

# **Thermochemical conversions of biomass residues to valuable fuels, chemicals and materials**

**Elmeri Pienihäkkinen**



**Aalto University**



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# **Thermochemical conversions of biomass residues to valuable fuels, chemicals and materials**

Elmeri Pienihäkkinen

A doctoral thesis completed for the degree of Doctor of Science to be defended, with the permission of the Aalto University School of School of Chemical Engineering, at a public examination held at the lecture hall Ke2 of the school on 10<sup>th</sup> of April 2026 at 12:00.

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Aalto University publication series

Doctoral Theses 85/2026

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ISBN 978-952-64-3088-1 (soft cover)

ISBN 978-952-64-3087-4 (PDF)

ISSN 1799-4934 (printed)

ISSN 1799-4942 (PDF)

<https://urn.fi/URN:ISBN:978-952-64-3087-4>

Punamusta Oy

2026

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**Author** Elmeri Pienihäkkinen

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**Name of the doctoral thesis** Thermochemical conversions of biomass residues to valuable fuels, chemicals and materials

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**Article-based thesis**

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**Number of pages** 93

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**Keywords** fast pyrolysis, biomass, residues, waste, thermochemical conversion

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As the pressure to reduce greenhouse gas emission grows, more interest towards sustainable bio-fuels and bio-chemicals has emerged. Fast pyrolysis is a robust liquefaction technique which can be used to turn biogenic solid wastes and residues into liquid intermediates (bio-oils). This is advantageous as liquids are much more easily utilizable in various chemical processes compared to solid waste. Ideally, sustainable non-edible and renewable lignocellulosic waste streams or industrial residues are used as feedstock for liquefaction to maximize the emission reductions, but the qualities of such feedstocks may be problematic from the scope of the processing. In this dissertation, fast pyrolysis of various lignocellulosic residues was studied in industrially relevant fluidized bed fast pyrolysis units. Target was to better understand the behavior of different residual feedstocks in the production of the fast pyrolysis bio-oils (FPBO), study the effect of feedstock pretreatment with low quality feeds and to improve understanding of the potential of FPBO and its further valorization into chemicals and materials. Most studied applications for FPBO are upgrading routes into transportation fuels but the focus on this thesis is in FPBO gasification to syngas and fractionation into chemicals, and materials.

Pretreatment of the lignocellulosic feeds was found to have both positive and negative effects depending on the starting feedstock and pretreatment severity. Alkali removal via mild acid leaching was found to significantly increase the organic bio-oil yield with high-alkali feedstocks. However, feeds, where alkali content was reduced below detection limits, were difficult to pyrolyze due to the bed agglomeration. The absence of alkali metals which are active in pyrolysis reactions may result in operational problems, while too large content of these alkali metals results in suboptimal bio-oil yield. Similar operational difficulties were observed also when fast pyrolysis of different hydrolysis lignins, by-products from the lignocellulosic ethanol production process, were studied. Hydrolysis lignin has gone rather severe pretreatment where a part of hemicelluloses and cellulose are removed from the feedstock prior to fast pyrolysis. The carbohydrate content of hydrolysis lignin had a clear correlation to its processability. More challenges were observed with lignin feedstocks having lower carbohydrate content. Increased amount of lignin caused problems through bed agglomeration. Additionally, rapid secondary reactions in the vapor phase resulted in deposit formation and pressure buildup in product gas lines, underlining the aspect that technical feasibility and readiness of lignin pyrolysis is still immature.

Regarding the FPBO valorization, the pathways studied in this dissertation were FPBO gasification into syngas and FPBO fractionation with subsequent use of obtained fractions in the phenolic resin synthesis. Results showed that the combination of fast pyrolysis with subsequent FPBO gasification provides a technically feasible and feedstock flexible solution to produce synthesis gas which can be used in the synthesis of fuels or various chemicals. FPBO fractions were also found to be potential substitutes for fossil phenol in phenolic resin production. All the produced resins performed well in dry conditions, but in wet conditions resins with the highest replacement ratio of 50 wt% had somewhat reduced strength. Although technical potential is promising, better understanding of techno-economic aspects of these routes will be needed.



# Acknowledgements

Experimental work for this dissertation was carried out at VTT Technical Research Centre of Finland Ltd. during 2019 – 2023. Work was carried out partly in EU funded projects, including 4REFINERY, BECOOL and ICEBERG, and partly in co-operation with industrial partners.

I want to thank my advisors, Anja Oasmaa and Taina Ohra-aho for all the help, support and advises given. I also want to express my gratitude towards colleague Christian Lindfors, who has supported and mentored me during my time at VTT, all the way from beginning when he hired me as a diploma thesis worker in 2018. I am also thankful for the supervising professor Ville Alopaeus for the interest and contribution towards this thesis.

I also want to thank all the technical people at VTT, including Joni Rantala, Pekka Saarimäki, Elina Raineva, Jaana Korhonen, Sirpa Lehtinen and all the others in VTT Bioruukki Pilot Centre. Without the technical and analytical expertise, experiments and research work would not have been possible. I also want to thank all the co-authors involved in the publications. The wide expertise available through international collaboration taught me a lot and made the work more meaningful and publications much more impactful.

Finally, I want to thank my parents from the encouragement to seek my own path, as well as my spouse and two children, for all the patience and support given.

Espoo, 15 October 2025  
Elmeri Otto Matias Pienihäkkinen



# List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their numerals

**I.** Pienihäkkinen, E., Lindfors, C., Ohra-aho, T., Lehtonen, J., Granström, T., Yamamoto, M., & Oasmaa, A. Fast Pyrolysis of Hydrolysis Lignin in Fluidized Bed Reactors. *Energy and Fuels*, 35, 14758–14769. 2021. <https://doi.org/10.1021/acs.energyfuels.1c01719>

**II.** Pienihäkkinen, E., Lindfors, C., Ohra-aho, T. & Oasmaa, A. Improving Fast Pyrolysis Bio-Oil Yield and Quality by Alkali Removal from Feedstock. *Energy and Fuels*, 36, 3654–3664. 2022. <https://doi.org/10.1021/acs.energyfuels.1c04331>

**III.** Pienihäkkinen, E., Leijenhörst, E.J., Wolters, W., Lindfors, C., Lahtinen, J., Ohra-aho, T. & Oasmaa, A. Valorization of Eucalyptus, Giant Reed *Arundo*, Fiber Sorghum, and Sugarcane Bagasse via Fast Pyrolysis and Subsequent Bio-Oil Gasification. *Energy and Fuels*, 36, 12021–12030. 2022. <https://doi.org/10.1021/acs.energyfuels.2c01968>

**IV.** Pienihäkkinen, E., Stamatopoulos, I., Krassa, P., Svensson, I., Ohra-aho, T., Lindfors, C. & Oasmaa, A. Production of pyrolytic lignin for the phenolic resin synthesis via fast pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 176, 106239. 2023. <https://doi.org/10.1016/j.jaap.2023.106239>



# Author's Contribution

## **Publication I:** Fast Pyrolysis of Hydrolysis Lignin in Fluidized Bed Reactors

E.P. contributed to the planning of the experiments, conducted most of the bench scale experiments, participated into pilot campaign, calculated and interpreted the results. C. L. planned the experiments with participation from T.O., J.L., T.G., M.Y., A.O and E.P. Regarding the manuscript preparation, E.P. wrote the manuscript while C.L., T.O., J.L. and A.O oversaw the work and contributed through commenting and review.

## **Publication II:** Improving Fast Pyrolysis Bio-Oil Yield and Quality by Alkali Removal from Feedstock

E.P. planned the experiments with participation from C.L., T.O. and A.O. In addition, E.P. conducted most of the bench scale experiments, participated into pilot campaign, calculated and interpreted the results and wrote the manuscript. C.L., T.O. and A.O, oversaw the work and contributed to the manuscript writing and review.

## **Publication III:** Valorization of Eucalyptus, Giant Reed Arundo, Fiber Sorghum, and Sugarcane Bagasse via Fast Pyrolysis and Subsequent Bio-Oil Gasification

E.P. contributed to the planning of the pyrolysis experiments together with C.L. and A.O., conducted most of the bench scale pyrolysis experiments with J.L., calculated and interpreted the results and wrote the manuscript together with E.J.L., who contributed to the bio-oil gasification. Bio-oil gasification experiment were planned and carried out by E.J.L. and W.W. Regarding the manuscript preparation, C.L., T.O. and A.O. commented and reviewed the manuscript.

## **Publication IV:** Production of pyrolytic lignin for the phenolic resin synthesis via fast pyrolysis

E.P. planned the pyrolysis and fractionation experiments together with C.L. and T.O., participated into pilot campaign and carried out the fractionation experiments. E.P. wrote the manuscript together with I.St. and P.K, who planned and carried out the resin synthesis experiments and with I.Sv., who planned and carried out the testing of the resins. A.O. oversaw the work and commented and reviewed the manuscript.



# List of Abbreviations and Symbols

AAEM	alkali and alkaline earth metal
AL	acid leached
BFB	bubbling fluidized bed
CFB	circulating fluidized bed
CAN	carboxylic acid number
CCR	Conradson carbon residue
DCM	dichloromethane
FPBO	fast pyrolysis bio-oil
sFPBO	stabilized fast pyrolysis bio-oil
FCC	fluid catalytic cracker
HMW	high molecular weight
HHV	higher heating value
LMW	low molecular weight
LHV	lower heating value
MCR	micro carbon residue
PF	phenol-formaldehyde
TAN	total acid number
TGA	thermogravimetric analyser
WS	water soluble
WIS	water insoluble



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# 1. Introduction

Actions to mitigate climate change require a move away from fossil fuels in energy, transportation, and chemical production. This increasing pressure to reduce greenhouse gas emissions has led to growing interest toward sustainable biofuels, bio-based chemicals and materials. One of the major challenges for this development is that current oil refining processes for fossil feedstocks have been honed over for decades and have been developed to be extremely energy- and feedstock-efficient. These processes, which effectively use the various fractions of crude oil in high-volume products such as transportation fuels, as well as in numerous lower-volume but higher value-added chemical applications, are also extremely cost effective, which makes the competition for bio-based alternatives very difficult.

Furthermore, fossil oils are generally more homogenous compared to their bio-based alternatives and consist largely of relatively simple hydrocarbons, while bio-based feedstocks have typically higher heteroatom content and chemical complexity. This is added challenge when bio-based hydrocarbons are targeted, but various chemical functionalities present in these bio-based feeds opens also possibilities to utilize them in wider range of various chemical syntheses. It is also important to understand that not only fuels, but majority of organic chemicals and polymers are made from fossil crude oil, and a complete phase-out of crude oil will require the development of alternative products or production methods for these products as well.

Despite these challenges, there is a strong demand for biofuels driven mainly through legislation. In EU, regulations, such as ReFuelEU Aviation and FuelEU Maritime promote the use of renewable and low-carbon fuels in aviation and maritime sectors [1,2]. Similar legislation does not yet exist for the chemical production, but for example, the Chemical Industry Federation of Finland has set a target of a carbon-neutral chemical industry in Finland by 2045 [3]. However, new legislation and financial incentives to utilize bio-based feedstocks are needed to achieve the targeted emission reductions.

Efficient utilization of non-edible lignocellulosic waste streams as feedstock is one of the most promising ways to maximize the emission reductions. [4] These feedstocks are also often cheap which makes them economically lucrative. However, solid lignocellulosic wastes and residues are challenging to utilize as such. Therefore, new primary conversion technologies capable to convert sustainable lignocellulosic wastes and residues into liquid intermediates have awakened interest as these liquid intermediates are potentially more easily utilizable especially

in existing chemical and petrochemical infrastructure. One potential technology for liquefaction is fast pyrolysis, which is a thermochemical conversion technology used to convert lignocellulosics into liquid products. Utilization of wastes is a great way to expand the feedstock pool for fast pyrolysis where rather pure wood, such as saw dust or forest thinnings, is the dominant feedstock at the industrial scale. However, low-quality waste streams with high concentrations of impurities are more problematic and challenging from the perspective of pyrolysis. Impurities and changing feedstock composition can have various effects affecting the fast pyrolysis process and quality of the produced fast pyrolysis bio-oils (FPBO). Therefore, better understanding of residue feedstock behavior and limitations during fast pyrolysis are needed.

## 1.1 Aim and scope of the research

The aim of the research was to i) improve the understanding of the behavior of waste and residual feedstocks and effect of pretreatment, ii) identify limitations of fast pyrolysis of these challenging feedstocks, and iii) develop valorization routes for produced fast pyrolysis bio-oils. Four peer reviewed publications are included in this dissertation. Targets of the publications are summarized below, and scope of research work and context of the publications are illustrated in Figure 1. Furthermore, key research questions and scientific contributions are listed in the Table 1.

Lignin rich residues are abundant industrial by-products which are currently combusted to heat and power and underutilized in the material and chemical applications. Therefore, **Publication I** is focused on the pyrolysis of hydrolysis lignin in the bench and pilot-scale units. Target was to assess the yield and quality of the produced FPBO and to overcome operational difficulties typical for lignin rich feedstocks. Fast pyrolysis of hydrolysis lignin was scaled-up to industrially relevant pilot scale unit, which made possible to assess the technical feasibility and readiness in longer term operation. There was no previously published research on the fast pyrolysis of hydrolysis lignin in pilot scale fluidized bed reactors.

Secondly, with forestry and agricultural residues, typical issue is their high inorganic content which reduces the FPBO yield and decreases its quality. Therefore, the key target in **Publication II** was to study the effect of inorganic removal, especially alkali and alkaline earth metals, prior to fast pyrolysis in bench and pilot-scale fast pyrolysis units. Effects of pretreatment to feedstock processability and to FPBO yield and quality were assessed. After bench scale experiments, pretreatment was scaled up to industrially relevant pilot scale unit, with the target to replicate the small-scale results and to assess the technical feasibility of the process with pretreated feed. To authors knowledge, pretreatment and fast pyrolysis was not carried out previously on such large scale in fluidized bed reactors.

Furthermore, bench scale pyrolysis of agricultural and forestry residues was studied in **Publication III** and the produced FPBOs were gasified into syngas which could be potentially used as feedstock for renewable chemicals. Target

was to assess suitability of selected residues in FPBO production and to assess the effect of varying FPBO quality into syngas yield and composition. Systemic study with same gasifier and with different FPBOs was lacking from the literature.

In the **Publication IV**, fast pyrolysis of waste wood was studied in the pilot scale unit and produced FPBO was valorized through fractionation and subsequent resin synthesis. Target was to utilize cheap waste wood and simple solvent-free water fractionation to produce FPBO fractions suitable for resins synthesis, which was not done previously in scientific literature.

**Table 1.** Key research questions of the publications.

Publication	Key research questions
I	<ul style="list-style-type: none"> <li>- How severe operational issues are faced in different type of fluidized bed reactors with hydrolysis lignin feedstock and how these issues can be tackled?</li> <li>- What is the yield and quality of FPBO from varying quality hydrolysis lignin?</li> </ul>
II	<ul style="list-style-type: none"> <li>- How much the pretreatment improves the FPBO yield from residue feeds with high ash contents?</li> <li>- How the FPBO quality changes due to the pretreatment?</li> <li>- How scalable the results are in longer term pilot scale operation?</li> </ul>
III	<ul style="list-style-type: none"> <li>- How comparable is the FPBO quality from various residual feeds and does the gasification performance of FPBOs change with the feedstock?</li> </ul>
IV	<ul style="list-style-type: none"> <li>- How the waste wood behaves in FPBO production in pilot scale?</li> <li>- How the fractionated pyrolytic lignin from waste wood derived FPBO performs in phenolic resins synthesis as phenol replacement?</li> </ul>
Publication	Scientific contribution
I	<ul style="list-style-type: none"> <li>- Mass balance and product quality data from pilot-scale circulating fluidized bed and bench-scale bubbling fluidized bed reactors in hydrolysis lignin fast pyrolysis.</li> <li>- Mass balance and product quality data from experiments with ethanol and steam as process additives in hydrolysis lignin fast pyrolysis.</li> <li>- Effect of hydrolysis lignin carbohydrate content to feedstock processability and to yield and quality of FPBO.</li> </ul>
II	<ul style="list-style-type: none"> <li>- Data from alkali and alkaline earth metal removal from lignocellulosic residues through nitric acid washing.</li> <li>- Bench- and pilot-scale mass balance data to highlight the benefit of increased FPBO yield when alkali and alkaline earth metal removal is carried out with high ash feedstocks.</li> <li>- Highlighting the negative effects of washing with low-ash feedstocks where removal of alkali and alkaline earth metals can increase the problems with processability through agglomeration issues.</li> <li>- Bench- and pilot-scale data to give attention to changes observed in FPBO and product gas quality.</li> </ul>
III	<ul style="list-style-type: none"> <li>- Bench-scale fast pyrolysis yield and product quality data from lignocellulosic residues.</li> <li>- Data from FPBO gasification with FPBOs from different origins.</li> <li>- Demonstration of feedstock flexibility of FPBO gasification by testing FPBOs from different origins in entrained flow gasifier.</li> </ul>
IV	<ul style="list-style-type: none"> <li>- Demonstration of suitability of demolition wood as fast pyrolysis feedstock in pilot-scale fast pyrolysis.</li> <li>- Data from FPBO quality and Demonstration of waste wood derived FPBO suitability in fractionation and subsequent phenolic resin synthesis.</li> <li>- Demonstration of produced resins in adhesive application.</li> </ul>

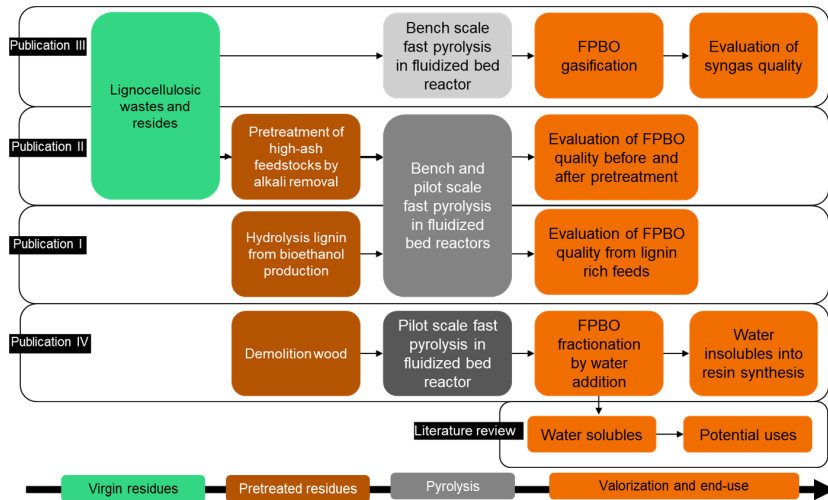


Figure 1. Illustration of the thesis structure.

## 1.2 Dissertation structure

Following the introduction in Chapter 1, basic principles of fast pyrolysis of biomass are reviewed and discussed in Chapter 2. In Chapter 3 selected valorization routes developed for the fast pyrolysis bio-oils are reviewed and discussed. Furthermore, sustainable feedstocks for fast pyrolysis are discussed, and the typical challenges and impurities present in waste and residue-based feedstocks are reviewed. In Chapter 4, materials and methods used in the experimental work are described. In Chapter 5, major results from the Publications I-IV will be summarized. Results include the feedstocks pretreatment results, fast pyrolysis experiments and product analyses, as well as fast pyrolysis bio-oil valorization experiments. Chapter 6 includes the concluding remarks of the dissertation work.

## 2. Fast pyrolysis of biomass

### 2.1 Principles of fast pyrolysis of biomass

In general, pyrolysis refers to thermal degradation of any given feed material in the absence of oxygen. When biomass is subjected to these conditions, it goes through thermal endothermic decomposition into three products: (1) solid char, (2) condensable product consisting of various organic components and water, and (3) permanent gases such as carbon monoxide, carbon dioxide, light hydrocarbons and hydrogen. In the case of fast pyrolysis or flash pyrolysis, high heating rates ( $> 500\text{--}1000\text{ }^{\circ}\text{C/s}$ ) and short vapor phase residence times ( $< 2\text{ s}$ ) are used to maximize the yield of condensable product [5,6]. Condensable product is often referred as bio-oil, pyrolysis oil, or pyrolysis liquid. Here, term fast pyrolysis bio-oil (FPBO) will be used. In addition to fast pyrolysis, different pyrolysis processes, such as slow pyrolysis to optimize the char yield by slower heating rates, exists [7], but focus on this dissertation is on the fast pyrolysis process. In this chapter basic principles of fast pyrolysis of biomass will be discussed.

#### 2.1.1 Process parameters affecting FPBO yield

Thermal fast pyrolysis can be classified as thermochemical liquefaction technique as the target product is liquid FPBO. However, like in all pyrolysis processes, three products are obtained also in the fast pyrolysis process: (1) char, (2) liquid from condensable vapors and aerosols, i.e. FPBO and (3) non-condensable gases. The product distribution can be altered by changing the process conditions. In general, lower process temperatures and longer residence times favor the production of char, high temperatures and longer residence times increase biomass conversion to gas, and intermediate temperatures and short vapor residence time are optimum for producing FPBO. [8]

##### *Effect of temperature and heating rate*

To maximise the FPBO production, critical step is to heat the feedstock particles rapidly into the optimal reaction temperature, which with lignocellulosic feeds is usually between  $450\text{ -- }500\text{ }^{\circ}\text{C}$ . High heating rate minimizes the char formation typical for lower processing temperature. For example, dehydration and cross-linking reactions occurring between  $250\text{ -- }350\text{ }^{\circ}\text{C}$  initiate char formation while cracking reactions responsible for volatile formation become more dominant at higher temperature. For these reasons, it is important to control the res-

idence time of solids at each temperature range [9]. Higher process temperature ( $> 500$  °C), on the other hand, can result into overcracking and extensive production of gases at the expense of FPBO yield [8].

To obtain high heating rates, feedstock particle size needs to be sufficiently small to minimize the heat transfer limitations within the particles. Additionally, the volatile species released within the feedstock particles need to travel through the shell of the char formed around the feedstock particle and this shell can be thicker with larger particles. Char can catalyze the dehydration of some primary pyrolysis products which furthermore can increase the water content of the produced FPBO [10]. For the same reason, it is important to rapidly separate the char from gases and vapors to avoid secondary char-catalyzed reactions in vapor space.

To achieve high heating rates needed in biomass fast pyrolysis, either fluidized bed or rotating cone reactors are used in the commercial scale [8]. Regarding the fluidized beds, one common configuration is circulating fluidized bed reactor where riser reactor is typically integrated with bubbling-bed combustor. This type of technology has been developed by Valmet and Ensyn [11]. In this configuration, the sand is heated in the combustor and circulated to riser to provide the heat needed in the endothermic pyrolysis reactions. Pyrolysis takes place in the riser where solid material is flowing upwards due to high fluidization gas flow rate. After the reactor, solids are separated from gas stream by cyclones and returned to combustor where the char is burned and bed material regenerated and reheated. Another commercial reactor type is rotating cone and this technology has been developed by BTG-Bioliquids [11]. In this reactor type, similar heat carrier solids circulation is used, but the difference is that solids are separated from the vapors already in the cone shaped reactor. No high velocity carrier gas to fluidize the bed is needed and thus the separation of product vapors from solids is simpler and easier. Char and non-condensable gases formed in the reactor can be burned in similar manner as in circulating bed reactor to provide the heat for the process [8].

#### *Formation of liquid intermediates and presence of aerosols*

It is important to understand that pyrolysis products are not fully in gaseous form during or after the pyrolysis reactions as molecules in various molecular sizes and boiling points are produced in cracking of the lignocellulosic macromolecules. Therefore, solid, liquid and gaseous pyrolysis products, formed in the primary and secondary cracking reactions, are present throughout the process. In addition to char, vapor and gases, significant amounts of persistent liquid aerosol droplets are formed during pyrolysis reactions [12].

One suggested mechanism for aerosol formation is the formation through a vapor-bubble collapse mechanism. This mechanism suggests that the aerosol droplets are formed from the molten liquid intermediate during thermal decomposition. Within the liquid intermediate, bubbles are formed, and when the bubbles are subsequently collapsed, an extending liquid jet is formed. This liquid jet eventually develops into a liquid aerosol droplet. [13–16] Especially lignin is prone to melting and studies indicate that lignin can be in completely fluid state already between 200 and 225 °C before mass loss even starts. Fluid lignin can

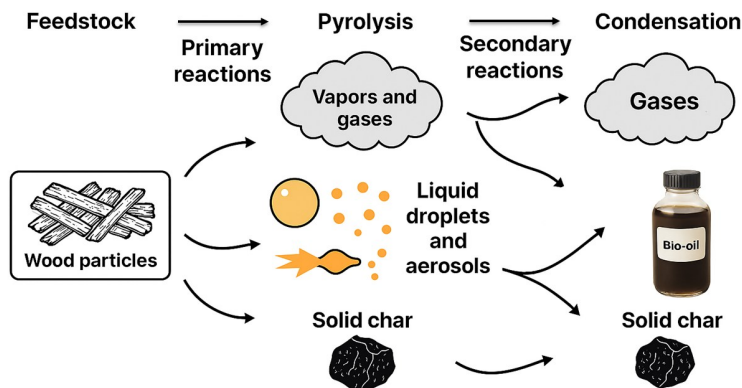
bubble and eject aerosol. Hemicellulose and cellulose on the other hand start to lose mass before full fluidity due to thermal instability and are less prone for bubbling. However, in case of biomass particles, where these components are present at the same time together with biomass ash, phenomena is more complex as interaction between the biomass components are evident. For example bubbling of lignin can facilitate ejection of aerosols containing both lignin and polysaccharide derived pyrolysis products although the polysaccharides are not that prone for melting and bubbling. [17–19]

Another proposed mechanism for aerosol formation is based on film-aerosol generation as a result of shear thinning of bubbles. This mechanism has been reported to produce smaller aerosol droplets than the vapor-bubble collapse mechanism. [20] Additionally, so called secondary aerosols can also be formed through condensation of pyrolysis vapors [21].

Presence of aerosols is important as they can increase the fouling and deposit formation in fluidized bed but especially in the products gas lines after the reactor, as aerosols can collide and attach to hot pipe surfaces forming eventually carbon deposits on pipe surfaces. Aerosols can also be challenging to recover after condensation. They have aerodynamics resembling the carrier gas and, therefore, easily escape collection equipment, such as condensers, scrubbers and spray towers frequently used in the collection of FPBO [12].

#### *Effect of residence time*

Another important parameter in the fast pyrolysis is the residence time of vapors in the process temperature. Once the vapors and aerosols are formed by the primary pyrolysis reactions of the lignocellulosic macromolecules, short vapor phase residence time is beneficial to reduce secondary pyrolysis reactions which decrease the FPBO yield. These secondary reactions can increase yields of char through condensation and polymerization reactions, and yield of gases through secondary cracking reactions. Therefore, rapid quenching of the pyrolysis vapors after the primary reactions is essential to maximize the FPBO yield and reduce secondary cracking before condensation of the vapors [9]. As mentioned earlier, it is also important to rapidly separate the char from gases and vapors to avoid secondary char-catalyzed reactions in vapor space.

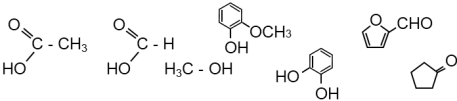
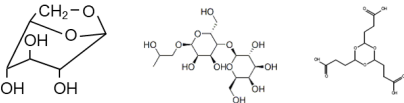

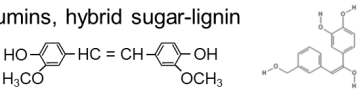


**Figure 2.** Schematic illustration of the pyrolysis reactions.

### 2.1.2 FPBO composition

Chemical composition of FPBOs is extremely complex and they include hundreds of different organics components originating from the lignocellulosic macromolecules. FPBO can be described as emulsion of aqueous solution of sugars and other small molecular weight oxygenates, and degraded pyrolytic lignin fragments. For further classification, the FPBO constituents can be generally divided into two major groups. The first group is the water solubles, which include polar oxygenated components originating mainly from the degradation reactions of polysaccharides. These components include acids, alcohols, aldehydes, ketones, furans, pyrans and mono- and oligomeric anhydrosugars. Additionally, water soluble phenols originating from lignin can be present. The second major component group is the water insolubles, which consists mainly of lignin derived oligomeric and polymeric matter, but also the water insoluble extractives such as resin acids, fatty acids, and hydroxy acids. In addition to components above, FPBO includes significant amounts of water, and low concentrations of inorganic solids and ash. [22–26]

**Table 2.** Typical FPBO constituents [22–26].

<b>Water solubles</b>		
Ether soluble light volatiles (acids, alcohols, aldehydes, ketones, furans, pyrans)	$\text{HO}-\text{C}(=\text{O})-\text{CH}_3$ $\text{HO}-\text{C}(=\text{O})-\text{H}$ $\text{H}_3\text{C}-\text{OH}$ 	
Sugar-type ether-insoluble components (mono- and oligosugars)		
<b>Water insolubles</b>		
Extractives (fatty acids, sterols, etc.)	$\text{CH}_3 - (\text{CH}_2)_n - \text{CO}_2\text{H}$ $n = 10-30$ $\text{HOCH}_2 - (\text{CH}_2)_n - \text{CO}_2\text{H}$ $n = 10-28$	
Dichloromethane soluble components	Phenolics Humins, hybrid sugar-lignin oligomers 	
Dichloromethane insoluble components	Heavy lignin-derived molecules, residual solids, highly dehydrated sugars	

Due to the various oxygenated and polar compounds present, FPBOs are immiscible with hydrocarbons. Reactive chemical functionalities of the FPBOs also increases problems with FPBO stability. FPBOs are not stable at room temperature and will go through aging reactions producing water and higher molecular weight components. Aging reactions are fastest within first week after liquid production and diminish over time. Due to this instability, FPBOs do not sustain heating without extensive aging and coking reactions. Additionally, highly oxy-

generated compounds and water reduce the heating value of FPBO when compared to hydrocarbon fuels. Volumetric energy density of the FPBOs is, however, higher when comparison is made with fast pyrolysis feedstock (e.g. wood, or straw) which makes the oils transport more feasible than the transportation of the initial lignocellulosic feedstocks. [27]

When the different fractions of the FPBO are in balance, FPBO will stay in one phase. However, phase stability can be easily disturbed. For example, if the FPBO water content is high enough, it will lead to phase separation into aqueous and organic fractions. Phase separation can be, for example, caused by the high feedstock moisture content. As the moisture from the feedstock ends up into the FPBO, feedstock moisture content does not typically exceed 10 wt% to avoid unnecessary high water content and possible phase separation of the FPBO. [28–30] Phase separation can also be achieved purposefully by water addition or it can take spontaneously place during the storage due to the aging reactions and water formation disturbing the phase equilibrium [31] Pyrolysis of lignin rich feedstocks can also result in two-phase product due to the large amount of water insoluble components present in the produced FPBO. Some typical properties of FPBOs are presented in Table 3.

**Table 3.** Some typical characteristics and properties of FPBOs [32].

Property	Typical range	Property	Typical range
water	20–30 wt %	HHV	14–19 MJ/kg
solids	<1 wt %	LHV	13–18 MJ/kg
ash	<0.3 wt %	pH	2–3
carbon	50–60 wt % (d.b.)	TAN	70–100 mg KOH/g
hydrogen	7–8 wt % (d.b.)	kinematic viscosity at 40 °C	15–40 mm <sup>2</sup> /s
nitrogen	<0.5 wt % (d.b.)	density at 15 °C	1.11–1.30 kg/dm <sup>3</sup>
oxygen	35–40 wt % (d.b.)	pour point	–9..–36 °C
sulfur	<0.05 wt % (d.b.)	MCR, CCR	17–23 wt %
Na, K, Ca, Mg	<0.06 wt % (d.b.)	flash point	40–110 °C
chlorine	<75 ppm	sustained combustibility	does not sustain combustion

d.b. = dry basis

## 2.2 Sustainable biogenic feedstocks

Assessing the feedstock sustainability is an important aspect when fast pyrolysis feedstocks are considered. All biogenic feedstocks are not automatically sustainable and the feedstock must meet certain sustainability criteria in order to be considered as sustainable for biofuel production. Aspects to be assessed include minimizing the change in land use, carbon accounting, biodiversity protection and social sustainability.

One way to approach this problem is to consider the available legislation in the energy sector. In this context especially within Europe, EU Renewable Energy Directive (RED III) and its Annex 9 are important as the Annex 9 establishes a list of sustainable feedstocks for biofuels, bioliquids, and biomass fuels used in the context of the European Union's renewable energy policy[33].

Annex 9 outlines specific types of feedstocks considered as sustainable. One important stream is agricultural residues, such as straw, husks, or bagasse, which do not require new land to be cultivated. Another important stream is forest residues and wood waste, including residues from forest management (like branches, leaves, and thinnings) that would otherwise go to waste. Also, non-food crops, such as crops not intended for human consumption, for example certain grasses or, dedicated energy crops, can be considered sustainable feedstocks if all the other sustainability criteria is met. Additionally waste oils and fats, such as cooking oils and animal fats, which can be used in biodiesel production, are included in Annex 9. However, food crop use should be avoided and certain feedstocks such as palm oil, has faced restrictions due to high deforestation linked to palm oil production.

From the perspective of fast pyrolysis, lignocellulosic materials are the most relevant feedstocks. Especially forestry residues, waste wood and agricultural residues are feedstocks that are abundantly available, currently underutilized and therefore possess potential to be valorized. Additionally, energy crops and other non-food crops can be lucrative feedstock, but it is important to assess that all the other sustainability criteria are fulfilled.

### 2.3 Challenges with residue-based feedstocks

Three major components of lignocellulosic biomasses are cellulose, hemicelluloses and lignin. In addition, other polymeric matter such as pectin, starch and proteins, as well as extractives and inorganic ash forming elements are present in the biomasses. Content of these can vary quite a lot depending on the botanical origin of the biomass. Additionally, contents can vary within the plants. For example softwood stem wood can have lower lignin, extractives and ash when compared to than bark of the same wood. Furthermore, lignin, hemicellulose, extractives and ash composition can be significantly different between different types of feedstocks. [34–36] Typical lignocellulosic compositions are presented in Table 4.

**Table 4.** Typical compositions of certain lignocellulosics.

Feedstock	Cellulose	Hemicellulose	Lignin	Extractive	Proteins / other organics	Inorganics	Reference
Woody feedstocks	40-45	25-35	20-30	2-5	<0.5 <sup>c</sup>	0.1 – 5	[36]
Non-woody feedstocks	30-45	20-35	10-25	5-15	5-10 <sup>c</sup>	0.5-10	[36]
Hard wood	40-45	25-35	20-30	3-4	~1 <sup>d</sup>	<0.5	[37]
Bark <sup>a</sup>	20-30	10-15	10-25	5-20	5-20 <sup>d</sup>	2-5	[37]
Forest residues <sup>a</sup>	35-40	25-30	20-25	~5	~3 <sup>d</sup>	~1	[37]
Hard wood <sup>b</sup>	43-47	25-35	16-24	2-8	n.r.	n.r.	[35]
Soft wood <sup>b</sup>	40-44	25-29	25-31	1-5	n.r.	n.r.	[35]
Bagasse <sup>b</sup>	40	30	20	10	n.r.	n.r.	[35]
Wheat straw <sup>b</sup>	30	50	15	5	n.r.	n.r.	[35]

a = depends greatly on the wood species, b = ash-free basis, c = proteins, d = other organics, n.r.= not reported

In this chapter, the focus is on the typical challenges with residue-based feedstocks which are related to impurities and lignin content of the feedstocks during pyrolysis. Typical inorganic impurities present in lignocellulosics and their effects in pyrolysis will be discussed in section 2.3.1., impurity characteristics for waste wood fraction are discussed in section 2.3.2, and finally, fast pyrolysis of lignin rich feedstock will be discussed in section 2.3.3.

### 2.3.1 Inorganic impurities and their effects in pyrolysis

One of the most important quality criteria for fast pyrolysis feedstock is the feedstock ash content. In biomasses, inorganic ash-forming elements include alkali and alkaline earth metals, transition and post-transition metals, as well as non-metals. Many of these elements are nutrients for the plants and therefore essential or beneficial for plant growth [38]. In fast pyrolysis, low-ash feeds are considered to be higher quality, due to the fact that increasing ash content can decrease the bio-oil yield [31,39], change the chemical composition of bio-oil [40], deactivate catalysts in catalytic pyrolysis [41] and increase the quantity of inorganic impurities in bio-oil [42]. However, when suitability of feedstock to fast pyrolysis are evaluated the ash composition is more important than the total ash content. Inorganic elements in biomasses are very versatile and certain inorganics play more significant role than others during the pyrolysis.

#### *Inorganics in lignocellulosics*

The most abundant inorganics in biomasses include elements such as Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn, and Ti [43], but origin of the elements can vary a lot. For example, natural inorganics are originating from the soil and are often essential minerals needed by the plants. These compounds can be formed within the biomass through plants own metabolism, or they can be formed outside the biomass and taken inside for example through water suspensions. Anthropogenic inorganics, on the other hand, are introduced to plants during harvesting, handling and processing. For example, fine sand particles can be attached to plant surfaces during processing [44].

Ash-forming elements contribute typically 1 - 10 % to biomass on a dry mass basis [36]. However, quantity and composition are highly dependent on the botanical origin of the feedstock, and high growing speed of the plant correlates with higher inorganic content. Furthermore, environmental conditions (site, climate, weather, soil) play a significant role in the concentration of inorganics as soil salinity and metal content has been proven to correlate with the inorganics content of plants. Additionally, vast precipitations can reduce the ash content and dry seasons can increase it.

Wood from temperate and cold climates can comprise 0.1 - 1 % ash while wood from tropical and subtropical climate with higher growth rates can comprise up to 5 % of ash [34]. Furthermore, agro-residues can comprise up to 20 % of ash in worst cases [45]. Within trees, there can be also variation in parts of the tree. Ash content is usually the highest in biologically active sections of three where nutrients are actively needed. For example, the fastest growing parts, such as

needles and leaves have higher ash content compared to bark, branches, roots and stem wood [35,46].

### *Inorganics during pyrolysis*

Most important impurities are alkali and alkaline earth metals (AAEM), K, Na, Ca and Mg, as these elements are abundant in lignocellulosic feeds and they possess catalytical activity during pyrolysis [47,48]. Si is another abundant element especially in straws, but from the scope of fast pyrolysis, it is considered to be inert material and therefore not as significant.

Patwardhan et al. [49] studied the effect of AAEM salts in pyrolysis of pure cellulose. All inorganic additives increased the formation of char and small molecular weight compounds such as glycoaldehyde, formic acid and acetol, with the expense of levoglucosan yield. Low dosages had already significant effect and ash content as low as 0.5 wt% changed the product distribution. K had the largest effect followed by Na to the levoglucosan yield. The effects of Ca and Mg were milder in lower salt concentrations, but with higher dosages differences to other cations were diminished. Authors postulated that inorganic cations can reduce the activation energy of competitive reactions from reactive cellulose intermediate and drive the reactions away from levoglucosan formation. Decreasing temperature was found to reduce the above-mentioned effects.

The effects of cation additives to pure hemicellulose degradation seem to be similar as with cellulose. Char and gas yields increase when cations are present. On the other hand, formation of small molecular weight components decreases, probably due to their further degradation to gases [50]. In the case of pure lignin, no significant changes in primary product distribution were observed when samples were impregnated with inorganics [51]. However, Oasmaa et al. [30] reported that lignin was cracked more with high ash feedstocks and produced bio-oil included less HMW lignin.

Furthermore, studies of de-ashed lignocellulosic feedstocks have shown similar results. Stefanidis et al. [40] and Mourant et al. [52], who compared the chemical composition of bio-oils from original feeds to de-ashed feeds reported that de-ashing increased the sugar concentrations of the FPBOs significantly. Additionally, concentrations of carbonyl compounds, such as furans and ketones, were increased in FPBOs by feedstock de-ashing, which indicates that cations can catalyze the homolysis of pyranose rings to carbonyl compounds in the expense of anhydrosugar formation [40]. Furthermore, de-ashing resulted in lower concentrations of phenolic compounds in FPBO, indicating that ash components indeed catalyze also the cracking of lignin. Especially calcium concentration was concluded to be significant in lignin cracking reactions [40]. Mourant et al. [52] reported that drastic changes in FPBO sugar compositions occurred already in low AAEM concentration and the most significant changes were observed when AAEM content increased from 0 to 0.2 w-%. On the other hand, increased concentration of phenolic compounds followed more linearly the increasing AAEM content. These results indicate that different elements are active in different reactions. Thus, the concentrations of inorganic elements are much more important than the total ash content of feedstock.

In addition to the catalytic effects discussed above, high ash content of feedstock typically increases also the inorganic content of produced FPBO. This can be an issue as many of the inorganics can be catalyst poisons if the FPBOs are further catalytically upgraded. [53]. Leijenhörst et al. (2016) reported that although AAEMs were predominantly retained in char, significant amount was also transferred into FPBO. Transfer rates of AAEMs were not equal. Larger portion of potassium and sodium compared to calcium and magnesium transferred into FPBO. Different solubilities of AAEM salts into FPBO can also affect on this. The average transfer rate of potassium and sodium was 8 % and with calcium and magnesium 2 % [42].

#### *Removal methods for inorganic impurities*

Abovementioned results indicated the catalytic activity of the AAEMs in biomass. These elements have also been problematic in combustion and gasification where they induce ash melting and deposit formation on heat exchange surfaces. Therefore, removal of biomass inorganics prior to thermochemical processes (combustion, gasification and pyrolysis) has been studied already from the 80's and 90's [47,54–56]. Additionally, metal removal from feedstock of pulping industry has been studied [57].

Main methods for removal are based on the water or acid leaching of biomass, which are gentle towards the structure of biomass but still efficient in inorganic removal [58]. These methods are effective as approximately 80 - 90 % of AAEMs in biomasses are in water- or acid-soluble form [45,46,48,52,59]. K and Na are easier to remove with water than Mg and especially Ca [46] due to the higher mobilities and different binding strengths of monovalent  $K^+$  and  $Na^+$ -ions compared to divalent  $Mg^{2+}$  and  $Ca^{2+}$ -ions [60]. Water-soluble inorganics are expected to largely be water-soluble salts and free ions in fluid matter of plant while acid soluble part can include salts and minerals only soluble in acids, but also water-soluble cations trapped in ion exchange matrix of biomass. The ion exchange capacity of plant fiber results from the presence of carboxylic acid groups in polysaccharides, mainly in hemicelluloses and in pectin substance [57]. Therefore, insoluble part of AAEMs can include insoluble salts and species strongly bound to organic molecules of biomass [44,46].

Jensen et al. (1998) reported that pyrolysis of leached wheat straw, with TG-FTIR (Thermogravimetric-Fourier-transform infrared spectroscopy), increased bio-oil formation from 32 to 64 wt% and reduced char formation from 20 to 12 wt%, compared to the pyrolysis of untreated wheat straw. Piskorz et al. (1989) reported significant improvement in FPBO yield and changes at chemical composition of produced liquids. After these initial experiments, leaching of inorganics from fast pyrolysis feedstock has been studied a lot [58,61]. These early findings have later been confirmed and now it is well known that catalytic activity of ash results in decreased FPBO yield and altered chemical composition. Organic liquid yields are higher with low ash than high ash feedstocks [22] and de-ashed feedstocks have been reported to give higher FPBO yields and lower water content in FPBOs [39,52,62].

### 2.3.2 Impurities present in waste wood fractions

On the EU level, the generation of non-hazardous waste wood from construction was approximately 8.5 million tons during 2020. Largest amount was produced in Germany (3.1 million tons), followed by Netherlands (1.6 million tons), and France (1.5 million tons). [63] Currently, the recycling rate of waste wood is low and most of it is used for energy. In some countries, waste wood is recycled into particle boards, but mainly rather clean fractions are used in these applications. [64] To increase the recycling rate of the end-of-life waste wood, utilization of chemical recycling technologies could be considered.

Impurities present in used wood are very versatile and can vary a lot depending on the origin of the used wood. Generally, these impurities can be divided into mechanical and chemical impurities. Mechanical impurities include components such as dirt and stones, as well as particles of plastic, metals, concrete and glass. Typical for the mechanical impurities is that these impurities can be separated from wood relatively easily by utilizing mechanical separation techniques such as sieving of stones or magnetic separation of metals. Chemical impurities on the other hand are often integral part of the wood material and can be chemically bonded into the wood structure, which makes the separation of these impurities from the wood much more difficult. Chemical impurities include paints, coatings, wood preservatives and wood adhesives.

In Finland, classification and guidelines have been developed for the waste wood in energy use. In this classification waste wood is divided into four different categories A, B, C and D, depending on the impurity content. This classification has been developed for the energy use only and is not applicable as such for the pyrolysis. However, classification provides useful framework to assess the quality of available used wood fractions. [65,66]

Class A used wood consists only of chemically untreated industrial side-streams or residues from forest and wood processing industry. Additionally, this class A can include segregated wood from sources such as parks, gardens and roadside management. Class A cannot contain any chemically treated wood and therefore only mechanical impurities can be present. [67]

Class B used wood contains chemically treated used wood fractions. However, class B cannot contain halogenated organic compounds, preservatives or impregnated wood. Additionally, limits for heavy metals cannot be exceeded. These limits are presented in the Table 5. Class B category can contain painted, coated or lacquered wood from industry. Proof of the origin is needed and the production process and separation of wood waste needs to be described. [67]

Class C on the other hand includes chemically treated wood which contains or can contain halogenated organic compounds or heavy metals because of treatment with coating or wood preservatives. However, impregnated wood is not allowed in this fraction. Additionally, wood fractions which origin is difficult to prove, is classified into class C category. For example, demolition wood from building demolition sites belongs to this category unless the quality is proven to be higher by analytics. Coatings and resins, such as phenol-formaldehyde (PF) or urea-formaldehyde resins in fiberboard and plywood fractions, as well as other impurities present in wastes can increase the complexity of pyrolysis

products even further [65,68,69] and can for example increase the nitrogen content of the pyrolysis products [70].

**Table 5.** Class B wastewood threshold values used in Finland. [67]

Property	Threshold value, dry basis	Threshold value to be checked to classified from class C to class B
Sulphur	≤ 0.2 wt%	x
Nitrogen	≤ 0.9 wt%	x
Potassium <sup>a</sup>	≤ 5000 mg/kg	
Sodium <sup>a</sup>	≤ 2000 mg/kg	
Chlorine	≤ 0.1 wt%	x
∑ Arsenic <sup>b</sup> + Chromium + Copper	≤ 70 mg/kg	x
Cadmium	≤ 1 mg/kg	x
Mercury	≤ 0.1 mg/kg	x
Lead	≤ 50 mg/kg	x
Zinc	≤ 200 mg/kg	x

<sup>a</sup> Threshold values for potassium and sodium are only recommendations to evaluate the combustion behaviour.

<sup>b</sup> As should not exceed 10 mg/kg (+30% accuracy of the measurement) for class B wood

Categories A and B are classified as solid biofuels and class C as solid recovered fuels and related standards are used. Solid fuels falling into class C should be incinerated according to waste incineration legislation. [67] Class D on the other hand is impregnated wood and is classified as hazardous waste. This category can contain significant quantities of toxic components such as arsenic or chromium. Examples include wood products designed for outdoor use e.g. wood in transmission and telephone line poles. [67] In Finland, arsenic was used for preserving timber until early 2000 and therefore will be still present in long lasting application although new products are not produced anymore.

### 2.3.3 Challenges with lignin rich feedstocks

One of the most studied pathways for lignin valorization is the depolymerization of the lignin via fast pyrolysis and a lot of efforts have been made to valorize different types of technical lignins in fluidized bed reactors. However, thermal processing of the lignin has been proven to be difficult. When Kraft lignin is heated, it undergoes softening and melting overlapped with depolymerization followed by solidification of the softened material [71] and similar behavior is also typical for lignin from soda pulping [72]. Formation of the gaseous products within the lignin melt results in large porous char agglomerates. [71,72] Due to melting phenomenon, Kraft lignin is especially difficult to feed into a fluidized bed with screw feeder and further problems are faced in the reactor, where char foam and agglomerates can easily lead to bed defluidization and cyclone failure. [73,74].

However, the type and source of the lignin feedstock has major effects into its chemical and molecular properties. [71,72] Major industry providing technical lignins is the pulp and paper industry, where alkaline sulfate pulping, i.e. Kraft-process, is the dominant process [75,76]. The growing biofuel markets have raised the volumes of cellulosic ethanol production industry, where the leading process is the mild acid treatment followed by the enzymatic hydrolysis [77] to

obtain fermentable sugars. As the pathways to lignin isolation from these processes are significantly different, also the obtained lignin qualities differ.

Depending on the source of lignin, chemical and structural properties of the lignin can change. For example, the hydrolysis lignin is reported to be more condensed and cross-linked and have higher content of phenolic hydroxyl groups compared to Kraft-lignin [71,78]. In addition, sulfur content in hydrolysis lignin is lower compared to Kraft-lignin [71], which is a benefit if catalytic upgrading processes for lignin derived liquids are considered [53]. There can be also significant differences in the carbohydrate content of lignin after different processes. Typically, the residual carbohydrate content of hydrolysis lignin is higher than in Kraft-lignin [73]. Hydrolysis lignin is also less prone to melt at least at pre-pyrolysis temperatures [71], and hence is significantly easier to process thermally compared to the Kraft lignin. However, similar problems with deflu-idization and agglomerate formation have been observed with hydrolysis lignin, but these operational problems are less severe compared to Kraft lignin fast pyrolysis [73]. Other characteristic of lignin behavior, observable with both Kraft and hydrolysis lignin, include the wide temperature range of lignin degradation (150 – 900 °C), which is challenging from the process optimization point of view [71,79–81].

Besides the operational problems, major issues in lignin conversion are its high oxygen content and highly aromatic structure, which during pyrolysis will produce a significant quantity of solid char through recombination of the radical intermediates [81]. If the aim is to maximize the liquid yield, additional hydrogen is needed [82–84]. Steam [85,86] and calcium formate [87,88] have been tested as hydrogen additives during biomass pyrolysis and increased liquid yields has been reported.

## 3. Valorization of the FPBOs

### 3.1 State of the art in FPBO utilization

The most mature technology for FPBO utilization is energy generation through combustion [89]. Fast pyrolysis of wooden biomasses and use of the produced fast pyrolysis bio-oils (FPBOs) as boiler fuel is technology that has entered the market and currently there is two biomass fast pyrolysis plants in operation in Europe. Standard EN 16900–2017, specifying the FPBO properties for the industrial boiler use, has been developed and published in 2017 [32,65]. Recently, Pyrocell and Preem have made advancements in the production of advanced biofuels through co-feeding the FPBO into a FCC system in Preems oil refinery [90,91]. Other less mature valorization pathways include hydroprocessing of FPBOs into advanced biofuels [92–95], and gasification into syngas [96].

However, from the perspective of energy generation, FPBOs as such are suboptimal due to the high oxygen and water content, poor thermal and storage stability as well as poor calorific value, when compared to hydrocarbon fuels. Although significant advancements have been made in the production of advanced biofuels from the FPBOs, production of hydrocarbons will always need removal of most of the oxygen which is major element in FPBOs (up to 45 wt%, dry basis). Due to these reasons, applications where chemical characteristic and oxygen content of FPBOs have also awakened research interest. Research for the utilization of FPBO in material application such as bitumen binder [97], in the production of carbons material [98] or in resins synthesis [99] has also been carried out, but to lesser extent.

### 3.2 FPBO hydroprocessing into transportation fuels

High oxygen content, high corrosivity and thermal instability has restricted the FPBO use as fuel. Additionally, FPBO is immiscible with hydrocarbons and therefore cannot be used as drop-in fuel. To improve the fuel qualities to correspond the demands of advanced transportation fuels, oxygen removal from FPBO is critical. Deoxygenation through hydroprocessing has been the most studied pathway to produced advance transportation fuels and this topic has been subjected for research already for several decades [92].

One of the key challenges in the FPBO hydroprocessing is the fact that these oils are not thermally stable. During heating FPBOs go through aging and re-polymerization reactions resulting into heavy coking. In catalytic fixed bed upgrading, this phenomenon results easily into fouling of the catalyst bed, loss of activation and reactor blockage. To overcome these issues, two-stage hydroprocessing, where stabilization by mild hydrotreatment (175 to 250 °C) is followed by more severe deoxygenation (350 to 400 °C), is needed. [92] Especially the sugar-type components present in FPBO withstand poorly elevated temperature needed in deoxygenation. The purpose of the mild hydrotreatment is typically to stabilize the thermally unstable components and not to remove oxygen extensively. For example, stabilization of sugars to sugar alcohols enables the stability needed in further and more severe deoxygenation treatment. [100]

Catalyst deactivation remains still an issue during the stabilization step and for example inorganic impurities and various heteroatoms present in FPBOs can reduce the activity. Additionally, even after higher temperature deoxygenation, stabilized and partly deoxygenated FPBO will contain significant amounts of oxygen (10 – 20 wt%), which needs to be removed if advanced transportation fuels are targeted. Stabilization and deoxygenation, however, makes the bio-oil more blendable with hydrocarbons which opens up possibilities to co-refine these liquids in existing oil refinery infrastructures. [100] Additionally, high carbon yields from FPBO to stabilized and deoxygenated products can be achieved.

In addition to fixed bed reactors, more plugging resistant reactor technologies, such as slurry-phase processes where the unsupported catalyst is dispersed with the feedstock, has been developed for FPBO stabilization step. Additional advantage of this slurry-phase processing is that new catalyst can be fed into reactor and the used catalyst could be potentially regenerated to overcome issues with catalyst deactivation. [101,102]. Stabilized FPBO (sFPBO) from slurry process can be deoxygenated further in fixed bed reactors. [103]. Dimitradis et al. (2023) reported mass and carbon yields for upgrading steps (slurry hydroprocessing and fixed bed hydrotreatment). Reported mass yield from FPBO to sFPBO was 57 wt% and yield from sFPBO to end product (3 wt% oxygen) was 92 wt%. Reported carbon yields were higher: 71 wt% and 96 wt% respectively for the different process steps.

### 3.3 FPBO gasification

Gasification of FPBOs into syngas has been studied by many research groups [96,104,105]. Syngas can be used as an energy source, or it can be converted into advanced biofuels via catalytic Fischer–Tropsch synthesis [106]. Production of methanol and ammonia with different catalytic systems has been also developed [106] as well as production of value-added chemicals, such lower olefins or higher alcohols [107]. Methanol can be further used to substitute fossil-based feeds in various syntheses to produce wide variety of different chemical products [106]. Key challenge in the catalytic conversion of syngas been the catalyst poisoning via the impurities present in the syngas. For example, sulphur species can be problematic. Hence, purification of syngas has been developed [108,109]

Furthermore, different fermentation-based processes have been developed with the target to reduce the cost of the syngas conversion into chemicals. Microbes used can also be more flexible towards conventional impurities present in the syngas [110].

In comparison to direct biomass gasification, the gasification of FPBO benefits from the fact that a large part of the tar precursors (primarily lignin[111]) does not enter the gasifier as it is converted to char in the pyrolysis process. Tar concentrations in FPBO gasification are therefore typically much lower than for direct biomass gasification which results into reduced operational problems due to the tar formation [112]. Furthermore, the separation of pyrolysis char and its use in carbon products possess potential to enhance the sustainability of the value chain. On the conceptual level, one of the key benefits of the FPBO gasification is that it can increase the economically available feedstock sources for large gasification plants. Unlike in the case of fast pyrolysis, where the FPBO transportation is a feasible solution and the utilization can be decoupled from the actual production process, gasification cannot be decoupled from the syngas utilization. Transportation of syngas is more challenging and therefore the syngas utilization must be done usually at the same site as the production. The economies of scale favor the large plant size, but the size of plant is typically restricted by the quantity of the economically available biomass resources[104]. Decentralized production of FPBO could increase the economically available biomass resources and give freedom to build larger gasification plants. Corrosive properties of the bio-oils can, however, be drawback if extensive transportation networks needs to be planned.[113,114]

As the plant size goes up, it is likely that there will be more variation in the type of available biomass feedstocks and FPBOs produced from them. These feedstocks could be blended already in the pyrolysis phase, or the produced FPBOs could be blended in centralized utilization sites[115–117]. In all scenarios, deep understanding of yields and compositions of the produced FPBOs from different feedstocks are important factors to help in the design of plants, which are capable of handling different feedstocks and product liquids. Several researchers published results on the gasification of pyrolysis oil in various gasifiers, including non-catalytic entrained flow systems[105,118–121] and various catalytic gasification systems[96,122–124]. Most research involved the gasification of wood derived pyrolysis oils, with some straw derived results included as well. However, a direct comparison of multiple residue-based feedstocks within the same system is not previously reported. This information is important if large scale gasification plants are considered, as the FPBO for such plant will likely come from different origins. This question was further explored in Publication III and is discussed in section 5.2.1.

### **3.4 FPBO valorization through fractionation**

FPBOs can phase separate for several reasons. Different bio-oil fractionation technologies, including solvent extractions, have been recently reviewed by

Chan et al.[125]. Main focus in the literature has been in the separation of pyrolytic lignin fragments and other phenolics from decomposition products of polysaccharides. Separation of lignin fraction from the FPBO is typically done by adding a solvent which forces the FPBO to phase separate into lignin rich and sugar rich fractions. Most simple solvent is water, but solvents such as ethyl acetate and n-butanol have also been used [29]. In this section, utilization of the different FPBO fraction will be discussed. As the utilization of the water insoluble lignin fraction is studied in the Publication IV and discussed more detail in the sections 5.2.2 and 5.2.3, more emphasis in the review is given to the utilization of the aqueous fraction to complete the fractionation scheme.

Addition of water into FPBP results in separation of FPBO into an aqueous and organic phase. Water soluble components, such as monomeric and oligomeric sugars originating from the thermal degradation of polysaccharides, are retained in aqueous phase while the organic phase is rich in hydrophobic pyrolytic lignin and extractives. When the water fractionation is considered, the composition of the aqueous phase and concentration of organics are highly dependent on the production process. The aqueous phase from the water induced bio-oil fractionation is naturally rich in water soluble bio-oil components, such as acids, alcohols, aldehydes, ketones, phenols, furans, pyrans, anhydrosugars and oligomeric sugar fragments. The quantity of the water affects the concentration of the organics, but it can also affect on the purity of obtained lignin fraction. If more water is used, less water-soluble impurities are present in the lignin fraction [126].

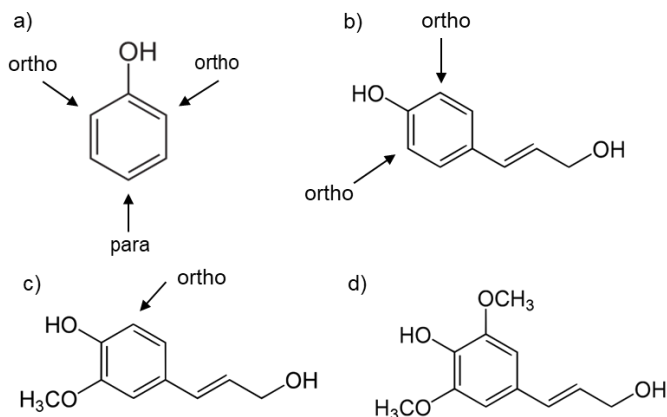
If the fractionation of the oil is targeted, utilization of moist feedstock in the pyrolysis could be also considered, as one of the main drivers for feedstock drying is the production of one-phase oil during pyrolysis. With moist feedstock, spontaneous phase separation can be achieved directly after fast pyrolysis when the product vapors, including the feed moisture, are condensed [127]. Liquid recovery and condensation systems need to be designed appropriately, and the energy demand of the pyrolysis will be increased as more water needs to be evaporated from the feedstock. However, in principle the energy needed for the evaporation can be recovered during the condensation of the vapors, but nevertheless the heat management of such a process needs careful consideration.

### 3.4.1 Water-insoluble phase from fractionation

Different valorization pathways for the lignin fractions have been studied in literature. On a wider level, lignin utilization in resin synthesis has awakened a lot of research interest and other technical lignins, such as Kraft-lignin and lignosulfonates, have been used to substitute fossil phenol in PF-resins [76]. Typically, the focus has been on the synthesis of resol type resins for adhesive use. These type of resins have a formaldehyde to phenol ratio greater than 1. If the ratio is below 1, produced resins are called novolac-type resins, which are used to create thermoset polymers, e.g. bakelite [128].

For the reaction of lignin with formaldehyde, free ortho-positions in aromatic ring are required [129]. Para-positions, available in simple phenols, are typically occupied by the alkyl side chain in lignin derived phenolics. This results in the

lower reactivity of lignin derived phenolics compared to simple phenol molecule. Furthermore, methoxy groups and/or covalent bonding between the lignin monomers on the ortho-sites can reduce the availability of the active sites even further. Available reaction sites in ortho- and para-positions in phenol and three common monolignols are depicted in Figure 3.



**Figure 3.** Available ortho- and para-sites depicted with arrows in a) phenol, b) paracoumaryl alcohol, c) coniferyl alcohol and d) sinapyl alcohol

In addition to the phenol-formaldehyde resins for adhesive use [99,130,131], use of lignin in epoxy resins [132] and polyurethanes [133,134], has been studied with the aim to increase the content of biogenic feeds in these products. Furthermore, additionally to common technical lignins, chemically modified lignins have been tested with the aim to increase the functionality and reactivity of lignins in the resin synthesis [135]. Pyrolysis can be considered as one of these methods since the molecular size of the lignin is reduced during pyrolysis, which can increase the lignin reactivity. Several research groups have applied different bio-oils from various slow and fast pyrolysis processes to PF-resin synthesis [99,128,136–142]. In addition to the whole bio-oils, separated lignin fraction from the bio-oil has been tested. For example, Aslan et al. (2015) substituted successfully 10 wt% of phenol by FPBO derived phenolic rich fraction in the synthesis of PF-resin. Sukhbaatar et al. (2009) separated the pyrolytic lignin from the pine wood FPBO by using mixture of water and methanol. Separated pyrolytic lignin was used to replace up to 30, 40 and 50 % of the phenol in PF resins and replacement rates up to 40 % showed good performance when the resins were evaluated as oriented strand board corelayer binders. However, resins with 50% lignin replacement were found to give inadequate internal bonding. Methanol can also be rather expensive solvent, at least when compared to water. Nevertheless, pyrolytic lignin, which can have reduced molecular size compared to other technical lignins, could be potential substitute for fossil phenol especially in synthesis of PF-resins.

Therefore, development of simple FPBO water fractionation and further utilization of the phenolic fraction in the PF-resin synthesis could be interesting and economically more lucrative option, especially if cheap waste lignocellulosics

can be utilized as a feedstock for FPBO production. This concept was further developed in Publication IV and is discussed in sections 5.2.2 and 5.2.3.

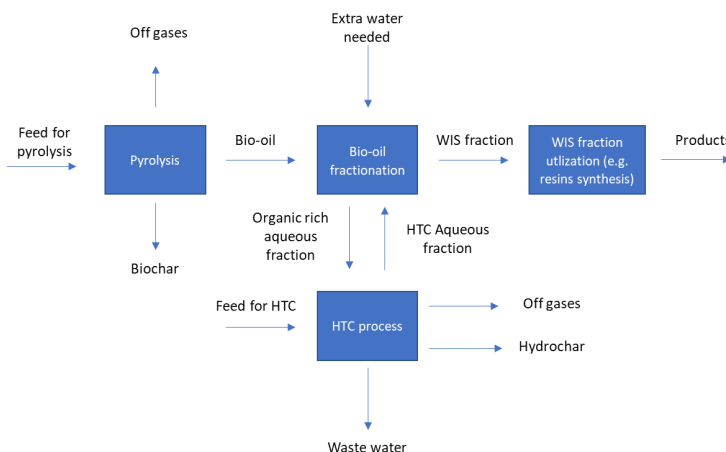
### 3.4.2 Water-soluble phase from FPBO fractionation

To make the fractionation process efficient, complete utilization of the bio-oil organics is necessary to achieve economically and ecologically sustainable and material efficient value chain. As the major fraction of the bio-oil organics are water soluble and in water fractionation they end up into the aqueous phase [127], the efficient utilization pathways for the organics in the water-soluble fraction is necessary. Therefore, it is important to map the potential processing pathways for pyrolysis derived aqueous phases, which is in the focus of this section.

#### *Hydrothermal carbonization*

In the literature, pyrolysis derived aqueous phase has been studied as reaction medium for HTC of biomass [145,146]. Hydrothermal carbonization (HTC) is a thermochemical process that converts various organic feeds, into a carbon-rich material known as hydrochar. HTC is carried out in liquid phase where water act as reaction medium. Moderate process temperatures of 180 – 260 °C are combined with high pressure keep the reaction medium, i.e. water, in liquid state. The potential applications for hydrochar are versatile and studied applications include uses as soil amendment, use in catalysis, use in the production of activated carbon, adsorption use in wastewater treatment as well as hydrochar use in the energy production[147].

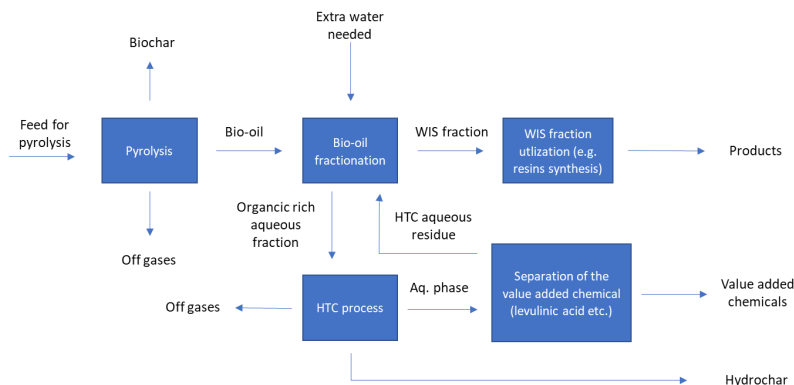
Instead of using pure water as reaction medium, there has been reports about accelerating the reaction rate in HTC of biomass by adding external acids or alkaline solution into the process [145,146]. As the pyrolysis derived aqueous phases are often acidic due to the carboxylic acids present, there could be added benefits in the use of this aqueous phase as reaction medium of HTC process. Schematic flow diagram of such a process is depicted in the Figure 4.



**Figure 4.** Flow diagram for aqueous fraction utilization as acidic reaction medium in the separate HTC process using its own biomass feedstock.

Drawback of the concept where HTC is coupled with fast pyrolysis is the added complexity when two separate processes are tightly attached to each other. Flexibility of the individual processes are reduced as the capacity of the HTC to deal with the aqueous phase will determine the FP aqueous phase production capacity. Additionally, the CAPEX and OPEX will be naturally higher, and the feedstock resourcing for two different types of process must be considered. This can limit the available plant sites significantly because the logistics of two different feedstocks will have their own limitations. Optimally, rather dry lignocellulosic feeds could be used for fast pyrolysis while slurries/sludges could be used for the HTC.

Another interesting option could be the design of HTC of the aqueous phase directly without any other separate feed for the HTC process (Figure 5). As the pyrolysis derived aqueous phases can be rich in pyrolytic sugars and other water-soluble organics, they possess potential for carbonization. For example, HTC of different sugars and pulp mill streams has been studied by Wikberg et al.[148], with the aim to produce hydrochar. Additionally, the HTC conditions combined with acidic environment and presence of sugars or polysaccharides, are suitable for levulinic acid, formic acid, furfural and hydroxymethyl furfural production[149,150]. Thus, direct HTC of pyrolysis derived aqueous stream could be an interesting method to enable co-production of hydrochar, levulinic acid and other value-added chemicals from pyrolytic sugars.



**Figure 5.** Flow diagram for the hydrochar production from the sugar rich aqueous fraction through HTC.

*Hydrogen production through aqueous phase and steam reforming*

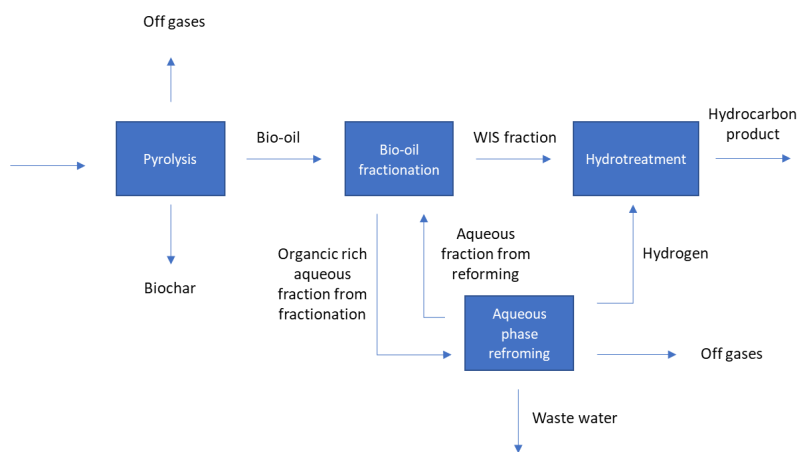
Aqueous phase reforming (APR) and steam reforming are processes which are developed to valorize oxygenated molecules and obtain a gas mixture rich in hydrogen[151]. Steam reforming and APR of the aqueous phase of the pyrolysis oils has been extensively studied by several research groups with the aim to convert the organics of the pyrolysis oil aqueous phase into hydrogen through catalytic process [151–167].

Steam reforming is done in gas phase and in high temperatures with the presence of the catalyst [153]. Disadvantage of the process is that high temperatures

affect the stability of the catalyst due to thermal cracking of the feedstock leading to coke formation. Additionally, hydrogen production by the parallel water–gas shift (WGS) reaction is unfavourable at high temperatures which reduces the hydrogen production efficiency. [168]

APR on the other hand is carried out in lower temperature at which reforming of oxygenated hydrocarbons and the water-gas-shift reaction are favored. Lower temperatures result in lower coke formation. Reaction pressure in APR is high to keep the reactants in liquid stated but conditions are still below critical point of pure water (374.2 °C and 221.2 bar). Additional advantage in these conditions is the suppression of an energetically demanding vaporization-step for the feedstock[168]. Disadvantage is that high pressure conditions are more demanding for materials, which can increase the CAPEX of these units. In both processes, hydrogen and carbon dioxide are produced among other gaseous and liquid products from organic components in aqueous phase. APR has potential to be a bit more energy efficient in hydrogen production while steam reforming is more mature are simpler technology.

On a concept level, hydrogen production from aqueous phase is a particularly interesting approach if the WIS fraction is further hydrotreated as this creates need for the hydrogen at the site. Therefore, hydrogen production from aqueous phase could provide the hydrogen needed for the hydrotreatment as illustrated in Figure 6. For example, Paasikallio et al.[152,153] studied the steam reforming of the aqueous fraction obtained from the fast pyrolysis and concluded that excess hydrogen production capacity could be reached for WIS hydrotreatment needs.



**Figure 6.** Flow diagram for hydrogen production through aqueous phase reforming.

#### *Hydrodeoxygenation of the aqueous fraction*

HDO of aqueous fraction has been studied by Sanna et al. [169]. Sanna et al. were able to produce oxygenated gasoline additives, such as alcohols and diols, from the pyrolysis derived aqueous fraction in a 2-stage continuous hydrogenation process.

As the pyrolysis derived organics are not thermally stable, direct high temperature hydrogenation of aqueous fraction is not feasible without unwanted coking reactions as discussed in section 3.2. Thus, two stage process was used and it consisted of separate low temperature hydrogenation (LTH) and high temperature hydrogenation (HTH) steps. LTH step converted the aldehydes, ketones, and sugars to their corresponding alcohols, such as ethylene glycol, propylene glycol and sorbitol, with some losses (7 %) to gases and solids. In LTH, a ruthenium catalyst supported with activated carbon was used at temperatures up to 125 °C.

In subsequent HTH step with platinum catalyst, thermally stable products from LTH were converted into diols and monohydric alcohols at more severe reaction conditions through hydrogenation and hydrogenolysis reactions. Up to 45% carbon present in the starting aqueous phase was successfully converted to gasoline blendstocks and C2 to C6 diols. The product distribution from HTH can be controlled varying the process pressure and 2<sup>nd</sup> stage temperature. High yields of gasoline blendstocks can be obtained by operating at low total pressure and high second stage temperature (e.g. 275 °C). Higher temperatures lead to deeper hydrogenation leaving less alcohols into the product liquids. High hydrogen pressure on the other hand is preferable in the 2-stage process as it suppresses the gaseous product formation and minimizes carbon loss into gas phase.

#### *Fermentation of the sugars into ethanol*

Fermentation of pyrolytic sugars is another topic where the water-soluble components of the pyrolysis bio-oils have been utilized [170–172]. The anhydrosugars found in bio-oils derived from the fast pyrolysis of lignocellulosic materials can be fermented to produce ethanol or lipids [170]. The challenge with the anhydrosugars present in the bio-oil derived aqueous fractions is that the common microorganisms used in the fermentation of the glucose into ethanol cannot utilize the anhydrosugars directly [173]. Acid hydrolysis can convert anhydrosugars into glucose, and to ferment these sugars, it is also necessary to remove the toxic compounds from the solutions. Phenols and acids present in the aqueous fraction are the main species inhibiting growth of the yeast *Saccharomyces cerevisiae*. [170]

Sukhbataar et al. [172] fermented hydrolyzed levoglucosan produced by fast pyrolysis of biomass into ethanol. Inhibitors were successfully removed from the bio-oil water fraction by extraction with n-butanol. However, the residual n-butanol was found to inhibit fermentation performance of *S. pastorianus*, and removal of n-butanol residues was needed to solve the inhibition issue. However, ethanol yields up to 98% were obtained with purified pyrolytic sugars. Although purification needs for fermentation are demanding, the technical potential to obtain high ethanol yield from pyrolytic sugars exists.

#### *Solvent extraction of the component groups*

Further solvent extraction of the aqueous fraction has also been studied. Generally, the solvent extractions proposed for the bio-oils has been deemed to be economically unfeasible at least with the common organic solvents due to the

high amounts of solvents needed to separate rather small amount of valuable components from the bio-oils [125]. The concentrations of the individual components within the bio-oils are typically very low, and the bio-oils contain groups of components with similar chemical properties, which makes the selective extraction of the compounds difficult. Same is true also for the bio-oil derived aqueous fractions due to the complex chemical nature of these streams, as discussed in the Chapter 2. Additionally, some of the most abundant compounds, such as glycolaldehyde, do not possess obvious market potential, although some research in valorization has been carried out[174].

Despite all the above, research with some common organic solvents such as toluene to separate phenolics [175], ethyl acetate to separate acetic acid[176] or n-butanol to separate furfural, 5-HMF, weak acids and phenolics[177] has been carried out with aqueous fractions derived from pyrolysis. In principle, these solvents work in the extraction process, but the economics of such process is questionable. Recently, several research groups have also used different water insoluble ionic liquids to separate components such as phenolics and aromatics[171,178,179] as well as acetic acid, glycolaldehyde and acetol[180]. Ionic liquids are an interesting option due to their negligible vapor pressure, which makes almost full recyclability of the solvent theoretically possible. However, thermal and chemical instability of certain ionic liquids can be problematic in solvent recycling. High recycling rates are often necessary due to the high cost of these liquids.

#### *Distillation/evaporation*

Bio-oil distillation has been proven to be very difficult because bio-oil are not thermally stable, and they cannot be fully vaporized[27,181]. However, evaporation has been used to valorize the pyrolysis derived aqueous fractions. For example, Rover et al.[182] demonstrated the production of crystallized levoglucosan through the fast pyrolysis of lignocellulosic biomass. Levoglucosan and other anhydrosugars, could be used as chemical building block for commercially important applications, including the manufacture of plastics, surfactants, explosives, propellants, resins, biodegradable polymers, antiviral agents, and other chiral bioactive natural products, if the production process would be competitive. Currently synthesis of levoglucosan is too expensive and limits its use as a chemical building block[182]. Evaporation could be easy and low severity treatment strategy to achieve sugar-rich syrup from the aqueous phases. However, before evaporation removal of water-soluble contaminants, i.e. phenolic monomers and light oxygenated compounds, may be necessary either by using solvent or adsorbents. [183].

## 4. Materials and methods

### 4.1 Feedstocks and characterization methods

The raw materials used in the Publications I-IV in the fast pyrolysis and pre-treatment experiments are listed in Table 6 with some common analyses. Different particle size feedstocks were used in different units due to the restrictions in feeding system and unit dimensions. In bench scale bubbling fluidized bed (BFB) unit, particle size used was 0.5 – 1 mm and in pilot scale circulating fluidized bed (CFB) particles below 3 mm were used. Fines were sieved to limit the carry-over of fine char particles through the cyclones into the produced fast pyrolysis bio-oil (FPBO). Generally, raw materials were dried below 10 wt% moisture before pyrolysis experiments. This was done to avoid excess water in the FPBO as the feed moisture ends up into the product liquid and can induce phase separation of FPBO. Analytical methods used in feedstock characterization are listed in Table 7. More detailed descriptions can be found from the Publications I-IV.

**Table 6.** Different feedstocks used in the Publications I-IV.

Type	Particle size, mm	Moisture, wt%	Volatiles wt% dry	C, wt% dry	H, wt% dry	N, wt% dry	O, wt% dry	Ash, wt% dry	Unit used	Publication
Lignin A	0.5 – 1	7.2	70.7	59.3	6.1	0.7	34	0.3	BFB	I
Lignin B	0.5 – 1	8.9	71.3	60.0	5.9	0.6	33	0.4	BFB	I
Lignin C	0.5 – 1	8.1	65.1	61.7	6.2	1.0	31	0.4	BFB	I
Lignin D	0.5 – 1	2.5	69.5	61.8	6.0	0.4	32	0.3	BFB	I
Lignin E	0.25 – 3	4.6	68.2	63.6	6.3	0.5	29	0.4	CFB	I
Forest residues	0.5 – 1	5.8	81.9	51.1	6.0	0.2	42	1.2	BFB	II
Eucalyptus residues	0.5 – 1	8.8	81.6	48.4	5.5	0.3	41	4.8	BFB	II
Wheat straw	0.5 – 1	8.0	80.5	45.7	5.5	0.3	42	6.1	BFB	II
Wheat straw	0.5 - 3	8.4	76.9	46.1	5.7	0.5	41	6.3	CFB	II
Oat straw	0.5 - 3	16.1	70.3	44.6	5.3	0.7	39	10.2	CFB	II
Arundo	0.5 – 1	6.4	76.3	47.8	5.6	0.3	42	4.4	BFB	III
Sorghum	0.5 – 1	6.2	77.3	45.5	5.7	0.8	43	5.3	BFB	III
Eucalyptus	0.5 – 1	6.4	80.6	49.5	5.8	0.2	43	1.6	BFB	III
Bagasse	0.5 – 1	7.4	83.7	48.4	5.8	0.2	43	2.2	BFB	III
Demolition wood	0.25 - 3	5.2	84.5	53.6	5.8	0.6	39	0.8	CFB	IV

**Table 7.** Feedstock analyses in Publications I-IV.

Property	Method	Publication
Ash, 550 °C	SFS-EN ISO 18122	I-IV
Moisture	SFS-EN ISO 18122	I-IV
Volatiles	SFS-EN ISO 18123	I-IV
C	SFS-EN 15104	I-IV
H	SFS-EN 15104	I-IV
N	SFS-EN 15104	I-IV
O	by difference	I-IV
Cl	SFS-EN ISO16994	II, III
S	SFS-EN ISO16994	II, III
Elements by IC	SFS-EN ISO 10304-1	II, IV
Elements by ICP-OES	SFS-EN ISO 11885	II, IV
Lignin and carbohydrates	Acid hydrolysis, monosaccharides by HPAEC. Klason lignin content i.e. the insoluble residue from the hydrolysis was determined gravimetrically. Acid soluble lignin was determined from the hydrolysate based on UV at 215 and 280 nm	I, II
HHV	SFS-EN 14918	I-III
LHV	SFS-EN 14918	I-III

#### 4.1.1 Feedstock leaching pretreatment and characterization

In the Publication II, leaching of ash and AAEMs from the pyrolysis feedstock was studied in laboratory, bench and pilot scales. Leaching was first optimized in the laboratory scale by studying the effect of temperature, residence time, as well as the amount and the acidity of leaching liquid. Nitric acid was used in the experiment. Other strong inorganic acids have also been proven to be effective in AAEM removal, but weak acids, such as acetic acid, need larger quantities of the acid are used. [184] Nitric acid was chosen for the experiments because potential traces of nitrogen were assessed to be less harmful for FPBO quality, compared to sulfur or chlorine traces from sulfuric acid or hydrochloric acid, respectively. Sulfur and chlorine can be severe catalyst poisons if further upgrading of the FPBO is considered. [53] Nitrogen can also be a catalyst poison, but as the quantity of nitrogen in biomass and FPBO is naturally much higher, potential acid traces have less severe effects on FPBO quality.

The most significant parameter to improve the total ash and AAEM removal in laboratory scale was the acidity of the leaching liquid. Potassium and sodium were largely removed by water washing, but magnesium and calcium not. Removal of calcium and magnesium was significantly enhanced in acidic conditions. With wheat straw, the differences in total ash removal with acid and water were minor because of high silica content in straw. However, lower AAEM levels were reached in acidic conditions also with wheat straw. Silicon is hardly soluble and removable by conventional leaching methods. Removal of silicon, however, is not crucial as silicon is considered as catalytically inert element during pyrolysis. [49] In addition to acidic conditions, increasing temperature was found to enhance the leaching efficiency with wood biomasses, but with wheat straw, room temperature was equally efficient. Short leaching time was found to be as efficient as longer time with all feedstocks under acidic conditions. Higher temperature is expected to increase the solubility of AAEMs and other inorganics

and enhance the leaching. The amount of acid is also a crucial aspect if ion-exchangeable cations are to be removed from the plant fibres, as the protons originating from the acid are needed in the ion-exchange process.

Based on the laboratory scale test, leaching parameter presented in the Table 8 were chosen for bench scale. In pilot scale, due to the equipment limitations, a larger amount of leaching liquid was used. Consistency, that is, the dry matter content of the liquid–straw suspension, was limited to 5 w % to ensure proper mixing and pumping of the suspension. Detailed description of leaching experiments is presented in Publication II.

**Table 8.** Leaching parameters in pilot and bench scale used in Publication II (© 2022 The Authors. Reprinted under license CC-BY 4.0.).

Sample	Temp. (°C)	Time (min)	Acid concentration (wt%)	Leaching liquid (B:LL)	Rinsing water (B:W)	Scale
Forest residues	50	30	1 %	1:10	1:10	BFB
Eucalyptus residues	50	30	1 %	1:10	1:10	BFB
Wheat straw	20	30	0.5 %	1:10	1:10	BFB
Oat straw for	20	30	0.5 %	1:20	1:20	CFB

B = biomass, LL = leaching liquid, W = water

Feedstocks composition before and after acid leaching is presented in Table 9. Based on the results, no large variations were seen in lignin or polysaccharide contents of the feeds. Volatile content was somewhat increased after the pretreatment which can be at least partly attributed to the removal of non-volatile ash elements. AAEM content was significantly reduced by the leaching pretreatment with all feedstocks. In addition, chlorine content was reduced by the pretreatment as expected, as the chlorine is largely in water soluble form in biomasses. Sulphur content was also reduced by the pretreatment.

**Table 9.** Feedstock analyses results before and after acid leaching for feedstocks used in bench and pilot scale experiments in Publication II (© 2022 The Authors. Reprinted under license CC-BY 4.0.).

	Forest residues	AL forest residues	Eucalyptus residues	AL eucalyptus residues	Wheat straw	AL wheat straw	Wheat straw	Oat straw	AL oat straw
Scale	Bench	Bench	Bench	Bench	Bench	Bench	Pilot	Pilot	Pilot
Moisture, wt%	5.8	6.7	8.8	3.8	8.0	6.5	8.4	16.1	10.0
Ash, wt% db	1.2	0.2	4.8	2.8	6.1	4.9	6.3	10.2	4.1
Volatiles, wt% dab	81.9	86.9	81.6	84.9	80.5	87.5	82.1	78.3	81.9
C, wt% dab.	51.7	50.9	50.8	50.0	48.7	48.9	49.2	49.7	50.3
H, wt% dab.	6.1	5.9	5.8	5.9	5.9	5.9	6.1	5.9	6.0
N, wt% dab.	0.2	0.1	0.3	0.3	0.3	0.2	0.5	0.8	0.6
O, as diff., wt%, dab.	42	43	43	44	45	45	44	43	43
Inorganic content									
K, mg/kg db.	700	bdl	2 600	400	7 600	300	9 900	40 200	2 400
Na, mg/kg db.	200	bdl	500	100	bdl	bdl	90	1 000	180
Ca, mg/kg, db.	1 300	bdl	7 500	800	1 700	100	3 600	2 600	610
Mg, mg/kg, db.	200	bdl	900	100	700	bdl	700	1 200	130
Si, mg/kg, db.	800	na	6 000	na	17 000	na	16 200	11 200	14 600
S, wt% db.	0.011	0.005	0.029	0.011	0.035	0.008	0.11	0.756	0.050
Cl, wt% db.	na	0.008	0.159	0.016	0.315	0.017	0.31	0.156	0.075
Chemical composition									
Total lignin, wt% dab.	30.0	29.1	36.9	31.3	24.5	25.2	n.m.	n.m.	n.m.
Klason lignin, wt% dab.	29.4	28.8	31.7	27.9	22.6	23.8	n.m.	n.m.	n.m.
Acid soluble lignin, wt% dab.	0.5	0.4	5.1	3.4	1.9	1.4	n.m.	n.m.	n.m.
Polysaccharides, wt% dab.	52.3	53.5	46.3	47.1	59.6	63.0	n.m.	n.m.	n.m.
Extractives, wt% dab.	1.1	0.7	0.9	0.8	1.1	0.7	n.m.	n.m.	n.m.

AL = acid leached, db. = dry basis, dab.=dry and ash-free basis

#### 4.1.2 Lignin feedstock characterization

In publication I, four different lignin batches (A, B, C and D) were pyrolysed in the bench scale unit and lignin E in pilot scale CFB unit. Detailed composition of lignin feedstocks is presented in Table 10. Hydrolysis lignin came from the St1 Cellulolix ethanol plant, which used pine (*Pinus sylvestris*) and spruce (*Picea abies*) sawdust as a raw material. Hydrolysis lignin can be considered to gone through rather severe treatment where large part of hemicellulose and cellulose are removed from the feedstock by acid hydrolysis prior to fast pyrolysis.

When compared to lignocellulosic residues, hydrolysis lignin contained, obviously, significantly more lignin and less carbohydrates. Additionally, lignin had higher carbon and lower ash and volatile contents. Carbohydrate content varied

significantly between the batches and changes were caused by the optimization work done in the upstream steam explosion and hydrolysis process.

**Table 10.** Composition of the lignin feedstock used in Publication I (© 2021 The Authors. Reprinted under license CC-BY 4.0.).

Feedstock	A	B	C	D	E
Pyrolysis unit	BFB	BFB	BFB	BFB	CFB
wt%, dry basis					
<b>Dry matter</b>	92.8	91.1	91.9	97.5	95.4
<b>Total lignin</b>	59.8	64.3	73.8	78.6	79.1
<i>Klason lignin</i>	58.7	63.5	72.6	77.7	77.9
<i>Soluble lignin</i>	1.1	0.8	1.3	0.9	1.2
<b>Carbohydrates</b>	38	34	23	18	19
<b>Moisture (TGA)</b>	6.1	8.6	7.5	4.6	4.6
<b>Carbon</b>	59.3	60	61.7	61.8	63.6
<b>Hydrogen</b>	6.1	5.9	6.2	6	6.3
<b>Nitrogen</b>	0.7	0.6	1	0.37	0.5
<b>Ash (550°C)</b>	0.3	0.4	0.4	0.3	0.4
<b>Volatiles</b>	70.7	71.3	65.1	69.5	68.2
<b>H/C, (mol/mol)</b>	1.23	1.17	1.20	1.16	1.18
<b>HHV, MJ/kg</b>	na	na	na	na	26.29
<b>LHV, MJ/kg</b>	na	na	na	na	24.92

## 4.2 Fast pyrolysis experiments

Fast pyrolysis experiments were carried out in bench and pilot scale pyrolysis units. Bench scale unit is bubbling fluidized bed reactor (BFB), and in pilot scale pyrolysis unit is circulating fluidized bed (CFB) system. To compare these units, key aspects and dimensions are listed Table 11. More detailed description of both units are given in following sections 4.2.1 and 4.2.2.

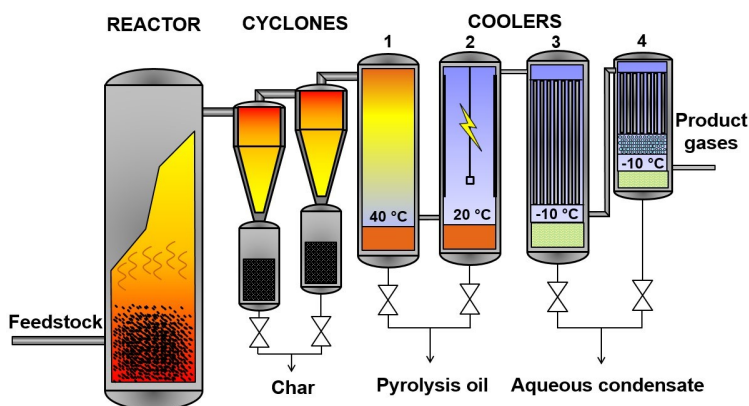
**Table 11.** Comparison of bench scale and pilot scale reactors.

Scale	Reactor type	Fluidization gas	Feed rate, kg/h	Reactor height, m	Reactor diameter, mm	Heating	FPBO condensation
Bench	BFB	Nitrogen	0.5-1.0	0.57	52	Electricity	Series of heat exchangers and electrostatic precipitator
Pilot	CFB	Circulated pyrolysis gases	15 – 20	9	64	Electricity / Pellet in combustor	Scrubbers and heat exchangers

### 4.2.1 Bench scale fast pyrolysis experiments

The bench-scale bubbling fluidized bed unit used in the fast pyrolysis experiments in publications I, II and III was used to screen the effect of changing feed quality and composition into FPBO yield and quality. Detailed description of the

unit can be found from Publications I-III. Schematic flow diagram of the unit is depicted in the Figure 7.



**Figure 7.** Schematic representation of the bubbling fluidized bed pyrolysis system.

The reactor was bubbling fluidized bed reactor white aluminium oxide was used as bed material. With lignocellulosic feeds, bed was fluidized by nitrogen. In Publication I with lignin feeds, steam/nitrogen and ethanol/nitrogen mixtures were also used as fluidization gases. Reactor diameter ( $d$ ) was 52 mm, the height ( $h$ ) 570 mm, and heat for the pyrolysis was provided from outside with four different electrical heating elements, which enable temperature control through the whole reactor length. Additionally in the case of lignin pyrolysis in Publication I, a mechanical mixer was inserted into the reactor to break lignin and bed material agglomerates caused by lignin melting and charring to avoid defluidization of the bed.

The reactor was operated at atmospheric pressure. With lignocellulosic feeds, reactor temperature of 480 °C was used as this is known to be very close to optimal temperature to maximise the FPBO yield [6,65]. With lignin rich feeds, larger variation of the temperature was tested. The superficial gas-phase residence time at the reactor conditions was 1 s and it was adjusted by the fluidization gas flow. Fluidization velocity was chosen to be short to maximize the FPBO yields. Feedstock was fed into the reactor by feed auger which was calibrated to the desired feed rate before the experiments.

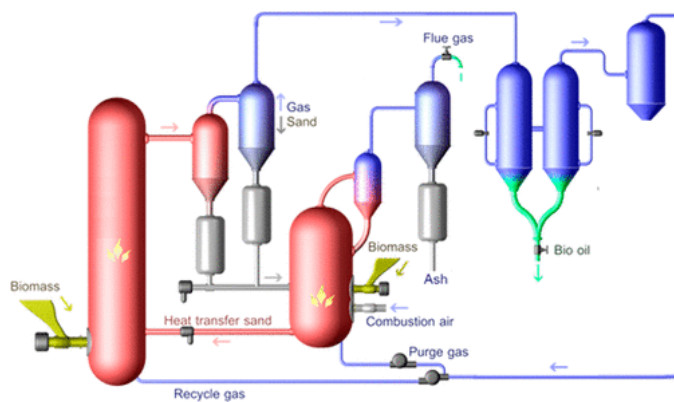
After the pyrolysis reactor, solid char was separated from the pyrolysis gases by cyclones. After the cyclones, hot vapors and gases were first cooled indirectly in cold water-cooled heat exchanger (40 °C), after which vapors and gases were passed through an electrostatic precipitator (20 °C) where aerosols from the gases were recovered. From the electrostatic precipitator (ESP) the non-condensed water and light organics were led to two glycol coolers (-10 °C); one-tube heat exchanger and a second smaller-tube heat exchanger filled with additional glass packings. The composition of the non-condensable gases was analyzed by a micro-GC.

After the pyrolysis experiments, the collected char and FPBO were weighed. Most of the organics ( $\approx 95$  wt %) were recovered in the water-cooled heat exchanger and electrostatic precipitator. The aqueous condensate recovered in the

glycol cooler contained 80–85 wt % of water. The liquid products recovered in the water-cooled heat exchanger and electrostatic precipitator were weighed and mixed before physicochemical characterization. The liquid recovered from the glycol coolers was weighed and treated separately. The liquid recovery system was rinsed after each experiment with a small amount of methanol to remove the condensed bio-oils from the walls of the condensers. The amount of pyrolysis liquid condensed on the walls was determined by evaporating the methanol from the washing liquid with a rotavapor, weighing the residue, and analyzing its water content. The total FPBO yield was the sum of all of these different recovered liquid fractions. Product yields are reported on a dry basis from the starting feedstock. Organic liquid yield refers to dry organics in the liquid fractions. Pyrolytic water refers to water formed in the pyrolysis reactions (pyrolytic water = total water in liquid products – moisture of the feedstock).

#### 4.2.2 Pilot scale fast pyrolysis experiments

Pyrolysis experiments at pilot scale in publication I, II and IV were carried out with the circulating fluidized bed (CFB) pilot unit with the feed capacity of 20 kg/h biomass feedstock. Target in the pilot scale was to scale-up the chosen feedstocks into larger scale to see how they behave in longer term operation in industrially relevant system. Additionally, target was production of larger quantities of samples for FPBO upgrading experiments. Schematic flow diagram of the unit is presented in the Figure 8.



**Figure 8.** Schematic representation of the bubbling fluidized bed pyrolysis system.

The reactor ( $d = 64$  mm,  $h = 9$  m) was operated at atmospheric pressure and heated with the hot sand from the combustor. Combustor was operated at 680 – 700 °C and sand temperature when entering the reactor was 650–680 °C. Sand used was quartz sand (0.1 – 0.6 mm,  $\rho = 2\,600$  g/dm<sup>3</sup>). The ground and sieved feedstock was introduced into the cold section of the riser reactor with a screw feeder and mixed with the cold fluidization gas stream coming from the reactor bottom. After the feedstock feeding point, feedstock particles were carried upwards by the fluidization gas to encounter the hot sand. Hot sand was

fed into the reactor with a screw feeder, and the reactor temperature was controlled with the sand flow rate. After the introduction of hot sand, the mixture of solids was carried through the reactor to the cyclones. During this time, most pyrolysis reactions took place. The used pyrolysis temperature was 480-500 °C, measured from the top part of the reactor, and the superficial fluidization gas velocity was 7 m/s. The main part of the char particles and heat transfer sand were removed by two cyclones from the hot product gases and vapors before entering the liquid recovery system.

In the liquid recovery system, two scrubbers and one cooler were used. The vapors were condensed by using the pyrolysis liquid as a cooling agent. The temperature of the scrubbers was kept at 40 °C. A part of the non-condensable gases was used for fluidization, and the rest was burned in the combustor. Most of the ash from the feedstock ended with the char in the combustor. The combustor was operated as a bubbling fluidized bed, and the temperature was controlled to 700 °C by feeding ground pellets into it. After the combustor, one cyclone and a hot gas filter were used to remove the fine dust and fly ash from the flue gases. Before the hot gas filter, flue gas was cooled to < 250 °C using a tube heat exchanger and water quench. Product yields are reported on the dry basis of the starting feedstock.

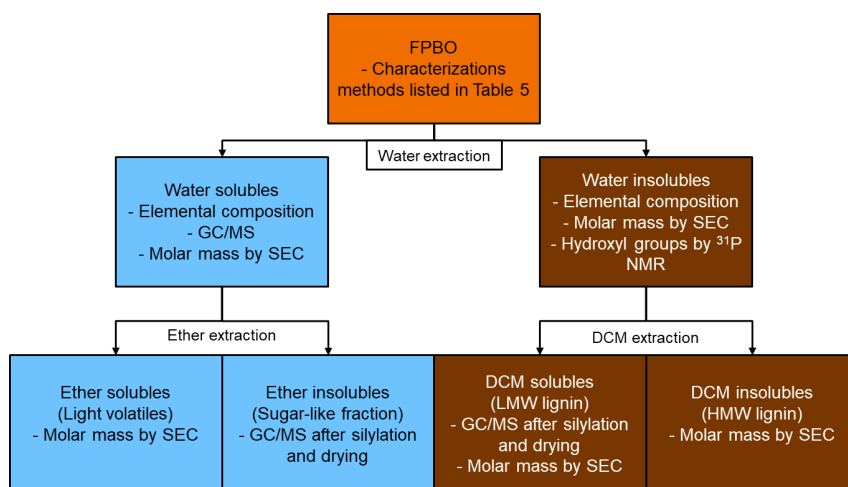
Yields from the pilot scale experiments were calculated for the stable operational periods. Stability of the operation was based on the stable reactor temperature and fluidization velocity during the balance period.

### 4.3 Characterization of the FPBOs

Physico-chemical characterization of the FPBO in Publications I-IV was carried out by employing standard methods [27] listed in Table 12. More detailed analytical descriptions can be found from the publications listed in table 7. Some analyses were carried out only after the solvent fractionation of the FPBO which was performed according to Oasmaa et al. [185] and presented in Figure 9. Shortly, this method is based on dividing the FPBO first into water soluble (WS) and insoluble fractions (WIS). WS fraction is further divided into ether soluble and insoluble fractions and WIS into ichloromethane (DCM) soluble and DCM insoluble fractions.

**Table 12.** FPBO analyses in Publications I-IV.

Property	Method	Publication
Water content	ASTM E 203	I-IV
C	ASTM D 5291	I-IV
H	ASTM D 5291	I-IV
N	ASTM D 5291	I-IV
O	by difference	I-IV
HHV	DIN 51900	I-IV
LHV	DIN 51900	I-IV
TAN/CAN/PN	modified ASTM D 664	I-IV
MCR	ASTM D 4530	I-IV
Ash	combusting the residue from the MCR determination in a muffle furnace at 775 °C	I-IV
Cl	DIN 51727 B:2011	I-III
Inorganics	DIN EN ISO 11885:2009	I, II
Chemical composition by solvent fractionation	Method according to Oasmaa et al. [184]. and Figure 9.	I-IV
Molar mass	Molar mass measurements were performed with size exclusion chromatography (SEC) described in Publication IV	IV
Phenolic and aliphatic hydroxyl groups	Phenolic and aliphatic hydroxyl groups and acids were analyzed by <sup>31</sup> P NMR described in Publication IV	IV
GC/MS	GC-MS was carried out for the different FPBO fractions after solvent fractionation procedure described in Publication IV	IV

**Figure 9.** Solvent fractionation and analytical methods used for different fractions.

## 4.4 FPBO valorization experiments

### 4.4.1 FPBO fractionation

In the publication IV, FPBO fractionation was studied. Target in the fractionation was to separate water insoluble pyrolytic lignin fraction (i.e. lignin bio-oil) to be used in the resin synthesis. Pyrolytic lignin fraction could be potential to substitute the fossil phenol, for example in the phenol-formaldehyde resins synthesis route studied in Publication IV.

After the pyrolysis experiment, the FPBO fractionation was carried out in 100 L Teflon coated vessel equipped with mixer. FPBO and water were weighted in the vessel to reach mass ratio of water and dry FPBO 1:1. Solution was mixed

for 1 h at room temperature. Larger quantities of water could help to produce purer pyrolytic lignin fraction, but to avoid excess water use and production of very diluted aqueous fraction, water addition was minimized. This was considered to be a beneficial approach from the point of view of process scale-up and economic considerations.

After mixing, the phases were let to settle. Aqueous phase, i.e., the top phase, was removed by a pump and the water insoluble viscous lignin bio-oil fraction was emptied from the valve located at the bottom of the vessel.

#### 4.4.2 Resin synthesis, characterization and validation

Synthesis experiments were started with the optimization of the synthesis conditions (e.g., reaction time, reagents' ratio). After the optimization step, phenol was gradually replaced by lignin bio-oil, and PF resins containing lignin bio-oil at 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt% (in relation to the mass of phenol), were produced. Detailed synthesis protocol can be found from the Publication IV, and only short description is given here. The steps in the synthesis are described below.

First, phenol, paraformaldehyde, lignin bio-oil and solvent were loaded in the reactor. The mixture was homogenized for 30 min with constant stirring and heated up to 40 °C to dissolve the reagents.

After the dissolution, first part of 50 wt% NaOH solution (1/3 of total amount) was added dropwise and the temperature was kept below 100 °C. After the addition of NaOH was completed, the mixture was heated gradually up to 90 °C, was kept under stirring for 60 min and then cooled down to 60–70 °C.

After cooling, the second part of NaOH solution (2/3 of total amount) was added dropwise and the mixture was heated stepwise up to 100 °C under stirring. Temperature was maintained at 100 °C for 1 h, until the free formaldehyde reached the desirable value (lower than 2.3% w/w). When the free formaldehyde content was below 2.3%, the mixture was cooled rapidly to room temperature to avoid unnecessary polycondensation reactions.

The produced resins were characterized by assessing their free formaldehyde content, non-volatile content, viscosity and pH. Formaldehyde content was measured to follow the reactivity of phenol and performance of synthesis. Non-volatile content was followed as higher value typically leads to better adhesion properties. Viscosity was followed as the high viscosity can limit the resin use in certain equipment and applications. pH was measured to assess the curing properties of the resins. Having a basic pH, resins can be cured by heating over 100 °C. At such temperature, the water is removed resulting in curing of the resin. Analysis are listed in Table 13 and more detailed method description can be found from the Publication IV.

The gluing performance of the resins was evaluated by measuring the tensile shear strength of lap joints formed by gluing 5 mm thick beech wood veneers (EN 205:2003). The resin to be tested was applied at 150 g/m<sup>2</sup> to both surfaces to be glued together and then in a hotplate press the laminate was cured at 200 °C and 20 bar for 5 min. Before cutting out the glued wood samples to be tested, the laminated wood was equilibrated at 20 °C and 65% relative humidity

for 7 days. Samples for humidity resistance were immersed in deionized water at 20°C for 24 h before testing.

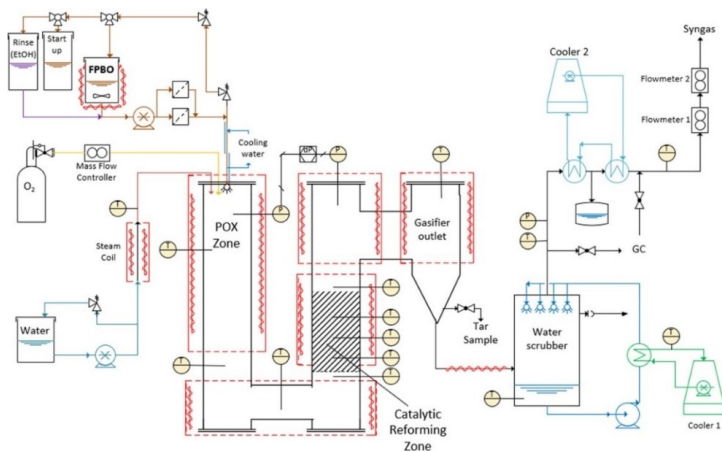
**Table 13.** Methods to characterized resins and validate resin performance.

Analysis	Method	Publication
Free formaldehyde	ISO 11402	IV
Non-volatile content	Kern DBS moisture analyser	IV
Viscosity	Brookfield RV DV-II+ Pro viscometer	IV
pH	Jenway 570 pH Meter	IV
IR spectra	Bruker ALLPHA II FT-IR spectrometer	IV
Gluing performance	EN 205:2003	IV

#### 4.4.3 FPBO gasification

Gasification of the FPBO for syngas production in Publication III was performed in a bench-scale system (Figure 10) converting about 3 kg FPBO/h. Detailed description of the unit is presented in the Publication III. The gasifier was preheated to the desired operating temperature (900 °C). Before gasification, 20 wt % bioethanol was mixed into the FPBO to reduce the viscosity and improve atomization in the bench-scale setup. For larger-scale gasifier systems, mixing ethanol is not required for processing and pure FPBO can be used. [105,119] The gasifier consists of two directly connected reactor zones. In the partial oxidation zone (POX zone), FPBO was atomized and mixed with oxygen and steam to form raw syngas, and in the fixed bed catalytic reforming zone, the hydrocarbons present in the raw syngas (tars, but also smaller hydrocarbons such as methane, ethene, etc.) are reformed to produce a clean syngas.

FPBO was supplied to the gasifier at a high pressure using a piston pump and atomized by using a spray nozzle. The atomized FPBO was mixed with pure oxygen and steam. The catalyst used in the reforming zone was a commercially available catalyst (ReforMax 330 LDP with nickel as the active component) purchased from Clariant. The hot syngas was cooled after the gasifier using a water scrubber and several indirect heat exchanges to further cool the gas to room temperature before analysis. Finally, the gas composition was measured to determine the H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> concentrations.



**Figure 10.** Schematic representation of the autothermal catalytic reforming system used in Publication III (© 2022 The Authors. Reprinted under license CC-BY 4.0.).

## 5. Results and discussion

### 5.1 Fast pyrolysis of biomass waste and residues

In this section, pyrolysis experiments with lignocellulosic residue, pretreated lignocellulosic residues, lignin rich residues and waste wood are discussed. Mass balances and composition of FPBO and gaseous pyrolysis products from different feedstocks will be compared. Results from the bench scale experiments in section 5.1.1 and results from pilot scale experiments in section 5.1.2.

#### 5.1.1 Comparison of feedstocks in bench scale BFB unit

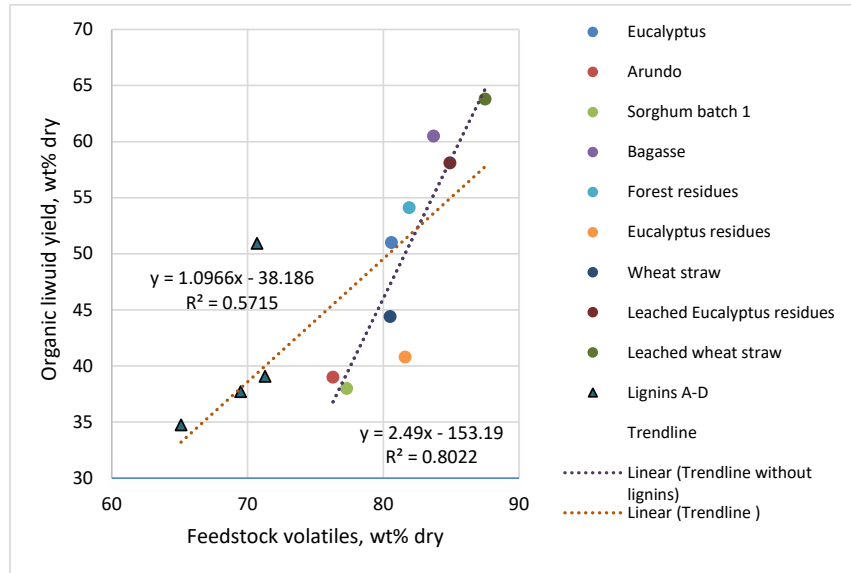
##### *Effect of feedstock and process parameters into FPBO yields*

In Publication I-III, bench scale fast pyrolysis experiments were carried out with forest residues, wheat straw, eucalyptus, eucalyptus residues, arundo, sorghum, bagasse and different hydrolysis lignin feeds. Lignocellulosic feeds were tested at 480 °C with and without pretreatment. Lignins were tested at 500 – 600 °C with and without additives. Mass balances from all bench scale pyrolysis experiments are presented in Table 14.

When the product yields from different feedstocks are compared, it can be seen that the organic liquid yields from bagasse and leached wheat straw runs were the highest (60.6 and 63.8 wt%, respectively). Lignin feeds on the other hand produced the lowest organics liquid yield. Similarly high FPBO yields have been also reported from bagasse pyrolysis in the literature. For example, Montoya et al.[189] reported FPBO yield of 70.9 wt% from bagasse in BFB reactor which is in similar range than was achieved in this study (69.7 wt%). Higher volatile content of bagasse is expected to explain the higher organic liquid yields [30]. In fact, organic liquid yield was found to correlate well with the volatile content of the tested feedstocks, especially when lignin feeds are excluded, as illustrated in Figure 11.

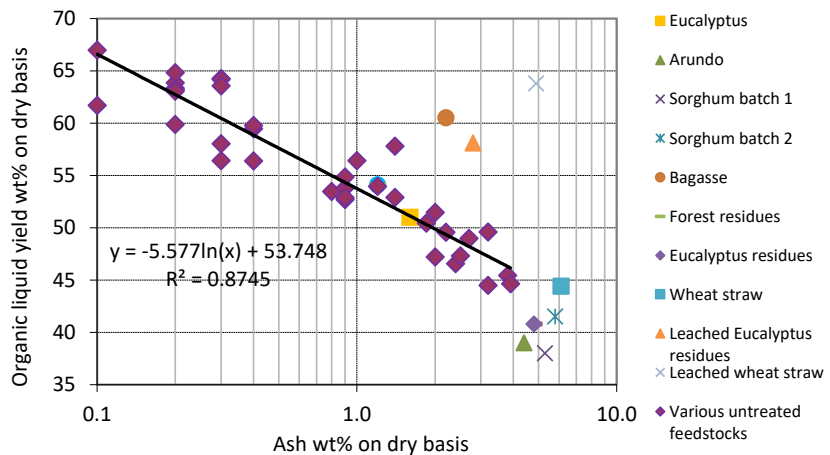
**Table 14.** Product yields calculated on dry basis for the bench-scale fast pyrolysis experiments at 480 °C. Lignins A-D were pyrolyzed at 500 °C. Standard deviation presented for the experiments where repetitions were done.

	T, °C	Additive feed rate, g/min	Char, wt%	Pyrolytic gases, wt%	Organic liquid, wt%	Pyrolytic water, wt%	Mass balance closure, wt%
Lignocellulosic feeds							
Bagasse	480	-	16.5 ± 0.8	11.4 ± 1.0	60.6 ± 1.3	9.1 ± 0.2	97.5 ± 1.3
Forest residues	480	-	17.1	12.3	54.1	11.9	95.4
Eucalyptus	480	-	20.3 ± 0.8	13.5 ± 1.6	51.1 ± 2.3	11.2 ± 0.8	96.1 ± 0.7
Sorghum	480	-	25.3 ± 1.1	16.4 ± 3.1	39.7 ± 3.3	12.2 ± 2.4	93.7 ± 5.7
Arundo	480	-	32.8	8.6	38.9	15.4	95.6
Eucalyptus residues	480	-	23.2	15.6	40.8	12.6	92.2
Leached Eucalyptus residues	480	-	19.3	7.6	58.1	11.8	96.8
Wheat straw	480	-	26.5 ± 2.4	11.4 ± 0.5	44.4 ± 1.1	12.2 ± 0.9	94.4 ± 2.5
Leached wheat straw	480	-	15.3	7.6	63.8	6.9	93.6
Lignin tests without additives							
Lignin A	500	-	24.0	5.5	50.9	6.8	87.2
Lignin B	500	-	29.8	5.4	39.1	16.4	90.7
Lignin C	500	-	32.9	10.1	34.7	9.2	86.9
Lignin D	500	-	34.2	9.8	39.8	5.1	88.9
Lignin D	550	-	34.9	10.0	41.4	6.0	92.3
Lignin D	600	-	32.3	11.2	41.7	5.2	90.4
Lignin tests with steam as additive							
Lignin D	500	3	34.9	10.0	41.4	6.0	92.3
Lignin D	550	3	32.3	11.2	41.7	5.2	90.4
Lignin D	600	3	31.2	17.5	32.4	10.2	91.2
Lignin D	500	6	38.0	8.1	40.8	9.7	96.6
Lignin D	500	9	36.9	6.2	46.0	4.1	93.3
Lignin tests with ethanol as additive							
Lignin D	500	0.4	32.4	10.8	41.7	9.6	94.4
Lignin D	550	0.4	31.8	12.3	42.2	9.0	95.4
Lignin D	600	0.4	30.2	20.9	34.7	9.8	95.6



**Figure 11.** Correlation of volatiles and organic liquid yield with feedstocks used in Publications I-III.

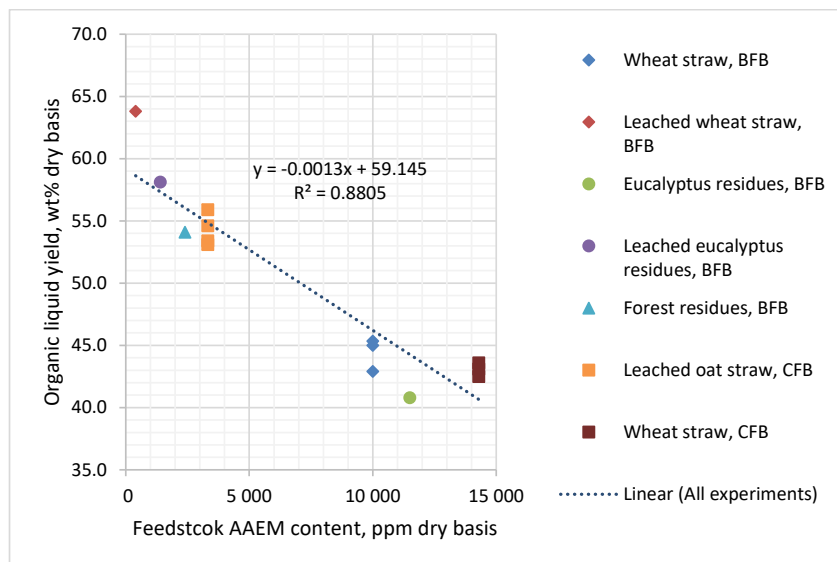
For comparison, organic liquid yields from lignocellulosics were also plotted as a function of ash content and is presented in Figure 12. While other feedstocks correlated rather well with previously published data, yield of bagasse, and acid leached feedstocks were significantly higher than could be expected only from the feedstock ash content, indicating that the ash composition is more important than the total ash content.



**Figure 12.** Organic liquid yields from feedstocks used in Publication II and III as a function of the ash content, with additional data from VTT's fluidized bed pyrolysis units.

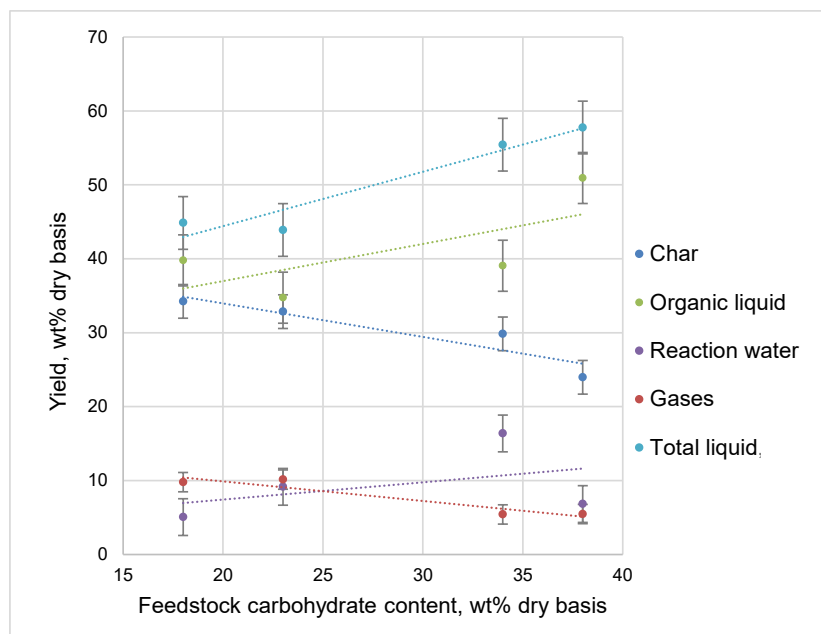
When this issue was further investigated with pretreated feedstocks, organic liquid yields were significantly higher than with their untreated counterparts. With pretreated feeds, organic liquid yield was also found to correlate with total alkali and alkaline earth metal (AAEM) content, which is illustrated in Figure

13, where also pilot data from section 5.1.2 is included. AAEM removal by acid leaching, increased the organic liquid yield by 42 % and 44 % for eucalyptus and wheat straw, respectively. Furthermore, the yield of char and gases were reduced with the leached feedstocks. With pyrolytic water, no clear trends in yield were observed. Similar organic liquid yield improvement has been reported by Stefanidis et al.[31] with high AAEM feedstock, but with feedstock lower in AAEMs, yield improvements have been milder [31,50].



**Figure 13.** Organic liquid yield as a function of feedstock AAEM content (K+Ca+Na+Mg) for the feedstocks used in Publication II (© 2022 The Authors. Reprinted under license CC-BY 4.0.).

Varying carbohydrate content of the lignins had also an effect on the product distributions as illustrated in Figure 14. With the highest feedstock carbohydrate content (lignin A) the highest organic liquid yields were reached. Additionally, gas and char yields were lower when carbohydrate content of the feed was higher. This is expected as lignin rich biomass feedstocks are known to produce more char[51,73], and carbohydrates more sugar-like liquid species, light oxygenates and gaseous products[50,186,187]. Total liquid, which is a sum of reaction water and organic liquid, was found to correlate even better with increasing carbohydrate content. Reaction water, i.e. water formed during pyrolysis reactions, showed no clear trends as a function of lignin used.



**Figure 14.** Product distribution from bench scale BFB experiments with different carbohydrate content lignins from Publication I (© 2021 The Authors. Reprinted under license CC-BY 4.0.).

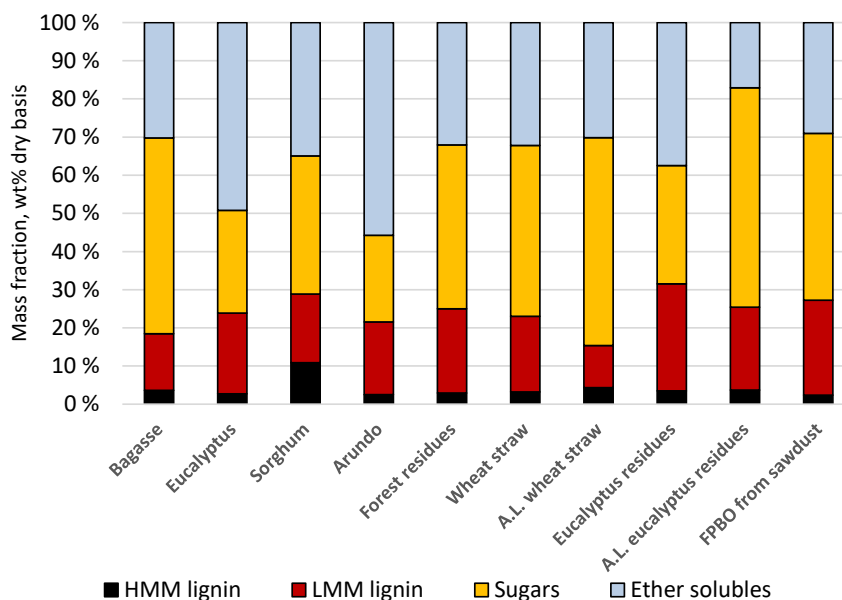
Result obtained from the thermal pyrolysis of hydrolysis lignin in BFB unit were well in line with previously published results with similar type of equipment. Nowakowski et al.[73] provided data from the thermal pyrolysis of softwood hydrolysis lignin in different BFB systems. Lignin contained 39.5%, carbohydrates which was comparable to Lignin A used in Publication I. Experiments were done at close to 500 °C (450 - 519 °C) and organic liquid yields varied between 24 - 48 wt% on dry basis. In these experiments, organic liquid yield achieved with lignin A was 51 wt% on dry basis, which is a bit higher than the range reported by Nowakowski et al. When compared to experiments with Kraft-lignin, which usually contains significantly less carbohydrates (< 5 wt%)[71,73], Tumbalam Gooty et al.[188] reported maximum organic liquid yield of 23.5 wt% on dry basis. Reactor temperature was 550 °C and reactor used was BFB reactor equipped with stirrer to break the lignin agglomerates. Purest lignin in our experiments was lignin D, where residual carbohydrate content was 18 wt% on dry basis. Organic liquid yield with lignin D was 40 wt% on dry basis. Lower carbohydrate content of Kraft-lignin is expected to explain lower yields, but also other chemical and structural differences, discussed also in section 2.3.2, can have effect on the pyrolysis performance and product yields [71].

#### *FPBO compositions from bench scale experiments*

Chemical compositions of FPBOs produced from lignocellulosics feeds in the bench scale experiments are presented in Figure 15. A major difference in chemical composition of the FPBOs is the high HMM (high-molecular-mass) fraction in sorghum FPBOs. Pyrolysis products of proteins and amino acids include many basic nitrogen compounds such as ammonia and amines[189]. Additionally, eucalyptus FPBOs contained high quantity of low molecular weight ether

soluble components and bagasse FPBO had higher sugar and lower lignin contents.

Main difference caused by the leaching pretreatment was the increased portion of the sugar fraction within the produced FPBOs. In addition, slight increase in high molecular weight (HMW) lignin was observed with leached feedstocks. Reduction in light volatile compounds and increase in low molecular weight lignin (LMW) were also observed. Regarding the chemical composition, results were in line with those presented in the literature where increased sugar content has been reported with different lignocellulosics feeds[40,52,190].



**Figure 15.** Chemical composition of FPBOs produced from lignocellulosic residues in Publication II and III. Reference data for sawdust FPBO acquired from Oasmaa et al.[30]. AL = acid leached.

FPBOs were further characterized for physical and chemical properties, and these results are presented in Table 15. Leaching pretreatment was observed to increase the oxygen content of the produced FPBOs. Increased oxygen content was seen also as lower heating value, and, additionally, micro carbon residue (MCR) was higher in FPBOs produced from leached feedstocks. Higher sugar content is expected to contribute to high MCR as sugars are known to be thermally unstable. Furthermore, sugars are rich in oxygen and therefore higher sugar content contributes to higher oxygen content of the FPBOs from leached feedstocks. Additionally, TAN was somewhat reduced in the FPBO produced from leached feedstocks, which could be attributed to reduced cracking of sugars to acids and lignin to low molecular weight phenolics. Sorghum on the other hand, had higher nitrogen content indicating potential presence of protein derived pyrolysis products. Agricultural residues are known to be rich in protein when compared to woody biomasses (Table 4).

Inorganic content of the FPBOs was also lower with leached feedstocks. Na was below detection limit in all samples, K was reduced below detection limit with leached eucalyptus and leached wheat straw, and large reduction in Ca content was observed with leached eucalyptus. In addition, S and Cl content were lower in leached feedstocks. FPBO from forest residues was lowest in all measured inorganics already without leaching, but the feedstock had also the lowest inorganic content at the beginning.

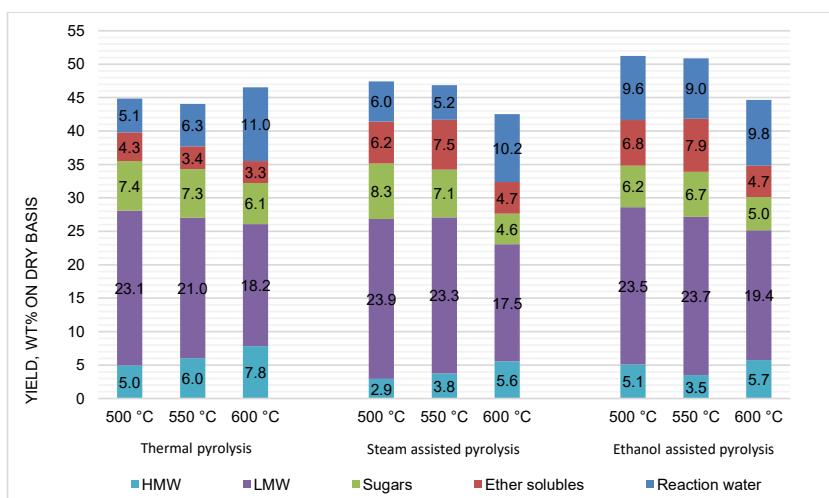
**Table 15.** Physical and chemical properties of fast pyrolysis bio-oils from BFB experiments on dry basis from Publication II (© 2022 The Authors. Reprinted under license CC-BY 4.0.).

Parameter	Forest residues	Eucalyptus residues	AL eucalyptus residues	Wheat straw	AL wheat straw	Arundo	Eucalyptus	Sorghum	Bagasse
Water, wt%	22.3	27.5	7.8	21.0	16.4	29.6	22.8	26.1	17.7
Ash, wt% dry	0.13	0.04	0.03	0.05	0.04	0.23	0.04	0.12	<0.01
MCR, wt% dry	25.1	24.4	31.2	23.7	27.4	23.6	24.1	23.7	25.2
C, wt% dry	57.8	57.5	53.5	54.9	51.0	58.5	55.7	56.0	53.3
H, wt% dry	6.3	6.8	6.2	6.8	6.1	6.7	6.7	6.9	6.2
N, wt% dry	0.1	0.4	0.3	0.3	0.1	0.4	0.3	1.2	0.2
O by difference, wt% dry	36	35	40	38	43	34	37	36	40
HHV, MJ/kg dry	24.3	24.1	21.7	22.7	20.4	24.5	23.2	23.9	21.8
LHV, MJ/kg dry	23.0	22.7	20.3	21.2	19.1	22.0	21.0	21.5	19.9
pH	2.6	3.1	2.5	2.5	2.3	2.9	2.8	3.5	2.3
TAN, mg/KOH/g dry	85.6	109.1	53.6	115.3	90.1	125	106	112	141
Carbonyls, mmol/g dry	3.6	4.4	3.9	6.6	7.3	5.3	5.4	5.7	6.8
Inorganic content									
K, mg/kg dry	bdl	48	bdl	28	bdl	n.m.	n.m.	n.m.	n.m.
Na, mg/kg dry	bdl	bdl	bdl	bdl	bdl	n.m.	n.m.	n.m.	n.m.
Ca, mg/kg dry	bdl	88	23	6	bdl	n.m.	n.m.	n.m.	n.m.
Mg, mg/kg dry	bdl	8	bdl	bdl	bdl	n.m.	n.m.	n.m.	n.m.
Si, mg/kg dry	bdl	bdl	bdl	bdl	bdl	n.m.	n.m.	n.m.	n.m.
S, mg/kg dry	80	197	128	256	139	480	187	714	169
Cl, wt% dry	0.009	0.040	0.023	0.061	0.010	0.037	0.031	0.018	0.016

AL = acid leached, bdl = below detection limit, n.m. = not measured

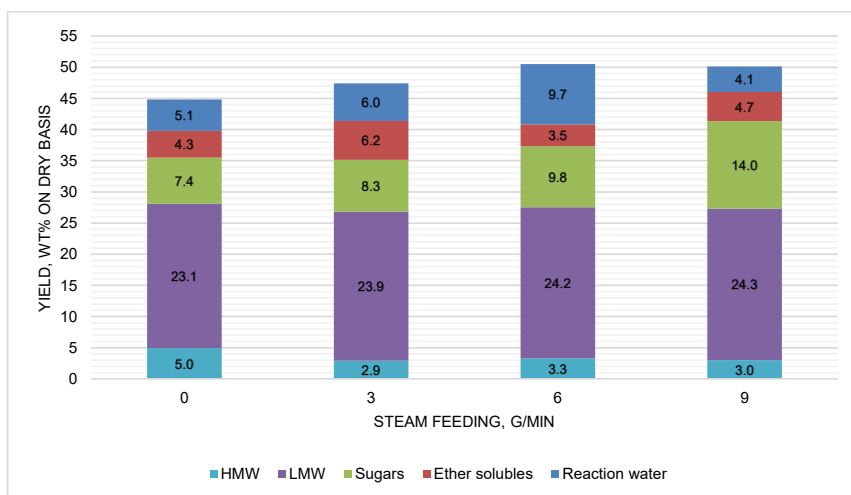
In the case of hydrolysis lignin, varying process temperature and additives were tested in the BFB unit with lignin D. Ethanol and steam were used with target to incorporate hydrogen from the additives into the produced FPBO. Chemical composition of product liquids on dry basis from bench scale thermal, steam and ethanol assisted pyrolysis is presented in Figure 16. Temperature was found to be the most important parameter and additives had only small effects. At higher temperature, the yield of LMW lignin, sugars and light water-soluble compounds decreased, while the yield of HMW lignin increased. Over cracking

of sugars, LMW lignin and light water solubles into gaseous components at 600 °C is likely reason for decreased organic liquid yields.



**Figure 16.** Total liquid composition and component yields on dry basis from the thermal, steam assisted and ethanol assisted pyrolysis experiments with lignin D from Publication I (© 2021 The Authors. Reprinted under license CC-BY 4.0.).

Furthremore, the effect on increasing share of steam in fluidization gas studied at the reactor temperature of 500 °C. Increasing share of steam was found to increase the sugar content in the organic liquid (Figure 17). Steam can perhaps stabilize the sugars in lower process temperature and prevent further secondary cracking reactions. Similar results have been reported with biomass pyrolysis by Kantarelis et al.[85]. Authors postulated that hindered dehydration reaction of sugars in the presence of steam could explain the higher sugar concentrations in FPBO.



**Figure 17.** Total liquid composition and component yields on dry basis from the steam assisted pyrolysis of lignin D with varying steam feed rate at 500 °C from Publication I (© 2021 The Authors. Reprinted under license CC-BY 4.0.).

Analysis results of the FPBOs produced in bench scale experiments from lignin D are presented in Table 16. FPBOs had significantly lower oxygen content compared to typical wood derived FPBOs. FPBOs from lignin D had oxygen content varying between 23 - 29 wt% on dry basis, while lignocellulosics tested had oxygen content of 35-43 wt% on dry basis (Table 15).

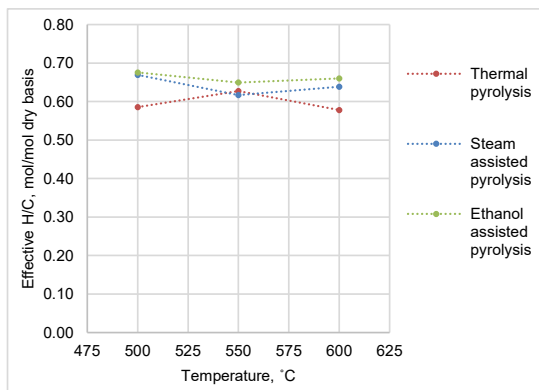
Reaction temperature and additives had an effect to oxygen content of the produced FPBOs. Lowest oxygen content was reached at 600 °C when additives were present. In thermal experiments the oxygen content of organics stayed nearly constant within the tested temperature range. Reduction in oxygen content is likely a result of cracking of oxygen rich sugars and ether solubles into gaseous products. As HMW and LMW lignin, which are lower in oxygen, are cracked to lesser extent, oxygen content of the liquid drops. Furthermore, when steam feed rate was increased, the produced FPBO contained more oxygen which is logical as the FPBOs contained also larger share of sugars as previously discussed.

When the effective molar H/C ratio, which takes into account also the oxygen content of the organic liquid and describes the liquid applicability as a refinery feed[191], is calculated and plotted in Figure 18, it can be seen that no major changes are caused by the increasing temperature nor by adding steam or ethanol into the system. Based on these calculations, it seems that no major transfer of hydrogen from the steam or ethanol into the pyrolysis liquid is occurring.

**Table 16.** Chemical characterization of the total organics and the heavy oil phase produced in bench and pilot scale from lignins D from Publication I (© 2021 The Authors. Reprinted under license CC-BY 4.0.).

Temperature, °C	500	550	600	500	550	600	500	500	500	550	600
Additive feed rate, g/min	-	-	-	3 <sup>a</sup>	3 <sup>a</sup>	3 <sup>a</sup>	6 <sup>a</sup>	9 <sup>a</sup>	0.4 <sup>b</sup>	0.4 <sup>b</sup>	0.4 <sup>b</sup>
Carbon, wt% dry basis	66.2	66.1	66.2	64.1	65.8	69.7	63.9	62.0	66.0	66.3	68.7
Hydrogen, wt% dry basis	6.6	6.8	6.5	7.1	6.8	6.6	6.4	7.4	7.0	6.9	6.8
Nitrogen, wt% dry basis	0.7	1.2	1.4	0.9	0.9	1.1	1.0	1.1	0.7	0.8	0.9
Oxygen by difference, wt% dry basis	27	26	26	28	27	23	29	29	26	26	24
H/C (mol/mol, dry basis)	1.19	1.22	1.17	1.32	1.22	1.13	1.19	1.43	1.27	1.24	1.18
O/C (mol/mol, dry basis)	0.31	0.30	0.29	0.33	0.31	0.25	0.34	0.35	0.30	0.29	0.26
Effective molar H/C	0.59	0.63	0.58	0.67	0.62	0.64	0.51	0.72	0.68	0.65	0.66

a=steam, b=ethanol



**Figure 18.** Effective H/C for the organics produced in thermal, ethanol and steam assisted pyrolysis in bench scale BFB experiments at varying temperatures with lignin D from Publication I (© 2021 The Authors. Reprinted under license CC-BY 4.0.).

### *Gaseous pyrolysis products from different feedstocks*

Non-condensable product gas compositions from bench scale experiments are presented in Table 17. Catalytic activity of ash and AAEMs can be also seen in the gas composition. Feedstocks higher in ash tend to produce more CO<sub>2</sub> as illustrated in Figure 19. The pretreated feedstocks stand out from untreated as more CO compared to CO<sub>2</sub> was formed with the leached feedstocks. Without leaching pretreatment, CO was more abundant. Cations present in the biomass seem to catalyze decarboxylation reactions, and when they are removed, decarboxylation reactions become dominant. This partly explains the higher oxygen content in leached feedstocks as less oxygen is removed in the gas phase in the form of CO compared to CO<sub>2</sub>.

Gas composition from lignin pyrolysis was significantly different compared to other feedstocks. With lignin, large quantity of methane was formed. CO<sub>2</sub> content was significantly less than with other feedstocks. Additionally, small quantities of light hydrocarbons were detected (3.2 - 5.9 vol-%).

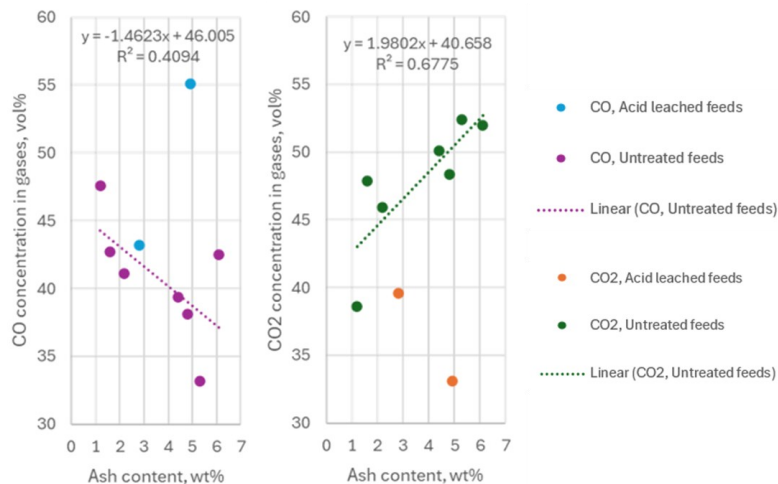
Furthermore, temperature had an effect on the gas yield in lignin pyrolysis, but also into the gas composition. Carbon dioxide was reduced in higher temperature with and without additives. Additionally, an increase in the light hydrocarbon content was observed when temperature increased. Hydrogen, on the other hand, increased from 4.0 to 9.4 vol-% in thermal experiments and from 4.3 to 12.1 vol-% when steam was present. In the experiment with ethanol, hydrogen content was high within the whole temperature range.

Steam feed rate had also a significant effect on the gas composition. Hydrogen content increased with increasing steam feed rate. Based on these results, it seems that the additives added hydrogen into the system, but no incorporation of hydrogen into pyrolysis liquid organics was occurring and hydrogen ended up mostly into gas phase as gaseous hydrogen.

**Table 17.** Composition of non-condensable gases from the bench scale pyrolysis experiments in Publications I-III. Standard deviation calculated for experiments where repetitions were available.

	Temperature	Additive feed rate	H <sub>2</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>	C2-C5 hydrocarbons
	°C	g/min	vol%	vol%	vol%	vol%	vol%
Eucalyptus	480	-	2.0±0.04	5.9±0.39	42.7±1.02	47.9±0.45	1.4±0.14
Arundo	480	-	1.6	6.6	39.4	50.1	2.4
Sorghum	480	-	8.1±0.15	3.7±0.12	33.2±0.45	52.4±0.76	2.6±0.05
Bagasse	480	-	3.7±0.01	5.9±0.17	41.1±0.25	45.9±0.42	3.5±0.01
Forest residues	480	-	3.5	8.6	47.6	38.6	1.7
Eucalyptus residues	480	-	4	8	38.1	48.4	1.5
AL eucalyptus residues	480	-	6.8	9.5	43.2	39.6	0.8
Wheat straw	480	-	0.9	3.4	42.5	52	1.1
AL wheat straw	480	-	2.3	7.4	55.1	33.1	2.2
Lignin D	500	-	4	24.7	39.9	27	4.1
	550	-	7.4	25.4	40.7	21.8	4.4
	600	-	9.4	23	40.9	19	5.8
	500	3 <sup>a</sup>	4.3	24.4	36.1	30.7	3.5
	550	3 <sup>a</sup>	7.3	22.7	37.2	27.7	4
	600	3 <sup>a</sup>	12.1	22.3	40.4	17.7	5.5
	500	6 <sup>a</sup>	5.6	21.6	35	31.9	3.2
	500	9 <sup>a</sup>	18.2	18.2	33.3	26.1	3.3
	500	0.4 <sup>b</sup>	14.9	22	33.2	24.8	4.3
	550	0.4 <sup>b</sup>	17.7	20.9	34.3	21.7	4.4
600	0.4 <sup>b</sup>	16.2	21.7	38.7	15.8	5.9	

AL=acid leached, a= steam, b = ethanol



**Figure 19.** Effect of ash into CO and CO<sub>2</sub> concentrations from the bench scale pyrolysis experiments in Publications I-III.

*Operational difficulties observed in the bench scale experiments*

Although promising results with pretreatment of wheat straw and eucalyptus were achieved in respect to FPBO yield and composition, pyrolysis of leached forest residues was not successful. Some of the biomass was “melted” and agglomerated on the heat carrier, which disturbed feed and temperature control of the reactor. This led eventually to termination of the experiment due to the bed defluidization and instability. After the reactor examination it was noted that forest residue particles were not pyrolyzed completely which led to clogging of the equipment. Feed material agglomerated onto the heat carrier and cyclones were blocked which resulted in the compromised solids removal.

Similar issues with de-ashed feeds have been reported by few other authors as well [194–197]. Generally, pyrolysis of untreated low-ash wood feedstock do not cause any problems during pyrolysis [22]. For example, heartwood chips can have ash content as low as 0.3 wt% (typically 0.3 - 0.7 wt%) and can be pyrolyzed without similar problems. However, alkali and alkaline earth metals are still present in measurable levels in these feedstocks [198], which is different compared to the acid leached forest residues in this study where alkali metals were reduced below detection limits. Based on the thermal degradation studies of pure biomass macromolecules, degradation of hemicellulose and cellulose should occur already at temperatures below 400 °C, but lignin degradation occurs on much wider temperature range (150 - 900 °C)[199]. Total absence of catalytically active ash elements might reduce the especially the lignin cracking which furthermore can severely affect the processability of feedstock [196]. Especially calcium has been reported to be active in the cracking of lignin into phenolic compounds [22,31]. Furthermore, lignin as such is prone to melting under heating and can form agglomerates in the fluidized beds [62,200,201].

Similar issues with bed agglomeration were also faced when hydrolysis lignin, but feedstock carbohydrate content was found to have significant effect on the processability. In the experiments with highest carbohydrate lignins, i.e. Lignin A, reactor was operated without bed agglomeration or defluidization problems. When carbohydrates decreased, more severe bed agglomerate issues were faced. Eventually with lignins C and D, severe bed agglomeration and defluidization was confronted, resulting into fluctuation of pressure difference over the fluidized bed, and into unstable reactor temperature. Mechanical mixer was installed into the reactor to break the char agglomerates. With mixer attached, stable operation was reached in the reactor. With lignins C and D, the deposit formation in the product gas line got also more severe and pressure build up rates were increased.

As noted in Table 10, hydrolysis lignin had a very low ash content. Efficient and complete lignin conversion may need catalytically active elements to be present [192]. This is supported by the fact that lignin melting has been reported to diminish by alkali metal impregnation. Especially calcium has been proven to be efficient to suppress the melting behavior [87,193]. In addition, during biomass pyrolysis, lignin is speculated to be released mainly as aerosols, which are ejected through bubble-formation process when carbohydrates are cracked into lighter compounds [16,194,195]. Lack of carbohydrates could reduce the release of lignin aerosols[16]. Therefore, a larger fraction of carbohydrates in

the feedstock could improve the processability through enhanced release of lignin aerosols.

### 5.1.2 Pilot scale fast pyrolysis experiments

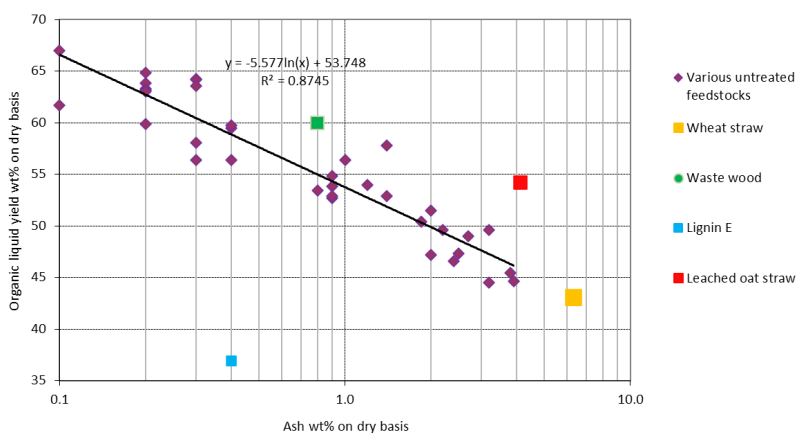
#### *Mass balances from pilot scale experiments*

Mass balances from pilot experiments are presented in Table 18. When the organic liquid yield from leached oat straw is compared with wheat straw, leached feedstock gave higher yield. Furthermore, when compared to feedstocks with similar ash contents, leached oat straw seems to give better yields than other feedstocks with similar ash content. (Figure 20). This is in line with the bench scale experiments and supports the conclusion that the AAEM concentrations are more important than the total ash content, although the total ash content correlates well with the organic liquid in the case of untreated feedstocks. Logical explanation for this is that the ash content in untreated feedstock can be expected to correlate with feedstock AAEM content as increasing quantity of AAEMs will contribute to higher ash content.

With waste wood, obtained organic liquid yield was high (60.0 wt% of dry feedstock on average). Yields were comparable with high quality feedstocks, such as pine saw dust or de-ashed straw [11,22,30,196]. On the other hand, lignin gave lower organic liquid yields as expected from the bench scale experiments. Char, organic liquid, reaction water, and gas yields were 43, 37, 11, and 11 wt %, respectively. In comparison, the same values from bench scale BFB experiments conducted at 500 °C were 34, 40, 5, and 10 wt %, respectively. The largest difference was in the char yield, which was significantly higher in the pilot experiment compared to bench scale experiments.

**Table 18.** Mass balances from the pilot test runs in Publications I, II and IV.

Feedstock	Stage	Balance period length (h)	Feed rate (kg/h)	T (°C)	Organic liquids (wt%, dry)	Pyrolytic water (wt%, dry)	Gases (wt%, dry)	Char by difference (wt%, dry)
Leached oat straw	1	9.1	18	480	55.9	10.2	12.1	21.8
	2	8.5	14.6	488	54.6	12.2	12.0	21.2
	3	8.9	14.7	499	53.1	14.0	13.1	19.8
	4	6.8	17.7	480	53.4	12.9	11.8	21.9
Untreated wheat straw	1	33.6	19.6	481	43.6	14.9	14.2	27.3
	2	14.4	19.1	481	43.1	16.8	15.6	24.5
	3	5.6	19.6	462	42.5	13.8	14.6	29.1
Waste wood	1	40	18.7	483	57.9	12.1	11.1	18.9
	2	40	20.4	480	62.0	11.3	11.0	15.7
Lignin E	1		15.5	525	36.9	10.6	11.4	41.1



**Figure 20.** Organic liquid yields from feedstocks used in pilot experiments in Publications I, II and IV as a function of the ash content, with additional data from VTT's fluidized bed pyrolysis units.

### *FPBO composition from pilot experiments*

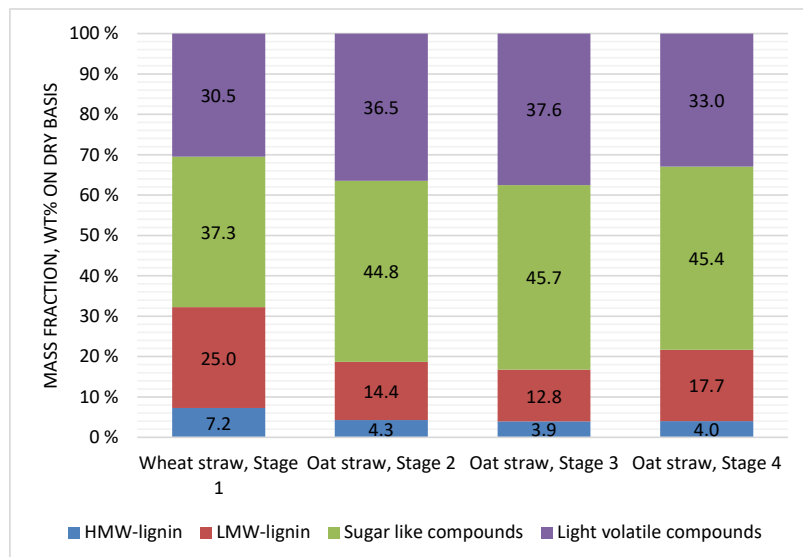
When the composition of produced FPBOs is considered, the results from the pilot scale experiments were generally in line with the bench scale results. Characterization of the FPBOs produced in pilot experiments are presented in Table 19. Waste wood derived FPBO was comparable to FPBO from low ash lignocellulosics. FPBO from Lignin E was similar in elemental composition as in the bench scale experiments. Compared to other FPBOs, lignin FPBO had lower acid number, which can be a result of lower quantities of carbohydrates, especially hemicelluloses, which contribute to the formation of organic acids during pyrolysis. Leached oat straw contained more sugars than the untreated wheat straw as can be seen in Figure 21.

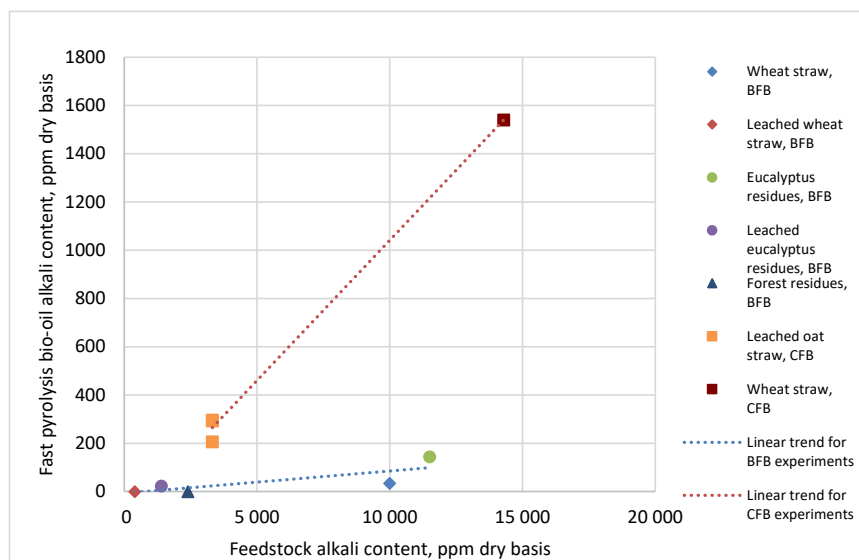
Additionally, leached feedstock produced FPBO with lower AAEM content. Average transfer rate of alkalis from leached feedstock to FPBO, were 20 %, 25 %, 12 % and 4 %, for calcium, magnesium, sodium and potassium, respectively. Transfer rates were larger than previously published results presented by Leijenhurst et al. [33]. However, Leijenhurst et al. used rotating cone and screw reactors which are different compared to the fluidized bed reactor. High fluidization gas rates can especially increase the char carry-over into the FPBO, and metals present in char can potentially be leached into FPBO. Therefore, removal of solids is critical when low AAEM content liquids are targeted [33]. Ash and inorganic content of the FPBOs were also higher in CFB pilot experiments compared to bench scale BFB experiments, as illustrated in Figure 22. Reason for this likely the better cyclone performance is smaller scale.

**Table 19.** Characterization of the produced fast pyrolysis bio-oils at the CFB pilot from Publication II (© 2022 The Authors. Reprinted under license CC-BY 4.0.).

	Unit	Wheat straw	Leached oat straw			Lignin E	Waste wood
		Stage 1	Stage 2	Stage 3	Stage 4		
Water	wt%	25.5	26.5	28.9	27.5	11.2	20.3
Ash	wt%, dry	0.90	0.46	0.42	0.34	0.05	0.08
MCR	wt%, dry	26.7	27.3	26.9	27.4	34.9	-
C	wt%, dry	56.5	54.7	54.6	55.2	69.9	53.8
H	wt%, dry	6.9	6.6	6.6	6.5	6.7	6.3
N	wt%, dry	0.8	0.8	0.7	0.8	0.7	0.6
Oxygen by difference	wt%, dry	35	38	38	38	23	39
Solids	wt%, dry	1.3	0.7	0.7	0.7	1.6	0.1
TAN	mg KOH/g, dry	84	72.0	73.0	70.8	44.9	176
Inorganic content							
K	mg/kg, dry	870	88	100	84	-	-
Na	mg/kg, dry	bdl	13	28	23	-	-
Ca	mg/kg, dry	520	150	130	80	-	-
Mg	mg/kg, dry	150	45	35	19	-	-
Si	mg/kg, dry	81	960	880	650	-	-
S	wt%, dry	0.11	0.09	0.09	0.10	-	-
Cl	wt%, dry	0.14	0.03	0.04	0.04	-	-

bdl = below detection limit

**Figure 21.** Fast pyrolysis bio-oil composition from the pilot experiments with wheat straw and leached oat straw on dry basis from Publication II (© 2022 The Authors. Reprinted under license CC-BY 4.0.).



**Figure 22.** Fast pyrolysis bio-oil AAEM content as a function of feedstock AAEM content in the BFB (blue trend line) and CFB (red trend line) units for the feedstocks used in Publication II (© 2022 The Authors. Reprinted under license CC-BY 4.0.).

### *Operational observations and discussion regarding waste wood pyrolysis*

Although good FPBO yields and FPBO quality was reached in pilot experiment with waste wood some operational issues were faced. Experiment consisted of two continuous 40-hour periods with 20-hour maintenance break between the operational periods.

The maintenance break during the pilot run was not planned and it was caused by the blockages in the liquid recovery system. A large amount of solid coke was formed in the first scrubber where the hot vapors were cooled and condensed. These solids blocked the top part of the scrubber and the pump lines in the bottom. During the maintenance break, the system was cleaned, but the phenomena repeated itself during the second 40 hours operational period. Although solids and coke formation in the scrubber is typical when the hot vapors are cooled down, this extensive solid formation has not been observed previously with biomass feedstock. One possible explanation could be that the impurities present in waste wood, such as resins, are contributing to the solids formation.

Nevertheless, high organic liquid yield achieved in pilot run confirmed potentiality of the waste wood derived feedstocks in the FPBO production. Better understanding of the impurity behaviour during pyrolysis and condensations phase is still needed to overcome the observed operational issues.

### *Operational observations and discussion regarding pretreated feedstocks*

In the pilot experiments with pretreated straw, issues were faced in the sand circulation during the pilot experiments which was identified to be caused by the blockages inside the sand pipe feeding the hot sand from the combustor into the reactor. Issues were expected to be a result of partly melted sticky ash re-

sulting from the pyrolysis feedstock. Similar problems were observed in the experiment with untreated wheat straw, but in this case also large agglomerates were found from the combustor afterwards. With leached oat straw, large agglomerates were not found, but it is suspected that ash can form sticky or adhesive melt that can glue sand particles together and disturb the sand flow.

Based on the literature, straw ash is known to have low melting point which can result in the formation of agglomerates at elevated temperatures[197]. Leaching of inorganics has also been shown to affect the melting behaviour of greenhouse residue ash [56]. Effects of leaching procedure to thermal behaviour of straw ash is still unclear, but changing inorganic content is expected to affect also the ash melting behaviour. Additives could furthermore reduce the melting induced operational problems[198].

Nevertheless, pilot run confirmed potential benefits of the pretreatment as pilot was operated with high liquid yield. Techno-economics of the pretreatment step still needs to be evaluated to assess the economic feasibility of the pretreatment. Additionally, if applications for FPBO derived sugars are developed, it will increase the attractiveness of the pretreatment as one of the key benefits of the pretreatment is increased sugar content in the FPBO.

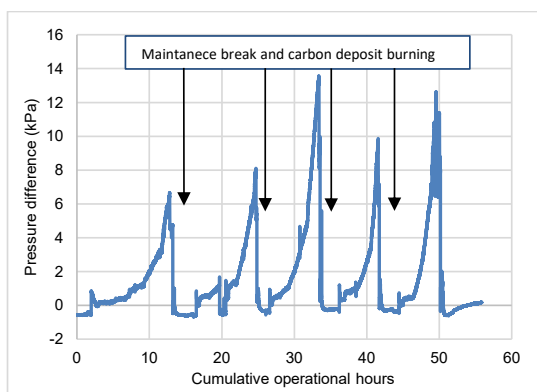
#### *Operational observations and discussion regarding lignin pyrolysis*

When the lignin E was tested in CFB pilot, bed agglomeration was not a problem. The reason for this is expected to be the different reactor configuration in pilot scale. High gas and particle velocities in the riser reactor can result in the breakage of the agglomerates. However, issues with deposit formation were emphasized in a 2 day long experiment carried out in a CFB pilot unit. Rapid deposit formation resulted in increased pressure build-up rate and shorter operational periods depicted in Figure 23. Repeating maintenance breaks were needed to burn the carbon deposits from the product gas lines and therefore the availability (hours in production/hours planned) of the system was only 64 %. The longest continuous period reached with feed rate of 15 kg/h was a bit over ten hours at the beginning of the test run.

Two mechanisms for deposits formation were suggested in Publication I: (1) collision and attachment of pyrolysis derived aerosols with pipe surfaces with subsequent charring of the droplets and (2) formation of soot and char from the secondary reactions of lignin derived vapors. Aerosol mechanism (1) seems to be more likely because soot particles (2) would be easily carried out by the gas flow all the way to liquid recovery. However, if aerosols form sticky carbon residue on the pipe surfaces, fine soot from the secondary reactions, or even fine char escaping the cyclones, can be more easily attached on the surfaces and contribute to the deposit formation. Aerosol mechanism (1) is also supported by the fact that the wood derived aerosols are rich in lignin fragments [12] and lignin oligomers can be ejected as aerosols through bubble-formation process[16]. Hence, feedstock rich in lignin could produce even larger fraction of aerosols capable to stick on pipe surfaces.

Short operational periods and reoccurring shutdowns and start-ups caused fluctuation in the process conditions. Reactor temperature varied from 511 to 538 °C, averaging on 525 °C. Despite these drawbacks, calculated mass balances

were comparable with the bench scale experiments. Char, organic liquid, reaction water and gas yields were 43, 37, 11, and 11 wt%, respectively, while in the bench scale BFB experiments at 500 °C yields of 34, 40, 5 and 10 wt%, respectively, were achieved. Positively, no lignin melting induced problems were faced in raw material feeding or in the reactor side. Lignin was fed into the cold section of the reactor, where cold fluidization gas carried the particles upwards prior to contact with hot sand. Additionally, the lignin quality is expected to have significant effects as no feeding problems were faced even in the bench scale BFB experiments. As Han et al.[71] reported, hydrolysis lignin is less prone to melt in pre-pyrolysis temperatures when compared to other types of technical lignins.



**Figure 23.** Pressure drop across the second cyclone during pilot experiment from Publication I (© 2021 The Authors. Reprinted under license CC-BY 4.0.).

These observed operational difficulties in pilot scale hydrolysis lignin fast pyrolysis underline the aspect that technical feasibility and readiness of lignin pyrolysis is still very questionable. Furthermore, low liquid and high char yield arises a question if lignin is more suitable for optimization of char and carbon production, instead of liquefaction through fast pyrolysis. Lignin carbonization and production of carbons suitable for energy storage applications could be another way to valorize the lignins through thermochemical processing [199].

## 5.2 Valorization of FPBOs

Valorization routes studied in this dissertation include the FPBO gasification, FPBO fractionation and use of pyrolytic lignin fraction in the synthesis of phenol formaldehyde resins. FPBO gasification is discussed in section 5.2.1, FPBO fractionation in section 5.2.2 and resin synthesis in section 5.2.3.

### 5.2.1 FPBO gasification into syngas

FPBOs produced in Publication III were subjected to gasification experiment with the target to prove the technical feasibility and assess the efficiency of FPBO gasification process with varying feedstocks. To ensure proper atomization of the FPBOs in the gasifier, 20 wt% of bioethanol was added to reduce the

viscosity of the FPBO and prevent formation of large droplets which are undesirable when full conversion is targeted. The viscosity requirement is particularly important for the small-scale system where the unit dimensions restrict the operation. For example, the viscosity can be problematic when pipe dimensions are small, and atomization can be improved with industrial nozzle systems. In full-scale gasifier pure FPBO is expected to be fed as such without any additives.

The composition of the gasifier feeds is presented in Table 20. FPBOs are named according to the original biomass feedstock with the bioethanol content to avoid confusing them to the corresponding FPBOs without additives. For Sorghum the FPBO from batch 1 and batch 2 were combined before mixing with the bioethanol.

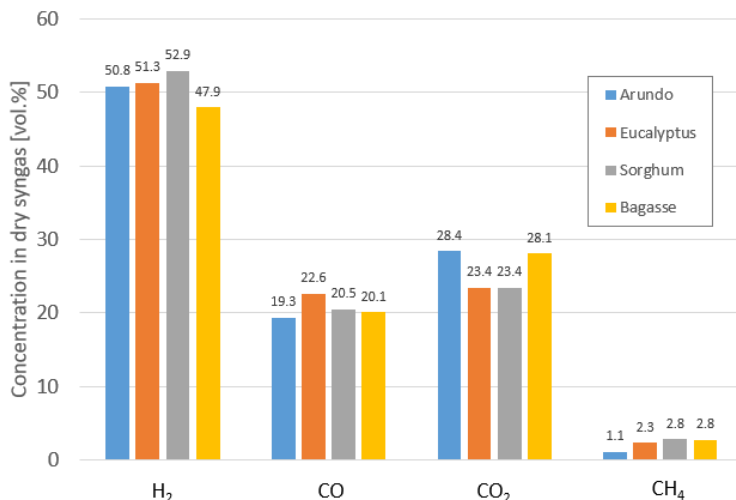
**Table 20.** Composition of the FPBOs as fed to the gasifier, all data on 'as received' basis from Publication III (© 2022 The Authors. Reprinted under license CC-BY 4.0.).

	Unit	Arundo20	Eucalyptus20	Sorghum20*	Bagasse20
Ethanol added	wt%	20	20	20	20
Carbon	wt%	43.4	45.8	42.9	44.8
Hydrogen	wt%	8.9	8.5	8.4	8.0
Nitrogen	wt%	0.4	0.3	0.7	0.2
Oxygen (by diff)	wt%	47.3	45.4	48.0	46.9
Water	wt%	22.9	19.8	25.6	14.8
LHV	MJ/kg	18.0	18.7	17.1	17.9
Viscosity (40 °C)	cSt	7	12	8	18
MCR	wt%	13	15	13	16

\* Sorghum oil from batch 1 and batch 2 was combined for the gasification tests.

For the gasification tests with FPBOs originating from Arundo, Eucalyptus and Sorghum steady-state was achieved rapidly and gas compositions were stable throughout the tests. For the bagasse there was a need to decrease the oxygen flow to the gasifier (from 1.3 kg/h to 1.1 kg/h) to prevent too high temperature in the partial oxidation zone. High temperatures are usually caused by bad atomization. When the FPBO is not properly atomized, part of the FPBO does not react quickly enough in the gasifier, which results in a lower apparent fuel to oxygen ratio and higher gasifier temperature. The higher viscosity observed with bagasse derived FPBO (20 vs. 7-12 cSt, Table 20) is a likely the cause of poor atomization.

The dry syngas composition for the four FPBOs is presented in Figure 24. Hydrogen content was around 50 vol% for all feedstocks, while CO and CO<sub>2</sub> content were in the ranges of 19-23% and 23-28 vol%, respectively. The concentrations of gas components, including H<sub>2</sub>, CO, CO<sub>2</sub> as well as H<sub>2</sub>O, were close to the thermodynamic equilibrium of the water-gas-shift reaction, which indicates good conversion FPBO into syngas. Methane, on the other hand, was present in low concentrations (1.1-2.8 vol%) in the syngas, which is above the equilibrium value predicted by the methane-steam-reforming equilibrium. Therefore, methane reforming was not complete, but this is, however, frequently observed in gasification systems.



**Figure 24.** Dry syngas composition obtained with the four FPBOs from Publication III (© 2022 The Authors. Reprinted under license CC-BY 4.0.).

When the total syngas production is considered, rate of gas production was similar with all FPBOs. Gas production was 1.71 Nm<sup>3</sup>/kg FPBO for Arundo, 1.75 Nm<sup>3</sup>/kg FPBO for Eucalyptus, 1.68 Nm<sup>3</sup>/kg FPBO for Sorghum and 1.68 Nm<sup>3</sup>/kg FBPO for bagasse. The carbon to gas ratio was 0.98 for Arundo, 0.94 for Eucalyptus, 0.94 for Sorghum and 0.98 for Bagasse 0.98. This ratio depends mostly on the atomization performance, which was optimized for these tests, but ratios can be considered to be good.

Similar gas compositions and gas productions observed in the experiments with different FPBOs show that the combination of fast pyrolysis and FPBO gasification can provide a feedstock flexible valorization route for FPBOs from different origins. Stable syngas production could open possibilities to convert the FPBO in feedstock for different fuels and chemicals as discussed in Chapter 3.

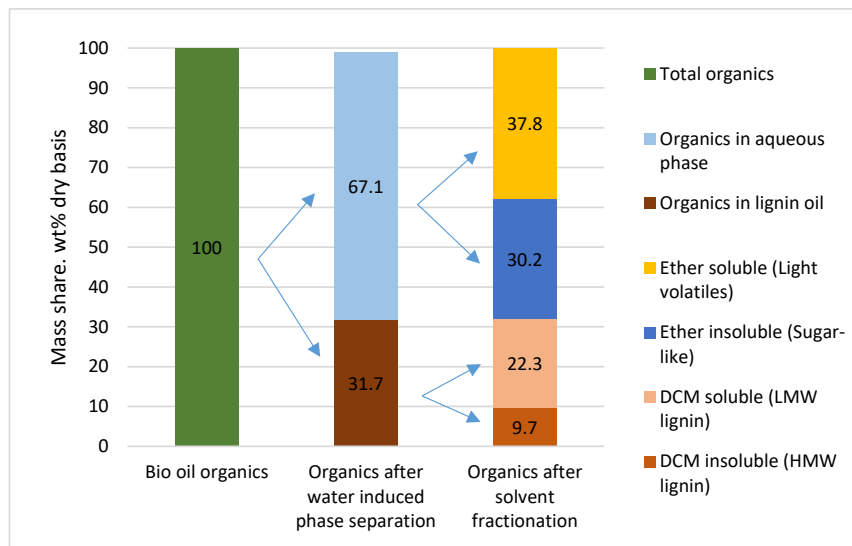
### 5.2.2 FPBO fractionation and characterization of the fractions

In the publication IV fractionation experiment were conducted with demolition wood based FPBO. Fractionation of water insoluble lignin bio-oil from water soluble fraction was conducted by adding water into the FPBO to achieve water/organics ratio of 1:1. Addition resulted into phase separation and FPBO organics were divided into water solubles and water insoluble fractions. Totally, 46.4 kg of pyrolysis oil with water content of 17.4 wt% was mixed with 30.2 kg of water and after mixing and settling, 62.2 kg of aqueous fraction and 13.7 kg of water insoluble lignin bio-oil fraction was obtained. Mass balances from the fractionation are presented in Table 21.

**Table 21.** Yield of different fractions from the fractionation of the pyrolysis oil by water addition from Publication IV (© 2023 The Authors. Reprinted under license CC-BY 4.0.).

	Water content	C	H	N	O	Total quantity	Water	Organics	Yield of organics, dry basis
	wt%	wt% dry	wt% dry	wt% dry	wt% dry	kg	kg	kg	wt% dry
<i>Materials IN</i>									
FPBO	17.5	52.0	6.4	0.6	41	46.4	8.1	38.3	-
Water	100	-	-	-	-	30.2	30.2	0.0	-
SUM	-	-	-	-	-	76.6	38.3	38.3	-
<i>Materials OUT</i>									
Aqueous fraction	58.7	48.7	5.2	1.3	45	62.2	36.5	25.7	67.1
Water insoluble fraction (lignin bio-oil)	11.5	66.8	6.7	0.9	26	13.7	1.6	12.1	31.7
SUM	-	-	-	-	-	75.9	38.1	37.8	98.8

When the division of the FPBO organics into different phases are considered, 31.7 wt% of organics was captured within the water insoluble lignin bio-oil fraction, meaning that 67.1 wt% of the organics ended up into the aqueous fraction. Organics of the aqueous fraction were richer in oxygen compared to water insoluble fraction (45 wt% vs. 26 wt%), whereas the water insoluble fraction was richer in carbon (66.8 wt% vs. 48.7 wt%). Results are logical, as the water-soluble organics in pyrolysis oils typically contain polar oxygen rich compounds, such as sugar derivatives, acids, aldehydes, ketones, furans and pyrans, while non-polar water insoluble lignin fragments with varying molecular size are richer in carbon [22]. For the detailed chemical characterization water soluble and insoluble fractions were further solvent fractionated and characterized according to scheme in Figure 8. Quantities of different fractions are illustrated in Figure 25. Concentrations of selected components quantified by GC/MS are presented in Table 22.



**Figure 25.** Distribution of organics during water induced bio-oil fractionation. Publication IV. DCM = dimethyl chloride, LMW = light molecular weight, HMW = high molecular weight

When the composition and quality of the water insoluble lignin bio-oil is assessed, the quantity of DCM solubles was higher compared to the DCM insolubles (22.3 vs. 9.7 wt%). According to the molecular mass analyses, DCM solubles were lower in molecular weight compared to the DCM insolubles, which is in line with solubility properties in DCM (Table 23). Based on the GC/MS, DCM solubles contained most of the lignin monomers and the extractives of the starting FPBO (Table 22). Additionally, some anhydrosugars were detected from the DCM solubles indicating incomplete separation of the water solubles and water insoluble fragments from each other. Further washing of water insoluble fraction could improve the purity and reduce the quantity of sugar derivatives. DCM insolubles on the other hand, consisted of oligomeric and polymeric components originating from the lignin structure, which are not detectable by GC/MS.

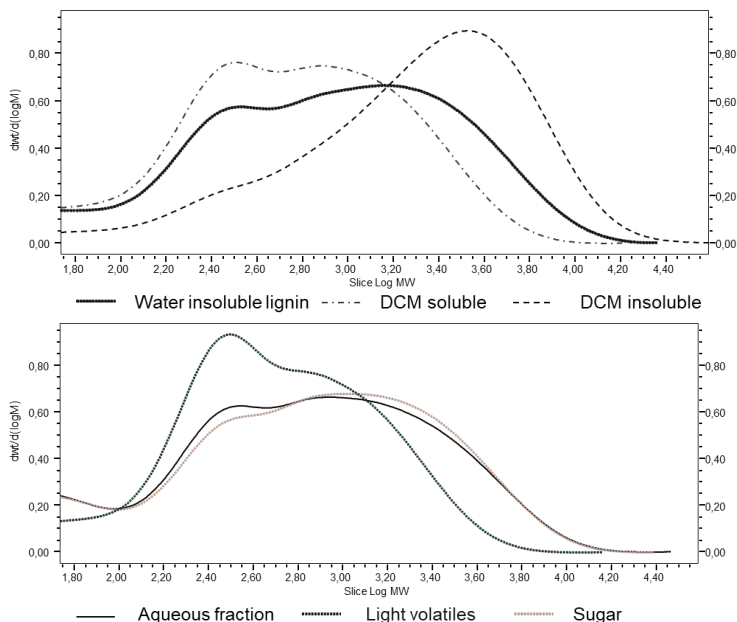
In the case of the aqueous fraction, the content of ether solubles was slightly higher than the ether insoluble (37.8 vs. 30.2 wt%). Additionally, ether solubles were lower in molecular weight compared to the ether insoluble fraction (Table 23). Furthermore, ether solubles were rich in low molecular weight oxygenates (acids, alcohols, ketones, aldehydes, and furans) while ether insolubles were rich in anhydrosugars and oligomeric fragments of polysaccharides (Table 22). Additionally, small quantities of lignin derived products could be determined from the water-soluble fraction due to the hydrophilicity of certain phenolic compounds.

**Table 22.** Identified GC-eluted organic compounds in different FPBO fractions from Publication IV (© 2022 The Authors. Reprinted under license CC-BY 4.0.).

Compounds	In dry FPBO, wt %	Compounds	In dry FPBO, wt %
Water soluble aqueous phase		Water insoluble lignin bio-oil	
<b>Light volatiles</b>	37.8	<b>DCM soluble (LMW lignin and extractives)</b>	22.3
Alcohols and acids	9.30	Lignin derived monophenols	0.9
- <i>Methanol</i>	0.60	- <i>Hydroxyphenylethanol</i>	0.07
- <i>2-Propanol</i>	2.10	- <i>Hydroquinone</i>	0.03
- <i>Acetic acid</i>	6.14	- <i>Catechol</i>	0.09
- <i>Propionic acid</i>	0.36	- <i>4-Methylcatechol</i>	0.08
Aldehydes, ketones, furans, pyrans	12.5	- <i>3-Methylcatechol</i>	0.02
- <i>Acetaldehyde</i>	0.18	- <i>Guaiacol</i>	0.03
- <i>Glycolaldehyde (dimer)</i>	7.38	- <i>4-Methylguaiacol</i>	0.07
- <i>1-Hydroxy-2-propanone (acetol)</i>	2.40	- <i>4-Ethylguaiacol</i>	0.02
- <i>Furfural</i>	0.18	- <i>Eugenol</i>	0.04
- <i>5-Hydroxymethylfurfural</i>	0.34	- <i>Isoeugenol</i>	0.11
Lignin derived monophenols	0.71	- <i>Vanillin</i>	0.08
- <i>Phenol</i>	0.03	- <i>Vanillic acid</i>	0.05
- <i>2-Methylphenol</i>	0.01	- <i>Acetylguaiacol</i>	0.04
- <i>3-Methylphenol</i>	0.01	- <i>Guaiacylacetone</i>	0.03
- <i>4-Methylphenol</i>	0.03	- <i>Dihydroconiferyl alcohol</i>	0.04
- <i>Guaiacol</i>	0.15	- <i>Coniferylaldehyde</i>	0.10
- <i>4-Methylguaiacol</i>	0.11	Dilignols	0.09
- <i>Eugenol</i>	0.02	- <i>4,4'-Dihydroxy-3,3'-dimethoxystilbene</i>	0.09
- <i>Isoeugenol</i>	0.13	Anhydrosugars	0.19
- <i>Vanillin</i>	0.18	- <i>1,6-Anhydro-β-D-mannopyranose</i>	0.05
- <i>Syringol</i>	0.02	- <i>1,6-Anhydro-β-D-glucopyranose (Levoglucozan)</i>	0.14
- <i>4-Methylsyringol</i>	0.01	Extractives and derivatives	0.58
<b>Ether insoluble (Sugar-like)</b>	30.2	- <i>Nonadioic acid</i>	0.03
Alcohols, acids, aldehydes	0.87	- <i>Oleic acid</i>	0.06
- <i>Ethyleneglycol</i>	0.13	- <i>Pimaric acid</i>	0.05
- <i>Glycolic acid</i>	0.19	- <i>Isopimaric acid</i>	0.03
- <i>Glycolaldehyde dimer</i>	0.31	- <i>Palustric acid</i>	0.02
- <i>1,4-anhydro-3-deoxypentitol-2-carboxylic acids</i>	0.16	- <i>Dehydrodehydroabietic acid</i>	0.05
Anhydrosugars	1.88	- <i>Dehydroabietic acid</i>	0.19
- <i>1,6-Anhydro-β-D-mannopyranose</i>	0.34	- <i>Abietic acid</i>	0.07
- <i>1,6-Anhydro-β-D-glucopyranose (Levoglucozan)</i>	1.45	- <i>7-Oxodehydroabietic acid</i>	0.08
- <i>Cellobiosan</i>	0.29	- <i>Unidentified LMW compounds in LMW lignin</i>	0.29
- <i>Unidentified LMW compounds in sugar fraction</i>	1.41	<b>DCM insoluble (HMW lignin)</b>	9.7

When the molar mass results of different fractions are considered more closely (Figure 26 and Table 23), it can be seen that especially the ether solubles contain more low molecular weight components compared to other analysed fractions.

Ether insoluble on the other hand are much higher in molecular weight supporting the presence of oligomeric sugars. From the DCM solubles and insoluble it can be seen that biomass lignin has been converted into low molecular weight fragments during pyrolysis ( $M_w = 1681$  Da,  $PD = 3.8$ ). For example, Crestini et al. [200] reported  $M_w = 6000$  and  $PD = 6.2$  for soft wood Kraft lignin, which is much higher than values measured for water insoluble lignin bio-oil. The low molecular weight with narrow polydispersity could be beneficial as they might increase the reactivity of the lignin if further syntheses are considered. Water insoluble lignin bio-oil was further tested in synthesis of phenol formaldehyde resins and the results are discussed in section 5.2.3.



**Figure 26.** Molecular masses of the different FPBO fractions. LMW = low molecular weight, HMW = high molecular weight. from Publication IV ((© 2023 The Authors. Reprinted under license CC-BY 4.0.),

**Table 23.** Number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and polydispersity ( $PD$ ) for the organics in different FPBO fractions from Publication IV (© 2023 The Authors. Reprinted under license CC-BY 4.0.).

	<b><math>M_n</math></b>	<b><math>M_w</math></b>	<b><math>PD</math></b>
Water insoluble lignin	441	1681	3.8
DCM insoluble	880	3241	3.7
DCM soluble	362	1018	2.8
Aqueous fraction	385	1476	3.8
Light volatiles	345	840	2.4
Sugars	394	1505	3.8

### 5.2.3 Resin production and validation

In the resins synthesis experiments in Publication IV, target was to synthesise resol-type phenol formaldehyde (PF) resins for adhesive use, meaning that resins have a formaldehyde to phenol ratio greater than 1. Synthesis of resoles is base-catalyzed. The base (NaOH) deprotonates phenol resulting in the formation of phenoxides, which are the reactive species in the synthesis. Delocalization of the formed negative charge, over the aromatic ring, activates the ortho- and para-sites of the phenolic ring, which react with formaldehyde and form the polymer chain. Water is typically used as a solvent in the synthesis of phenol formaldehyde resin, since the final resin is water soluble. [129].

The extracted water insoluble lignin bio-oil from fractionation experiments carried out in section 5.2.2 was used to substitute fossil phenol in the PF-resin synthesis. Water content of lignin bio-oil was 11.5%wt. Aliphatic and phenolic OH's were analyzed by P NMR to determine reactive sites for the crosslinking reactions with formaldehyde. P NMR results are presented in Table 24. For the reaction of lignin with formaldehyde, free ortho positions in aromatic ring are required. Based on the NMR results lignin contained four different phenolic OH's in which the *p*-hydroxyphenyl, catechols and guaiacyl type phenolic OH's contained the important reactive sites. The number of reactive sites in lignin was 3.11 mmol/g. Although the main reactive phenolic species in the lignin bio-oil originates from the lignin structure, the lower concentration impurities present in lignin bio-oil, such as organic acids, alcohols, ketones and sugar derivatives (e.g., acetic acid, glycolaldehyde), can also participate in the polycondensation reactions under the synthesis conditions, and be incorporated in the polymer chain [201].

**Table 24.** Aliphatic and phenolic OH's (mmol/g lignin) of the water insoluble lignin bio-oil from Publication IV (© 2023 The Authors. Reprinted under license CC-BY 4.0.).

	Aliphatic OH	Carboxylic acid	Condensed + syringyl OH	Guaiacyl	Catechols	<i>p</i> -OH-phenyl	Reactive sites
pyrolysis lignin	1.63±0.11	0.62±0.02	1.12±0.06	0.91±0.02	0.96±0.06	0.38±0.03	3.11*

\* Reactive sites calculated from the guaiacyl, catechol and *p*-OH phenyl type units.

#### *Optimization of the resin synthesis*

In the resin synthesis experiments with lignin bio-oil, phenol was gradually replaced by lignin bio-oil with replacement rates of 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt%. PF-lignin bio-oil resins syntheses were successful. Resin characterization is presented in Table 25. All produced PF-lignin bio-oil resins exhibited sufficiently low free formaldehyde values. The pH of all resins was alkaline, around 9.5 to 10.9 and the non-volatile content of the obtained resins was close to 50%. Increasing share of lignin bio-oil was, however, observed to correlate with higher viscosity of the final resin. Resins produced with 40% and 50% replacement rates exhibited very high viscosity (almost in the form of a paste) and it was necessary to dilute the samples to obtain a resin with acceptable viscosity.

**Table 25.** Characterization results of produced PF resins and lignin bio-oil based PF resins. Solvent used was H<sub>2</sub>O from Publication IV (© 2023 The Authors. Reprinted under license CC-BY 4.0.).

Trial	Lignin wt% (as replacement of phenol)	Solid content (wt%)	Free Formaldehyde (%)	Viscosity (cP @ 25°C)	pH
3	0	50.15	0.39	75	10.4
7	10	48.80	0.32	542	10.9
8	20	48.70	0.36	142	10.4
9	30	48.76	0.27	6820	10.2
10 <sup>a</sup>	40	24.38	0.14	194	10.2
11 <sup>a</sup>	50	24.18	0.18	110	9.8

a = resins diluted to 50%, due to the high viscosity of the produced resin. Initial solid content 49.66% for resin 10 and 49.76% for resin 11,

Due to the high viscosities with highest phenol replacement rates, further optimization was carried out with the target to lower the viscosity of the resins. High viscosities are undesirable as they may limit the use of resin in certain applications. Additionally, high viscosity of fresh resin is undesirable as PF-resins are known for their poor stability which can result in further viscosity increase during storage. Therefore, the target in the further optimization work was to increase the solvent content aiming to achieve lower viscosities values, without significantly decreasing the non-volatile content as it is known that high non-volatile content of the PF-resins can lead to better adhesion properties. Results of further optimization are presented in Table 26.

In the trials 12 and 13 (Table 26), viscosities of the resins were adjusted by adding deionized water into the resin to achieve non-volatile content of 40 %. In trials 14, 15 and 16, the effect of the solvent type and different solvent mixtures were tested. Mixture of H<sub>2</sub>O/n-butanol was tested in these trials. When a mixture of H<sub>2</sub>O/n-butanol (ratio 70:30 wt/wt) was used in the synthesis, resins with the desirable viscosity, improved storage stability and low free formaldehyde content were obtained. With lower n-butanol addition, higher viscosities were observed.

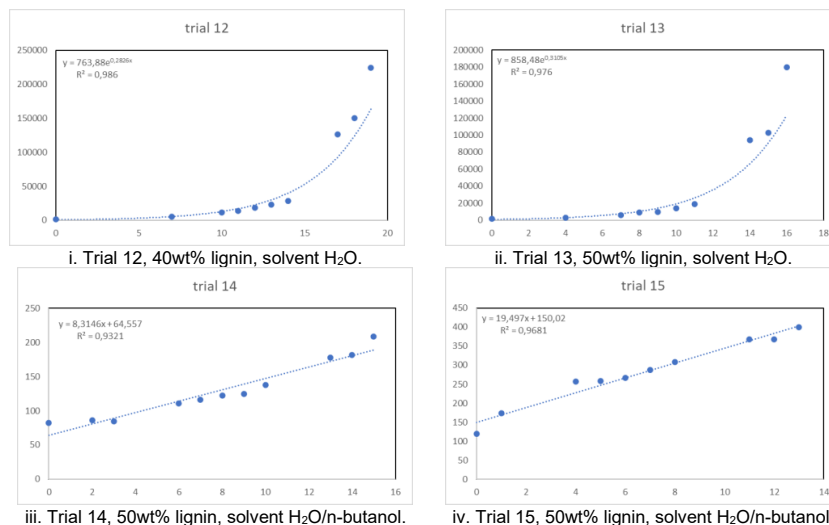
**Table 26.** Characterization results of produced PF-lignin bio-oil resins. Solvent used H<sub>2</sub>O and H<sub>2</sub>O/n-Butanol (70:30 wt/wt) from Publication IV (© 2022 The Authors. Reprinted under license CC-BY 4.0.).

Trial	Solvent	Lignin fraction wt% (as replacement of phenol)	Free formaldehyde (%)	N.V.%	Viscosity (cP)
12 <sup>a</sup>	H <sub>2</sub> O	40	0.23	39.02	1100
13 <sup>b</sup>	H <sub>2</sub> O	50	0.18	38.18	1440
14 <sup>c</sup>	H <sub>2</sub> O/n-Butanol	50	0.76	41.50	82.5
15 <sup>d</sup>	H <sub>2</sub> O/n-Butanol	50	0.50	46.71	119
16 <sup>e</sup>	H <sub>2</sub> O/n-Butanol	50	0.45	50.47	4280

a = diluted resin with 40 wt% lignin bio-oil (solvent H<sub>2</sub>O), b = diluted resin with 50 wt% lignin bio-oil (solvent H<sub>2</sub>O), c = use of H<sub>2</sub>O/n-Butanol at ratio 70:30 combined with lower N.V.% content, d = use of H<sub>2</sub>O/n-Butanol at ratio 70:30, e = use of H<sub>2</sub>O/n-Butanol at ratio 95:5.

Furthermore, the storage stability of the resins with H<sub>2</sub>O and H<sub>2</sub>O/n-butanol mixture as solvent were assessed by following the viscosity change during a two week test period. Evolution of viscosities during storage in room temperature is presented in Figure 27. From the results it can be seen that the presence of n-

butanol has positive effects on the storage stability of the resins. When H<sub>2</sub>O is used as solvent, viscosity of the resins increases exponentially, and increase becomes very rapid when storage time exceeds 12 days. On the other hand, when mixture of H<sub>2</sub>O/n-butanol is used, viscosity increase seems to be linear during the same storage period. Additionally, viscosity increases at much lower rate, suggesting that the mixture H<sub>2</sub>O/n-butanol can successfully prolong the storage stability of PF-lignin resin with relatively high non-volatile content of 47%, allowing storage for 2 weeks before its use in the targeted application.



**Figure 27.** Plots of resin viscosities (cP @ 25°C) vs storage time (days). Resins were stored at room temperature from Publication IV (© 2023 The Authors. Reprinted under license CC-BY 4.0.).

#### *Validation of the resins in adhesive use*

The gluing performance of the produced resins was evaluated by measuring the tensile shear strength of lap joints formed by gluing 5 mm thick beech wood veneers (EN 205:2003). With the PF-lignin bio-oil resins, all the produced resins fulfilled a dry strength limit of  $\geq 10$  N/mm<sup>2</sup>, and wet strength limit  $\geq 7$  N/mm<sup>2</sup> was fulfilled by the resins with the replacement ratio up 40 wt%. Resins with replacement ratio of 50 wt% had somewhat reduced wet strength (EN 12765: 2001).

With the highest phenol replacement rate (50 wt% substitution in trial 11) the wet strength was somewhat reduced (6 N/mm<sup>2</sup>) but good dry strength of over 14 N/mm<sup>2</sup> was achieved. Similarly, good results were achieved with the n-butanol optimized resins 14 and 15, both with 50 wt% phenol replacement rate (Table 27). The dry strength was just over 10 N/mm<sup>2</sup>, but the wet strength was below 7 N/mm<sup>2</sup> for both samples. It should be added that, on average, resin 14 showed 100% and resin 15 70% detached wood failure in dry conditions and respectively 80 and 70% wood failure at wet conditions. The results presented here confirm a promising potential of pyrolysis derived lignin bio-oil in phenolic wood adhesives, at least in dry conditions.

**Table 27.** Tensile strength of dry/wet sample 14 and sample 15 resins. Average values of 5 samples from Publication IV (© 2023 The Authors. Reprinted under license CC-BY 4.0.).

Resin sample	Tensile shear strength, dry (N/mm <sup>2</sup> )	Tensile shear strength, wet (N/mm <sup>2</sup> )
14	10.9	4.3
15	10.8	6.0

## 6. Conclusions

In this dissertation, fast pyrolysis of various biogenic residues was studied in industrially relevant fluidized bed fast pyrolysis units. Target was to better understand the limitations of the different waste and residual feedstocks in the production of fast pyrolysis bio-oils (FPBOs) and in their further upgrading into chemicals and materials. The scope of the studies included the review of value chain from the pretreatment of the pyrolysis feedstocks to the end use of FPBO in gasification and resin synthesis.

Pre-treatment of the lignocellulosic feeds was found to have both positive and negative effects depending on the starting feedstock. With high alkali feeds, alkali removal via mild acid leaching was found to increase the organic liquid yield and especially the sugar content in the FPBOs was higher. Furthermore, the results with high-alkali feeds were scalable to the pilot scale (20 kg/h) unit. Pre-treated straw was successfully pyrolyzed, although some ash-melting derived issues were faced on the combustor side of the process. On the other hand, low-alkali feeds, where alkali content was reduced below detection limits after the pretreatment, were difficult to pyrolyze due to the bed agglomeration. The complete absence of alkali metals which are active in pyrolysis reactions may result in operational problems, while too large content of alkali metals results in suboptimal bio-oil yield.

Similar operational issues related to agglomeration were observed with fast pyrolysis of different hydrolysis lignins in bench scale (1 kg/h) bubbling fluidized bed reactor. Hydrolysis lignin has gone through rather severe pretreatment where large parts of hemicelluloses, cellulose and ash are removed from the feedstock prior to fast pyrolysis. The carbohydrate content of hydrolysis lignin had a clear correlation to its processability. More challenges were observed with lignin feedstocks having lower carbohydrate content and higher amount of lignin. This caused problems through char formation induced bed agglomeration. In bench scale unit, bed agglomeration issues were tackled by attaching a mechanical mixer into the fluidized bed reactor to break the sand-char agglomerates. In pilot scale, bed agglomeration was not an issue as due to the higher gas velocities used in circulating fluidized bed configuration, larger forces were applied to sand and lignin particles. Furthermore, the constant regeneration of bed material through combustion helped with the agglomeration issues. On the other hand, rapid secondary reactions in the vapor phase, which were present in both units, resulted in deposit formation and pressure buildup in product gas lines, which shortened stable operational periods. These observed operational

difficulties in pilot scale underline the aspect that technical feasibility and readiness of lignin pyrolysis still has unresolved research issues. Furthermore, low liquid and high char yield raises the question if lignin is more suitable for char and carbon than liquid production.

Most studied applications for bio-oils are upgrading routes into transportation fuels but focus on this thesis was in other valorization routes. First routes studied was bio-oil gasification into syngas. Results showed that the combination of fast pyrolysis with subsequent bio-oil gasification provides a technically feasible and feedstock flexible solution. FPBOs produced from different residues performed similarly in the production of synthesis gas which can be further converted to fuels or various chemicals.

Second studied valorization pathway focused on the FPBO fractionation and subsequent use of obtained fractions in the phenolic resin synthesis. Feedstock used was waste wood, which was converted into FPBO with high yield in pilot scale. Yield achieved confirmed the potential of the waste wood in the FPBO production. However, issues were faced in the liquid recovery where blockage formation in the scrubber was observed. One possible explanation could be that the impurities present in waste wood, such as resins, are contributing to the solids formation but better understanding of the impurity behavior during pyrolysis and condensations phase is still needed to overcome the observed operational issues. In resin synthesis, waste wood FPBO fractions were found to be a potential substitute for fossil phenol in phenolic resin production. All the produced resins performed well at dry conditions, but at wet conditions resins with the highest replacement ratio of 50 wt% had somewhat reduced strength. Although technical potential is promising, better understanding of techno-economic aspects of these routes will be needed in the future.

When the future of the fast pyrolysis is considered, pyrolysis processes need to be developed to be more material efficient. Instead of incineration of the side-streams, such as char and gases, side-streams should be utilized to produce added-value products. Needed energy could be met instead by introducing green energy through electricity. This would improve the sustainability and carbon footprint of the process concepts if more of the biomass content can be converted into long lasting products. Side-stream utilization and process electrification are aspects that need attention in the fast pyrolysis related research in the future.

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**Aalto DT 85/2026**

ISBN 978-952-64-3088-1

ISBN 978-952-64-3087-4 (pdf)

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