bigger anhydrosugars to crack further, for example to levoglucosan. Just like levoglucosan, the recovery of glucose decreased with an increase in the potassium concentration in cellulose and eventually approached zero, even under the extreme conditions applied in the screen-heater.

It is remarkable how fast the potassium catalysed reactions are (milliseconds) and the low concentrations of at which those reactions become destructive to anhydrosugars. Literature shows that with increasing AAEM concentrations in cellulose, the yield of levoglucosan decreased sharply (see Table A.1 in Appendix A). For example, the levoglucosan yields decreased from 0.25 kg kg⁻¹ (400 mg kg⁻¹ ash) to 0.02 kg kg⁻¹ (2200 mg kg⁻¹ ash) at 500 °C and 100 kPa^[223,224]. Patwardhan et al.^[210] reported constant concentration (not yield) of levoglucosan when the potassium concentration increased from 3000 mg kg⁻¹ to 11800 mg kg⁻¹. Taking into account the oil yield, it is also likely that the levoglucosan yield decreases further as the potassium concentration increased. When

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Figure 4.14A: Levoglucosan yield as a function of potassium concentration in cellulose, in screen-heater and fluidised bed, at the T_{FS} of 530 °C

Figure 4.14B: Glucose recovery after hydrolysis of oil as a function of potassium concentration in cellulose, in screen-heater and fluidised bed, at the T_{FS} of 530 °C

translating these findings to the real biomass, it can be concluded that it is impossible to produce high yields of anhydrosugars from untreated biomass which has typically 10000 mg kg⁻¹ AAEM. Removal (or passivation) of AAEMs from (or in) the biomass is therefore mandatory.

Levoglucosan pyrolysis

It was previously shown that levoglucosan could be completely evaporated in vacuum^[225] and atmospheric pressure^[148]. To obtain more information on the reactions of this important compound, it was pyrolysed in the screen-heater ($T_{FS} = 530\text{ °C}$; 0.5 kPa and 100 kPa). The potassium concentration in the levoglucosan feedstock was 1 mg kg⁻¹ (pure levoglucosan) and 1000 mg kg⁻¹. At both pressures (0.5 kPa and 100 kPa), levoglucosan without potassium could be completely recovered ($R_{\text{Levoglucosan}}$), see Figure 4.15A. When potassium was added, only a small amount of gas and char were produced at 0.5 kPa, and the oil was solely comprised of levoglucosan. When the pressure was increased to 100 kPa, and the potassium concentration to 1000 mg kg⁻¹, only half of the levoglucosan was recovered (Figure 4.15A), and noticeable amounts of char and gas were produced (Figure 4.15B). This can again be explained by the faster escape rate of levoglucosan from the hot reacting particle at 0.5 kPa compared to at 100 kPa (factor 10, see Table 4.2). In other words, levoglucosan escaped the hot screens, at 0.5 kPa, even before the potassium became catalytically active. Although levoglucosan could be completely evaporated at 100 kPa, in the absence of potassium (1 mg kg⁻¹), only half of the original levoglucosan was recovered in oils obtained from 1000 mg kg⁻¹ potassium infused levoglucosan, pointing again towards very fast catalytic reactions. Note, in the nearly absent vapour phase reactions, destruction of levoglucosan at 100 kPa can solely be ascribed to intra-particle (catalytic) reactions.

Light oxygenates (screen-heater, 530 °C and 0.5 kPa)

An important effect of AAEMs on cellulose pyrolysis is the ability to catalyse dehydration and ring fragmentation reactions of the anhydrosugars^[219,226]. Levoglucosenone was chosen to represent the products of dehydration reactions, while the products of fragmentation reactions are represented by acetol and hydroxyacetaldehyde^[121,174]. The yields of these compounds, calculated based on three experiments performed under identical conditions, and the corresponding standard deviation on the mean are reported in Table B.6 of Appendix B.

The yield of levoglucosenone increased from 0.003 kg kg⁻¹ to 0.01 kg kg⁻¹ with an increase in the potassium concentration up to 1000 mg kg⁻¹, while no levoglucosenone

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Figure 4.15A: Levoglucosan recovery as a function of potassium concentration in levoglucosan and pressure in screen-heater, at the T_{FS} of 530 °C

Figure 4.15B: Effect of pressure on oil, char and gas yields at constant potassium concentration in levoglucosan; in screen-heater, at the T_{FS} of 530 °C

was detected at 10000 mg kg⁻¹ potassium concentration. Levoglucosenone has probably reacted away to form solid residue and/or decomposed to other compounds such as water, gas and light oxygenates. It is worth mentioning that in the case of levoglucosan pyrolysis, no levoglucosenone production was observed. Similar levoglucosenone yields were reported by Zhou et al.^[107] in the temperature range between 400 and 600 °C. In the range of 1 mg kg⁻¹ to 1000 mg kg⁻¹ of potassium concentration the acetol yield remained low (<0.0025 kg kg⁻¹), and it increased rapidly to 0.02 kg kg⁻¹ at 10000 mg kg⁻¹ potassium concentration. Piskorz et al.^[223] observed acetol yield of 0.007 kg kg⁻¹ for cellulose containing 400 mg kg⁻¹ ash, and it increased (0.032 kg kg⁻¹) with an increase in the ash content (2200 mg kg⁻¹ ash).

In the case of 1 mg kg⁻¹ and 10000 mg kg⁻¹ potassium in cellulose, the hydroxyacetaldehyde yield was 0.11 kg kg⁻¹, and it passed through a maximum (0.16 kg kg⁻¹) at 100 mg kg⁻¹ potassium concentration. The yield of hydroxyacetaldehyde reported in the literature lies in the range between 0.016 kg kg⁻¹ to 0.16 kg kg⁻¹, see Table A.3 in Appendix A. The difficulties in determining the hydroxyacetaldehyde yield by gas chromatography have been elaborated in Chapter 3; thus, the direct comparison between the hydroxyacetaldehyde yields reported in this work and the literature is not possible. Nevertheless, principal component analysis (see loading matrix in Section A.3.2 of Appendix A) suggests that the yield of hydroxyacetaldehyde is directly proportional to the ash content of cellulose.

In summary, based on the production of levoglucosenone and char, dehydration reactions of anhydrosugars are more pronounced at higher potassium concentrations. Ring fragmentation reactions lead to an unequivocal increase in the gas and acetol yields with an increase in the potassium concentration. The hydroxyacetaldehyde yield was found to be independent of the potassium concentration in cellulose.

4.3.5 Influence of different anions

Cellulose was impregnated with different potassium salts (K₂CO₃, KCl or KOH) while keeping the concentration of potassium constant (1000 mg kg⁻¹) to investigate the influence of different anions on the pyrolysis products. All cellulose samples were pyrolysed at 530 °C and two pressures (0.5 kPa and 100 kPa). Figure 4.16A and 4.16B (Table B.7 in Appendix B) show the yield of oil, solid residue and gas, at 0.5 kPa and 100 kPa, as a function of the different anions, respectively. The error bars shown in Figure 4.16A and 4.16B represent the standard deviation on mean, calculated based on 6 and 3 experiments at 0.5 kPa and 100 kPa, respectively.

At 0.5 kPa, comparable mass balance closures of ~0.84 kg kg⁻¹ were obtained.

However, at 100 kPa the mass balance closure decreased by 0.1 kg kg⁻¹ to 0.75 kg kg⁻¹. Different anions appeared to have no effect on the mass balance closure (Figure 4.16A and 4.16B). The char and gas yields did not differ much between the experiments performed at a given pressure for all three anions. The oil yield decreased when the pressure was increased to 100 kPa, which can mainly be attributed to the increasing loss of water and light oxygenates. The obtained oil was analysed for the levoglucosan yield and glucose recovery.

In Figure 4.17A to 4.18B, the levoglucosan yields and the glucose recovery, obtained at 0.5 kPa and 100 kPa, are plotted for three different anions. There was almost no effect of pressure on the levoglucosan production, and a small decrease in glucose recovery was observed at 100 kPa compared to at 0.5 kPa for all three different anions. It was observed that CO₃²⁻ was the least active anion in reducing the levoglucosan as well as the hydrolysable anhydrosugar yields, while no significant difference between the catalytic activity of Cl⁻ and OH⁻ was observed. A similar observation was made for the levoglucosan yield by Patwardhan et al.^[210].

DFT calculations suggest that cations can form cation-carbohydrate complexes. In general, cations are more active in forming salt-carbohydrate complex than anions^[227]. A theoretical study by Mayes et al.^[108] shows that distinct anions have a different affinity towards the cation. They also reported that anions are primarily involved in binding with their counter cation and compete with cation-carbohydrate complex reactions instead of influencing cellulose pyrolysis chemistry directly^[108]. Nevertheless, more detailed research (experimental and theoretical) is needed to gain a deeper understanding to investigate the role of different anions.

Figure 4.16A: Oil, char and gas yields for different anions with constant potassium concentration. $P = 0.5$ kPa and at $T_{FS} = 530$ °C

Figure 4.16B: Oil, char and gas yields for different anions with constant potassium concentration. $P = 100$ kPa and at $T_{FS} = 530$ °C

Figure 4.17A: Levoglucosan yield for different anions with constant potassium concentration. $P = 0.5 \text{ kPa}$ and at $T_{\text{FS}} = 530 \text{ }^\circ\text{C}$

Figure 4.17B: Levoglucosan yield for different anions with constant potassium concentration. $P = 100 \text{ kPa}$ and at $T_{\text{FS}} = 530 \text{ }^\circ\text{C}$

Figure 4.18A: Glucose recovery for different anions with constant potassium concentration. $P = 0.5 \text{ kPa}$ and at $T_{\text{FS}} = 530 \text{ }^\circ\text{C}$

Figure 4.18B: Glucose recovery for different anions with constant potassium concentration. $P = 100 \text{ kPa}$ and at $T_{\text{FS}} = 530 \text{ }^\circ\text{C}$

4.4 Conclusions

In the first part of the chapter, the fast pyrolysis of Avicel PH 101 cellulose has been studied in a screen-heater (heating rate $\sim 5000\text{ }^{\circ}\text{C s}^{-1}$, 0.5 kPa pressure and fast quenching at $\sim -180\text{ }^{\circ}\text{C}$), while varying the temperature and maximising the escape rate of products from the reacting cellulose particle. In the second part, the effects of three different potassium salts on the primary reactions of cellulose pyrolysis are investigated at $530\text{ }^{\circ}\text{C}$. Also, the obtained results are compared with the pyrolysis, at 100 kPa, carried out in the same screen-heater (at lowered escape rate of products) and in a bench scale fluidised 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 pure cellulose (1 mg kg^{-1} potassium), in the broad temperature range of 370 to $765\text{ }^{\circ}\text{C}$, into hydrolysable sugars with a high and constant yield ($60\% - 70\%$ on carbon basis) while producing only a limited amount of light oxygenates and gas. Below $450\text{ }^{\circ}\text{C}$ solid residue was found, which turned out to be unconverted cellulose, not char. The results indicate that depolymerisation to anhydrosugars (DP_1 to $DP_{>11}$) is a true primary reaction, while gas formation not and that char formation can be, as was already known, avoided. Evidence is accumulating that both the distribution of the produced anhydrosugars and the mass loss rate of cellulose is determined by the interplay between the chemistry, 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.

The catalytic effects of potassium on cellulose fast pyrolysis are evident, even in the timescale of milliseconds. In screen-heater (at 0.5 kPa), as a function of potassium concentration, a $\sim 50\%$ reduction in the oil yield, a significant increase in the gas yield (<0.01 to 0.15 kg kg^{-1}) and a decreased glucose recovery (70% to almost zero) was observed. These findings show that the destruction of anhydrosugars, by the catalytic activity of potassium, predominantly takes place at the hot reacting particle to produce other products such as water, light oxygenates and gases. Identical char yields obtained in fluidised bed and screen-heater for a given potassium concentration indicate that the char formation reactions are not affected by the escape rate of other products. Generalising, for the low AAEMs content feedstock, reducing pressure, i.e. enhancing the escape rate of products from the hot reacting particle, may improve the oil and sugar yields to a certain extent. However, the removal (or passivation) of AAEMs from (or in) the mineral-rich feedstock, before pyrolysis, is mandatory to obtain high oil and sugar yields.

Nomenclature

A	m^2	Area available for heat transfer
α	$W m^{-2} K^{-1}$	Heat transfer coefficient
B	$^{\circ}C s^{-1}$	Heating rate of the screens.
B'	$^{\circ}C s^{-1}$	Cooling rate (measured) of the screens after the holding time
C_p	$J kg^{-1} K^{-1}$	Heat capacity of the sample
E_1	$J mol^{-1}$	Activation energy of reaction 1
E_2	$J mol^{-1}$	Activation energy of reaction 2
E_3	$J mol^{-1}$	Equal to E_2
E_4	$J mol^{-1}$	Overall k lower than k_2
ΔH_2	$J kg^{-1}$	the enthalpy of the reaction / evaporation
ΔH	$J kg^{-1}$	the enthalpy of the evaporation
$k_{1,0}$	s^{-1}	Pre-exponential constant of reaction 1
$k_{2,0}$	s^{-1}	Pre-exponential constant of reaction 2
$k_{3,0}$	s^{-1}	10 % of $k_{2,0}$ (arbitrary choice)
$k_{4,0}$	s^{-1}	Overall k lower than k_2
M_C	kg	the mass of cellulose
$M_{C,0}$	kg	Initial mass of the cellulose
M_{AC}	kg	the mass of active cellulose
$M_{AC,0}$	kg	Initial mass of the active cellulose
M_S	kg	the mass of sample
$M_{S,0}$	kg	Initial mass of the sample
M_{DP_1}	kg	the mass of DP_1
$M_{DP_1,0}$	kg	Initial mass of DP_1
$M_{DP_{\geq 2}}$	kg	the mass of $DP_{\geq 2}$
$M_{DP_{\geq 2},0}$	kg	Initial mass of $DP_{\geq 2}$
T_C	K	Model I: temperature of the sample (cellulose + active cellulose) Model II: temperature of the sample (cellulose + $DP_{\geq 2}$ + DP_1)
T_S	K	Temperature of the screen
$T_{C,0}$	K	Initial temperature of the sample (cellulose + active cellulose)
$T_{S,0}$	K	Initial temperature of the screen
T_{set}	K	Set-point of the screen temperature
T_r	K	the reaction temperature
t_h	s	Holding time
X	—	the conversion on mass basis

Y_{DP_1}	$kg\ kg^{-1}$	The yield of DP_1 in oil on cellulose basis
$Y_{DP_{\geq 2}}$	$kg\ kg^{-1}$	The yield of $DP_{\geq 2}$ in oil on cellulose basis

C_5

C₅

Fast pyrolysis of lignins with different molecular weight: experiments and modelling

Abstract

Lignins with number averaged molecular weights between 350 Da and 1900 Da were characterised and subsequently pyrolysed in a screen-heater at pressures of 0.5 kPa and 100 kPa between 425 °C and 793 °C. Upwards of 530 °C, the temperature turned out to have only a minor influence on the yields and composition of the oils produced. Clear trends were observed as a function of the molecular weight and pressure – 1) at increasing molecular weight of the lignin, the oil yield decreases while yields of char and gas increase, 2) the molecular weight of the oil is lower for oils produced at 100 kPa as compared to the ones obtained at 0.5 kPa, 3) above a certain molecular weight of the lignins, ~400 Da for 100 kPa and ~800 Da for 0.5 kPa, the molecular weight of the oil becomes independent of the molecular weight of the lignin. A mathematical model has been developed, which includes three concurrently occurring processes, viz. cracking and polymerisation reactions and removal, hence mass transport, of unconverted lignin and reaction products from the reaction zone. This model can describe all the trends observed experimentally and provides, after parametrisation, reasonable qualitative predictions of the yield and molecular weight of the oils. Knowledge of the role of the interplay between mass transport and chemistry in the pyrolysis process is further accumulating, and from this the development of lignin valorisation can avail. For instance, it has become clear that in the pyrolysis process the molecular weight of lignin oil, which is an important characteristic for the upgrading of the oil to chemicals and/or fuels, can be steered with the pressure.

This chapter is based on:

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5.1 Introduction

Lignin is an amorphous, highly cross-linked, hetero-polymer that provides structural integrity and stiffness to plant cell walls^[10]. It is the most abundant naturally occurring aromatic polymer and it accounts for ~30% of all organic carbon in the biosphere^[228]. Typically, it is burned as a low-value fuel, however, being aromatic in nature, it could be a potential source of mono-aromatics and other value-added chemicals^[229–231].

Lignin is isolated from biomass via several methods such as kraft, organosolv, ball milling, and cold-water precipitation of pyrolytic lignin^[14,15,125]. The extent to which the structure of native lignin is preserved is controlled by the severity of the isolation method^[15,16,232]. Milled wood lignin (MWL), obtained by Björkman's method, is considered to represent native lignin most accurately^[17].

Starting in the 1970's, the fast pyrolysis process has been studied extensively to liquefy and depolymerise lignin in various experimental devices^[12,86,233–238]. Aligning the results obtained in the different reactor systems used is difficult. For example, with respect to the production of mono-aromatics yields of up to 20% were reported in micro-pyrolysers^[239,240], whereas in screen-heaters and fluidised beds typical yields were only 1 to 4%^[236,241,242]. Oil yields as high as 80% were obtained in screen-heaters under vacuum conditions^[225,242] while in the other reactors the maximum yield was limited to 40%^[240,241,243,244]. There is also no consensus on the chemical mechanisms leading to monomers and oligomers. Patwardhan et al.^[240] claimed that monomeric compounds are the primary products of lignin pyrolysis and that they polymerise during condensation of the vapours (to oil) to form oligomers. Contrary, Piskorz et al.^[52] postulated that oligomers eject from pyrolysing biomass particles, which was later verified experimentally by Small-Angle Neutron Scattering (SANS) analysis by Fratini et al.^[53] and by Montoya et al.^[55] for lignin, and by Teixeira et al.^[54] for cellulose.

Models for lignin pyrolysis range from weight loss kinetic models^[87,245–248], lumped component class models^[249–251], via population balance calculations over the molecular weight distribution of the reacting lignin^[115,116], to models combining a structural description of lignin with the reactivity of linkages between the lignin building blocks^[113,252]. Weight loss kinetics models are always based on low heating rate data and use experimentally observed yields of volatile species to estimate kinetic parameters to simulate slow pyrolysis of lignin. These models can predict the non-isothermal weight loss of the reacting lignin and yields of volatile species (e.g. gases, methanol). However, they cannot predict the oil yield nor the molecular weight distribution of the oil, which limits their applicability. The lumped class models of Faravelli et al.^[250], Hough et al.^[251], and Dussan

et al.^[249] use experimentally obtained and/or theoretically (group contribution method and/or density functional theory) calculated kinetic parameters to predict the yields of oil (light and heavy), char, and gas as well as weight loss kinetics. The experimentally obtained kinetic parameters were derived under slow pyrolysis conditions. These models use complex reaction networks, composed of more than a hundred series/parallel primary and/or secondary reactions. As input, the lumped class models use a simplified lignin structure, while the models of Klein et al.^[252] and Yanez et al.^[113,253] use the spruce lignin structure proposed by Freudenberg^[11] and an artificially generated structure of wheat straw lignin, respectively. In the latter, probabilities of reactions pathways are assigned based on experimental observations as well as theoretical calculations. The model of Klein et al.^[252] uses empirically obtained kinetic parameters, and their values are used as an initial estimate in the model of Yanez et al.^[113]. These models predict the temporal evolution of the yields of major product fractions and the molecular weight of the liquid and gaseous products. However, they do not capture the influence of mass transfer. The population balance model of Avni et al.^[116], originally developed for coal pyrolysis, assumes the cracking of weak bonds and transport of volatile products away from the reacting lignin. Interestingly, their model captures the effect of the external pressure on the product yields. Solomon et al.^[115,116] have described the transport of species by using Fick's law of diffusion, where the diffusion coefficient is a function of pressure, temperature and molecular weight.

This paper aims at advancing the understanding of lignin pyrolysis in order to increase the valorisation of this abundant natural aromatic resource. We assume that, like for cellulose (Chapter 4), the pyrolysis of lignin is controlled by the interplay of chemical reactions taking place in the liquid/solid state and the removal rate of compounds from the reaction zone. If this hypothesis is true, then the product yields and molecular weight distribution of the produced oil depend on the molecular weight (distribution) of the lignin feedstock and the bond type interconnecting the aromatic units. For lignin pyrolysis, the dominant reactions with respect to molecular weight distribution of the oil produced can be generalised into cracking and polymerisation reactions. To investigate this hypothesis, 14 lignins with a mass average molecular weight ranging from 588 to 3596 Da were characterised. Secondly, the lignins were pyrolysed in a screen-heater designed to minimise non-isothermality and to maximise the quenching rate of products (and unconverted lignin) after leaving the reaction zone^[119]. Temperatures (425 °C - 793 °C) and pressures (0.5 kPa and 100 kPa) were varied in order to map the operating window and to further analyse the aforementioned interplay. Finally, the experimental results were compared with a mathematical model including the aforementioned chemical reactions and mass transfer.

In the literature, numerous studies^[232,237,239,244,254–262] compared the pyrolysis of various lignins which were chosen based on either their source and/or isolation methods, while we are the firsts, to the best of our knowledge, to interpret the results on the basis of the molecular weights of the lignins. The developed population balance model is relatively simple compared to lumped class and linkage reactivity based models and has the easily measurable molecular weight distribution of lignin as the main input.

5.2 Lignins

Physical characteristics such as elemental composition, aromaticity, mass average molecular weight ($\langle M_w \rangle$), polydispersity values, and content of β -O-4 linkages present in lignins are presented in Table 5.1. Note, all lignin samples were dried for 12 h in a vacuum oven (<0.5 kPa, 20°C) before any analysis and pyrolysis experiment.

As can be seen, MWL has an oxygen content of 33% which is considerably higher compared to the other lignins. The oxygen content of the other lignins (i.e. SL, SOL, WSL, PL) is quite comparable. SL has the highest carbon content. Furthermore, all lignins have similar hydrogen ($\sim 6\%$), and nitrogen ($<1\%$) content. The ash content of all lignins is lower than 5 mg kg^{-1} , and therefore it has assumed that it does not affect the pyrolysis outcome.

In the case of WSL, the ratio of light fraction (L) to a heavy fraction (H) is 1:1, whereas for both pyrolytic lignins it is in the range of 0.65:0.35 (See Table C.1). The molecular weights of light and heavy fractions are presented in Table 5.1. Note, the fractionation experiments were performed twice to check the reproducibility. The standard deviation in the yields of light fractions and heavy fractions, obtained from two separate fractionation experiments, was below 1% for all fractioned lignins.

As can be seen, the MWL is the heaviest lignin (3596 Da) studied in this work. The $\langle M_w \rangle$ of both pyrolytic lignins (PL1 and PL2) is ~ 9.5 times lower than the MWL. Three organosolv lignins (SL, SOL and WSL) had their $\langle M_w \rangle$ between 2000 Da and 2500 Da. The $\langle M_w \rangle$ of light fractions (2,5,8,11) are notably lower than their parent lignins (1,4,7,10) and much lower than the heavy fractions (3,6,9,12).

The poly-dispersity of 2.5 and high $\langle M_w \rangle$ of MWL, indicates that MWL is mainly composed of high molecular weight compounds originating from native lignin as well as low molecular weight compounds. Organosolv lignins have polydispersity around ~ 2.1 . The polydispersity values of light fractions (2,5,8,11) are much smaller than the corresponding heavy fractions (1,4,7,10). The M_w D of all lignins (VWD response) are presented in Section C.5 of Appendix C.

The MWL lignin has the highest abundance of β -O-4 linkages namely 34.5 per 100 aromatic units. This value is close to the values typically reported for the softwood lignins, which are in the range of 45 to 50^[13,263]. In three organosolv lignins (SL, SOL, WSL), the abundance of β -O-4 linkage is in the range from 1.8 to 8.6 per 100 aromatic units. Expectedly, in pyrolytic lignin (10) no traces of β -O-4 linkages were observed, which is in line with the literature^[126].

In summary, these lignins have the same aromaticity as indicated by their equal H/C ratio (~ 1.1), despite originating from three different isolation processes and differ uniquely in their molecular weights (588 Da to 3596 Da, $\langle M_w \rangle$). Only MWL stands out for having the highest amount of β -O-4 linkages, while pyrolytic lignin represents the other end of that spectrum, i.e. no β -O-4 linkages. This set of lignins is envisaged to be a powerful tool to test the validity of the hypothesis discussed in the introduction with respect to the influence of the molecular weight (distribution) on the pyrolysis process.

Table 5.1: Characterization of lignins

Lignin	Code	C	H	O ^a	N	H/C	<M _w > ^b	D	β -O-4 linkages
-	-	%, on mass basis, dry				mol mol ⁻¹	Da	-	per 100 Ar units
SL	1	66.9	6	27	0.1	1.1	2515	2.1	1.8
L-SL	2	-	-	-	-	-	1591	1.7	-
H-SL	3	-	-	-	-	-	3462	1.8	-
WSL	4	64.8	5.8	28.6	0.8	1.1	2043	2.0	8.6
L-WSL	5	-	-	-	-	-	1449	1.7	-
H-WSL	6	-	-	-	-	-	2601	2.0	-
PL1	7	68.1	6.3	25.5	0.1	1.1	725	1.5	-
L-PL1	8	-	-	-	-	-	670	1.5	-
H-PL1	9	-	-	-	-	-	1047	1.6	-
PL2	10	64.8	6.5	28.6	0.1	1.2	616	1.6	0
L-PL2	11	-	-	-	-	-	588	1.6	-
H-PL2	12	-	-	-	-	-	1241	2.0	-
SOL	13	63.9	5.7	30.3	0.1	1.1	1858	2.2	7.8
MWL	14	60.7	6.3	33	<0.1	1.2	3596	2.5	34.5

^a Oxygen content by difference: (100 - C - H - N)^b <M_w> is calculated from UV detector response

- Not measured

5.3 Modelling

The model consists of population balances for the reacting lignin and the produced oil. In Figure 5.1, the model is schematically presented. The population balances are made over segments called DP_i where i refers to the number of monomer units out of which the lignin molecules in a segment DP_i are build-up. In a segment DP_i the lignin molecules are identical linear polymers. The molecular weight of a monomeric unit is set to 200 Da corresponding to the molecular weight of a typical building block alcohol of lignin, i.e. sinapyl alcohol (210 Da).

The following processes are considered for each segment of reacting lignin: cracking reactions, polymerisation reactions and removal (transport) from the reaction zone of unreacted lignin and reaction products. It is assumed that this is the minimal set of reactions and mass transport needed for predicting yields of oil and char and the molecular weight distribution of oil. For these processes experimental proofs are available. Cracking reactions are evident from the yield of lower DP_i fractions in the oil as compared to their presence in the feedstock (see Figure C.1A and C.1B). Washing the char with tetrahydrofuran showed a liquid fraction that contained larger molecules than present in the feed (see Figure C.16), hence polymerisation reactions must have taken place. Reactions in the vapour phase outside the particle are excluded by the low hot vapour residence time (~ 20 ms). It could be that vapours react while still in/on the hot sample. Therefore, cracking and polymerisation reactions used in the model must be considered as a lumped description of these reactions in the liquid/vapour/solid state of the hot reacting sample. Transport of molecules from the reaction zone is obvious as oil was collected at the cold vessel wall. It is assumed, based on experimental verification^[120], that there are no reactions in the vapour phase and in the oil phase which is condensed on the cold vessel wall. Consequently, for the oil product, only the transport of molecules from the reacting lignin sample is considered. Cracking and mass transport were also included in the population balance model of Solomon et al.^[115], though the mass transport was described differently.

The DP_i grid ranges from $i = 1$ to $i = 2 i_{max}$ with i_{max} being 50 in the standard simulations ($DP_{max} = 10000$ Da). In the model, the bins between DP_{max+1} to $2DP_{max}$ represent char. The characteristics of the molecules in the char bins are – 1) they do not react and 2) they cannot leave the hot reacting lignin. Without these assumptions i.e. without char bins, zero char production is predicted by the model. Summarizing, char is set to be equivalent to the $> DP_{50}$ molecules in the calculation domain. This is a rather a blunt assumption, however, it can be argued that molecules with $DP_{>25}$ will eventually react to char due to their very low likelihood of leaving the reaction zone,

Figure 5.1: Schematics of the model

especially for 100 kPa experiments. It should be noted that the molecules in the char bins (DP_{max+1} to $2DP_{max}$) have same structure as that of molecules present in the reacting lignin (DP_i to DP_{max}). The cross-linking reactions of the molecules are not included in the model.

Mole balance:

The mole balances for the segment DP_i of the reacting lignin (C_i^L) and oil (C_i^O) are given by Eq. 5.1 and Eq. 5.2:

$$\frac{dC_i^L}{dt} = -E_i + K_i + P_i \quad (\text{Eq. 5.1})$$

$$\frac{dC_i^O}{dt} = E_i \quad (\text{Eq. 5.2})$$

Where, E_i is the rate of transport of DP_i from the reacting lignin to oil, K_i is the net rate at which different DP_i are formed during cracking reactions, and P_i is the net rate at which different DP_i are formed during polymerisation reactions. The mathematical description of these three processes will be discussed in following paragraphs.

Transport from the reaction zone:

It is assumed that a single first order equation can describe these processes:

$$E_i = k_{T,i} C_i^L \quad (\text{Eq. 5.3})$$

$$k_{T,i} = e^{-Ai} + B \quad (\text{Eq. 5.4})$$

The exponential term describes the evaporation and/or sublimation rate which is, as the molecular weight and the pressure affect the diffusion coefficient^[115,116], higher for lighter molecules and at lower pressure. B is included to allow a fixed, DP_i independent, ejection rate. In simulations, the value of B was set to 0.02 and 0 for 0.5 kPa and 100 kPa experiments, respectively. Transport away from the reaction front is expected to be faster at lower pressure. Instead of using a flux equation for the escape rate, like the film model used by Solomon^[115], a purely mathematical approach is used (see Eq. 5.3 and Eq. 5.4) that does include the effects described above. This is rationalized by the expectedly very vigorous mass transport under the conditions applied, which is not captured by

simplified models like the film model. In literature, the transport of species has been described by Darcy's law^[95] or modified Clausius–Clapeyron equation^[264]. Formation of bubbles was observed on the reacting lignin (at 100 kPa), which points towards vigorous mass transport and to the generation of aerosols (see Figure C.17). For DP_{max+1} to $2DP_{max}$ bins, i.e. for char, the transport rate is set to zero. The green arrows in Figure 5.1 represents DP_i dependent transport rates of molecules, highest for DP_1 and lowest for DP_{max} .

Cracking:

The following first order reaction describes cracking:

$$R_{K,i} = k_K C_i^L \quad (\text{Eq. 5.6})$$

It is assumed that only the bonds connecting the monomer units present in the DP_i segment can be cracked. Therefore, the segment DP_i can crack in $\frac{(i-1)!}{(i-2)!} = (i-1)$ different ways. It is also assumed that all possibilities of cracking have the same likelihood, i.e. the rate constant k_K , is the same for all cracking reactions. Under these assumptions the cracking rate K_i^c of DP_i becomes,

$$K_i^c = (i-1)R_{K,i} = (i-1)k_K C_i^L \quad (\text{Eq. 5.7})$$

DP_i is also formed by cracking reactions. Obviously, DP_i can only be formed from a segment DP_j with $j > i$. The rate of formation of DP_i by cracking is given by:

$$K_i^f = 2 \sum_{j=i+1}^{i_{max}} k_K C_j^L \quad (\text{Eq. 5.8})$$

It is set in the model that char (DP_{max+1} to $2DP_{max}$) does not crack and therefore the sum in Eq. 5.8 runs until i_{max} . Eq. 5.7 and Eq. 5.8 are also used by Solomon et al.^[115]. Combining Eq. 5.7 and Eq. 5.8 gives the overall reaction rate of DP_i due to cracking:

$$\begin{aligned}
K_i &= K_i^f - K_i^c \\
&= \left\{ 2 \sum_{j=i+1}^{i_{max}} k_K C_j^L \right\} - (i-1)k_K C_i^L \\
&= \left\{ 2 \sum_{j=i+1}^{i_{max}} \left(\frac{1}{j-1} K_j^c \right) \right\} - K_i^c
\end{aligned} \tag{Eq. 5.9}$$

For example, DP_1 and DP_7 are formed by consumption of DP_8 in a cracking reaction, see Figure 5.1.

Polymerisation:

The following second order reaction describes polymerisation:

$$R_{P,i} = k_P C_j^L C_{i-j}^L \tag{Eq. 5.11}$$

It is assumed that all molecules in segments between DP_1 to DP_{max} will polymerize with each other, in all possible combinations, to form polymerisation products which are not bigger than $2DP_{max}$. As previously mentioned, the DP_{max+1} to $2DP_{max}$ segments do not take part in polymerisation reactions but will be formed as a product, which represents char. Like in case of cracking, all polymerisation possibilities have the same likelihood i.e. the reaction rate constant, k_P , is the same for all polymerisation reactions. Thus, the rate of consumption of DP_i in polymerisation reactions can be written as follows.

$$P_i^c = \left\{ \sum_{j=1}^{i_{max}} k_P C_i^L C_j^L \right\} + k_P C_i^L C_{j=i}^L \quad 1 \leq i \leq i_{max} \tag{Eq. 5.12}$$

For example, DP_3 and DP_5 are consumed in a polymerisation reaction to form DP_8 , see Figure 5.1. Also, DP_i will be formed by polymerisation, e.g. DP_{20} is formed as a result of polymerisation reaction between DP_8 to DP_{12} (Figure 5.1). The rate at which DP_i is formed by polymerisation is described by the following equation, in which $k_P C_j^L C_{i-j}^L = 0$ for all combinations with $(i-j) > DP_{max}$, i.e. products larger than

$2DP_{max}$ cannot be formed.

$$P_i^f = \begin{cases} \sum_{j=1}^{\frac{i-1}{2}} k_P C_j^L C_{i-j}^L & \text{if } i \in (2\mathbb{Z} + 1) \wedge \mathbb{Z} \geq 1 \wedge 3 \leq i \leq (2i_{max} - 1); \\ \sum_{j=1}^{\frac{i}{2}} k_P C_j^L C_{i-j}^L & \text{if } i \in 2\mathbb{Z} \wedge 2 \leq i \leq 2i_{max} \end{cases} \quad (\text{Eq. 5.13})$$

The net reaction rate of DP_i by polymerisation is given by combining Eq. 5.12 and Eq. 5.13,

$$P_i = P_i^f - P_i^c \quad (\text{Eq. 5.14})$$

Discretization of GPC chromatogram:

The way in which $M_w D$ of lignin or pyrolysis oil, in terms of $w(\log M)$, is calculated has been described elsewhere^[265].

$$m(M)_q = \frac{w(\log M)}{\ln 10} \quad (\text{Eq. 5.15})$$

Mass corresponding to each molecular weight slice (q) between 1 Da and 10000 Da is calculated and then subsequently discretised into 50 segments of 200 Da. The mass fraction of DP_i is calculated,

$$w_i = \frac{m_i}{\sum_{i=1}^{50} m_i} \quad (\text{Eq. 5.16})$$

Note, the $M_w D$ s, in terms of mass fractions (w_i), of all lignins and experimentally obtained pyrolysis oils presented in this work (Figure 5.2A, Figure 5.2B and Figure C.2 to C.15) are calculated by using this procedure. These discretised mass fractions of each DP_i segments were converted to corresponding mole fractions by Eq. 5.17,

$$\omega_i = \frac{\frac{w_i}{M_{w,DP_i}}}{\sum_{i=1}^{50} \frac{w_i}{M_{w,DP_i}}} \quad (\text{Eq. 5.17})$$

Initial conditions:

The mole fraction of each DP_i is used to calculate the molar concentrations of the DP_i 's in the lignin feedstock.

$$C_{i,feed}^L = \frac{\omega_i^L N_{total}}{V_L} = \frac{\omega_i^L \frac{m_L}{M_n^L}}{V_L} \quad (\text{Eq. 5.18})$$

The molar concentration distribution of the lignin is the initial condition for C_i^L with $1 \leq i \leq i_{max}$.

$$C_{i,t=0}^L = C_{i,feed}^L \quad 1 \leq i \leq i_{max}$$

For the char bins, i.e. the segments between DP_{max+1} to $2DP_{max}$

$$C_{i,t=0}^L = 0 \quad (i_{max} + 1) \leq i \leq 2i_{max}$$

Note, the $M_w D$ of a lignin sample obtained from the GPC depends on – 1) packing material of the column, 2) geometry of column, 3) eluent and its flow rate, and 4) detector type^[265–267]. At $t = 0$ the concentration of each DP_i in the oil is zero:

$$C_{i,t=0}^O = 0 \quad 1 \leq i \leq i_{max}$$

Numerical method:

The model equations were solved in the coding environment of Matlab®2017a. The numerical integration was carried out with the built-in ode23tb solver which is especially suited for stiff systems and is based on the trapezoidal rule with a second order backward difference approximation.

Characteristics of the model:

The model has two important characteristics:

1. The predictions of C_i^L and C_i^O at $t = \infty$ are invariant to the multiplication of the constants $k_{T,i}$, k_P and k_K with the same factor (for details see Section C.6.2 in Appendix C).
2. Changing the computational grid by changing the starting point of the char bins (remaining the final grid points) does not influence the predictions after fitting $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$ as long as the starting DP_i of the char bins corresponds with a mass fraction of zero of that DP_i in the lignin feed (for details see Section C.6.2 in Appendix C).

Post-processing:

The mass fraction and mole fraction of the DP_i segments in the oil are given by:

$$w_{i,cal,t=\infty}^O = \frac{C_{i,t=\infty}^O M_{w,DP_i}}{\sum_{i=1}^{i_{max}} C_{i,t=\infty}^O M_{w,DP_i}} \quad (\text{Eq. 5.19})$$

$$\omega_{i,cal,t=\infty}^O = \frac{\frac{w_{i,cal,t=\infty}^O}{M_{w,DP_i}}}{\sum_{i=1}^{i_{max}} \frac{w_{i,cal,t=\infty}^O}{M_{w,DP_i}}} \quad (\text{Eq. 5.20})$$

The $\langle M_w \rangle$ and $\langle M_n \rangle$ of the oil is calculated as follows:

$$\langle M_{w,t=\infty} \rangle = \sum_{i=1}^{i_{max}} w_{i,cal,t=\infty}^O M_{w,DP_i} \quad (\text{Eq. 5.21})$$

$$\langle M_{n,t=\infty} \rangle = \sum_{i=1}^{i_{max}} \omega_{i,cal,t=\infty}^O M_{w,DP_i} \quad (\text{Eq. 5.22})$$

The oil and char yields are calculated with the following equations:

$$Y_{Char,cal,t=\infty} = \frac{\sum_{i=i_{max}+1}^{2i_{max}} C_{i,t=\infty}^L M_{w,DP_i}}{\sum_{i=1}^{i_{max}} C_{i,t=\infty}^O M_{w,DP_i} + \sum_{i=i_{max}+1}^{2i_{max}} C_{i,t=\infty}^L M_{w,DP_i}} \quad (\text{Eq. 5.23})$$

$$Y_{Oil,cal,t=\infty} = 1 - Y_{Char,cal,t=\infty} \quad (\text{Eq. 5.24})$$

Parameter estimation:

$$f_i = \sum \left\{ \left(w_{i,exp}^O - w_{i,cal,t=\infty}^O \right)^2 + \left(Y_{Char,exp} - Y_{Char,cal,t=\infty} \right)^2 \right\} \quad (\text{Eq. 5.25})$$

As mentioned before, the predictions of C_i^L and C_i^O at $t = \infty$ are invariant to multiplication the constants $k_{T,i}$, k_P and k_K with the same factor. This in combination with the fact that the experimental method does not allow the determination of the temporal evolution of oil and char yield, instead final yields ($t = \infty$) are obtained, leads to the restriction that it is not possible to determine all three constants by fitting them to the experimental results. In fact, it is only possible to determine the ratio of the constants, here expressed as $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$.

For each lignin, the experimental results were fitted to the model using $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$ as parameters. This is called the individual fit procedure. The objective function for this (Eq. 5.25) is comprised of – 1) the sum of squared difference between the M_wD of experimentally obtained oil and calculated, and 2) the squared difference between the experimentally obtained and calculated char yield. Note, as mentioned in Section 5.4.1, some of the volatile products (potential oil) could not be recovered, and therefore, the char yield is used in the minimization routine since it was measured more accurately compared to oil yield. Parameters estimation is carried out with the Matlab in-built optimisation function lsqnonlin. 95% confidence intervals for each parameter were determined by the built-in Matlab function nlparci.

$$g = \sum_{j=1}^n f_j \quad (\text{Eq. 5.26})$$

In order to estimate a single set of values of $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$ per pressure, describing pyrolysis of all lignins studied in this work, the objective function shown in Eq. 5.26 is used, where n represents the number of lignins. This is what is called the total fit procedure.

5.4 Experimental results

5.4.1 Mass balance closures

The mass balance closure for individual pyrolysis experiments carried out at 0.5 kPa was between 0.87 kg kg⁻¹ and 0.97 kg kg⁻¹, while for 100 kPa experiments a slight decrease in mass closure (0.8 kg kg⁻¹ – 0.88 kg kg⁻¹) was observed. This decrease can be accounted for the observation that at 100 kPa more pyrolysis products condensed on the gas sampling line, thermocouple, and pressure sensor line instead of on the wall. Light organics (e.g. formic acid, formaldehyde) and water were most likely (partly) lost during gas sampling and during the dismantling of the setup, which explains that the closure was always below 100%. The number of experiments performed for each lignin, under identical conditions, were at least 3. Except, in the case of MWL only two experiments were performed at both pressures because of its limited availability. Reproducibility of the experiments was satisfactory as shown in the Table C.3. The error bars on yields (Figure 5.3A to 5.3C and Figure 5.5) and $\langle M_n \rangle$ of the oils (Figure 5.4) represent the standard deviations on the mean.

5.4.2 Molecular weight distribution of oils at 530 °C

In Figure 5.2, the M_wD of two lignins (11 and 14) and their oils produced at 0.5 kPa and 100 kPa are plotted. Also, model predictions are shown. Because these two lignins are entirely different from each other regarding their $\langle M_w \rangle$, $\langle M_n \rangle$, M_wD and β -O-4 linkage content, they were selected to illustrate the observed differences in pyrolysis behaviour. In the case of lignin-11, the M_wD of the oils nearly overlapped with the M_wD of the parent lignin (Figure 5.2A). On the contrary, a significant shift towards the lower molecular weight region was observed in the M_wD for the of lignin-14 oils as compared to the feedstock (Figure 5.2A). For lignin-14, the oil obtained at 0.5 kPa was heavier than the oil obtained at 100 kPa.

5.4.3 Lumped product yields at 530 °C

In Figure 5.3A to 5.3C, oil, char and gas yields are plotted as a function of the $\langle M_n \rangle$ of the lignin. At both pressures, a decrease in oil yield was observed with an increase of the $\langle M_n \rangle$ of lignin. At 100 kPa lower oil yields were achieved than at 0.5 kPa. This difference in oil yield became wider with an increase in $\langle M_n \rangle$ of the lignins. At both pressures, the oil yields obtained for the light fractions (2,5,11) were higher than the yields achieved for their parent lignins (1,4,10) and their respective heavy fractions (3,6,12). For low $\langle M_n \rangle$ lignins (<500 Da), high oil yields of up to 0.96 kg kg⁻¹ were

Figure 5.2A: $M_w D$ of lignin 11 and its oils

Figure 5.2B: $M_w D$ of lignin 14 and its oils

achieved at 0.5 kPa and decreased to 0.78 kg kg⁻¹ at 100 kPa. In the case of high $\langle M_n \rangle$ lignins (>500 Da), a significant drop in oil yield was observed (0.32 kg kg⁻¹) at 100 kPa compared to the 0.5 kPa experiments. In the literature, oil yields of ~ 0.12 kg kg⁻¹ (at 100 kPa)^[268] and ~ 0.8 kg kg⁻¹ (~ 0.5 kPa)^[87,225,242] in screen-heater reactors, ~ 0.55 kg kg⁻¹ in a tubular reactor^[236], and ~ 0.40 kg kg⁻¹ in a fluidised bed reactor^[241,244] were reported.

Also at both pressures, the char yield increased with the increase in $\langle M_n \rangle$ of the lignins. For low molecular weight lignins (<500 Da), the char yields were below 0.1 kg kg⁻¹, while the difference between the char yields obtained at 0.5 kPa and 100 kPa was small. In the case of lignins heavier than 500 Da, char yields increased significantly especially for experiments performed at 100 kPa. At both pressures, the char yields obtained for the light fractions (2,5,11) were lower than the yields achieved for their parent lignins (1,4,10) and their respective heavy fractions (3,6,12). In the literature, char yields of ~ 0.75 kg kg⁻¹ in TGA^[241,247,269,270], ~ 0.45 kg kg⁻¹ (at 100 kPa)^[268] and ~ 0.12 kg kg⁻¹ (~ 0.5 kPa)^[225,242] in screen-heater reactors, 0.22 kg kg⁻¹ (0.5 kPa) to 0.35 kg kg⁻¹ (100 kPa) in a modified pyroprobe reactor^[75], ~ 0.35 kg kg⁻¹ in a tubular reactor^[236], and ~ 0.35 kg kg⁻¹ in a fluidised bed reactor^[241,244] were reported.

Only a small amount of gases (~ 0.025 kg kg⁻¹) were produced for all lignins during pyrolysis at 0.5 kPa. A marginal increase, if at all, in gas yield was observed at 100 kPa. Gases produced during pyrolysis were mainly CO₂ and CH₄, while CO was only present in trace quantities. In literature, at ~ 530 °C similar gas yields were obtained by Iatridis et al.^[268] and Zhou et al.^[242] in screen-heater reactors and by Lou et al.^[236] in a tubular reactor. Contrary, gas yields up to ~ 0.25 kg kg⁻¹ and ~ 0.30 kg kg⁻¹ were reported in micro-pyrolysers^[240,271] and TGA^[272], respectively.

5.4.4 The average molecular weight of oils at 530 °C

Figure 5.4 shows the $\langle M_n \rangle$ of the oils as a function of the $\langle M_n \rangle$ of the lignins. At both pressures, the oils obtained from pyrolysis of low $\langle M_n \rangle$ lignins (<500 Da) showed no significant reduction in $\langle M_n \rangle$ as compared to their parent lignins (data close to parity line). From ~ 500 Da and above, the oils seemed to have a constant $\langle M_n \rangle$ which was independent of the $\langle M_n \rangle$ of the lignin. This trend was most clearly observed at 100 kPa. At 0.5 kPa, larger deviations in molecular weights of oils were observed, which might be explained by the random ejection of molecules from the reacting lignin. It is worth noticing that the yields and the $\langle M_n \rangle$ of the oils obtained from lignin 14 (richest in β -O-4 linkages) do not deviate from the trend as observed for other lignins.

Figure 5.3A: Oil yield as a function of $\langle M_n \rangle$ of the lignins. The numbers in the symbols refer to the lignins listed in Table 5.1

Figure 5.3B: Char yield as a function of $\langle M_n \rangle$ of the lignins. The numbers in the symbols refer to the lignins listed in Table 5.1

Figure 5.3C: Gas yield as a function of $\langle M_n \rangle$ of the lignins. The numbers in the symbols refer to the lignins listed in Table 5.1

Figure 5.4: Experimentally obtained $\langle M_n \rangle$ of oils obtained at 0.5 kPa and 100 kPa as a function of the $\langle M_n \rangle$ of the lignins

Effect of temperature

Figure 5.5 shows the oil, char and gas yields obtained from the pyrolysis of lignin-13 versus the final screen temperature (T_{FS}), at two different pressures. The experiments were carried out in a temperature range between 425 °C and 793 °C. Figure 5.5 shows that char yield decreased with an increase in T_{FS} , at both pressures. It can be seen that at 0.5 kPa, the maximal amount of gases were produced above the T_{FS} of 530 °C and their yield remained independent of T_{FS} after that. At 100 kPa, the gas yield was below 0.06 kg kg⁻¹ until 530 °C and thereafter it increased significantly to 0.17 kg kg⁻¹ (at 793 °C). It can be seen that at 0.5 kPa, 0.62 kg kg⁻¹ of oil yield was achieved at 425 °C and above 530 °C it became constant at a value of ~ 0.8 kg kg⁻¹. At 100 kPa, the oil yield was independent of T_{FS} , i.e. it remained constant at 0.46 kg kg⁻¹ - 0.49 kg kg⁻¹. Similarly, Lou et al.^[273] observed a constant yield of oil (~ 0.5 kg kg⁻¹) in a wide temperature range. The effect of T_{FS} on the $\langle M_n \rangle$ of oils collected from the pyrolysis of lignin 13 is presented in Figure 5.6, showing independence at 100 kPa and a slight increase with increasing T_{FS} at 0.5 kPa. A similar trend was observed for pyrolysis of kraft lignin by Ben et al.^[274] at 100 kPa.

Figure 5.5: Oil, char, and gas yields as a function of the final mesh temperature (T_{FS}) obtained for lignin 13

Figure 5.6: $\langle M_n \rangle$ of oil obtained from lignin 13 as a function of T_{FS} at 0.5 kPa and 100 kPa

5.5 Discussion

5.5.1 Chemical reactions and mass transport

C₅

As mentioned in the introduction, we hypothesize that, like for cellulose (Chapter 4), lignin pyrolysis cannot be described solely by chemical reactions. Instead, there is an interplay of chemistry and mass transport. As previously mentioned, the fact that the oil is collected indicates that mass transport of compounds away from the reaction front is taking place. Due to the influence of pressure on the escape rate - the higher rate at lower pressure - heavier oils are expected at lower pressure. This behaviour was observed in the lignin pyrolysis experiments – lighter oils were collected at 100 kPa (~400 Da) than at 0.5 kPa (~800 Da), see Figure 5.4. At both pressures, the oil yields measured for the low $\langle M_n \rangle$ lignins (<500 Da) were high (Figure 5.3A), and no significant change in their $\langle M_n \rangle$ was observed compared to the $\langle M_n \rangle$ of the parent lignins (Figure 5.4). This indicates that these low $\langle M_n \rangle$ lignins are mainly evaporating/sublimating/ejecting while the extent of reactions, in particular, cracking reactions, is limited. On the contrary, for high $\langle M_n \rangle$ lignins, the obtained oil yields were (much) higher than the mass fraction of lights in the feed (Figure C.1A and C.1B), and a noticeable decrease in $\langle M_n \rangle$ of oils compared to the feedstock (Figure 5.4), affirms the presence of cracking reactions. Because the reactions take place on the reacting lignin (in the liquid and/or solid phase), it is not expected that the pressure influences their rates. At lower pressures, the likelihood of char production decreases (as observed experimentally, see Figure 5.3B) because of the rate of mass transport away from the reacting lignin increases leaving less time for polymerisation. More char (Figure 5.3B) and less oil (Figure 5.3A) at increasing $\langle M_n \rangle$ can be explained by the fact that heavier molecules have more possibilities (more reactions) to form char in combination with a lower escape rate. Heavier oils at a higher temperature (see Figure 5.6) is not expected when only considering chemical reactions, but can be explained by a higher escape rate of heavy molecules from the reacting sample at higher temperatures.

The main experimental trends can be summarised as – 1) the lower the pressure, the higher (or lower) the oil (or char) yield, 2) the lower the pressure, the heavier the collected oil, 3) the heavier the lignin, the higher the char yield, 4) heavier oil at higher temperature all support that pyrolysis of lignin is influenced by the interplay of chemistry and mass transport. It is also clear that the molecular weight distribution of the lignin is not the only parameter controlling the pyrolysis yields and oil M_w . For instance, lignin 5 and 13 having similar $\langle M_n \rangle$ but different oil and gas yields, which may arise from their structural differences.

5.5.2 Modelling

Fitting each lignin individually to the model results in $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$ values per lignin that predict the char yield very accurately (Figure 5.7A). For 100 kPa experiments, the predicted $\langle M_n \rangle$ of oils also match very well with the experimental values, while they are slightly under-predicted for 0.5 kPa experiments (Figure 5.7B). This mismatch in the predictions can be a result of the random ejection of heavier molecules which is difficult to describe. Also, the $M_w D$ is predicted fairly well as can be seen in Figure 5.2A and 5.2B (Figure C.2 to C.15). The range of fitted $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$ are listed in Table 5.2 (individual fit), and in Table C.4 in Appendix C they are listed per lignin with their 95% confidence intervals. As expected $\frac{k_{T,avg}}{k_P}$ is significantly higher at 0.5 kPa due to the higher escape rate at lower pressure. The variation in $\frac{k_K}{k_P}$ between the pressures is small, which should be the case as this is a ratio of pressure independent reactions. As the range of the parameters is not that large for the individual fits, it has been attempted to fit a single $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$ per pressure for all the lignins together, which is referred to as the total fit procedure (see Table 5.2 for the values). This results, on average, in a poor prediction of $\langle M_n \rangle$ and char yield (Figure C.22A and C.22B). However, the macro trends are still predicted.

From the individual fits, it is found that the ratio $\frac{k_K}{k_P}$ is a function of $\langle M_n \rangle$ of the lignins (Figure C.23). $\frac{k_K}{k_P}$ decreases with an increase in $\langle M_n \rangle$, i.e. larger DP_i molecules present in the lignin tend to polymerise faster than described in the original model. No clear relation was observed between the values of $\frac{k_{T,avg}}{k_P}$ and $\langle M_n \rangle$ for 0.5 kPa experiments, while for the 100 kPa experiments the values are independent of $\langle M_n \rangle$ of lignins. The fitted $\frac{k_K}{k_P}$ as a function of $\langle M_n \rangle$ of the lignins together with $\frac{k_{T,avg}}{k_P}$ (see Table 5.2, total fit) are used as input for the model. The predicted char yields and $\langle M_n \rangle$ of oils are monotonous in nature and follow the experimentally observed trend (Figure 5.7C and 5.7D). However, it can be seen that $\langle M_n \rangle$ of oils are under-predicted and char yields are over-predicted at 0.5 kPa.

After parameterisation, predicted char yields and $\langle M_n \rangle$ of the oils as a function of temperature match the experimentally obtained values (Figure C.24A and C.24B). It can be seen from Figure C.25A that the values of $\frac{k_{T,avg}}{k_P}$ increase as a function of temperature (especially at 0.5 kPa) indicating a stronger increase of the mass transport rate with temperature as compared to the polymerisation rate. With the increase in temperature the values of $\frac{k_K}{k_P}$ increased, while they were similar at both pressures for a any given temperature (Figure C.25B). This indicates that the ratio of reaction rate constants ($\frac{k_K}{k_P}$) is a function of temperature and is not affected by the pressure, as was also assumed.

Table 5.2: The values of $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$ at 0.5 kPa and 100 kPa

Fit procedure	$\frac{k_{T,avg}}{k_P}$ mole m ⁻³	$\frac{k_K}{k_P}$ mole m ⁻³
P = 0.5 kPa		
Individual fit	4 to 16	27 to 96
Total fit	10 ^a (± 0.6) ^b	39 (± 0.01) ^b
P = 100 kPa		
Individual fit	2 to 5	24 to 81
Total fit	3 ^a (± 0.2) ^b	42 (± 0.3) ^b

^a Values of $\frac{k_{T,avg}}{k_P}$ used with correlation for model predictions in Figure 5.7C and 5.7D

^b Values in parentheses are the 95% confidence intervals on the ratios

Concluding, after parameterisation of each lignin individually the model describes the experiments very well. However, it is not able to provide good quantitative predictions for all the lignins tested based on a single set of $\frac{k_{T,avg}}{k_P}$ (T and P dependent) and $\frac{k_K}{k_P}$ (T dependent). This could obviously be explained by the lignins tested being different in other aspects than the M_wD, e.g. chemical structure. However, including a $\frac{k_K}{k_P}$ relation accounting for a relatively higher polymerisation rate for larger molecules results in a reasonable qualitative and quantitative description. The model including this relation can be used to predict yields and the M_wD of oil based on the M_wD of the lignin feedstock. It must, however, be noted that the measured M_wD of the feedstock depends on the GPC/SEC machine and method used. As a result, $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$ which are obtained by fitting will also depend on the GPC/SEC machine and method.

5.5.3 Process considerations

Depolymerisation of lignin is proposed for the production of fuels and platform chemicals^[13,233,238,263,275,276]. The results obtained in this paper show that under (very) fast heating conditions and minimal chemical activity in the vapour/gas phase, pressure can steer the molecular weight of the oil. All technical lignins with $\langle M_n \rangle > 800$ Da result in an $\langle M_n \rangle$ of the oil that depends on the pressure, but is invariant to the M_wD of the feedstock. At atmospheric pressure the oil is rather light, dominated by monomers to trimers, which is beneficial for the production of chemicals. Potentially, high pressure lignin pyrolysis may favour the production of monomers, however, experimental investigation is needed to gain further insights. Light oil comes, however, at the expense of

Figure 5.7A: Parity plots in which the experimental char yields are plotted against their predicted values using individual fit procedure

Figure 5.7B: Parity plots in which the experimental $\langle M_n \rangle$ of oils (B) are plotted against their predicted values using individual fit procedure

Figure 5.7C: Char yields, experimental and model prediction using the correlation

Figure 5.7D: $\langle M_n \rangle$ of oils, experimental and model prediction using the correlation

lower oil yields and higher char yields. Nevertheless, also light oil can also be produced with a yield exceeding 50% under the tested conditions. There is a clear effect of the $\langle M_n \rangle$ of the feedstock and the oil and char yields. If possible, a light feedstock should be selected as this will increase the oil yield. At low pressures, in our case 0.5 kPa, the oil is heavier, but its yield is considerably higher. These conditions may be interesting for fuel production. Also a process, in which first as high as possible oil yield is achieved at low pressure followed by further tuning of the product distribution in the vapour/gas phase can be considered.

5.6 Conclusions

In this work, lignins having number averaged molecular weight between 350 Da and 1900 Da were pyrolysed between 425 °C and 793 °C and pressures of 0.5 kPa and 100 kPa. It was found that – 1) With an increase in number averaged molecular weight, oil yield decreased, and char and gas yields increased, 2) At higher pressures (100 kPa) lighter oils were collected than at 0.5 kPa, 3) Above 500 Da (at 100 kPa) and 1000 Da (at 0.5 kPa) the molecular weights of oils became independent of the number averaged molecular weight of the parent lignins, and 4) Heavier oils were collected with an increase in temperature. Based on the gathered experimental evidence of cracking and polymerisation reactions, and mass transport of species from the reacting lignin, a population balance model, which includes these processes, was developed. After parameterisation and by using the molecular weight distribution of lignin as an input, the model predicts all experimentally observed trends. It is noteworthy that the model also predicts the char yields and the number averaged molecular weight of oils reasonably for lignins, for which the β -O-4 linkage content varies significantly.

The present contribution highlights that during fast pyrolysis of lignin the temperature alone has a limited impact on the oil yield and the number averaged molecular weight of the oils. The molecular weight distribution is one of the most important characteristics of the lignin, which has a significant influence on the pyrolysis product distribution. Modelling results show that heavier molecules tend to polymerise faster than lighter molecules, which results in higher char yields. The pressure, at which the pyrolysis is carried out, is certainly the most influencing process parameter, which alters the transport rate of molecules away from the reaction front, thereby, changing their residence time in the hot reaction zone. It can be considered as the main steering wheel to manipulate the product yields and the number averaged molecular weight of the oils.

Nomenclature

A, B		Parameters used to describe the transport rate of DP_i
C_i^L	$mole\ m_L^{-3}$	Molar concentrations of DP_i in reacting lignin at $t = t$
$C_{i,feed}^L$	$mole\ m_L^{-3}$	Molar concentrations of DP_i in lignin feedstock
$C_{i,t=0}^L$	$mole\ m_L^{-3}$	Molar concentrations of DP_i in lignin at $t = 0$
C_i^O	$mole\ m_L^{-3}$	Molar concentrations of DP_i in oil at $t = t$
$C_{i,t=0}^O$	$mole\ m_L^{-3}$	Molar concentrations of DP_i in oil at $t = 0$
$C_{i,t=\infty}^O$	$mole\ m_L^{-3}$	Molar concentrations of DP_i in oil at $t = \infty$
$C_{i,t=\infty}^L$	$mole\ m_L^{-3}$	Molar concentrations of DP_i in lignin at $t = \infty$
DP_i	-	Degree of polymerisation with i number of monomers
E_i	$mole\ m_L^{-3}\ t^{-1}$	Transport rate of DP_i from the reacting lignin to cold glass wall at $t = t$
K_i	$mole\ m_L^{-3}\ t^{-1}$	Overall cracking rate of DP_i at $t = t$
$k_{T,i}$	t^{-1}	Evaporation/sublimation/ejection rate constant of DP_i
k_K	t^{-1}	First order cracking reaction rate constant
k_P	$mole\ m_L^{-3}\ t^{-1}$	Second order polymerisation reaction rate constant
$m(M)_q$	g	Mass corresponding to each molecular weight slice (q)
m_i	g	Mass corresponding to each DP_i obtained after discretization
m_L	g	Total mass of lignin pressed between the two screens
M_{w,DP_i}	Da	Molecular weight of each DP_i
M_w	Da	Molecular weight
$\langle M_n \rangle$	Da	Number average molecular weight
$\langle M_w \rangle$	Da	Mass average molecular weight
$M_w D$	-	Molecular weight distribution
$\langle M_n^L \rangle$	Da	$\langle M_n \rangle$ of lignin calculated from GPC chromatogram after discretization
$\langle M_{n,t=\infty}^O \rangle$	Da	Calculated $\langle M_n \rangle$ of oil at $t = \infty$
$\langle M_{w,t=\infty}^O \rangle$	Da	Calculated $\langle M_w \rangle$ of oil at $t = \infty$
ω_i	-	Mole fraction of each DP_i
ω_i^L	-	Mole fraction of each DP_i present in lignin
$\omega_{i,cal,t=\infty}^O$	-	Calculated mole fraction of each DP_i present in oil at $t = \infty$
N_{total}	$mole$	Initial number of moles of lignin
P_i	$mole\ m_L^{-3}\ t^{-1}$	Overall polymerisation rate of DP_i at $t = t$
$R_{K,i}$	$mole\ m_L^{-3}\ t^{-1}$	Cracking reaction rate of each DP_i
$R_{P,i}$	$mole\ m_L^{-3}\ t^{-1}$	Polymerisation reaction rate for each DP_i
V_L	m_L^3	Volume of lignin pressed between the two screens

$w(\log M)_q$	-	Molecular weight distribution corresponding to each molecular weight slice (q)
w_i	-	Mass fraction of each DP_i in lignin or pyrolysis oils
$w_{i,exp}^O$	-	Mass fraction of each DP_i present in oil obtained from experiments
$w_{i,cal,t=\infty}^O$	-	Calculated mass fraction of each DP_i present in oil at $t = \infty$
$Y_{Char,exp}$	$kg\ kg_L^{-1}$	Experimentally obtained char yield
$Y_{Char,cal,t=\infty}$	$kg\ kg_L^{-1}$	Calculated char yield at $t = \infty$
$Y_{Oil,cal,t=\infty}$	$kg\ kg_L^{-1}$	Calculated oil yield at $t = \infty$

Superscripts/subscripts

L	Lignin
O	Oil
c	Consumption
f	Formation

C_6

C₆

On the effect of ether linkages in
lignin on the product yields and the
molecular weight of pyrolysis oils
using HSQC NMR

Abstract

Aromatic units in lignin are connected by ether and carbon linkages. Ether linkages are considered to play an essential role in depolymerisation of lignin by pyrolysis with a goal to obtain high liquid yields and especially high yields of mono-phenolic compounds. In this chapter, five lignins, with the varying number of ether linkages and molecular weights were used as feedstock for experiments in a screen-heater (0.5 kPa and 100 kPa) at the T_{FS} of 530 °C. The lignin feedstock and their pyrolysis oils were characterised by HSQC NMR to study the effect of ether linkages on the oil and char yields and average molecular weights of the oils. It was demonstrated that a high escape rate (at 0.5 kPa) of pyrolysis products away from the hot reacting particle, results in oil which still contains a significant amount of molecules with ether linkages. Also, it is shown that the amount of ether linkage in the lignins hardly has any effect on the char and oil yields and the number average molecular weight of the oils.

6.1 Introduction

The lignin content of biomass varies from 15 to 40%^[277–279]. Coumaryl, coniferyl, and sinapyl alcohols, the precursors of lignin, are interconnected by various linkages, broadly classified into two types, namely, ether linkages (e.g. β -O-4, α -O-4) and carbon linkages (e.g. β -1, α -1, 5-5')^[13,263,278,280]. Characterisation of the lignin structure using nuclear magnetic resonance (NMR) spectroscopy started in the late 1960s^[281–283] and NMR characterisation of pyrolysis oils in the mid-1980s^[284–286]. Lately, advancements have been made in characterisation and quantification of linkages in lignin and pyrolysis oils derived from it, using ^1H , ^{13}C , ^{19}F , ^{31}P and HSQC NMR techniques^[274,278,287–293]. In most of these studies, lignins isolated via different methods and/or source are characterised, from which it is concluded that different isolation methods result in lignins with different amounts of ether bonds due to the destructive nature of the isolation process^[293–295]. Note that milled wood lignin, obtained by Björkman's method, is considered to represent native lignin most accurately^[17]. In this work, pyrolysis oils obtained under different pyrolysis conditions are qualitatively compared with their feed lignin to identify the structural alterations. It is reported in the literature that the cleavage of ether linkages is a primary decomposition reaction^[274] and new aliphatic and aromatic C-H linkages are formed by cleavage and rearrangement ether linkages and methoxyl groups, respectively^[274].

In Chapter 5, the oil and char yields and the molecular weight of the oils are interpreted as a function of the molecular weight of lignins. For the depolymerisation of lignin to platform chemicals, inter-unit linkages need to be cleaved, and the formation of new bonds (polymerisation) should be minimised. The main goal of this chapter is to investigate the effect of pyrolysis on the cleavage of ether linkages. Moreover, the effect of the number of ether linkages in lignin on the yields of oil and char and the average molecular mass of oils is investigated. To do so, five different lignins (1,4,10,13 and 14) from Table 5.1 of Chapter 5, and their corresponding pyrolysis oils, obtained from screen-heater (0.5 kPa and 100 kPa) experiments, were characterised and quantified by HSQC NMR. By varying the pressure during pyrolysis, the escape rate of molecules from the hot reacting particle was varied, which has shown previously to play an important role in the outcome of lignin pyrolysis, see Chapter 5.

6.2 Results and discussion

Five lignins (1,4,10,13 and 14) with varying content of ether linkages were selected from Table 5.1 of Chapter 5. These lignins and their pyrolysis oils, produced at the T_{FS} of 530 °C in a dedicated screen-heater at two pressures (0.5 kPa and 100 kPa), were characterised by quantitative CMPG-improved HSQC 2D NMR. For the details of the NMR machine settings, see Section 2.4.7 of Chapter 2. Briefly, this method compensates for the influence of $^1J_{CH}$ and J_{HH} couplings on signal volumes. Two regions of interests were considered: ether linkage region (δ_C/δ_H 50-90/2.5-5.8) and building block unit region (δ_C/δ_H 90-150/5-8.5).

The β -aryl ether (β -O-4, A), phenylcoumaran (β -5', B) and resinol (β - β ', C) are the most important among the inter-unit linkages (marked in red colour), while p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) are the building blocks of lignin, as shown in Figure 6.1. The cross-peaks representing different ether linkages and building block units were assigned based on the literature^[274,293]. Note, although the phenylcoumaran (B) and resinol (C) substructures have carbon linkages, they were used to characterise the ether linkages in the respective substructure (Figure 6.1). The distribution of building blocks as a molar percentage and the content of ether linkages per 100 aromatic units were determined by the integration method described by Constant et al.^[293]. The reproducibility of the 2D NMR experiments was tested by analysing lignin 4 three times, and the obtained standard deviation on the means for three ether linkages was $\leq 1\%$. Considering the long measurement time per sample (~24 h) and the reproducibility of the 2D NMR experiments, other lignins and their oils were analysed only once. Two experimenters integrated the recorded spectrum of each sample, and the average values are reported in Table 6.1.

$$X_{ether} = 1 - \frac{A_A + A_B + A_C}{A_{A,0} + A_{B,0} + A_{C,0}} Y_{Oil} \quad (\text{Eq. 6.1})$$

FTIR analysis showed that the β -O-4 linkages (at 1120 cm^{-1} ^[296]) were absent in the chars obtained from the pyrolysis of lignins (data not shown here). Therefore, the conversion of ether linkages (X_{ether}) can be estimated by using Eq. 6.1, where $A_{A,0}$, $A_{B,0}$ and $A_{C,0}$ are the abundance of ether linkages in lignin; A_A , A_B and A_C are the abundance of ether linkages in oil obtained at a given pressure; Y_{oil} is the oil yield obtained from the pyrolysis of lignin at a given pressure.

Figure 6.1: Linkages/substructures identified in lignin; β -aryl ether (A), phenylcoumaran (B), resinol (C), p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S)

Table 6.1: Abundances of ether linkages and building blocks in lignins and their pyrolysis oils

Lignin Code	SL 1		WSL 4		SOL 13		MWL 14		
	Feed	0.5 kPa	100 kPa	Feed	0.5 kPa	100 kPa	Feed	0.5 kPa	100 kPa
Ether linkages (per 100 aromatic units) ^a									
β -aryl ether (A)	1.8	0.0	0.0	8.6	3.9	0.0	7.8	3.9	0.0
Phenylcoumaran (B)	4.9	2.4	0.2	6.2	4.3	0.0	2.9	1.7	0.5
Resinol (C)	1.2	0.6	0.0	1.6	1.2	0.0	6.3	2.9	1.5
Total	7.8	3.0	0.2	16.5	9.4	0.0	17.0	8.6	2.0
Aromatic units (%) ^b									
p-Hydroxyphenyl (H)	0	0	0	7	7	9	0	0	0
Guaiacyl (G)	100	100	100	54	52	46	29	37	32
Syringyl (S)	0	0	0	39	41	45	71	63	68
							2	2	1
							6	2	2
							92	96	97

^a Linkage abundance calculated from the oil spectrum is multiplied by the oil yield to obtained linkage content on lignin basis^b Molar percentage (H + G + S = 100)

From Table 6.1, it can be seen that lignin 14 has the highest total number of ether linkages among other lignins. The total number of ether linkages are significantly lower in organosolv lignins compared to lignin 14. The cross peaks of three ether linkages were not observed in the spectrum of pyrolytic lignin (lignin 10), hence, not presented in Figure 6.2 and Table 6.1. Absence of β -aryl ether, phenylcoumaran and resinol in pyrolytic lignins is reported in the literature^[126,286,290]. Like reported in the literature^[293–295], this result shows that with an increase in the severity of the isolation process, the content of ether linkages in (isolated) lignin decreases.

Figure 6.2A presents the conversion of ether linkages during the pyrolysis of four lignins (1, 4, 13 and 14). At 0.5 kPa, the conversion of ether linkages was between 43% to 73%, whereas it was ~96% at 100 kPa. At 0.5 kPa, lower conversion of ether linkages can be explained by the rapid removal of molecules containing ether linkages from the hot reaction zone. Otherwise, as a result of the longer residence time of molecules on/in hot reacting particle at 100 kPa, nearly all ether linkages were cleaved.

In Figure 6.2B to 6.2D, experimentally obtained oil and char yields and the number average molecular weight ($\langle M_n \rangle$) of the oils (per pressure) are plotted as a function of the content of ether linkages in lignins and the pressure during pyrolysis. It can be seen that at both pressures, the product yields and the number average molecular weight of the oils were (nearly) independent of the number of ether linkage in the feedstock lignin.

At 0.5 kPa and 100 kPa, the molecular weight distribution (M_w D) of oils obtained from the pyrolysis of lignin 10 overlapped significantly with that of the feedstock, see Figure 5.2A in Chapter 5. In other words, during pyrolysis lignin 10 escaped hot screens without undergoing reactions, especially cracking reactions. Consequently, the $\langle M_n \rangle$ of oils, obtained at both pressures, was similar to that of lignin 10, and high oil and low char yields were observed.

The distribution of p-hydroxyphenyl, guaiacyl and syringyl units in lignin vary based on the type of biomass, i.e. softwood, hardwood, grasses^[278]. In three softwood lignins studied in this work, i.e. lignin 1 (spruce wood) and lignin 10 and 14 (pinewood), guaiacyl units were predominantly present, see Table 6.1. The cross peaks of all three building blocks were detected in wheat straw lignin (4). A similar observation was made by Constant et al. and Zeng et al. for grass-derived lignins^[293,297]. Lignin 13, derived from a mixture of three hardwoods, was abundant in syringyl units.

In the literature, it is reported that under pyrolysis conditions, p-hydroxyphenyl and guaiacyl units have a higher tendency for condensation reactions compared to syringyl units^[286,298]. However, the following trends, contradictory to the literature, were

Figure 6.2A: Conversion of ether linkages in different lignins

Figure 6.2B: Experimental oil yields against the abundance of ether linkages of lignins

Figure 6.2C: Experimental char yields against the abundance of ether linkages of lignins

Figure 6.2D: $\langle M_n \rangle$ of oils against the abundance of ether linkages of lignins

observed: 1) At 0.5 kPa and 100 kPa, the molar percentage of guaiacyl units in oil increased for lignin 13 and remained constant for lignin 14, and 2) despite having similar content of guaiacyl units, significantly different char yields were seen for lignin 1 and 14. A plausible explanation for these difference can be ascribed to the aspects such as the presence of hydroxyl groups at the α or β carbon in ether linkage^[299] and the reactivity of other linkages/substructures (e.g. cinnamyl alcohol end-groups, ferulate) present in lignin. In the author's opinion, a further experimental investigation is needed to elucidate these observed trends.

6.3 Conclusions

In this chapter, five lignins and their pyrolysis oils obtained in screen-heater at two pressures (0.5 kPa and 100 kPa) were analysed by HSQC NMR. At 0.5 kPa, lower conversion of ether linkages was observed ($\sim 60\%$) compared to that of observed at 100 kPa, as a result of rapid removal of molecules (containing ether linkages) away from the hot reaction front. The yields of oil and char and the number average molecular weight of oils were found to be independent of the number of ether linkages in the lignin feedstock.

C_7

C₇

Effect of pressure on the fast
pyrolysis of acid-leached bagasse
and pine wood:
experiments and modelling

Abstract

Pyrolysis of acid-leached bagasse has been carried out in the pressure range of 0.005 to 100 kPa in a screen-heater, designed for nearly isothermal operation and rapid quenching of reaction products. At the lowest pressure, i.e. by maximising the escape rate of products away from the hot reaction zone, 73% of the poly- C_6 -sugars in the feed were recovered in the liquid product as C_6 -anhydrosugars (C_6aS) with degree of polymerization between 1 and 6 (DP_1 - DP_6). A mathematical model, including reactions and mass transfer, was able to predict the measured decrease in the total yield of C_6aS and the shift to lighter C_6aS in the DP -distribution as a function of increasing pressure. The effect of the hot vapour residence time on the DP -distribution of the C_6aS was investigated by pyrolysing in a fluidised bed. At identical pressure and temperature the total yield of C_6aS was the same for the screen-heater and fluidized bed while the DP -distribution shifted to DP_1 as a result of the higher hot vapour residence time in the fluidized bed, which could be described by assuming first order kinetics for all possible cracking reactions of C_6aS in the vapour phase.

7.1 Introduction

Fast pyrolysis is a thermochemical conversion processes, in which biomass is converted at ~ 500 °C in the absence of oxygen, to form oil, char and gas. Typically, the bio-oil produced is a complex mixture of hundreds of oxygenated organic compounds. A considerable amount of studies has been reported on the production of targeted compounds such as mono-phenols and sugars. For instance, pyrolytic sugars (e.g. glucose, xylose, mannose) can be upgraded to ethanol or platform chemicals^[200–203]. In this chapter, we focus on the production of anhydrosugars via pyrolysis of lignocellulosic biomass.

In most previous studies^[71,74,173,174,300,301], fast pyrolysis of biomass was studied in a wide range of reactor temperature (360 to 650 °C) at a constant pressure of 100 kPa. Contrary, only a few accounts are available on the pyrolysis of biomass at reduced pressure^[75,152,225,302–308], and in most of these studies^[225,302–306,308] pyrolysis was carried out at a single (reduced) pressure. Amutio et al.^[152] studied the effect of pressure (25 kPa and 100 kPa) in a continuous conical spouted bed reactor for the pyrolysis of pine wood, from which they showed that the pressure has little effect on the yields of the lumped products liquid (oil), char and gas. They performed pyrolysis of hybrid poplar over a wide range of pressure (0.4 to 100 kPa)^[75] and quantified monomeric and dimeric anhydrosugars present in the oil. Pecha et al. reported an increase in the DP_1 (levoglucosan) yield of a factor two, while the yield of larger anhydrosugars diminished with increasing the pressure from 0.4 to 100 kPa.

This work aims at advancing the understanding of the role of pressure during the fast pyrolysis of biomass. It is well known that alkali and alkaline earth metals (AAEMs) show strong catalytic activity with respect to the pyrolysis reactions, particularly the decomposition of sugars^[61,62,64,66,68,136,153,309]. In fact, we did not observe a significant effect of pressure on the yields of DP_1 - DP_6 C₆aS for pinewood and bagasse with 549 and 5032 ppm AAEMs, respectively (Table D.2 and Table D.4 in Appendix D). Therefore, in order not to be hindered by these catalytic effects acid-leached, hence AAEMs lean, biomass was used in this study.

Like seen in the case of cellulose (Chapter 4) and lignin (Chapter 5), we propose that the competition between mass transport and chemical reactions steers the pyrolysis of biomass with respect to the product slate of sugars. Experimentally obtained yields of C₆aS, obtained in a screen-heater are compared with a mathematical model, which includes chemical reactions and transport of products away from the reaction zone. Additionally, a comparison is made between pyrolysis experiments, performed under the identical conditions, in the screen-heater and a fluidised bed to evaluate the influence

of hot vapour residence time on the product distribution.

7.2 Mass balance and reproducibility

The mass balance closure of acid-leached bagasse (see Table 7.1 for characterisation) pyrolysis experiments, performed in screen-heater in a pressures range between 0.005 to 100 kPa, were in the range of 0.86 to 0.93 kg kg⁻¹. Pyrolysis of acid-leached pinewood (see Table 7.1 for characterisation) was carried out in a screen-heater (0.2, 55 and 100 kPa) at 485 °C, of which the mass balance closures were in the range between 0.74 to 0.91 kg kg⁻¹. An observed decrease in the mass balance closure, with an increase in pressure, can be ascribed to the observation that more pyrolysis products condensed on the gas sampling line, thermocouple, and pressure sensor line instead of on the cold vessel wall. Also, light organic compounds and water were most likely (partly) lost during gas sampling and the dismantling of the setup. Minimally 3 experiments were performed for both feedstock for each condition. Reproducibility of the experiments was satisfactory as shown in Table D.1 and Table D.3 in Appendix D.

Because of the limited availability of acid-leached pinewood, only one pyrolysis experiment was performed, at 485 °C and 55 kPa, in the fluidised bed, of which mass balance closure was 0.94 kg kg⁻¹. However, its reproducibility was judged by 5 pyrolysis experiments of untreated pinewood in the continuous fluidised bed at 485 °C and 55 kPa. The yields and standard deviation on mean of wet oil, char and gas were 0.62 kg kg⁻¹ ($\pm$ 0.01), 0.12 kg kg⁻¹ ($\pm$ 0.01), 0.20 kg kg⁻¹ ($\pm$ 0.01). This shows that the reproducibility of experiments was satisfactory.

7.3 Modelling

To interpret the experimentally observed yields of C_6aS a modified version of our previously developed model for the pyrolysis of lignin (Chapter 5), is used. The schematic representation of the model is presented in Figure 7.1. On/in the particle, C_6aS depolymerize (red arrows Figure 7.1) to C_6aS with lower degree of polymerization, react to other products U (purple arrows), or escape from the reaction zone by mass transfer (green arrow). Whether or not U stays on the particle is of no concern for this study. U is a mathematical sink that represents the experimentally observed char, light volatiles and gas. Depolymerisation is assumed to be a first order process, and all reactions have the same likelihood, i.e. the same rate constant (k_K). Decomposition reactions of C_6aS to U are also assumed to follow first order kinetics and to have the same rate constant (k_U). The transport of C_6aS by evaporation/sublimation/ejection is described by Eq. 7.1. Note that $k_{T,avg}$ is a simple average of transport rate of individual escape rates of C_6aS varying in DP between 1 and 6, as calculated by Eq. 7.2.

$$k_{T,i} = e^{-Ai} \quad 1 \leq i \leq 6 \quad (\text{Eq. 7.1})$$

$$k_{T,avg} = \frac{\sum_{i=1}^6 k_{T,i}}{6} \quad (\text{Eq. 7.2})$$

It is assumed that DP_7 is the initial state of the biomass because C_6aS bigger than DP_6 were not detected in collected oils (see Section D.2 in Appendix D). Note that the experimental method (in screen-heater) does not allow the determination of the temporal evolution of products. Instead, final yields ($t = \infty$) are obtained, which leads to the restriction that it is not possible to determine all three constants ($k_{T,avg}$, k_U and k_K) by fitting them to the experimental results. It is only possible to determine the ratio of the constants $\frac{k_K}{k_K + k_U}$ and $\frac{k_{T,avg}}{k_K + k_U}$, for details see Section D.3.1 of Appendix D.

Vapour phase depolymerisation reactions of C_6aS are also assumed to be the first order, and all possibilities have the same likelihood, i.e. the same rate constant k_V . For interpretation of the screen heater experiments only $k_{T,avg}$, k_U and k_K are considered, while for the fluidized bed k_V is included.

Figure 7.1: Schematic representation of the model

7.4 Results and discussion

Table 7.1 shows the total ash content and its composition present in the biomass before and after acid leaching. The values reported in the table are the averages determined based on triplicates. It can be seen that the total ash content of bagasse and pinewood decreased after acid leaching by 68% and 77%, respectively, while 95% and 88% removal of total AAEMs content for bagasse and pinewood was achieved, respectively.

Table 7.1: Total ash content and its composition present in the biomass after acid leaching

		Bagasse		Pinewood	
		Untreated	Acid-leached	Untreated	Acid-leached
Compositional analysis (kg kg ⁻¹ dry ash and extractive free biomass) ^a					
Glucose		0.49	0.5	0.53	0.53
Xylose		0.23	0.24	0.04	0.04
Galactose		0	0	0.01	0.01
Arabinose		0.03	0.02	0.01	0.01
Mannose		0	0.01	0.12	0.12
Lignin		0.25	0.23	0.29	0.29
Ash analysis					
		Untreated	Acid-leached	Untreated	Acid-leached
Ash ^b	wt. %	1.85	0.59	0.43	0.10
Na⁺	mg kg ⁻¹	2657	100	37	10
K⁺	mg kg ⁻¹	1461	102	207	24
Mg²⁺	mg kg ⁻¹	-	-	28	5
Ca²⁺	mg kg ⁻¹	914	37	277	26
Total	mg kg ⁻¹	5032	239	549	65

^a taken from [62]

^b Including all inorganic materials (metals, Si, etc.)

- Not detected

7.4.1 Anhydrosugars

In this section, the C₆aS yields obtained from bagasse and pinewood are presented. The HPLC chromatograms of the water-soluble fraction of pyrolysis oil were integrated as described elsewhere^[120]. The *DP*₁ yields are absolute values, while for *DP*_{≥2} C₆aS the yields are referred as estimated since minor compounds (partially) co-elute with these bigger C₆aS^[120] and Chapter 3). Presence of up to *DP*₆ sugars in the oil, obtained from bagasse and pinewood, was confirmed by the direct infusion mass spectrometry (Section D.2 in Appendix D).

It is worth mentioning that from the pyrolysis of Avicel PH 101, C₆aS with *DP* up to 11 were found in the oil^[120,192,193,223,224,310], whereas from biomass, *DP*₆ was the biggest detected C₆aS. This difference might be explained the structural differences between the Avicel PH 101 and native cellulose. In this line of reasoning, it takes longer time before C₆aS can escape the hot reacting particle because of the hindrance created by the lignin present in the cell wall of the biomass particle as compared to Avicel PH 101. As a result of which bigger C₆aS undergo depolymerisation reactions to form smaller *DP* C₆aS. Moreover, Avicel PH 101 is one of the purest form of cellulose, and hence its pyrolysis is not affected by lignin or any other contaminant. In the literature, during the pyrolysis of biomass, presence of C₆aS up to *DP*₃ in the oil is reported^[61,136,142,143], while we are the firsts, to the best of our knowledge, to report the presence of up to *DP*₆ C₆aS from the biomass pyrolysis. The presence of bigger C₆aS (up to *DP*₆) in biomass-derived oils emphasises the role of random scission of native cellulose, which was previously concluded for microcrystalline cellulose^[120,192,193,223,224,310], however, the unzipping mechanism, proposed by Golova et al.^[311], still cannot be excluded.

Effect of pressure in screen-heater experiments

In Figure 7.2, the total yield of C₆aS (expressed on the fraction of C₆ sugars in bagasse) and the mass fraction of *DP*₁ in C₆aS are plotted against the pressure. At 0.005 kPa, 73% of C₆ sugars from biomass were selectively converted to C₆aS during pyrolysis. Upon increasing the pressure to 10 kPa, the yield of total C₆aS dropped to the value of ~0.5 kg kg⁻¹, and upwards 20 kPa only a small decrease in the yield to ~0.42 kg kg⁻¹ was observed. The mass fraction of *DP*₁ increased as a function of pressure from 0.13 to ~0.42. It is worth mentioning that, even at 100 kPa, the major fraction of the C₆aS is composed of *DP*_{≥2} C₆aS. Note that, between 10 and 20 kPa, a step change in the yield of C₆aS (or *DP*₁ mass fraction) was observed. Between 20 to 100 kPa, the yield of remained (nearly) constant, while the *DP*₁ mass fraction increases from 0.32 to ~0.41. This trend is in line with the results of Pecha et al.^[75] reported an increase in the *DP*₁

Figure 7.2: C₆aS yield (on C₆ sugars in bagasse) and the mass fraction of DP₁ in C₆aS, experimental and calculated using the correlation, as a function of pressure; obtained in the screen-heater; T_{FS} = 515 ± 15 °C

(levoglucosan) yield (on poplar wood basis) from 0.06 kg kg⁻¹ (0.4 kPa) to 0.1 kg kg⁻¹ (100 kPa), while the yield of DP_{≥2} C₆aS diminished. Note, a similar observation was made for acid-leached pinewood, see Table D.5 in Appendix D.

To support the interpretation of the experimentally observed trends the model was used without cracking in the vapour phase, i.e. $k_V = 0$, which is a valid assumption for the screen-heater^[119,120]. An attempt was made to fit a single $\frac{k_K}{k_K + k_U}$ and $\frac{k_{T,avg}}{k_K + k_U}$ for all pressures, which is referred to as the total fit procedure (for values see Table 7.2). This resulted into a poor prediction of the yield of C₆aS and the DP₁ mass fraction (see Figure D.10) because the escape rate of C₆aS is a function of pressure, and hence a single value of $\frac{k_{T,avg}}{k_K + k_U}$ cannot capture it.

Next, $\frac{k_K}{k_K + k_U}$ obtained from the total fit procedure was set to a fixed value, which is rationalized by the pressure independence of k_K and k_U (first order reactions), to obtain $\frac{k_{T,avg}}{k_K + k_U}$ per pressure, called as the individual fit procedure. The values of $\frac{k_{T,avg}}{k_K + k_U}$ obtained from the individual fit procedure decreased as a function of increasing pressure. The range of fitted $\frac{k_{T,avg}}{k_K + k_U}$ (individual fit) is presented in Table 7.2, and in Table D.7 of Appendix D they are listed per pressure with their 95% confidence intervals. With the fitted $\frac{k_{T,avg}}{k_K + k_U}$ as a function of pressure (Figure D.12) and fixed $\frac{k_K}{k_K + k_U}$ (obtained from total fit procedure), the model predicted the experimentally observed trends correctly (Figure 7.2).

With $\frac{k_K}{k_K+k_U} > 0.5$ and fitted $\frac{k_{T,avg}}{k_K+k_U}$, the model over predicts the DP_1 mass fraction. Thus, $\frac{k_K}{k_K+k_U} = 0.3$ indicates that the reactions forming other products are always faster than the depolymerisation reactions of C_6aS . Until 10 kPa, the mass transport of C_6aS away from the reaction front is the dominant process, see Figure D.12. In other words, the likelihood of depolymerisation reactions forming smaller DP C_6aS and other products is small, which consequently results in high yield of C_6aS and low DP_1 mass fraction. As shown in Figure D.12, the rate of mass transport at 10 kPa is higher than that at 20 kPa, while at 20 kPa, the escape rate of C_6aS becomes equal to that of the sum of reactions ($\frac{k_{T,avg}}{k_K} \approx 1$). This suggests that, at 20 kPa, reactions of C_6aS proceed at the similar rate (not the same) that of mass transport, whereas at 10 kPa mass transport rate is higher compared to the reaction rates. Thus, as a result of decreased mass transport rate between 10 and 20 kPa, a step drop in the yield of C_6aS (or the DP_1 mass fraction) was observed. Upwards 20 kPa, $\frac{k_{T,avg}}{k_K+k_U}$ was found to be (nearly) constant (Figure D.12), showing no significant change in the escape rate of C_6aS away from the reacting particle. Thus, in the pressure range between 20 and 100 kPa, due to the similar mass transport rate of C_6aS and likelihood of reactions on/in the reacting particle, a constant yield of C_6aS and DP_1 mass fraction was observed.

Table 7.2: The values of $\frac{k_K}{k_K+k_U}$ and $\frac{k_{T,avg}}{k_K+k_U}$ obtained at a constant T_{FS} of 515 °C

Fit procedure	$\frac{k_{T,avg}}{k_K+k_U}$	$\frac{k_K}{k_K+k_U}$
Total fit	0.7 (± 0.3) ^a	0.3 (± 0.05) ^a
Individual fit	1.9 (± 0.9) ^a – 0.4 (± 0.1) ^a	0.3 ^b

^a Values in parentheses are the 95% confidence intervals

^b Value of $\frac{k_K}{k_K+k_U}$ from the total fit procedure used in the individual fit procedure to estimate $\frac{k_{T,avg}}{k_K+k_U}$ per pressure

Effect of hot vapour residence time

Figure 7.3: DP distribution of anhydrosugar (experimental and calculated) on C₆ sugars basis, obtained from pyrolysis of pinewood at 485 °C and 55 kPa in screen-heater and fluidised bed

Figure 7.3 presents the DP-distribution of obtained from pyrolysis of pinewood at 485 °C and 55 kPa in screen-heater and fluidised bed. As can be seen that the anhydrosugars present in the fluidised bed oil were predominantly composed of DP₁ and DP₂, while bigger C₆aS (DP_{≥3}) were present in small or traces quantities. Contrary, the yield of DP₁ observed in screen-heater was a factor of ~2 lower compared to the fluidised bed oils, while the yield of DP₂ was highest (~0.17 kg kg⁻¹ C₆ sugars). The cumulative yield of DP₃ and DP₄ C₆aS was ~0.1 kg kg⁻¹ C₆ sugars, and the presence of DP_{>4} C₆aS was marginal. However, it is important to mention that despite a significant difference in the DP distribution, the total yield of C₆aS yields from screen-heater and the fluidised bed was ~0.39 kg kg⁻¹ C₆ sugars.

At identical pressure, it is fair to assume that the mass transport rate of products away from the reacting biomass particle is identical in the screen-heater and fluidised bed. Assuming that, the remarkable difference in the DP-distribution can be ascribed solely to the different hot vapour residence time of products in these two reactors; screen-heater (~20 ms) and the fluidised (~1 s.). Since the DP-distribution of C₆aS in the fluidised bed could not be measured after ~20 ms, the experimentally obtained DP-distribution in screen-heater is used as model input for vapour phase cracking reactions. Fitting the vapour phase cracking reaction rate constant to a value of

$k_v = 0.8 \pm 0.1 \text{ s}^{-1}$, accurately predicted the DP-distribution observed in the fluidised bed, see Figure 7.3. Note, for the prediction of C₆aS DP-distribution of for the screen-heater experiment of acid-leached pinewood, shown in Figure 7.3, newly fitted values for acid-leached pinewood of $\frac{k_{T,\text{avg}}}{k_K + k_U}$ (0.3 ± 0.05) and $\frac{k_K}{k_K + k_U}$ (0.1 ± 0.01) were used.

Scott et al. and Graham et al. varied the hot (700 °C) vapour residence time of the products between 30 to 900 ms during the pyrolysis of cellulose^[57,312]. They observed that between 30 to 300 ms, the gas yield increased at the expense of liquid products and above 300 ms the lumped products yields remain constant. Hoekstra et al. performed the pyrolysis of pinewood in a fluidised bed at 500 °C, in which the hot vapour residence time of products was varied between 1.5 to 16.5 s^[58]. Upwards ~ 4.5 s, the authors reported no change in the lumped product yields, while the DP_1 anhydrosugar (levoglucosan) yield was found constant over the entire range of hot vapour residence time. Like reported in previous studies, also in this work, a decrease in the oil yield was seen with increasing hot vapour residence time (Table D.3 in Appendix D); however, a similar yield of C₆aS was observed in screen-heater and fluidised bed. Gathered experimental evidence shows that bigger C₆aS (DP_{≥2}) undergo depolymerisation reactions in the hot vapour phase to form smaller DP C₆aS, and reconfirms the previous claim that DP_1 anhydrosugar is thermally stable in the time scale of a few seconds^[58,313]. These findings also show that the volatile products (e.g. light oxygenated compounds), which can be considered as light oil, are most likely converted to gaseous species in the hot vapour phase leading to lower oil yields in the fluidised bed.

7.5 Conclusions

In this chapter, the effect of pressure on the fast pyrolysis of acid-leached biomass is studied in a dedicated screen-heater (heating rate $\sim 5000\text{ }^{\circ}\text{C s}^{-1}$, fast quenching at $\sim 180\text{ }^{\circ}\text{C}$, $T_{\text{FS}} = 515\text{ }^{\circ}\text{C}$), while varying the system pressure (0.005 to 100 kPa). It was found that: 1) at the lowest pressure, 73% of the poly- C_6 -sugars in the feed were recovered in the liquid product as C_6 -anhydrosugars (C_6aS), while the mass fraction of DP_1 was only 10%, 2) With increasing pressure, upwards 20 kPa, the yield of C_6aS was reached a plateau value of $\sim 40\%$ and shift towards lighter C_6aS in the DP-distribution was observed. A mathematical model, including depolymerisation and decomposition reactions of C_6aS , and mass transport, could predict, after parameterisation, the effect of pressure on the yield of C_6aS and the DP_1 mass fraction in the DP-distribution. Modelling results show that the pressure strongly affects the mass transport of products away from the hot reacting particle, consequently, changing the likelihood of chemical reactions.

Pyrolysis (at $485\text{ }^{\circ}\text{C}$ and 55 kPa) of pinewood in screen-heater and fluidised bed resulted in the similar yields of C_6aS with distinctively different DP distribution, the former being richer in $\text{DP}_{\geq 2}$ than the latter. As a result of the long hot vapour residence time (screen-heater: $\sim 20\text{ ms}$ vs fluidised be: $\sim 1\text{ s}$), other volatile species (e.g. light oxygenated compounds) decompose to gas (or water) leading to lower oil yields, and depolymerisation of bigger C_6aS ($\text{DP}_{\geq 2}$) takes place to form lower DP C_6aS .

C_8

Conclusions and outlook

Lignocellulosic biomass, one of the environmentally friendly and renewable resources, is widely recognised as a promising way of addressing the problem of climate change by partially replacing finite fossil-based energy sources. Fast pyrolysis is one of the promising technologies in which lignocellulosic biomass is decomposed, at ~ 500 °C and in the absence of oxygen, to produce oil, char and gas. Pyrolysis oil is a complex mixture of organic compounds of different chemical classes such as phenols, aldehydes, anhydrosugars. The pyrolysis of lignocellulosic biomass and its building blocks is governed by the three simultaneously occurring processes, which are 1) chemical reactions (cracking, polymerisation), 2) heat transfer and 3) mass transfer by evaporation, sublimation, random ejection (e.g. aerosols).

A dedicated screen-heater reactor was used, which was designed: 1) to minimise non-isothermality (5000 °C s^{-1}), 2) to minimise reactions inside the reacting particle by maximising the escape rate of products away from the reaction zone, and 3) to minimise reactions outside the reacting particle by minimising hot vapour residence time (~ 20 ms) and fast quenching of the products (~ 180 °C). Specific tests were performed in a fluidised bed to investigate the effect of hot vapour residence time ($1 - 2$ s). The obtained pyrolysis products were characterised by qualitative and quantitative analysis. Suitability of gas chromatography for quantitative analysis of levoglucosan and hydroxycetaldehyde was evaluated.

The work presented in this thesis focuses on advancing the current understanding of the chemistry and transport processes, and their interplay during fast pyrolysis of cellulose, lignin and lignocellulosic biomass. Mapping the yields of the building blocks of lignocellulosic biomass, i.e. (anhydro)sugars and aromatics, shall provide deeper insights into the role of the aforementioned interplay.

Anhydrosugars

The production of anhydrosugars from cellulose (Avicel PH 101) and lignocellulosic biomass was studied under various conditions (350 to 765 °C and 0.005 to 100 kPa) to gain an understanding of the underlying interplay between the chemistry and transport processes.

In screen-heater, at ~ 520 °C, by maximising the escape rate of products (< 0.5 kPa) and quick quenching of products (~ 20 ms), the anhydrosugar yields obtained from pure cellulose and acid-leached biomass were 85 wt.% (on cellulose) and 73 wt.% (on C_6 sugars in acid-leached bagasse), respectively. Decreasing the escape rate of products away from the hot reacting particle, i.e. higher pressure during pyrolysis reduced the total yield of anhydrosugars and facilitated the depolymerisation of higher DP anhydrosugars to form smaller ones. For example, cellulose: 70% (0.5 kPa) to 50% (100 kPa); acid-leached

bagasse: 73% (0.005 kPa) to 40% (100 kPa)

The presence of oligo-anhydrosugars of the degree of polymerisation (DP) up to 6 for acid leached bagasse and even up to 11 for pure cellulose were observed. These finding showed that, at the hot reacting particle, the random chain scission is the dominant mechanism during the fast pyrolysis of pure cellulose and C₆ sugars in biomass. However, the role of unzipping mechanism cannot be excluded.

From the pyrolysis of cellulose it was also found that, upwards 550 °C, the depolymerisation reactions become very fast causing the conversion rate to be limited by the heat transfer and due to which the average reaction temperature becomes constant. Consequently, the selectivity of anhydrosugars (DP₁, DP₃ and DP₄₋₅) was found to be independent of the final screen temperature and the conversion of cellulose was finished in the heating trajectory.

The effect of hot vapour residence time was studied by pyrolysing in the fluidised bed (screen heater: ~20 ms vs fluidised bed: 1 – 2 s). Note, the heating rate of the sample in both reactors was comparable. At identical pressure and temperature, increasing the hot vapour residence time of volatile products did not decrease the total yield of anhydrosugar. It was found that the bigger anhydrosugars (DP_{≥2}) depolymerise in the hot vapour phase to form smaller DP anhydrosugars.

The catalytic effects of potassium (for cellulose) and of AAEMs (for biomass) on the sugar production were evident even in the timescale of milliseconds. Consequently, for cellulose, a ~50% reduction in the oil yield, a significant increase in the gas yield (<0.01 to 0.15 kg kg⁻¹) and a decrease in glucose recovery (70 % to almost zero) were observed. Pyrolysis at reduced pressure, i.e. by fast removal of products from the hot reaction zone, can improve the sugar yields only for low AAEMs content feedstock (~0.01 wt.%). Therefore, a pre-treatment step is mandatory for AAEMs rich feedstock (>0.1 wt.%) if the aim is to produce sugars.

It can be said that the fast pyrolysis behaviour of pure cellulose (Avicel PH 101) and the C₆ sugars in lignocellulosic biomass are similar in multiple aspects.

Oudenhoven et al. have shown that by pyrolysing acid-leached biomass in a fluidised bed at 480 °C, sugar recovery up to 40% can be achieved^[71]. In this work, acid-leached biomass particles of ~80 μm (no capillaries^[314]) were pyrolysed in screen-heater at 515 °C with reduced pressure (0.005 kPa), i.e. maximised escape rate of products away from the hot reacting particle. Consequently, ~50% sugar recovery has been achieved from the pyrolysis of biomass. A further increase in pyrolysis temperature would reduce sugar recovery^[71]. Therefore, in the author's view, improving sugar recovery from

biomass beyond 50% will be challenging.

Phenolic compounds

The production of phenolic compounds was studied from isolated lignin. For the investigation, lignins isolated via cold water precipitation of pyrolysis oil, organosolv process and milled wood process were used. The molecular weights of isolated lignins were between 350 and 1900 Da, and the number of ether linkages varied between 0 to 60 per 100 aromatic units.

In this work, 3.5 wt.% yield of mono-phenolic compounds was achieved from sigma organosolv lignin in a screen-heater (420 °C and 100 kPa), whereas for milled wood lignin (richest in ether linkages) it was <1 wt.%. It was found that due to the influence of pressure on the mass transport rate, at higher pressure lighter oils (~400 Da) and lower pressure heavier oils (~800 Da) were collected. At any given pressure, lighter molecules rapidly escape from the hot reacting particle, restricting the extent of cracking reactions, thereby, hindering the production of mono-phenolic compounds (DP₁). The molecular weight distribution was found to be one of the important characteristics of the lignin feedstock. Modelling results showed that the heavier molecules tend to polymerise faster than lighter molecules. HSQC NMR analysis of lignins and its oils showed that the yields of oil and char and the number average molecular weight of oils were found to be independent of the number of ether linkages in the lignin feedstock. The system pressure was identified as the main steering wheel to manipulate the product yields and the molecular weight distribution of the oils.

In the literature, it is considered that the pyrolysis of lignin follows the radical mechanism and the radicals formed during pyrolysis supposedly favour different reaction pathways, e.g. hydrogen abstraction to form mono-phenolic compound or termination to form a heavy molecule. These radical reactions can take place in/on the hot reacting particle or outside, i.e. in the (hot) vapour phase, or during oil recovery. However, from the experimental results of this thesis, no conclusions can be drawn regarding these radical reactions. Further research is needed to get deeper insights into the competing reaction pathways. New insights can be gained by: 1) adding radical stabilising agent during lignin pyrolysis which may prevent unwanted coupling reactions of radicals, 2) *in situ* NMR/EPR lignin pyrolysis shall provide real-time occurring changes in lignin structure as well as in the radical concentrations.

It appears that, under the pyrolysis conditions studied in this work, the production of dimeric, trimeric (or bigger) phenolic compounds is being favoured over mono-

phenolic compounds. This raises the question of whether fast pyrolysis of lignin is the way forward for the production of mono-phenolic compounds. Solely from the perspective of the mono-phenolic compound yields obtained from the fast pyrolysis of lignin, other options appear more lucrative. Rahimi et al. showed that lignin could be converted to 52% mono-phenolic compounds by oxidation of β -O-4 linkages followed by cleavage with formic acid^[315]. Shuai et al. have shown that the addition of formaldehyde during biomass pre-treatment produces lignin, which can be converted to 78% mono-phenolic compounds via hydrogenolysis^[316].

Main message

The fast pyrolysis of lignocellulosic biomass and its building blocks is undoubtedly governed by the interplay between the chemistry, heat transfer and mass transfer. As already known, high heating rates ($5000\text{ }^{\circ}\text{C s}^{-1}$) of the sample are required to maximise the production of oil. The hot vapour residence time (1 – 2 s) does not affect the total anhydrosugar yields, however, it affects the DP distribution of anhydrosugars. The molecular weight (distribution) of isolated lignins is one of the important parameter, which has a significant influence on the pyrolysis product distribution. Below $500\text{ }^{\circ}\text{C}$, the temperature of the pyrolysis was found to have a significant impact on the yields of oil and the composition of the oil. Upwards $550\text{ }^{\circ}\text{C}$, the reactions become very fast, causing conversion rate to be limited by the heat transfer rate, consequently making the actual reaction temperature constant. Resultantly, a further increase in temperature does not affect the yield of oil and its composition. The system pressure is the key parameter, which alters the residence time of products in/on the hot reacting particle, thereby, providing a means to steer the yields and composition of the products of pyrolysis.

Appendices

C_3

A

C_4

B

C_5

C

C_7

D

A

Supporting information for Chapter 3

A

A.1 Literature data

In this section, yields of levoglucosan (LG) and hydroxyacetaldehyde (HA) reported in the literature are presented. The summary presents the name of the feedstock, its ash content, temperature and pressure of pyrolysis experiment, reactor type, and the yields of LG (or HA) determined by GC and/or LC. In the cases of the samples, where their ash content was not reported, cross-referred articles were looked up to find the details. Note, the yields reported in Table A.1 to A.4 are based on the feedstock basis. Additionally, the pressure during the pyrolysis was assumed to be 10^5 Pa, unless otherwise mentioned in the research article. The data reported in Table A.1 to A.4 was used for the principal component analysis (PCA), Section A.3 of this appendix for the details.

A.1.1 Levoglucosan

Cellulose

Table A.1: Levoglucosan yield reported in the literature (feedstock: cellulose)

Author, Year, Ref.	Specifics	Ash mg kg ⁻¹	Temperature °C	Pressure Pa	Reactor type	GC wt.% of cellulose	LC
Shafizadch 1973 ^[139]	Whatman chromatographic cellulose powder	0.015	300	100000	Pyrex tube	3.6	
	Whatman chromatographic cellulose powder	0.015	300	200	Pyrex tube	28.1	
Shafizadch 1979 ^[140]	Avicel crystalline	0.004	400	200	Pyrex tube	49	
	Whatman No 41	0.01	400	200	Pyrex tube	38	
	Whatman CF11	0.015	500	200	Pyrex tube	34	
	Baker TLC crystalline	0.05	400	200	Pyrex tube	51	
Radlein 1987 ^[136]	Avicel pH 102	0.01	500	100000	Fluidized Bed		8.6
	SS 144	0.06	500	100000	Fluidized Bed		7
Piskorz 1989 ^[64]	Avicel pH 102	0.01	500	100000	Fluidized Bed		26.9

Julien 1991 ^[141]	SS 144	0.06	500	100000	Fluidized Bed	7
	Sigma cellulose	0.02	525	100000	Thermobalance	33
	Sigma cellulose	0.2	525	100000	Thermobalance	3.7
	Filter paper	0.01	530	100000	Tubular reactor	50
Luo 2004 ^[144]	Avicel PH 101	0.02	450	15000	Belt conveyor type pyrolyzer	48
Kwon 2007 ^[145]	Avicel PH 101	0.02	450	600	Belt conveyor type pyrolyzer	40
	Avicel PH 101	0.02	500	100000	PyGCMS	62.9
	Avicel PH 101	0.02	500	100000	Fluidized Bed	42
	Avicel PH 101	0.02	500	100000	PyGCMS	62.9
Patwardhan 2009 ^[148] Patwardhan 2011 ^[149]	Merck	0.04	500	100000	Tubular reactor	3.6
	Avicel PH-105 (20 l/m)	0	500	100000	PyGCMS	41
	Avicel PH-102 (90 l/m)	0.01	500	100000	PyGCMS	39.5
	Avicel PH-101 (50 l/m)	0.02	500	100000	PyGCMS	40
Collard 2012 ^[155] Ronse 2012 ^[159]	Sigmacell Type 50 (50 l/m)	0.05	500	100000	PyGCMS	24
	Avicel - Ca infused	0.1	550	100000	Fixed Bed	0.1
	Avicel - NH4 infused	5	500	100000	Fixed Bed	0.1
	Sigmacell Type 50 (50 l/m)	0.05	500	100000	PyGCMS	56
Zhang 2014 ^[175] Zhou 2014 ^[107] Wang 2014 ^[174] Gong 2014 ^[178] Westerhof 2016 ^[130]	Sigmacell Type 50 (50 l/m)	0.05	500	100000	PyGCMS	56.8
	Avicel PH 101	0.005	500	100000	Wiremesh	25
	Avicel PH 101	0.005	500	100000	Wiremesh	20
	Avicel PH 101	0.005	535	100000	Wiremesh	27.5
Proano-Aviles 2017 ^[48]	Avicel PH 101	0.005	535	500	Fluidized Bed	40
	Avicel PH 101	0.005	535	100000	Wiremesh	19
	Avicel PH 101	0.005	535	100000	Wiremesh	33
	Sigmacell Type 50 (50 l/m)	0.05	500	100000	PyGCMS	63.5

Marathe 2017 ^[185]	Avicel PH 101	0.005	535	100000	Fluidized Bed	35
	Avicel PH 101	0.01	535	100000	Fluidized Bed	20
	Avicel PH 101	0.1	535	100000	Fluidized Bed	7
	Avicel PH 101	0.005	535	500	Wiremesh	19.7
	Avicel PH 101	0.005	535	100000	Wiremesh	31
	Avicel PH 101	0.01	535	500	Wiremesh	9.8
	Avicel PH 101	0.01	535	100000	Wiremesh	17
	Avicel PH 101	0.1	535	500	Wiremesh	7.8
	Avicel PH 101	0.1	535	100000	Wiremesh	8
	Avicel PH 101	1	535	500	Wiremesh	0.5
Pecha 2017 ^[187]	Avicel PH 101	1	535	100000	Wiremesh	1
	Avicel PH 101	0.005	500	400	Modified pyroprobe	18
	Avicel PH 101	0.005	500	100000	Modified pyroprobe	28

Biomass

Table A.2: Levoglucosan yield reported in the literature (feedstock: biomass)

Author, Year, Ref.	Specifics	Ash mg kg ⁻¹	Temperature °C	Pressure Pa	Reactor type	GC	LC wt.% of biomass
Radlein 1987 ^[136]	Poplar wood	0.46	500	100000	Fluidized Bed		1
Piskorz 1989 ^[64]	Cellulose Sherbrooke	0.4	500	100000	Fluidized Bed		9.3
	Poplar wood	0.46	500	100000	Fluidized Bed		3.04
	Cellulose Sherbrooke	2.5	500	100000	Fluidized Bed		0
Piskorz 1998 ^[142]	Poplar saw dust	0.46	504	100000	Fluidized Bed		3
	Spruce saw dust	0.5	500	100000	Fluidized Bed		4
	Sunflower hulls	4	500	100000	Fluidized Bed		0.3
	Sorghum bagasse	9.2	510	100000	Fluidized Bed		1.7
	Wheat chaff	22.5	515	100000	Fluidized Bed		2
Scott 1999 ^[143]	Flax Shives	2.7	500	100000	Fluidized Bed		0.6
Brown 2001 ^[61]	Switchgrass	3.1	500	100000	Fluidized Bed		10.58
	Cornstover	4.2	500	100000	Fluidized Bed		11.89
	Switchgrass	4.5	500	100000	Fluidized Bed		22.12
	Cornstover	5	500	100000	Fluidized Bed		15.64
	Switchgrass	5.1	500	100000	Fluidized Bed		2.31
	Cornstover	5.9	500	100000	Fluidized Bed		1.63
Mullen 2008 ^[146]	Switchgrass	0.01	500	100000	Fluidized Bed		6.38
	Alfalfa early bud	0.28	500	100000	Fluidized Bed		0.14
	Alfalfa full flower	0.3	500	100000	Fluidized Bed		0.37
He 2009 ^[147]	Switchgrass	2.62	500	100000	Fluidized Bed		0.78
Azeez 2010 ^[150]	Spruce	0.4	470	100000	Fluidized Bed		4.5

Boateng 2010 ^[151]	Beech	0.7	470	100000	Fluidized Bed	2.4
	Corn cob	1.2	470	100000	Fluidized Bed	1.2
	Albizia	1.8	470	100000	Fluidized Bed	1.4
	Irolo	3.5	470	100000	Fluidized Bed	1.1
	Camelina press cake	4.96	500	100000	Fluidized Bed	1.48
	Pennycress seed	6.02	500	100000	Fluidized Bed	0.81
	Pennycress press cake	12.08	500	100000	Fluidized Bed	2.06
	Defatted pennycress press cake	12.27	500	100000	Fluidized Bed	2.44
	Pinewood	0.5	500	25000	Conical spouted bed	3.27
	Pinewood	0.5	500	100000	Conical spouted bed	2.78
Amutio 2011 ^[152]	Mallee wood	0.02	500	100000	Fluidized Bed	5.4
	Mallee wood	0.12	500	100000	Fluidized Bed	3
	Mallee wood	0.2	500	100000	Fluidized Bed	3
	Mallee wood	0.67	500	100000	Fluidized Bed	3
	Pinewood	0.26	480	100000	Fluidized Bed	3
Westerhof 2011 ^[154]	Beech wood	0.97	500	100000	Tubular reactor	0.51
	Switchgrass	3.5	650	100000	Tubular reactor	0.54
	Poplar	5.1	650	100000	Tubular reactor	0.35
	Corn stalks	5.3	650	100000	Tubular reactor	0.01
	Douglas Fir	0.3	430	100000	Auger reactor	4
Pollard 2012 ^[158]	Red oak	0.3	500	100000	Fluidized Bed	2.3
	Pecrin free beet pulp	0.8	500	100000	Fluidized Bed	1.34
	Beet pulp	3.6	500	100000	Fluidized Bed	0.27
	Miscanthus sinensis	3.37	500	100000	Fluidized Bed - cylindrical	10.44
Liaw 2012 ^[157]						
Aho 2013 ^[160]						
Bok 2013 ^[161]						

Burler 2013 ^[163]	Miscanthus sinensis	3.37	500	100000	Fluidized Bed - rectangular	9
	Spruce	0.26	470	100000	Fluidized Bed	2.2
	Salix	1.16	470	100000	Fluidized Bed	0.79
Burler 2013 ^[162]	Miscanthus	3.43	470	100000	Fluidized Bed	0.41
	Wheat straw	3.76	470	100000	Fluidized Bed	0.26
	Spruce	0.26	470	100000	PyGCMS	3.14
Greenhalf 2013 ^[164]	Salix	1.16	470	100000	PyGCMS	1.09
	Miscanthus	3.43	470	100000	PyGCMS	0.43
	Wheat straw	3.76	470	100000	PyGCMS	0.36
Hwang 2013 ^[165]	Beech wood	0.96	520	100000	PyGCMS	0.01
	Willow SRC	2.96	520	100000	PyGCMS	0.09
	Miscanthus	4.46	520	100000	PyGCMS	0.02
Kantarelis 2013 ^[166] Li 2013 ^[167]	Wheatstraw	4.89	520	100000	PyGCMS	0.01
	Switch grass	5.73	520	100000	PyGCMS	0.73
	Yellow poplar wood	0.17	470	100000	Fluidized Bed	11.94
Oudenhoven 2013 ^[168]	Yellow poplar wood	0.45	470	100000	Fluidized Bed	1.77
	mixture of pine and spruce	0.31	500	100000	Fluidized Bed	0.09
	Loblolly pinewood	0.07	450	100000	Auger reactor	7.24
Zhou 2013 ^[169]	Loblolly pinewood	0.25	450	100000	Auger reactor	3.82
	Lignocell - Pinewood	0.02	530	100000	Fluidized Bed	17
	Lignocell - Pinewood	0.04	530	100000	Fluidized Bed	17.6
Alvarez 2014 ^[170]	Lignocell - Pinewood	0.53	530	100000	Fluidized Bed	3.4
	Douglas Fir	0.3	500	100000	Auger reactor	5.5
	Douglas Fir	0.3	500	100000	Fluidized Bed	3.5
	Rice husk	12.9	500	100000	Conical spouted bed	0.54

Kelkar 2014 ^[171]	Indiangrass	500	100000	PyGCMS	2.8
	Miscanthus	500	100000	PyGCMS	2.5
	Deertongue	500	100000	PyGCMS	2.8
	Sandreed	500	100000	PyGCMS	2.7
	Big bluestem	500	100000	PyGCMS	2.7
	Sideoats grama	500	100000	PyGCMS	2.9
	Coastal panicgrass	500	100000	PyGCMS	2.5
	Switchgrass	500	100000	PyGCMS	2.9
	HWE-Sugar maple	550	100000	PyGCMS	11.97
	Hybrid poplar	550	100000	PyGCMS	6.48
Mante 2014 ^[172]	Debarked sugar maple	550	100000	PyGCMS	4.45
	Sugar maple with bark	550	100000	PyGCMS	3.54
	Willow	550	100000	PyGCMS	3.2
	WILL-I	550	100000	PyGCMS	4.31
	Switchgrass	550	100000	PyGCMS	2.76
	Red oak	500	100000	Fluidized Bed	5
	Douglas fir	500	100000	Wiremesh	828
	Douglas fir	500	100000	Wiremesh	5.52
	Eucalyptus	500	100000	Conical spoured bed	2.04
	Spruce wood	500	100000	Fluidized bed	2.37
Amutio 2015 ^[176] Charon 2015 ^[177]	Beechwood	500	100000	Fluidized bed	1.59
	Wheat straw	500	100000	Fluidized bed	0.72
	Sugarcane bagasse	500	100000	PyGCMS	23.45
	Sugarcane bagasse	500	100000	PyGCMS	11.68
	Sugarcane bagasse	500	100000	PyGCMS	4.95
	Shrub willow	500	100000	PyGCMS	2.1
Jiang 2015 ^[179]					
Serapiglia 2015 ^[180]					

Yildiz 2015 ^[181]	Pinewood	0.33	500	100000	Mixer reactor	3.22	
Hwang 2016 ^[182]	Geodae-Uksae 1	1.5	500	100000	Fluidized Bed	0.53	
Wang 2016 ^[72]	Cotton straw	5.71	500	100000	Fluidized Bed		10
Zheng 2016 ^[183]	Pine	0.1545	500	100000	PyGCMS	4	
	Eucalyptus	0.2244	500	100000	PyGCMS	4.1	
	Straw	3.4642	500	100000	PyGCMS	1.6	
Guizani 2017 ^[73]	Beech wood	0.5	500	100000	Drop tube reactor		13.5
Jiang 2017 ^[184]	Corn cob	3.3	500	100000	PyGCMS	16.87	
	Corn cob	3.8	500	100000	PyGCMS	12.71	
	Corn cob	5.5	500	100000	PyGCMS	8.25	
	Corn cob	5.7	500	100000	PyGCMS	4.44	
	Corn cob	6.5	500	100000	PyGCMS	2.31	
	Corn cob	6.6	500	100000	PyGCMS	1.8	
	Corn cob	10.5	500	100000	PyGCMS	0.85	
Montoya 2017 ^[74]	Sugarcane bagasse	3.9	500	100000	Hot plate reactor		7.5
Oh 2017 ^[186]	Radiata pine	0.2	430	100000	Fluidized Bed	0	
	Corn cob	2.2	430	100000	Fluidized Bed	0	
	Palm kernel shell	5.4	430	100000	Fluidized Bed	0	
Pecha 2017 ^[75]	ball milled poplar	2.72	500	400	Modified pyroprobe		6
	ball milled poplar	2.72	500	25000	Modified pyroprobe		6.2
	ball milled poplar	2.72	500	50000	Modified pyroprobe		8
	ball milled poplar	2.72	500	75000	Modified pyroprobe		8
	ball milled poplar	2.72	500	100000	Modified pyroprobe		10
Ren 2017 ^[191]	Pinewood	0.58	500	100000	Fluidized Bed	2	
	Pine bark	1.7	500	100000	Fluidized Bed	2.3	
Alvarez 2018 ^[188]	Orange waste	2.3	500	100000	Conical spouted bed	0.24	

Chandler 2018 ^[189]	Arundo Donax	1.7	500	100000	Fluidized Bed	0.2
Maduskar 2018 ^[49] Savou 2018 ^[190]	Arundo Donax	3.9	500	100000	Fluidized Bed	0.1
	Loblolly pinewood	0.65	500	100000	PHASR	5.4
	Sugarcane bagasse	10	500	100000	Tubular reactor	0.4
	Sugarcane bagasse	12.8	500	100000	Tubular reactor	0.1

A.1.2 Hydroxyacetaldehyde

Cellulose

Table A.3: Hydroxyacetaldehyde yield reported in the literature (feedstock: cellulose)

Author, Year, Ref.	Specifics	Ash mg kg ⁻¹	Temperature °C	Pressure Pa	Reactor type	GC wt.% of cellulose	LC
Radlein 1987 ^[136]	Avicel pH 102	0.01	500	100000	Fluidized Bed		8.6
	SS 144	0.06	500	100000	Fluidized Bed		15.3
Piskorz 1989 ^[64]	Avicel pH 102	0.01	500	100000	Fluidized Bed		8.6
	SS 144	0.06	500	100000	Fluidized Bed		15.3
Julien 1991 ^[141]	Sigma cellulose	0.2	525	100000	Thermobalance		11.13
	Sigma cellulose	0.02	525	100000	Thermobalance		0
Luo 2004 ^[144]	Filter paper	0.01	530	100000	Tubular reactor	3.5	
Parwardhan 2009 ^[148]	Avicel PH 101	0.02	500	100000	PyGCMS	6.69	
Parwardhan 2011 ^[149]	Avicel PH 101	0.02	500	100000	Fluidized Bed	5.4	
	Avicel PH 101	0.02	500	100000	PyGCMS	6.7	
	Sigmacell Type 50 (50 lfm)	0.05	500	100000	PyGCMS	6	
Ronsse 2012 ^[159]	Avicel PH-101 (50 lfm)	0.02	500	100000	PyGCMS	15	
	Avicel PH-102 (90 lfm)	0.01	500	100000	PyGCMS	11	
	Avicel PH-105 (20 lfm)	0	500	100000	PyGCMS	16	
Collard 2012 ^[155]	Merck	0.04	500	100000	Tubular reactor	1.59	
Zhang 2014 ^[175]	Sigmacell Type 50 (50 lfm)	0.05	500	100000	PyGCMS	7.2	
Zhou 2014 ^[107]	Sigmacell Type 50 (50 lfm)	0.05	500	100000	PyGCMS	7.88	
Westerhof 2016 ^[130]	Avicel PH 101	0.005	535	100000	Fluidized Bed	6	
	Avicel PH 101	0.005	535	500	Wiremesh	2	

Pecha 2017 ^[187]	Avicel PH 101	0.005	535	100000	Wiremesh	2
	Avicel PH 101	0.005	500	400	Modified pyroprobe	6.25
	Avicel PH 101	0.005	500	100000	Modified pyroprobe	6.25

Biomass

Table A.4: Hydroxyacetaldehyde yield reported in the literature (feedstock: biomass)

Author, Year, Ref.	Specifics	Ash mg kg ⁻¹	Temperature °C	Pressure Pa	Reactor type	GC	LC wt.% of biomass
Radlein 1987 ^[136]	Poplar wood	0.46	500	100000	Fluidized Bed		8.86
Piskorz 1989 ^[64]	Cellulose Sherbrooke	2.5	500	100000	Fluidized Bed		17.1
	Cellulose Sherbrooke	0.4	500	100000	Fluidized Bed		15.2
Piskorz 1998 ^[142]	Poplar wood	0.46	500	100000	Fluidized Bed		10.03
	Poplar saw duct	0.46	504	100000	Fluidized Bed		10
	Spruce saw dust	0.5	500	100000	Fluidized Bed		7.7
	Sorghum bagasse	9.2	510	100000	Fluidized Bed		7.2
	Wheat chaff	22.5	515	100000	Fluidized Bed		6.5
Scott 1999 ^[143] Brown 2001 ^[61]	Sunflower hulls	4	500	100000	Fluidized Bed		0.8
	Flax Shives	2.7	500	100000	Fluidized Bed		1.4
	Switchgrass	5.1	500	100000	Fluidized Bed		7.05
	Switchgrass	4.5	500	100000	Fluidized Bed		1.55
	Switchgrass	3.1	500	100000	Fluidized Bed		4.72
Mullen 2008 ^[146]	Cornstover	5.9	500	100000	Fluidized Bed		6.84
	Cornstover	5	500	100000	Fluidized Bed		2.66
	Cornstover	4.2	500	100000	Fluidized Bed		4.01
	Switchgrass	0.01	500	100000	Fluidized Bed		2.4
	Alfalfa early bud	0.28	500	100000	Fluidized Bed		0
He 2009 ^[147] Azeez 2010 ^[150]	Alfalfa full flower	0.3	500	100000	Fluidized Bed		0
	Switchgrass	2.62	500	100000	Fluidized Bed		6.53
	Beech	0.7	470	100000	Fluidized Bed		7.9

Boateng 2010 ^[151]	Spruce	0.4	470	100000	Fluidized Bed	9.8
	Irolo	3.5	470	100000	Fluidized Bed	7
	Albizia	1.8	470	100000	Fluidized Bed	6.7
	Corn cob	1.2	470	100000	Fluidized Bed	5.1
	Pennycress press cake	12.08	500	100000	Fluidized Bed	0
	Defatted pennycress press cake	12.27	500	100000	Fluidized Bed	0
	Pennycress seed	6.02	500	100000	Fluidized Bed	0
	Camelina press cake	4.96	500	100000	Fluidized Bed	0
	Pinewood	0.26	480	100000	Fluidized Bed	1
	Douglas Fir	0.3	430	100000	Auger reactor	1.1
Westerhof 2011 ^[154] Liaw 2012 ^[157] Collard 2012 ^[155] Cordella 2012 ^[156]	Beech wood	0.97	500	100000	Tubular reactor	0.72
	Corn stalks	5.3	650	100000	Tubular reactor	0
	Poplar	5.1	650	100000	Tubular reactor	2
	Switchgrass	3.5	650	100000	Tubular reactor	1.11
	Beet pulp	3.6	500	100000	Fluidized Bed	4.52
	Pectin free beet pulp	0.8	500	100000	Fluidized Bed	6.5
	Spruce	0.26	470	100000	Fluidized Bed	6.13
	Salix	1.16	470	100000	Fluidized Bed	3.44
	Miscanthus	3.43	470	100000	Fluidized Bed	2.64
	Wheat straw	3.76	470	100000	Fluidized Bed	2.29
Kantarelis 2013 ^[166] Butler 2013 ^[162]	mixture of pine and spruce sawdust	0.31	500	100000	Fluidized Bed	0.02
	Spruce	0.26	470	100000	PyGCMS	12.74
	Salix	1.16	470	100000	PyGCMS	7.43
	Miscanthus	3.43	470	100000	PyGCMS	6.37
	Wheat straw	3.76	470	100000	PyGCMS	6.57
	Big bluestem	1.07	500	100000	PyGCMS	5.8
Kelkar 2014 ^[171]						

Mante 2014 ^[172]	Coastal panicgrass	1.2	500	100000	PyGCMS	6.1
	Deertongue	0.9	500	100000	PyGCMS	4.7
	Indiangrass	0.86	500	100000	PyGCMS	6.4
	Miscanthus	0.89	500	100000	PyGCMS	5.9
	Sandreed	0.93	500	100000	PyGCMS	6.6
	Sideoats grama	1.11	500	100000	PyGCMS	5.4
	Switchgrass	1.45	500	100000	PyGCMS	6.3
	Hybrid poplar	0.43	550	100000	PyGCMS	11.04
	WILL-1	1.89	550	100000	PyGCMS	10.74
	Willow	1.43	550	100000	PyGCMS	9.72
	Sugar maple with bark	0.96	550	100000	PyGCMS	9.33
	Debarked sugar maple	0.81	550	100000	PyGCMS	11.76
	HWE-Sugar maple	0.38	550	100000	PyGCMS	12
	Switchgrass	2.99	550	100000	PyGCMS	7.34
	Beechwood	0.76	500	100000	Fluidized bed	1.11
	Spruce wood	0.44	500	100000	Fluidized bed	2.74
Charon 2015 ^[177]	Wheat straw	5.3	500	100000	Fluidized bed	0.8
	Pinewood	0.33	500	100000	Mixer reactor	0.67
	Pine	0.1545	500	100000	PyGCMS	2
	Eucalyptus	0.2244	500	100000	PyGCMS	1.9
Guizani 2017 ^[73]	Straw	3.4642	500	100000	PyGCMS	0.9
	Beech wood	0.5	500	100000	Drop tube reactor	0.07
	Corn cob	2.2	430	100000	Fluidized Bed	4.39
	Palm kernel shell	5.4	430	100000	Fluidized Bed	0.36
Oh 2017 ^[186]	Radiata pine	0.2	430	100000	Fluidized Bed	5
	Pinewood	0.58	500	100000	Fluidized Bed	5.7
Ren 2017 ^[191]

Montoya 2017 ^[74]	Pine bark	1.7	500	100000	Fluidized Bed	3.06
Savou 2018 ^[90]	Sugarcane bagasse	3.9	500	100000	Hor plate reactor	4
	Sugarcane bagasse	12.8	500	100000	Tubular reactor	0.1
	Sugarcane bagasse	10	500	100000	Tubular reactor	0.1

A.1.3 Analysis methods

Gas chromatography methods/systems

Table A.5 presents the summary of GC systems reported in the literature. Note, in this summary only those articles are added, in which at least one of (following) five details are reported – 1) solvent, 2) chromatographic column, 3) polarity of the column, 4) temperature of the injection port/section, and 5) the GC oven temperature ramp.

Table A.5: Literature summary of GC systems; chromatographic columns, its polarity, injection port/section temperature and oven temperature ramp

Author, Year, Ref.	Solvent	Column	Polarity	T _{injector} °C	GC oven temperature ramp
Shafizadeh 1973 ^[139]	-	3% SE-52 silicone gum on Chromosorb Wax	-	-	-
Shafizadeh 1979 ^[140]	-	3% SE-52 silicone gum on Chromosorb Wax	-	-	-
Wheeler 1997 ^[317]	Methanol	Agilent J&W DB-1701	Low to medium	250	45°C (4 min) → 280°C at 3 °C min ⁻¹ (15 min)
Branca 2003 ^[197]	Methanol	CP-Sil 19 CB	Medium	250	45°C (4 min) → 260°C at 3 °C min ⁻¹ (15 min)
	Acetone	Agilent J&W DB-1701	Low to medium	235	45°C (4 min) → 235°C at 3 °C min ⁻¹ (13 min)
Luo 2004 ^[144]		SUPELCO/WAX @10	Polar		
Patwardhan 2009 ^[148]	Acetone	Ultra Alloy 5	Extremely low	300	35°C (3 min) → 130°C at 5 °C min ⁻¹ → 250°C at 20 °C min ⁻¹ (2 min)
He 2009 ^[147]	-	Rtx-1701	Medium	260	45°C (5 min) → 250°C at 5 °C min ⁻¹ (8 min)
Azeez 2010 ^[150]	Acetone	Ultra Alloy 5	Extremely low	250	45°C (4 min) → 280°C at 4 °C min ⁻¹ (20 min)

Boateng 2010 ^[151]	Acetone	Agilent J&W DB-1701	Low to medium	250	45°C (4 min) → 280°C at 3 °C min ⁻¹ (20 min)
Mourant 2011 ^[153]	Methanol	Agilent HP-5 MS	Non-polar	200	
Patwardhan 2011 ^[149]	Acetone	Ultra Alloy 5	Extremely low	300	35°C (3 min) → 130°C at 5 °C min ⁻¹ → 250°C at 20 °C min ⁻¹ (2 min)
Westerhof 2011 ^[154]	Methanol	Agilent HP-5 MS	Non-polar	200	-
Gollard 2012 ^[155]	Acetone	Agilent J&W DB-1701	Low to medium	250	#1: 45°C (4 min) → 120°C at 3°C min ⁻¹ → 270°C at 20 °C min ⁻¹ #2: 45°C (4 min) → 250°C at 3 °C min ⁻¹ → 270°C at 20 °C min ⁻¹ (60 min)
Cordella 2012 ^[156]	-	MDN-5S (Supelco) fused-silica	-	-	#1: 50°C (5 min) → 310°C at 5 °C min ⁻¹ (3 min) #2: 50°C (5 min) → 310°C at 10 °C min ⁻¹ (3 min)
Liaw 2012 ^[157]	Methanol	Agilent HP-5 MS	Non-polar	200	40°C (1 min) → 280°C at 3 °C min ⁻¹ (10 min)
Pollard 2012 ^[158]	Methanol	CP-Sil 19 CB	Medium	250	45°C (4 min) → 235°C at 3 °C min ⁻¹ (13 min)
Ronsse 2012 ^[159]	Acetone	Ultra Alloy 5	Extremely low	300	35°C (3 min) → 130°C at 5 °C min ⁻¹ → 250°C at 20 °C min ⁻¹ (2 min)
Bok 2013 ^[161]	-	DB-5MS	Non-polar	250	50°C (5 min) → 280°C at 3 °C min ⁻¹ (20 min)
Butler 2013 ^[162]	-	VF-1701ms	Medium	-	45°C (4 min) → 280°C at 3 °C min ⁻¹ (20 min)
Butler 2013 ^[162]	Acetone	Agilent J&W DB-1701	Low to medium	-	-
Greenhalf 2013 ^[164]	Ethanol	Varian factorFour	Low	275	45°C (2.5 min) → 250°C at 5 °C min ⁻¹ (7.5 min)
Hwang 2013 ^[165]	Acetone	Agilent J&W DB-5	Non-polar	300	50°C (5 min) → 280°C at 3 °C min ⁻¹ (10 min)
Kantarelis 2013 ^[166]	-	Agilent J&W DB-1701	Low to medium	250	45°C (4 min) → 280°C at 3 °C min ⁻¹ (20 min)
Li 2013 ^[167]	Dichloromethane	Agilent J&W DB-5	Non-polar	270	40°C (4 min) → 280°C at 5 °C min ⁻¹ (15 min)
Oudenhoven 2013 ^[66]	Methanol	Agilent HP-5 MS	Non-polar	250	45°C (4 min) → 280°C at 3 °C min ⁻¹ (20 min)

Shaik 2013 ^[168]	Methanol	Agilent J&W DB-1701	Low to medium	250	45°C (5 min) → 250°C at 3 °C min ⁻¹ (5 min)
Zhou 2013 ^[169]	Methanol	SPBZ-5	Non-polar	250	25°C (1 min) → 40°C (4 min) at 20 °C min ⁻¹ → 130°C at 6 °C min ⁻¹ → 200°C at 25 °C min ⁻¹ (1 min)
Kelkar 2014 ^[171]	-	Rtx-1701	Medium	280	40°C → 270°C at 8 °C min ⁻¹
Mante 2014 ^[172]	-	Agilent J&W DB-1701	Low to medium	275	40°C (1 min) → 130°C at 6 °C min ⁻¹ → 275°C at 10 °C min ⁻¹ (20 min)
Rover 2014 ^[173]	Methanol	CP-Sil 19 CB	Medium	250	45°C (4 min) → 235°C at 3 °C min ⁻¹ (13 min)
Wang 2014 ^[174]	Methanol	Agilent HP-5 MS	Non-polar	200	40°C (1 min) → 190°C at 3 °C min ⁻¹ → 280°C at 20 °C min ⁻¹ (10 min)
Zhang 2014 ^[175]		ZB-1701 Phenomenex	Medium	300	50°C → 300°C at 5 °C min ⁻¹ (5 min)
Zhou 2014 ^[107]		ZB-1701 Phenomenex	Medium	250	35°C (3 min) → 300°C at 5 °C min ⁻¹ (4 min)
Charon 2015 ^[177]	Acetone	VF-1701ms	Medium	250	45°C (4 min) → 280°C at 4 °C min ⁻¹ (20 min)
Collard 2015 ^[155]	Acetone	Agilent J&W DB-1701	Low to medium	250	#1: 45°C (4 min) → 120°C at 3 °C min ⁻¹ → 270°C at 20 °C min ⁻¹ #2: 45°C (4 min) → 250°C at 3 °C min ⁻¹ → 270°C at 20 °C min ⁻¹ (60 min)
Jiang 2015 ^[179]	-	HP-INNOWax	High	240	50°C (2 min) → 90°C at 10 °C min ⁻¹ → 129°C at 4 °C min ⁻¹ → 230°C at 8 °C min ⁻¹ (29 min)
Kumagai 2015 ^[318]	-	InertCap 5MS/Sil	Low	-	-
Serapiglia 2015 ^[180]	-	Rtx-1701	Medium	260	45°C (5 min) → 280°C at 3 °C min ⁻¹ (20 min)
Yildiz 2015 ^[181]	Tetrahydrofuran	Rtx-1 PONA	Non-polar	-	40°C → 300°C at 3 °C min ⁻¹
	Tetrahydrofuran	BPX50	Medium	-	40°C → 300°C at 3 °C min ⁻¹
Hwang 2016 ^[182]	Acetone	-	-	250	50°C (5 min) → 280°C at 3 °C min ⁻¹ (10 min)
Westerhof 2016 ^[130]	Methanol	Agilent HP-5 MS	Non-polar	250	45°C (4 min) → 280°C at 3 °C min ⁻¹ (20 min)
Zheng 2016 ^[183]	-	HP-INNOWax	High	-	-

Jiang 2017 ^[184]	-	HP-INNOWax	High	240	50°C (2 min) → 90°C at 10 °C min ⁻¹ → 230°C at 8 °C min ⁻¹ (29 min)
Montoya 2017 ^[74]	Methanol	Rxt-5Sil MS	Low	250	50°C → 250°C at 10 °C min ⁻¹ → 320°C at 20 °C min ⁻¹ (20 min)
Oh 2017 ^[186]	-	Agilent HP-5 MS	Non-polar	-	35°C (10 min) → 150°C at 2 °C min ⁻¹ → 280°C at 20 °C min ⁻¹ (10 min)
Pecha 2017 ^[187]	-	Rtx-1701	Medium	-	45°C (10 min) → 250°C at 3 °C min ⁻¹ (5 min)
Pecha 2017 ^[75]	-	Rtx-1701	Medium	-	45°C (10 min) → 250°C at 3 °C min ⁻¹ (5 min)
Proano-Aviles 2017 ^[48]	-	ZB-1701 Phenomenex	Medium	-	-
Ren 2017 ^[191]	Acetone	Agilent J&W DB-1701	Low to medium	-	45°C (4min) → 250°C at 3 °C min ⁻¹ (20 min)
Chandler 2018 ^[189]	-	Rxt-5Sil MS	Low	300	45°C (4 min) → 300°C at 10 °C min ⁻¹ (5 min)
Maduskar 2018 ^[49]	-	Agilent HP-5 MS	Non-polar	320	70°C → 250°C at 20 °C min ⁻¹
Savou 2018 ^[190]	-	InertCap 5MS/Sil	Low	-	50°C (5 min) → 320°C at 5 °C min ⁻¹ (10 min)

Liquid chromatography methods/systems

Table A.6 presents the summary of LC systems reported in the literature. Note, in this summary only those articles are added, in which at least one of (following) four details are reported – 1) chromatographic column, 2) temperature of the column, 3) mobile phase, and 4) the flowrate of the mobile phase.

Table A.6: Literature summary of LC systems; chromatographic columns, its temperature, mobile phase and its flowrate

Author, year, Ref.	Column	T _{column} °C	Mobile phase	Flowrate mL min ⁻¹
Radlein 1987 ^[136]	Bio Rad Aminex HPX-87H	65	0.07 N Phosphoric acid	0.72
Piskorz 1989 ^[64]	Bio Rad Aminex HPX-87H	65	0.07 N Phosphoric acid	0.72
Julien 1991 ^[141]	Bio Rad Aminex HPX-97P	-	Water	-
Piskorz 1998 ^[142]	Bio Rad Aminex HPX-87H	65	0.07 N Phosphoric acid	0.72
Scott 1999 ^[143]	Bio Rad Aminex HPX-87H	65	0.07 N Phosphoric acid	0.72
Brown 2001 ^[61]	Bio Rad Aminex HPX-87H	65	0.07 N Phosphoric acid	0.72
Kwon 2007 ^[145]	Shimadzu CLC-NH2	-	70%:30% (v/v) Acetonitrile : Water	-
Mullen 2008 ^[146]	Bio Rad Aminex HPX-87H	30	0.07 N Phosphoric acid	1
Aho 2013 ^[160]	Bio Rad Aminex HPX-87C	80	Calcium sulphate	1.2
Wang 2014 ^[174]	Bio Rad Aminex HPX-87P	-	Water	0.4
Gong 2015 ^[178]	Dionex CarboPac PA200	-	100 mM Sodium hydroxide	0.5
Wang 2016 ^[72]	XBridge TM Amide C18	25	90%:10% (v/v) Methanol : Water	0.5
Westerhof 2016 ^[130]	Agilent Hi-Plex Pb	70	Water	0.6
Guizani 2017 ^[73]	Bio Rad Aminex HPX-87H	-	0.07 N Phosphoric acid	0.6
Marathe 2017 ^[185]	Agilent Hi-Plex Pb	70	Water	0.6
Montoya 2017 ^[74]	Bio Rad Aminex HPX-87H	80	Water	2

Pecha 2017 ^[75]	Bio Rad Aminex HPX-42C	85	Water	0.6
Pecha 2017 ^[187]	Bio Rad Aminex HPX-42C	85	Water	0.6

- Not reported

A.2 Welch's t -test

As reported in the Table A.1 to A.4, the yields of LG and HA were determined by either gas GC or by LC. For the yields of both compounds (LG and HA), obtained from cellulose and biomass, and determined by GC and LC, population means were calculated. Subsequently, Welch's t -test was used to find whether the two populations, i.e. all yields determined by GC (population 1) and by LC (population 2), have equal means. The t -test and p -values were determined by using Matlab 2017a inbuilt function `ttest2`.

A.3 Principal component analysis (PCA)

A.3.1 Procedure

Table A.7: Example of transformed data set used for PCA

Yield	Ash	Temperature	Pressure	Reactor type	Analytical technique
wt. %	mg kg ⁻¹	°C	Pa	-	-
8.6	0.01	500	100000	1	2
15.3	0.062	500	100000	1	2
.	.	.	.	.	.
.	.	.	.	.	.
6.25	0.005	500	400	2	1
6.25	0.005	500	100000	2	1

Principal component analysis (PCA) was used to identify the dominant factors affecting the yields of both species (LG and HA) reported in the literature. For PCA, it was assumed that the yields (Y) of the species was affected by five factors – 1) Ash content (A), 2) Temperature (T), 3) Pressure (P), 4) Reactor type (R), and 5) Analytical technique (AT). Note, no distinction is made between individual cellulose (or biomass) samples, and it was assumed that their heterogeneity is captured by their ash content. For each reactor type a unique integer code (starting from 1) was assigned. Similarly, for GC and LC numeric codes 1 and 2 were assigned, respectively. For PCA, data reported in the Table A.3 was transformed into Table A.7. Similarly, Table A.1, Table A.2, and Table A.4 were also transformed. PCA was carried out in Matlab 2017a by using in built function `pca`.

In order to take into account the large numerical differences in the data, each

variable in the transformed tables, was scaled by using following equation,

$$z = \frac{x - \mu}{\sigma} \tag{Eq. A.1}$$

Where z is the scaled value, x is the original value, μ is the mean of the population and σ is the standard deviation of the population.

A.3.2 Loading matrices

Below are the loading matrices obtained for LG and HA, from both feedstock (cellulose and biomass).

Cellulose - Levoglucosan

	<i>Y</i>	<i>A</i>	<i>T</i>	<i>P</i>	<i>R</i>	<i>AT</i>
<i>Y</i>	1.00	−0.31	−0.18	−0.01	−0.18	−0.46
<i>A</i>		1.00	0.06	0.07	−0.14	−0.11
<i>T</i>			1.00	0.33	0.15	0.44
<i>P</i>				1.00	−0.16	−0.06
<i>R</i>					1.00	0.16
<i>AT</i>						1.00

Cellulose - Hydroxyacetaldehyde

	<i>Y</i>	<i>A</i>	<i>T</i>	<i>P</i>	<i>R</i>	<i>AT</i>
<i>Y</i>	1.00	0.27	−0.49	0.24	−0.52	0.29
<i>A</i>		1.00	0.05	0.20	0.04	0.44
<i>T</i>			1.00	−0.21	0.56	0.00
<i>P</i>				1.00	−0.22	0.19
<i>R</i>					1.00	−0.36
<i>AT</i>						1.00

Biomass - Levoglucosan

	<i>Y</i>	<i>A</i>	<i>T</i>	<i>P</i>	<i>R</i>	<i>AT</i>
<i>Y</i>	1.00	−0.16	0.03	−0.07	0.01	0.22
<i>A</i>		1.00	0.12	0.03	0.06	0.08
<i>T</i>			1.00	0.01	0.41	−0.05
<i>P</i>				1.00	0.00	−0.22
<i>R</i>					1.00	−0.23
<i>AT</i>						1.00

Biomass - Hydroxyacetaldehyde

Note, the pressure was excluded from PCA since it was constant throughout the dataset, see Table A.4.

	<i>Y</i>	<i>A</i>	<i>T</i>	<i>R</i>	<i>AT</i>
<i>Y</i>	1.00	−0.25	0.02	0.11	0.13
<i>A</i>		1.00	0.11	−0.03	0.11
<i>T</i>			1.00	0.51	−0.01
<i>R</i>				1.00	−0.48
<i>AT</i>					1.00

A.4 Pure compound calibration

A.4.1 Levoglucosan

Figure A.1A: Levoglucosan (LG) calibration on LC

Figure A.1B: Levoglucosan (LG) calibration on GC

A.4.2 Hydroxyacetaldehyde

Figure A.2A: Hydroxyacetaldehyde (HA) calibration on LC

Figure A.2B: Hydroxyacetaldehyde (HA) calibration on GC

A.4.3 Retention time

In Table A.8, the retention time of levoglucosan (LG) and hydroxyacetaldehyde (HA) in GC and LC systems are presented.

Table A.8: Retention time of levoglucosan (LG) and hydroxyacetaldehyde (HA) in GC and LC

Compound	GC	LC
	min	
LG	55.5	31.2
HA	6.4	16.25

A.5 Proof of cellobiosan depolymerisation

Figure A.3: Chromatogram recorded by FID after injecting a cellobiosan solution

Cellobiosan, diluted in methanol, was injected into the GC and the chromatogram recorded by the FID is presented in Figure A.3. Presence of levoglucosan in the chromatogram was confirmed by comparing the retention time of the standard. The concentration of cellobiosan in methanol was 1.4 wt.%. In Table A.9, the mass (and moles)

of cellobiosan and levoglucosan before (and after) GC analysis, and conversion of cellobiosan are presented. Conversion of cellobiosan is estimated based on the assumption that cellobiosan only reacts to levoglucosan.

Table A.9: Mass (and moles) of cellobiosan and levoglucosan before (and after) GC analysis and conversion of cellobiosan

	Unit	Cellobiosan	Levoglucosan	Methanol
Molar mass	g mole ⁻¹	324	162	32
Before GC analysis	g	0.087	0	6.0269
	mole	0.00027		
After GC analysis	g	0	0.024	
	mole		0.000150	
Conversion	%	28		

A.6 Isolation, identification and quantification

A.6.1 Method: Proton Nuclear magnetic resonance (¹H NMR)

¹H NMR spectra were recorded on a Bruker Avance II 600 MHz NMR spectrometer (14.1 T), using a 5 mm triple nucleus TXI ¹H-¹³C/¹⁵N/²H probe and Avance III 400 MHz NMR spectrometer (9.4 T) provided with a broadband BBFO probe. Both spectrometers are equipped with a *z* gradient coil, producing a maximum gradient strength of 50 gauss cm⁻¹.

A.6.2 Isolation

Figure A.4 presents the LC chromatograms (RI detector) of the water-soluble fraction of pyrolysis oils obtained from the cellulose (pure and 1000 mg kg⁻¹ potassium infused) at 530 °C in a fluidized bed. Note, spectra in Figure A.4 are shown for the qualitative comparison only. It can be seen that with an increase in the potassium concentration in cellulose, anhydrosugars disappeared and a peak (retention time: 16.25 min, highlighted in the gray area) became prominent, referred as unknown in Figure A.4.

In order to identify and eliminate the possibility of co-elution of more than one compound at the same retention time, the unknown peak was isolated from the pyrolysis oil by the following procedure. The concentrated solution (40 wt.%) of oil in deionised water was prepared and was injected into LC. Because of the dead volume of the LC system, the sample was collected from the waste tubing line after the delay of 1.6 min

Figure A.4: LC chromatograms of oils obtained from cellulose (pure and 1000 mg kg⁻¹ potassium infused) pyrolysed in a fluidised bed at 530 °C

(between 17.3 min and 18.8 min). Isolated unknown compound(s) was reanalysed by LC to confirm the isolation. After that, deionised water from isolated fraction was removed by purging dry nitrogen (~4 h) until dry crystalline solids were precipitated. Precipitated solids were dissolved in deuterium oxide (D₂O) and were subsequently analysed by the ¹H NMR) spectroscopy.

A.6.3 Identification

Figure A.5: Chemical structures of A) Hydroxyacetaldehyde, B) Glycolaldehyde dimer, and C) Ethane-1, 1, 2-triol

The ^1H -NMR spectrum (Figure A.6) shows two main intense peaks corresponding with the compound of interest, which was isolated by using LC. In the spectrum, traces of other compounds (small peaks) can be observed. The peak at 9.59 ppm corresponds with the aldehydic proton (Figure A.5-A) and the peak at 4.4 ppm corresponds with CH_2 protons (Figure A.5-A). However, the intensity of these peaks is 11 times smaller than the intense peaks. The more intense peaks match with the structure showed in Figure A.5-B as it will be explained below. The first mentioned peaks in the ^1H NMR) spectrum suggest the presence of hydroxyacetaldehyde, but mainly the dimeric structure (Figure A.5-B).

To unequivocally assign the intense peaks with the dimeric structure, homonuclear and heteronuclear 2D NMR experiments were acquired. ^1H , ^1H -COSY NMR spectrum below (Figure A.7) shows correlation between CH_2 and CH corresponding to the dimeric structure. Excluding the small peak at 4.4 ppm that does not show any correlation peak, according with the expected for the glycolaldehyde structure.

Heteronuclear correlation, ^1H , ^{13}C HSQC NMR spectrum is shown in Figure A.8. The correlation peaks indicate unequivocally the assignation to the dimeric structure. Due to the edition of peaks in the HSQC pulse sequence acquired, it was possible to differentiate peaks due to CH_2 and CH, present at the dimeric and no at the monomeric structure. Since HSQC is an inverse NMR technique, also the correlation due to trace peaks were observed.

Finally, to prove the assignment of the peaks through NMR, we acquired spectra of glycolaldehyde in D_2O and methanol- d_4 . For the spectrum in D_2O we were able to identify the same situation observed in the isolated peak. However, in the case of methanol- d_4 the chemical shift observed matches better with the structure shown in Figure A.5-C. Note that the multiplicity observed in the methanol- d_4 spectrum is similar to the dimeric structure, however, the chemical shift is different. In methanol- d_4 are misfit, due to different environment (because of the solvent) and also to different structure. Therefore, non-aqueous conditions lead to dimeric structure and methanolic conditions can lead to triol structure (see Figure A.5-C). However, in all of the spectra the monomeric glycolaldehyde is observed in a ratio approximated to 1:10 (or even higher).

Figure A.6: ^1H NMR spectra of isolated peak in D_2O

^1H NMR: (600 MHz, D_2O) δ 9.59 (s, 1H), 5.01 (t, J = 5.1 Hz, 1H), 4.403 (s, 2H), 3.48 (d, J = 5.1 Hz, 2H)

Figure A.7: ^1H , ^1H -COSY NMR spectrum. ^1H , ^1H -COSY (600 MHz, D_2O) showed the correlation peaks between 5.01 and 3.48 ppm

Figure A.8: ^1H , ^{13}C -HSQC NMR spectrum of isolated peak in D_2O . ^1H , ^{13}C -HSQC: ^1H NMR (600 MHz, D_2O) and ^{13}C NMR (151 MHz, D_2O) showed the following proton-carbon correlation peaks: 5.01 and 89.75, 3.48 and 64.64

Figure A.9: In D₂O: ¹H NMR (400 MHz, D₂O) δ 4.93 (t, 1H), 4.70 (D₂O, 4.33 (s, 2H), 3.39 (d, 2H)

Figure A.10: In Methanol-d₄: ¹H NMR (400 MHz, MeOD) δ 5.59 (s, 2H), 4.90 (D₂O, 4.54 (t, 1H), 3.46 (d, 2H), 3.33. Note, H₂O peak arising from the solvent (MeOD).

A.6.4 Quantification

It can be seen from Figure A.4 that hydroxyacetaldehyde (in dimer form) partially overlapped cellobiosan peak, especially in the oils obtained from pure cellulose. Thus, in order to quantify the hydroxyacetaldehyde yield following integration procedure was followed. Figure A.11A shows the LC chromatogram of the hydroxyacetaldehyde (in dimer form), of which retention time is 16.25 min (maximum). Because of the fact that no other compound elutes after hydroxyacetaldehyde (see Figure A.4) following integration method was developed and used. The peak was integrated into two separate parts, namely right area (RA) and left area (LA). From a seven point calibration (see Figure A.2A) it was found that the ratio between the RA and LA is ~ 1.6 and was independent of hydroxyacetaldehyde concentration, see Figure A.11B. Thus, for oils only RA was determined and LA was computed using the ratio ($LA = RA/1.6$). The total area under the peak was determined by adding RA and LA, which was used for the quantification of the hydroxyacetaldehyde.

Figure A.11A: LC chromatogram of hydroxyacetaldehyde

Figure A.11B: The ratio between right area (RA) and left area (LA) as a function of hydroxyacetaldehyde concentration

A.7 Examples of GC chromatogram

Figure A.12A: GC chromatograms of cellulose (1 mg kg⁻¹ K⁺) derived oil recorded by FID

Figure A.12B: GC chromatograms of cellulose ($1000 \text{ mg kg}^{-1} \text{ K}^+$) derived oil recorded by FID

Figure A.12C: GC chromatograms of biomass derived oil (Exp 1) recorded by FID

B

Supporting information for Chapter 4

Table B.1: Oil, char, gas, CO and CO₂ yields as a function of potassium concentration in cellulose in screen-heater. T_{FS} = 530 °C

K ⁺ concentration in cellulose mg kg ⁻¹	Oil	Char	Gas kg kg ⁻¹ cellulose	CO	CO ₂
Screen-heater, P = 0.5 kPa					
1	0.96 ± 0.03	0	0.01 ± 0	0.003 ± 0.001	0.005 ± 0.002
100	0.89 ± 0.03	0.01 ± 0.01	0.01 ± 0	0.007 ± 0.002	0.007 ± 0.001
1000	0.76 ± 0.03	0.05 ± 0.01	0.03 ± 0	0.012 ± 0.003	0.017 ± 0.001
10000	0.52 ± 0.02	0.15 ± 0.02	0.1 ± 0.02	0.037 ± 0.008	0.059 ± 0.014
Screen-heater, P = 100 kPa					
1	0.86 ± 0.04	0.01 ± 0	0.02 ± 0.01	0.013 ± 0.006	0.01 ± 0.003
100	0.73 ± 0.03	0.01 ± 0	0.04 ± 0.01	0.012 ± 0.003	0.009 ± 0.001
1000	0.67 ± 0.01	0.04 ± 0	0.05 ± 0	0.016 ± 0.003	0.013 ± 0.001
10000	0.57	0.16	0.16	0.058	0.1

Table B.2: Oil, char and gas yields as a function of potassium concentration in cellulose in fluidised bed. $T_{FS} = 530\text{ }^{\circ}\text{C}$

K⁺ concentration in cellulose	Oil	Char	Gas
mg kg ⁻¹	kg kg ⁻¹ cellulose		
1	0.73	0.01	0.12
100	0.63	0.03	0.24
1000	0.60	0.04	0.22

Table B.3: Levoglucosan yield and glucose recovery after hydrolysis of oil, as a function of potassium concentration in cellulose; in screen-heater and fluidized bed. $T_{FS} = 530\text{ }^{\circ}\text{C}$

K⁺ concentration in cellulose	$\frac{C_{Glucose}}{C_{Cellulose}}$	Levoglucosan
mg kg ⁻¹	kg kg ⁻¹ cellulose	
Screen-heater, P = 0.5 kPa		
1	0.66 ± 0.02	0.2 ± 0.03
100	0.49 ± 0.04	0.1 ± 0.01
1000	0.3 ± 0.03	0.08 ± 0.02
10000	0.04 ± 0.02	0.01 ± 0.01
Screen-heater, P = 100 kPa		
1	0.45	0.31
100	0.35	0.17
1000	0.22	0.08
10000	0.03	0.01
Fluidized Bed Reactor		
1	0.45	0.35
100	0.30	0.20
1000	0.07	0.07

Table B.4: Levoglucosan recovery ($R_{\text{Levoglucosan}}$) as a function of potassium concentration in levoglucosan and pressure in screen-heater. $T_{\text{FS}} = 530^\circ\text{C}$

K⁺ concentration in levoglucosan	$R_{\text{Levoglucosan}}$
mg kg ⁻¹	kg kg ⁻¹ levoglucosan
Screen-heater, P = 0.5 kPa	
1	0.88
1000	0.89
Screen-heater, P = 100 kPa	
1	0.89
1000	0.48

Table B.5: Effect of pressure on oil, char and gas yields at constant potassium concentration in levoglucosan in screen-heater. $T_{\text{FS}} = 530^\circ\text{C}$

P	Oil	Char	Gas
kPa	kg kg ⁻¹ levoglucosan		
Levoglucosan + 1000 mg kg ⁻¹ potassium (K ₂ CO ₃)			
<0.5	0.94 ± 0.05	0.03 ± 0	0.01 ± 0
100	0.77 ± 0.03	0.05 ± 0.01	0.06 ± 0.02

Table B.6: Levoglucosenone, acetol and hydroxyacetaldehyde yields as a function of potassium concentration in cellulose in screen-heater. $T_{\text{FS}} = 530^\circ\text{C}$ and P = 0.5 kPa

K⁺ concentration in cellulose	Levoglucosenone	Acetol	Hydroxyacetaldehyde
mg kg ⁻¹	kg kg ⁻¹ cellulose		
1	0.002 ± 0	0.002 ± 0.001	0.11 ± 0.01
100	0.003 ± 0	0.002 ± 0	0.16 ± 0.01
1000	0.01 ± 0.001	0.002 ± 0	0.14 ± 0.01
10000	0	0.023 ± 0.001	0.12 ± 0.01

Table B.7: Oil, char, gas, glucose recovery after hydrolysis of oil and levoglucosan yield for different anions with constant potassium concentration (1000 mg kg⁻¹) in cellulose. T_{FS} = 530 °C

Anion	Oil	Char	Gas kg kg ⁻¹ cellulose	$\frac{C_{Glucose}}{C_{Cellulose}}$	Levoglucosan
-					
		Screen-heater, P = 0.5 kPa			
CO ₃ ²⁻	0.76 ± 0.03	0.05 ± 0.01	0.03 ± 0	0.3 ± 0.03	0.08 ± 0.02
Cl ⁻	0.76 ± 0.05	0.03 ± 0.01	0.04 ± 0.01	0.17 ± 0.01	0.03 ± 0
OH ⁻	0.75 ± 0.05	0.03 ± 0.02	0.05 ± 0.01	0.13 ± 0.03	0.04 ± 0
		Screen-heater, P = 100 kPa			
O ₃ ²⁻	0.67 ± 0.01	0.04 ± 0	0.05 ± 0	0.22	0.08
Cl ⁻	0.65 ± 0	0.03 ± 0.01	0.03 ± 0.02	0.15	0.039
OH ⁻	0.57 ± 0.01	0.05 ± 0	0.07 ± 0.02	0.11	0.043

B

C

Supporting information for Chapter 5

C.1 Fractionation efficiencies

Fractionation experiment efficiencies for different lignins are presented in Table C.1.

Table C.1: Fractionation efficiencies of lignin

Lignin	Code	L : H
-	-	kg : kg
SL	1	0.41 : 0.59
WSL	4	0.5 : 0.5
PL1	7	0.66 : 0.34
PL2	10	0.63 : 0.37

C.2 Effect of temperature

Table C.2 presents the lumped product yields obtained from the lignin 13 as a function of T_{FS} .

Table C.2: Oil, char and gas yields, $\langle M_w \rangle$ and polydispersity values of oils obtained at the T_{FS} of 530 °C

T _{FS}	Y _{Oil,exp}	Y _{Char,exp}	Y _{Gas,exp}	<M _{w,exp} >	D
°C	wt.% on lignin			Da	-
P = 0.5 kPa					
425	62 ± 5	30 ± 4	1 ± 1	736	1.5
513	78 ± 1	14 ± 2	1 ± 1	804	1.5
640	84 ± 3	8 ± 1	2 ± 1	874	1.5
779	81 ± 5	8 ± 1	2 ± 1	952	1.6
P = 100 kPa					
433	46 ± 0.2	36 ± 1	5 ± 0.3	440	1.2
523	46 ± 2	32 ± 2	6 ± 1	454	1.2
630	49 ± 2	22 ± 2	11 ± 2	500	1.3
793	47 ± 4	18 ± 1	17 ± 1	494	1.4

C.3 Experimental yields, $\langle M_w \rangle$ and polydispersity values of oil

Table C.3: Oil, char and gas yields, $\langle M_w \rangle$ and polydispersity values of oils obtained at the T_{FS} of 530 °C

Lignin	Code	P = 0.5 kPa					P = 100 kPa				
		$Y_{Oil,exp}$	$Y_{Char,exp}$ wt.% on lignin	$Y_{Gas,exp}$	$\langle M_{w,exp} \rangle$ Da	$\mathcal{D}$	$Y_{Oil,exp}$	$Y_{Char,exp}$ wt.% on lignin	$Y_{Gas,exp}$	$\langle M_{w,exp} \rangle$ Da	$\mathcal{D}$
-	-	-	-	-	-	-	-	-	-	-	-
SL	1	75 ± 3	15 ± 2	1 ± 1	1511	1.9	40 ± 3	42 ± 2	3 ± 2	716	1.5
L-SL	2	86 ± 2	5 ± 2	0.1 ± 0.1	1147	1.5	52 ± 7	29 ± 1	5 ± 2	699	1.5
H-SL	3	66 ± 6	20 ± 3	1 ± 2	1950	2.2	32 ± 4	46 ± 5	2 ± 1	571	1.3
W-SL	4	81 ± 3	8 ± 2	1 ± 1	1521	2.0	45 ± 2	32 ± 8	3 ± 4	609	1.4
L-W/SL	5	93 ± 1	4 ± 0.2	1 ± 0.2	1208	1.6	55 ± 2	21 ± 1	4.5 ± 0.4	664	1.5
H-W/SL	6	74 ± 3	15 ± 1	2 ± 0.3	1554	2.1	44 ± 5	39 ± 1	3 ± 3	578	1.4
PL1	7	94 ± 1	2 ± 0.8	0	595	1.4	-	-	-	-	-
L-PL1	8	93	1	0	643	1.5	-	-	-	-	-
H-PL1	9	-	-	-	-	-	63	23	2	565	1.4
PL2	10	90 ± 10	3 ± 3	0.3 ± 0.3	619	1.6	80 ± 1	7 ± 2	1 ± 0.5	450	1.4
L-PL2	11	92	0.3	0.1	556	1.5	78	8	0.5	464	1.4
H-PL2	12	96	2	0.1	986	1.8	76	11	0	492	1.3
SOL	13	78 ± 1	14 ± 3	2 ± 0.9	1138	1.9	46 ± 2	32 ± 2	6 ± 1	502	1.4
MWL	14	70 ± 2	18 ± 0.3	3 ± 0.8	1135	1.9	47 ± 7	32 ± 2	4 ± 0.1	580	1.4

-Not reported

C.4 Oil yield as a function of lights in the feed

Figure C.1A and C.1B presents the experimental oil yields as a function of the mass fractions of lights in the lignins. Lights were defined as: $DP_{\leq 4}$ for 0.5 kPa and $DP_{\leq 2}$ for 100 kPa. The boundaries of the mass fraction in the lignins were chosen because the $\langle M_n \rangle$ of oils obtained at 0.5 kPa was ~ 800 Da and at 100 kPa was ~ 400 Da, see Figure 5.4 in Chapter 5.

Figure C.1A: Experimental oil yield as a function of the mass fractions of lights ($\leq DP_4$) in the lignins at 0.5 kPa

Figure C.1B: Experimental oil yield as a function of the mass fractions of lights in the lignins at 100 kPa

C.5 M_wD plots of all lignins

The M_wD of all lignin and their oils (experiment and model) are shown in Figure C.2 to Figure C.15. For model predictions, parameters obtained from the individual fit procedure are used.

Figure C.2: $M_w D$ of lignin 1 and its oils

Figure C.3: $M_w D$ of lignin 2 and its oils

Figure C.4: $M_w D$ of lignin 3 and its oils

Figure C.5: $M_w D$ of lignin 4 and its oils

Figure C.6: $M_w D$ of lignin 5 and its oils

Figure C.7: $M_w D$ of lignin 6 and its oils

Figure C.8: M_wD of lignin 7 and its oil

Figure C.9: M_wD of lignin 8 and its oil

Figure C.10: M_w D of lignin 9 and its oil

Figure C.11: M_w D of lignin 10 and its oils

Figure C.12: $M_w D$ of lignin 11 and its oils

Figure C.13: $M_w D$ of lignin 12 and its oils

Figure C.14: $M_w D$ of lignin 13 and its oils

Figure C.15: $M_w D$ of lignin 14 and its oils

C.6 Model

C.6.1 Experimental proof of polymerisation and bubble formation

The char, obtained from the pyrolysis of lignin 1, trapped between the screens was washed with THF. Figure C.16 presents the M_w D of the THF soluble fraction of the char and the lignin 1. Note, the response of THF soluble fraction of char has been scaled to that of lignin 1 for comparison purpose only. However, it is worth mentioning that no THF soluble species in char were observed by Shrestha et al.^[319] after pyrolyzing lignin at 400 °C.

Figure C.16: M_w D of lignin 1 and tetrahydrofuran soluble fraction of its char obtained at 100 kPa

Figure C.17 shows the formed bubbles in the lignin melt during the pyrolysis of lignin 13 at 530 °C and at 100 kPa.

Figure C.17: Formed bubbles in the lignin melt during the pyrolysis of lignin 13 at 530 °C and at 100 kPa

C.6.2 Model characteristics

Invariant predictions: Multiplying rate constants with the same factor

Lignin pyrolysis (excluding gas formation reactions) can be simplified to two parallel first and second order reactions, as shown in Figure C.18.

Figure C.18: Schematic representation of lignin pyrolysis; oil (O) and char (C) formation reactions are of 1st and 2nd order, respectively

Rate equations for lignin, oil and char are as follows, where k_1 is a sum of transport rate constant and cracking rate constant and k_2 represents the polymerisation rate constant.

$$\frac{dC_L}{dt} = -k_1 C_L - k_2 C_L^2 \quad (\text{Eq. C.1})$$

$$\frac{dC_O}{dt} = k_1 C_L \quad (\text{Eq. C.2})$$

$$\frac{dC_C}{dt} = k_2 C_L^2 \quad (\text{Eq. C.3})$$

Analytical solutions of Eq. C.1, Eq. C.2, and Eq. C.3 with $C_L(0) = C_{L,0}$, $C_O(0) = 0$ and $C_C(0) = 0$, respectively, are as follows,

$$C_L = \frac{k_1 C_{L,0}}{e^{k_1 t}(k_1 + k_2 C_{L,0}) - k_2 C_{L,0}} \quad (\text{Eq. C.4})$$

$$C_0 = \frac{k_1}{k_2} \left\{ \ln \left(\frac{e^{k_1 t}(k_1 + k_2 C_{L,0}) - k_2 C_{L,0}}{k_1} - k_1 t \right) \right\} \quad (\text{Eq. C.5})$$

$$C_C = C_{L,0} - C_L - C_O \quad (\text{Eq. C.6})$$

at $t \rightarrow \infty$

$$Y_{Char} = 1 + \frac{k_1}{k_2 C_{L,0}} \ln \left(\left| \frac{k_1}{k_1 + k_2 C_{L,0}} \right| \right) \quad (\text{Eq. C.7})$$

As can be seen from the char yield formula (Eq. C.7), at $t = \infty$ the char yield is only a function of the ratios of the rate constants, i.e. k_1 and k_2 , for a given initial concentration of lignin ($C_{L,0}$). Thus, transport of molecules, cracking reactions and polymerisation reactions are interdependent and hence predictions remain unaffected when all rates ($k_{T,avg}$, k_K , k_P) are multiplied by a same factor. The different processes occurring during lignin pyrolysis should be compared based on rate ratios, i.e. $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$. Simulations were carried out for atmospheric pressure experiments of lignin 4 to demonstrate this characteristic for the full model described in the Chapter 5, see Figure C.19A and C.19B. Note, as the value of multiplication factor increased, population balance equations reached faster to steady state solution.

Figure C.19A: Effect of multiplication factor on the calculated char yield

Figure C.19B: Effect of multiplication factor on the calculated $\langle M_n \rangle$ of oils

Length of computational grid

One of the parameters in the model is the length of whole grid, i.e. DP_1 to $2DP_{\max}$. In all standard simulations the value of the $i_{\max}$ was set at 50 ($DP_{\max} = 10000 Da$), thereby, the char bins were between $(DP_{\max} + 1)$ to $2DP_{\max}$. However, it can be argued that molecules bigger than $DP_{>25}$, being not present in the oil (especially at 100 kPa), can be treated as a char. Hence, a sensitivity analysis was carried out to investigate the effect grid length on the model predictions i.e. char yield and the $\langle M_n \rangle$ of the oil. In these simulations the length of whole grid (DP_1 to $2DP_{\max}$) was varied between 50 to 100. For example, for $i_{\max} = 25$, the computational grid ended at 50 and char bins were between DP_{26} to DP_{50} . During this analysis, a set of parameters was estimated for each whole grid, i.e. 50. Simulations were carried out for lignin 1, at 0.5 kPa and 100 kPa.

Figure C.20A: Effect of grid length on the calculated char yield

Figure C.20B: Effect of grid length on the calculated $\langle M_n \rangle$ of oils

At both pressures, the predicted char yields are independent of the grid length and match accurately with the experimental values, i.e. 0.15 kg kg^{-1} (0.5 kPa) and 0.42 kg kg^{-1} (100 kPa), see Figure C.20A. Similarly, the predicted $\langle M_n \rangle$ of the oils remain constant as a function of the grid length at both pressures, see Figure C.20B. As the length of the computational grid decreases, an increase in the values of $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$ was observed. It can be seen that at 0.5 kPa the values of $\frac{k_K}{k_P}$ are higher than for 100 kPa and they increase proportionally. The transport rate becomes increasingly dominant over polymerisation for smallest char grid of 25 bins (26-50), especially for 0.5 kPa experiments (see Figure C.21A and C.21B).

Figure C.21A: Effect of grid length on $\frac{k_{T,avg}}{k_P}$

Figure C.21B: Effect of grid length on $\frac{k_K}{k_P}$

C.6.3 Individual fit procedure

The values of $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$ for each lignin obtained from the individual fit procedure for 0.5 kPa and 100 kPa experiments are presented below in Table C.4. It also presents the 95% confidence intervals of the ratios.

Table C.4: Values of $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$ for each lignin obtained from the individual fit procedure

Pressure		P = 0.5 kPa		P = 100 kPa	
Lignin	Code	$\frac{k_{T,avg}}{k_P}$	$\frac{k_K}{k_P}$	$\frac{k_{T,avg}}{k_P}$	$\frac{k_K}{k_P}$
-	#	mole m ⁻³	mole m ⁻³	mole m ⁻³	mole m ⁻³
SL	1	15 ± 2	33 ± 3	4 ± 0.4	25 ± 3
L-SL	2	16 ± 4	47 ± 7	4 ± 0.5	35 ± 4
H-SL	3	16 ± 2	27 ± 1	3 ± 0.7	24 ± 3
WSL	4	15 ± 3	43 ± 5	3 ± 0.9	35 ± 4
L-WSL	5	16 ± 6	52 ± 11	4 ± 0.4	43 ± 5
H-WSL	6	13 ± 1	35 ± 3	3 ± 0.4	30 ± 3
PL1	7	4 ± 1	87 ± 25	-	-
L-PL1	8	5 ± 1	96 ± 35	-	-
H-PL1	9	-	-	3 ± 0.5	44 ± 5
PL2	10	5 ± 0.2	92 ± 11	2 ± 0.3	81 ± 8
L-PL2	11	4 ± 0.4	38 ± 4	5 ± 3	55 ± 0.04
H-PL2	12	10 ± 1	74 ± 11	3 ± 0.01	65 ± 7
SOL	13	8 ± 1	43 ± 4	2 ± 0.8	39 ± 4
MWL	14	9 ± 0.8	40 ± 3	3 ± 0.6	37 ± 4

C.6.4 Model predictions with total fit procedure

The char yields and the $\langle M_n \rangle$ of oils predicted using the total fit procedure are presented in Figure C.22A and C.22B, respectively.

Figure C.22A: Char yields, experimental and calculated from total fit procedure, as a function of the $\langle M_n \rangle$ of the lignins

Figure C.22B: $\langle M_n \rangle$ of oils, experimental and calculated from total fit procedure, as a function of the $\langle M_n \rangle$ of the lignins

C.6.5 Correlation between $\frac{k_K}{k_P}$ and $\langle M_n \rangle$ of lignins

The relation between $\frac{k_K}{k_P}$ and $\langle M_n \rangle$ of lignins obtained from the individual fits is presented in Figure C.23. Also, the coefficient of determination (R^2) and the values of slope and intercept of the linear fit are shown.

Figure C.23: Correlation between $\frac{k_K}{k_P}$ and $\langle M_n \rangle$ of lignins

C.6.6 Effect of T_{FS} on the model predictions, and $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$

The parity plots (Figure C.24A and C.24B) of the experimental char yields (A) and $\langle M_n \rangle$ of oils (B) are plotted against their predicted values obtained as a function of T_{FS} , at 0.5 kPa and 100 kPa.

The values of $\frac{k_{T,avg}}{k_P}$ and $\frac{k_K}{k_P}$ obtained, after parameterization, as function of T_{FS} are presented in the Figure C.25A and C.25B, respectively.

Figure C.24A: Parity plots in which the experimental char yields are plotted against their predicted values obtained as a function of T_{FS}

Figure C.24B: Parity plots in which the experimental $\langle M_n \rangle$ of oils are plotted against their predicted values obtained as a function of T_{FS}

Figure C.25A: The values of $\frac{k_{T,avg}}{k_P}$ as a function of T_{FS}

Figure C.25B: The values of $\frac{k_K}{k_P}$ as a function of T_{FS}

D

Supporting information for Chapter 7

D.1 Experimental data

Each data point reported in Table D.1 to Table D.4 is an average of minimum three experiments. The calculated standard deviation on the mean is also presented. The data reported in Table D.3 and Table D.5 for acid-leached pinewood in fluidised bed is based on a single experiment because of the limited availability of the feedstock.

Bagasse

Table D.1: Yields of oil, char, gas, water-insoluble compounds (WIS) obtained from pyrolysis of acid-leached bagasse as a function of pressure in screen-heater ($T_{FS} = 515 \pm 10$ °C)

Pressure kPa	Y_{Oil}	Y_{Char} wt.% on d.a.f. bagasse	Y_{Gas}	Y_{WIS}
0.005 ± 0.00	91.3 ± 1.2	4.6 ± 0.2	0.5 ± 0.0	17.2 ± 1.6
0.2 ± 0.03	85.6 ± 2.0	5.0 ± 0.4	0.5 ± 0.1	15.6 ± 2.3
2 ± 0.03	87.9 ± 0.5	3.5 ± 0.1	3.2 ± 0.6	22.1 ± 0.5
10 ± 2.5	91 ± 3	3 ± 0	3 ± 0	14 ± 0.2
21 ± 1.08	78.7 ± 2.3	9.3 ± 1.4	1.9 ± 0.4	11.8 ± 2.2
38 ± 0.30	78.5 ± 2.7	9.0 ± 1.6	2.5 ± 0.8	17.7 ± 1.3
60 ± 0.10	81.5 ± 2.9	8.7 ± 1.5	2.3 ± 0.3	18.2 ± 1.3
81 ± 1.01	79.4 ± 1.4	7.4 ± 0.5	2.9 ± 0.8	17.6 ± 1.2
101 ± 1.39	72.8 ± 2.4	8.2 ± 0.9	4.7 ± 0.3	13.3 ± 2.9

Table D.2: Yield of C₆ anhydrosugars (C₆aS) and DP₁ mass fraction obtained from pyrolysis of acid-leached bagasse as a function of pressure in screen-heater (T_{FS} = 515 ± 10 °C)

Feedstock		Untreated bagasse				Acid-leached bagasse			
Pressure	±	Y _{C₆aS}	±	f _{DP₁}	±	Y _{C₆aS}	±	f _{DP₁}	±
kPa		wt.% on C ₆ sugars		-		wt.% on C ₆ sugars		-	
5x10 ⁻³	0.00	25.2	0.2	0.08	0.0	73	3	0.13	0.01
0.2	0.03	16.4	1.3	0.06	0.3	67	2	0.14	0.00
2	0.03	22.0	2.9	0.05	0.3	62	2	0.18	0.00
10	2.5	-	-	-	-	51	3	0.27	0.01
20	1.08	10.2	0.9	0.10	0.3	42	2	0.32	0.00
40	0.30	10.3	1.3	0.11	0.5	42	1	0.35	0.01
60	0.10	6.8	2.2	0.15	0.1	38	1	0.42	0.00
80	1.01	8.5	1.2	0.14	0.1	38	2	0.43	0.01
100	1.39	8.1	0.8	0.15	0.0	35	1	0.39	0.00

Pinewood

Table D.3: Yields of oil, char, gas and water-insoluble compounds (WIS) obtained from pyrolysis of acid-leached pinewood as a function of pressure in screen-heater and fluidised bed (T = 485 °C)

Pressure	Y _{Oil}	Y _{Char}	Y _{Gas}	Y _{WIS}
kPa	wt.% on d.a.f. bagasse			
Screen-heater				
0.3 ± 0.01	83.7 ± 1.4	7.1 ± 2.2	0.5 ± 0.0	10.2 ± 0.8
55 ± 0.05	76.2 ± 1.3	8.9 ± 0.0	1.5 ± 0.2	12.7 ± 0.9
100 ± 1.3	63.6 ± 2.0	8.2 ± 0.1	2.1 ± 0.1	9.0 ± 1.0
Fluidised bed				
55	62	12	19	7.9

Table D.4: Yield of C₆aS and DP₁ mass fraction obtained from pyrolysis of acid-leached pinewood as a function of pressure in screen-heater (T_{FS} = 485 ± 10 °C)

Feedstock	Untreated pinewood			Acid-leached pinewood		
	0.5 kPa	55 kPa	100 kPa	0.5 kPa	55 kPa	100 kPa
Pressure						
Y _{C₆aS}	0.22 ± 0.01	0.18 ± 0.02	0.18 ± 0.00	0.47 ± 0.03	0.40 ± 0.01	0.31 ± 0.00
f _{DP₁}	0.06 ± 0.01	0.16 ± 0.03	0.28 ± 0.02	0.11 ± 0.02	0.28 ± 0.01	0.44 ± 0.01

Table D.5: The yield of anhydrosugars obtained from the pyrolysis acid-leached pinewood at 485°C and 55 kPa

DP of anhydrosugars		Yield (kg kg ⁻¹ on C ₆ sugars)	
-		Screen-heater	Fluidised bed
1		0.11	0.26
2		0.17	0.11
3		0.08	0.01
4		0.03	0.00
5		0.00	0.00
6		0.00	0.00
Total		0.4	0.38

D.2 Direct infusion mass spectrometry

In this section, direct infusion mass spectrometry of water-soluble fraction of bio-oils and fingerprinting (MS^2) of anhydrosugars is presented. For the details of the method see Section 2.4.5 in Chapter 2.

Table D.6 presents the molar mass (m/z) and NH_4^+ (or Na^+) adduct molar mass corresponding to different DPs, which were found in the oil as well as in MS^2 spectra. Different DPs found in the spectra are highlighted in a red ellipse, see Figure D.1 to Figure D.3.

Table D.6: Molar mass (m/z) and NH_4^+ (or Na^+) adduct molar mass corresponding to different DPs

DP	Name	Molar mass or m/z	DP with NH_4^+	DP with Na^+
-	-	Da	Da	Da
1	Levoglucosan	162	180	185
2	Cellobiosan	324	342	
3	Cellotriosan	486	504	
4	Cellotetrasan	648	666	
5	Cellopentasan	810	828	
6	Cellohexasan	972	990

Figure D.1: Mass spectrum of oil (water-soluble fraction), in a positive ion, obtained from acid-leached bagasse in a screen-heater at 0.005 kPa; TFS = 515°C

Figure D.2: Mass spectrum of oil (water-soluble fraction), in a positive ion, obtained from acid-leached pinewood in a screen-heater at 55 kPa; TFS = 485°C

Figure D.3: Mass spectrum of oil (water-soluble fraction), in a positive ion, obtained from acid-leached pinewood in a fluidised bed at 55 kPa and 485°C

Figure D.4: Product spectra from MS2 experiments for DP_2 in a positive ion

Figure D.5: Product spectra from MS2 experiments for DP3 in a positive ion

Figure D.6: Product spectra from MS2 experiments for DP4 in a positive ion

Figure D.7: Product spectra from MS² experiments for DP₅ in a positive ion

Figure D.8: Product spectra from MS2 experiments for DP6 in a positive ion

D.3 Model description

D.3.1 Model characteristic

Pyrolysis of C_6 sugars in biomass can be simplified to three series-parallel first order reactions, as shown in Figure D.9.

Figure D.9: Schematic representation of C_6 sugars (in biomass) pyrolysis

Rate equations for C_6 sugars (S), intermediate C_6aS (I), C_6aS (AnS) and other products (U) are as follows, where k_1 is a depolymerisation rate constant, k_2 represents mass transport rate of C_6aS away from the reaction front, and k_3 is the rate constant for decomposition reactions.

$$\frac{dC_S}{dt} = -k_1 C_S \quad (\text{Eq. D.1})$$

$$\frac{dC_I}{dt} = k_1 C_S - k_2 C_I - k_3 C_I \quad (\text{Eq. D.2})$$

$$\frac{dC_{AnS}}{dt} = k_2 C_I \quad (\text{Eq. D.3})$$

$$\frac{dC_U}{dt} = k_3 C_I \quad (\text{Eq. D.4})$$

Analytical solutions of Eq. D.1, Eq. D.2, Eq. D.3 and Eq. D.4 with $C_S(0) = C_{S,0}$, $C_I(0) = 0$, $C_{AnS}(0) = 0$ and $C_U(0) = 0$, respectively, are as follows,

$$C_S = C_{S,0} e^{-k_1 t} \quad (\text{Eq. D.5})$$

$$C_I = \frac{k_1 C_{S,0}}{k_2 + k_3 - k_1} \left(e^{-k_1 t} - e^{-(k_2 + k_3)t} \right) \quad (\text{Eq. D.6})$$

$$C_{AnS} = \frac{k_1 C_{S,0}}{k_2 + k_3 - k_1} \left(\frac{e^{-(k_2 + k_3)t}}{k_2 + k_3} - \frac{e^{-k_1 t}}{k_1} \right) + \frac{k_2}{k_2 + k_3} \quad (\text{Eq. D.7})$$

$$C_U = C_{S,0} - C_S - C_I - C_{AnS} \quad (\text{Eq. D.8})$$

at $t \rightarrow \infty$

$$Y_{AnS} = \frac{k_2}{k_2 + k_3} \quad (\text{Eq. D.9})$$

From Eq. D.9, it can be seen that, at steady state, the yield of C₆aS is only a function of the mass transport rate of anhydrosugars (k_2) and decomposition rate constant (k_3). It is important to note that this analytical solution only computes the yield of C₆aS.

The experimental method does not allow the determination of the temporal evolution of products. Instead, final yields ($t = \infty$) are obtained, leads to the restriction that it is not possible to determine all three constants ($k_{T,avg}$, k_U and k_K) by fitting them to the experimental results. Since the aim is to predict both the yield of C₆aS and the mass fraction of DP₁ in C₆aS, inclusion of depolymerisation reaction rate constant (k_K) becomes necessary. Therefore, it was decided that the different processes occurring during the pyrolysis of C₆ sugars should be compared based on $\frac{k_K}{k_K + k_U}$ and $\frac{k_{T,avg}}{k_K + k_U}$.

D.3.2 Description

Particle level

Mass balance

The mass balances for DP_1 to DP_7 and other products (U) are presented below.

$$\frac{dm_{DP_i}^P}{dt} = (K_i^f - K_i^c) - E_i - U_i \quad 1 \leq i \leq 6 \quad (\text{Eq. D.10})$$

$$\frac{dm_{DP_i}^P}{dt} = K_i^c \quad i = 7 \quad (\text{Eq. D.11})$$

$$\frac{dU}{dt} = \sum_{i=1}^6 U_i \quad (\text{Eq. D.12})$$

$$\frac{dm_{DP_i}^O}{dt} = E_i \quad 1 \leq i \leq 6 \quad (\text{Eq. D.13})$$

Transport

The transport of C_6aS , by evaporation/sublimation/ejection, is described by a single first order equation.

$$E_i = k_{T,i} m_{DP_i}^P \quad 1 \leq i \leq 6 \quad (\text{Eq. D.14})$$

$$k_{T,i} = e^{-Ai} \quad 1 \leq i \leq 6 \quad (\text{Eq. D.15})$$

Depolymerisation

Depolymerisation is assumed to be a first order process, and all possibilities have the same likelihood, i.e. the rate constant k_K , is the same for all depolymerisation reactions. Note that the DP_1 segment do not depolymerise further.

$$K_i^f = k_K 2 \sum_{j=i+1}^7 \frac{i}{j} m_{DP_j}^P \quad 1 \leq i \leq 6 \quad (\text{Eq. D.16})$$

$$K_i^c = k_K (i - 1) m_{DP_i}^P \quad 1 \leq i \leq 6 \quad (\text{Eq. D.17})$$

Decomposition

Decomposition reaction of each C_6aS assumed to follow first order kinetics, and all decomposition reactions have the same rate constant, k_U . Furthermore, it is assumed that once the other products are formed, they do not take part in any reactions and remain at the reacting particle.

$$U_i = k_U m_{DP_i}^P \quad 1 \leq i \leq 6 \quad (\text{Eq. D.18})$$

Initial conditions

The initial masses of C_6aS (DP_1 to DP_6) on the hot reacting particle and in the oil are,

$$m_{DP_i, t=0}^P = m_{DP_i, t=0}^O = 0 \quad 1 \leq i \leq 6$$

The fraction of C_6 sugars present in bagasse or pinewood is used as an initial mass of DP_7 , see Table 1.

$$m_{DP_i, t=0}^P = f_{C_6} \quad i = 7$$

The mass fraction of other products is

$$U_{t=0} = 0$$

Post-processing

Eq. D.19 and Eq. D.20 calculate the yield of C_6aS and the mass fraction of DP_1 in C_6aS , respectively.

$$Y_{C_6aS, cal, t=\infty} = \frac{\sum_{i=1}^6 m_{DP_i, t=\infty}^O}{m_{DP_7, t=0}^P} \quad (\text{Eq. D.19})$$

$$f_{DP_1, cal, t=\infty} = \frac{m_{DP_1, t=\infty}^O}{\sum_{i=1}^6 m_{DP_i, t=\infty}^O} \quad (\text{Eq. D.20})$$

Parameter estimation

$$h_j = \sum \left\{ (f_{DP_1,exp} - f_{DP_1,cal,t=\infty})^2 + (Y_{C_6aS,exp} - Y_{C_6aS,cal,t=\infty})^2 \right\} \quad (\text{Eq. D.21})$$

$$g = \sum_{j=1}^n h_j \quad (\text{Eq. D.22})$$

The objective function for this (Eq. D.21) is comprised of – 1) the sum of the squared difference between the experimentally obtained and calculated mass fraction of DP₁, and 2) the squared difference between the experimentally obtained and calculated C₆aS yield.

At a constant temperature, parameters k_U and k_K are constant and are independent of pressure. To estimate a single value of $\frac{k_K}{k_K+k_U}$ over the entire pressure range, the objective function shown in Eq. D.22 is used where n represents each pressure; this is called the total fit procedure. The experimental results obtained at each pressure were fitted to the model, with $\frac{k_K}{k_K+k_U}$ the value obtained from the total fit procedure, to obtain $\frac{k_{T,avg}}{k_K+k_U}$ using the objective function shown in Eq. D.21. This called the individual fit procedure. Parameters estimation is carried out with the Matlab built-in optimisation function `lsqnonlin`. 95% confidence intervals for each parameter were determined by the built-in Matlab function `nlparci`.

Hot vapour phase

Mass balance

$$\frac{dm_{DP_i}^V}{dt} = k_V \left[2 \sum_{j=i+1}^6 \frac{i}{j} m_{DP_i}^V - (i-1) m_{DP_i}^V \right] \quad 1 \leq i \leq 6 \quad (\text{Eq. D.23})$$

Initial conditions

Since the DP distribution of C_6aS in the fluidised bed could not be measured after ~ 20 ms, the DP distribution of experimentally obtained in screen-heater is used as initial conditions.

$$m_{DP_1, t=0}^V = 0.112$$

$$m_{DP_2, t=0}^V = 0.169$$

$$m_{DP_3, t=0}^V = 0.082$$

$$m_{DP_4, t=0}^V = 0.029$$

$$m_{DP_5, t=0}^V = 0.005$$

$$m_{DP_6, t=0}^V = 0.005$$

Numerical method

The model equations were implemented in the coding environment of Matlab®2017a. The numerical integration was carried out with the built-in ode45 solver which is based on the explicit Runge-Kutta method.

Parameter estimation

$$h = \sum \left(m_{DP_i,exp}^V - m_{DP_i,cal,t=\infty}^V \right)^2 \quad (\text{Eq. D.24})$$

The objective function for this (Eq. D.24) is comprised of the sum of the squared difference between the experimentally obtained (in fluidised bed) and calculated masses of DP₁ to DP₆. The experimental DP distribution of C₆aS was fitted to the model to obtain the value of k_V . Parameters estimation is carried out with the Matlab in-built optimisation function lsqnonlin. 95% confidence interval for k_V was determined by the built-in Matlab function nlparci.

Results

Total fit procedure

The C₆aS yield (on C₆ sugars in acid-leached bagasse) and the mass fraction of DP₁ in C₆aS predicted using the total fit procedure are presented in Figure D.10.

Figure D.10: C₆aS yield (on C₆ sugars in acid-leached bagasse) and the mass fraction of DP₁ in C₆aS, experimental and calculated using the total fit procedure, as a function of pressure

Individual fit procedure

Figure D.11: Parity plot in which the experimental C_6aS yield (on C_6 sugars in acid-leached bagasse) and the mass fraction of DP_1 are plotted against their predicted values using individual fit procedure

Parity plot of the experimental C_6aS yield (on C_6 sugars in acid-leached bagasse) and the mass fraction of DP_1 against their predicted values using individual fit procedure are presented in Figure D.11. The values of $\frac{k_{T,avg}}{k_K+k_U}$ per pressure obtained using the individual fit procedure are presented in Table D.7.

Table D.7: Values of $\frac{k_{T,avg}}{k_K+k_U}$ per pressure obtained using the individual fit procedure

Pressure kPa	$\frac{k_{T,avg}}{k_K+k_U}$ -
0.005	1.9 ± 0.9
0.5	1.5 ± 0.5
2	1.2 ± 0.3
10	0.8 ± 0.2
20	0.5 ± 0.2
40	0.5 ± 0.1
60	0.4 ± 0.1
80	0.4 ± 0.1
100	0.4 ± 0.1

Correlation between $\frac{k_{T,avg}}{k_K+k_U}$ and pressure

Figure D.12: Values of $\frac{k_{T,avg}}{k_K+k_U}$ obtained using individual fit procedure as a function of the pressure with fixed $\frac{k_K}{k_K+k_U}$ obtained from total fit procedure

Nomenclature

A	-	Parameter used to describe the transport rate of DP_i
C_S	$mole\ m^{-3}$	Molar concentration of C_6 carbohydrates in simplified model at $t = t$
$C_{S,0}$	$mole\ m^{-3}$	Molar concentration of C_6 carbohydrates in simplified model at $t = 0$
C_{AnS}	$mole\ m^{-3}$	Molar concentration of C_6aS in simplified model at $t = t$
$C_{AnS,0}$	$mole\ m^{-3}$	Molar concentration of C_6aS in simplified model at $t = 0$
C_I	$mole\ m^{-3}$	Molar concentration of intermediate C_6aS in simplified model at $t = t$
$C_{I,0}$	$mole\ m^{-3}$	Molar concentration of intermediate C_6aS in simplified model at $t = 0$
C_U	$mole\ m^{-3}$	Molar concentration of other products in simplified model at $t = t$
$C_{U,0}$	$mole\ m^{-3}$	Molar concentration of other products in simplified model at $t = 0$
E_i	$kg\ s^{-1}$	Transport rate of DP_i from the reacting particle to cold glass wall at $t = t$
f_{C_6}	-	Fraction of C_6 sugars in biomass
$f_{DP_1,exp}$	-	Experimentally obtained mass fraction of DP_1 in C_6aS
$f_{DP_1,cal,t=\infty}$	-	Calculated mass fraction of DP_1 in C_6aS at $t = \infty$
K_i	$kg\ s^{-1}$	Overall depolymerisation rate of DP_i at $t = t$
k_1, k_3	s^{-1}	First order rate constants reactions in simplified model
k_2	s^{-1}	First order rate constants of transport in simplified model
$k_{T,i}$	s^{-1}	Evaporation/sublimation/ejection rate constant of DP_i
k_K	s^{-1}	First order depolymerisation rate constant
k_U	s^{-1}	First order decomposition rate constant
k_V	s^{-1}	First order vapour phase depolymerisation rate constant
$m_{DP_i}^P$	-	Mass fraction of DP_i at the reacting particle at $t = t$
$m_{DP_i,t=0}^P$	-	Mass fraction of DP_i at the reacting particle at $t = 0$
$m_{DP_i}^O$	-	Mass fraction of DP_i at the cold glass wall at $t = t$
$m_{DP_i,t=0}^O$	-	Mass fraction of DP_i at cold glass wall at $t = 0$
$m_{DP_i,t=\infty}^O$	-	Mass fraction of DP_i at cold glass wall at $t = \infty$
$m_{DP_i}^V$	-	Mass fraction of DP_i in the hot vapour phase at $t = t$
$m_{DP_i,exp}^V$	-	Experimentally obtained mass fraction of DP_i in the hot vapour phase
$m_{DP_i,cal,t=\infty}^V$	-	Mass fraction of DP_i in the hot vapour phase at $t = \infty$
U_i	$kg\ s^{-1}$	Overall decomposition rate of DP_i at $t = t$

$Y_{C_6aS,exp}$	$kg\ kg^{-1}$	Experimentally obtained yield of C ₆ aS
$Y_{C_6aS,cal,t=\infty}$	$kg\ kg^{-1}$	Calculated yield of C ₆ aS at $t = \infty$

Superscripts

c	Consumption
f	Formation

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List of publications

Publications

- [1] R.J.M. Westerhof, S.R.G. Oudenhoven, **P.S. Marathe**, M. Engelen, M. Garcia-Perez, Z. Wang, S.R.A. Kersten, The interplay between chemistry and heat/mass transfer during the fast pyrolysis of cellulose, *Reaction Chemistry & Engineering* 1 (2016) 555-566, DOI: 10.1039/C6RE00100A
- [2] **P.S. Marathe**, S.R.G. Oudenhoven, P.W. Heerspink, S.R.A. Kersten, R.J.M. Westerhof, Fast pyrolysis of cellulose in vacuum: The effect of potassium salts on the primary reactions, *Chem. Eng. J. (Lausanne)* 329 (2017) 187-197, DOI: 10.1016/j.cej.2017.05.134
- [3] **P.S. Marathe**, R.J.M. Westerhof, S.R.A. Kersten, Fast pyrolysis of lignins with different molecular weight: Experiments and modelling, *Appl. Energy* 236 (2019) 1125-1137, DOI: 10.1016/j.apenergy.2018.12.058
- [4] **P.S. Marathe**, A. Juan, X. Hu, R.J.M. Westerhof, S.R.A. Kersten, Evaluating quantitative determination of levoglucosan and hydroxyacetaldehyde in bio-oils by gas and liquid chromatography, *J. Anal. Appl. Pyrolysis* (2019), DOI: 10.1016/j.jaap.2019.02.010
- [5] M. Pala, **P.S. Marathe**, X. Hu, F. Ronsse, W. Prins, S.R.A. Kersten, J.P. Lange, R.J.M. Westerhof, Recycling of product gas does not affect fast pyrolysis oil yield and composition (*Manuscript submitted*)
- [6] **P.S. Marathe**, R.J.M. Westerhof, S.R.A. Kersten, Effect of pressure on the fast pyrolysis of acid-leached bagasse and pine wood: experiments and modelling (*Manuscript in preparation*)

Poster presentation

- [1] **P.S. Marathe**, S.R.G. Oudenhoven, R.J.M. Westerhof, S.R.A. Kersten, Effect of Alkali and Alkaline Earth Metals (AAEMs) on Cellulose Pyrolysis, European Biomass Conference and Exhibition 2016, Amsterdam, The Netherlands
- [2] **P.S. Marathe**, T.C. Derks, R.J.M. Westerhof, S.R.A. Kersten, Effect of Pressure on Fast Pyrolysis of Untreated and Acid Leached Bagasse, National Process Technology Symposium 2018, Enschede, The Netherlands

Oral presentation

- [1] **P.S. Marathe**, A. Juan, R.J.M. Westerhof, S.R.A. Kersten, The interplay between chemistry and heat/mass transfer during pyrolysis of lignin, Pyro2018, Kyoto, Japan

About the author

Pushkar was born on 16th August 1988 in Mumbai, India, where he attended secondary school. After the conclusion of schooling in 2004, he went to the Bharati Vidyapeeth Institute of Technology (BVIT), New Mumbai and obtained a Diploma in Chemical Engineering in 2007.

Pushkar obtained Bachelors in Chemical Engineering in 2010 from the University of Mumbai. During bachelor studies, he did an internship at the Indian Institute of Technology, Bombay (IITB) on the topic 'Reactive Distillation' under the guidance of Prof. Dr S.M. Mahajani.

He worked as a Research Assistant at the Institute of Chemical Technology, Matunga (ICT) on the research project titled - Novel solvents for CO₂ capture from flue gas, under the guidance of Assoc. Prof. Dr P.D. Vaidya for 9 months (January to September 2011).

Pushkar started his master's studies in 2011 at the Technical University of Dortmund, Germany (TUD). During his master's studies, he had an opportunity to work as a Process Intern at the Electrolysis Division of the ThyssenKrupp Uhde GmbH, Dortmund and Bayer MaterialScience, Leverkusen. The M.Sc. was concluded in October 2014 with the thesis titled - Investigations on the effectiveness of latent heat storage by hybrid adsorbent-PCM particles, under the guidance of Prof. Dr D.W. Agar.

Since January 2015 he started working as a PhD student at the University of Twente on the NWO Research project titled – Fundamentals of Fast Pyrolysis, under the guidance of Prof. Dr S.R.A. Kersten and Dr R.J.M. Westerhof. The work performed during his PhD is written down in this thesis.

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