Conversion of Biomass to Renewable Liquid Feedstocks in Pyrolysis-based Applications

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To my beloved family
“Why do we fall? So we can learn to pick ourselves up.”

- Alfred Pennyworth, Batman Begins
Abstract

The production of chemicals and fuels currently rely on fossil resources which are associated with global warming as well as economic and political instabilities. The demand for renewable alternatives is increasing as legislations on greenhouse gas emissions are becoming more stringent. Biomass is the main renewable carbonaceous feedstock that can be converted into chemicals and fuels. Pyrolysis allows the conversion of biomass to liquid feedstocks that could substitute the reliance on fossil crude. However, liquids originating from pyrolysis of biomass have unfavourable characteristics with respect to technical requirements from end-users. Therefore, further research and development of the biomass-to-liquid conversion is needed to enhance the quality of derived liquids. By developing liquefaction processes based on the influence of the biomass characteristics on the derived products, the conversion routes can be optimized to produce targeted precursors. In this dissertation, the selective conversion of lignocellulosic biomass into renewable liquid feedstocks by combining pyrolysis with upstream and downstream process modifications was experimentally investigated.

Pre-treatment of biomass in aqueous solutions of organic acids found in the pyrolysis liquid was investigated to reduce the ash content in biomass, known for catalyzing the cracking of pyrolysis vapors. Results show that the major fraction of ash can be removed without affecting the volatile matter of biomass. The composition of pyrolysis liquids derived from pre-treated biomass is significantly different to raw biomass, with increased selectivity of anhydrosugars and suppression of low molecular weight compounds such as carbonyls.

Stepwise pyrolysis was investigated to produce multiple fractionated liquids with compositions based on the thermal stability of the biomass polymers. A process concept of two pyrolysis units connected in-series, operating at 200 to 300 °C and 550 °C, respectively, was investigated. The results show that stepwise pyrolysis can be used to concentrate chemical compounds into fractionated liquids without reducing the total amount of liquid derived from biomass. However, complete separation of chemicals in a two-step pyrolysis setup faces technical difficulties due to the overlap in thermal decomposition temperatures of the biomass polymers.

Catalytic pyrolysis was studied for the production of aromatic hydrocarbons from biomass. Metal-doped zeolitic catalysts were prepared and studied based on the catalyst activity and the deactivation characteristics. Fe and Ni were impregnated into HZSM-5 followed by catalytic pyrolysis and investigation of the liquid and coke properties. The coke composition reflects the catalytic activity observed for upgraded
liquids. Metal-doping promotes the conversion of vapors into aromatic hydrocarbons, increases the catalyst deactivation rate, and alters the catalyst regeneration conditions.

The influence of the vapor composition fed for catalytic upgrading was studied by comparing the differences when using the pre-treated demineralized biomass mentioned above and raw biomass in catalytic pyrolysis. For ex-bed catalytic pyrolysis at 600°C using HZSM-5, pre-treated biomass results in higher conversion of biomass to aromatic hydrocarbons compared to raw biomass. This could be explained by a favorable composition of secondary pyrolysis vapors from pre-treated biomass for catalytic upgrading over HZSM-5.

Lastly, a continuous ex-situ catalytic fast pyrolysis process was experimentally investigated. The performance of HZSM-5 for continuous upgrading of pyrolysis vapors was evaluated by varying the biomass feeding rate to the pyrolyzer followed by upgrading over a fixed amount of catalyst. The results indicate the significance of the biomass-to-catalyst ratio in the design of large-scale processes in terms of the magnitude of catalytic conversion of pyrolysis vapors.

**Keywords:** Pyrolysis; Biomass; Pre-treatment; Stepwise Pyrolysis; Catalytic Pyrolysis
Sammanfattning


Förbehandling av biomassa i en vattenbaserad vätska innehållande organiska syror som förekommer i pyrolysoljan undersöktes för att minska halten aska i biomassa. Aska bidrar till katalytisk krackning av pyrolyssångor. Resultaten visar att en majoritet av askan kan separeras från biomassa utan att påverka dess innehåll av flyktiga komponenter. Sammansättningen av pyrolysolja från förbehandlad biomassa skiller sig från rå biomassa, med en ökad andel anhydrosocker och en minskning av lågmolekylära föreningar såsom karbonyler.


Katalytisk pyrolys undersöktes för framställning av aromatiska kolväten från biomassa. Metall-impregnerade zeolitiska katalysatorer framställdes och utvärderades utifrån sina katalytiska egenskaper såsom aktivitet samt deaktivering. Fe och Ni impregnerades i HZSM-5 följt av katalytisk pyrolys och analys av uppgradерad olja samt bildat koks. Kokssammansättningen hos en katalysator speglar dess aktivitet för
uppgradering av olja. Metallimpregnering av en katalysator bidrar till en ökad omvandling av pyrolysångor till aromatiska kolväten, ökar katalysatordeaktivering genom koksning, samt ändrar dess egenskaper vid regenerering. 

Påverkan av sammansättningen på pyrolysångor som passerar genom en katalysatorbädd undersöktes genom att jämföra skillnader mellan användning av den förbehandlade biomassa som nämns ovan med rå biomassa. Katalytisk pyrolys vid 600 °C i en ex-bäddsuppsättning med HZSM-5 ger en högre omvandling av biomassa till aromatiska kolväten med förbehandlad biomassa jämfört med rå biomassa. Detta kan förklaras genom en fördelaktig sammansättning hos pyrolysångorna som passerar genom katalysatorbädden efter att ha genomgått sekundära pyrolysisreaktioner.

Slutligen undersöktes en kontinuerlig process för ex-situ katalytisk snabbpyrolys genom experimentella försök. HZSM-5:s prestanda för att kontinuerligt uppgradera pyrolysångor utvärderades genom att variera flödet av biomassa följt av katalytisk uppggrading över en konstant mängd katalysator. Resultaten indikerar vikten av den signifikanta påverkan som förhållandet mellan biomassa och katalysator har i processen för katalytisk omvandling av pyrolysångor till aromatiska kolväten.

Nyckelord: Pyrolys; Biomassa; Förbehandling; Stegvis Pyrolys; Katalytisk Pyrolys
Acknowledgements

I would like to express my gratitude to my supervisor, Docent Weihong Yang, for giving me the opportunity to join his research group, to conduct the research presented in this thesis, and for offering his continuous support during the PhD studies. Also, I would like to thank my colleagues at KTH and the co-authors of the Supplements presented in this thesis. Without your company, support and constructive criticism this journey would have been less adventurous and fruitful.

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I would also like to thank all teachers and friends who have been part of my school years from elementary school up to now. Special and extra warm thanks goes to my teacher in upper secondary school, Linda Jonsson, who introduced me to the beauty of Chemistry. When looking back at the million choices tempting a teenager student, I here identify a clear milestone which has led to this doctoral thesis. I have pursued my passion to Chemistry and Nature ever since.

Special thanks go to my friends for your continuous indirect and social support when not at work. You bring that extra joy and laughter needed to relax my mind during these research studies.

I would like to acknowledge my deepest gratitude to my beloved family for your endless love and support to reach for the sky and to find myself in situations beyond my wildest dreams. Thanks to my parents, Eva and Roger, for always being there. Thanks to my brother, John, for our phenomenal balance of brotherhood and competition during childhood. Finally, I would like to thank the love of my life, Lisa, for always being with me through fire and flames and for always supporting my goals. I love you all.
List of Scientific Supplements in the Thesis


V. **H. Persson**, S. Gulshan, R. Svanberg, W. Yang, ”Production of renewable aromatic hydrocarbons by ex-situ catalytic fast pyrolysis of biomass in a combined fluidized bed and fixed bed system”. Submitted to *Energy & Fuels*.

**Contribution statement:**

Supplement I, IV, V: Performed experiments, analysed data, prepared and reviewed the manuscript.

Supplement II: Performed experiments, analysed data (excl. solvent extraction method), prepared and reviewed the manuscript.

Supplement III: Performed experiments (excl. metal-impregnation of catalysts and coke extraction), analysed data (excl. FTIR), prepared and reviewed the manuscript.
List of Scientific Contributions not included in the Thesis


Presentations at Conferences

Oral Presentations


H. Persson, T. Han, W. Yang, ”A study on influences of torrefaction to enhance the chemical characteristics of pyrolytic liquids from fast pyrolysis of palm kernel shells”. Presented at Biofuels and Bioenergy 2017, Dubai, United Arab Emirates 27th April 2017.


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<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AAEMs</td>
<td>Alkali- and Alkaline Earth Metals</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>BFB</td>
<td>Bubbling Fluidized Bed</td>
</tr>
<tr>
<td>BTX</td>
<td>Benzene Toluene Xylenes</td>
</tr>
<tr>
<td>CFP</td>
<td>Catalytic Fast Pyrolysis</td>
</tr>
<tr>
<td>d.b.</td>
<td>Dry basis</td>
</tr>
<tr>
<td>DAF</td>
<td>Dry Ash Free</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DTG</td>
<td>Differential Thermogravimetry</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GC/MS</td>
<td>Gas Chromatography/Mass Spectrometry</td>
</tr>
<tr>
<td>He</td>
<td>Helium</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric Acid</td>
</tr>
<tr>
<td>KF</td>
<td>Karl Fischer</td>
</tr>
<tr>
<td>KTH</td>
<td>Kungliga Tekniska Högskolan</td>
</tr>
<tr>
<td>LGA</td>
<td>Levoglucosan</td>
</tr>
<tr>
<td>MAHs</td>
<td>Monocyclic Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>Micro-GC</td>
<td>Micro-Gas Chromatography</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>ms</td>
<td>Millisecond</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>n.d.</td>
<td>Non-detectable</td>
</tr>
<tr>
<td>NH₃-TPD</td>
<td>NH₃-Temperature Programmed Desorption</td>
</tr>
<tr>
<td>PAHs</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>PKS</td>
<td>Palm Kernel Shells</td>
</tr>
<tr>
<td>Pt</td>
<td>Platina</td>
</tr>
<tr>
<td>Py-GC/MS</td>
<td>Pyrolysis-Gas Chromatography/Mass Spectroscopy</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>SDG</td>
<td>Sustainable Development Goal</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TAN</td>
<td>Total Acid Number</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>WHSV</td>
<td>Weight Hourly Space Velocity</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight percentage</td>
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1. Introduction

1.1 Introduction

The demand for renewable energy and materials is increasing as legislations to reduce greenhouse gas emissions are becoming more stringent. The European Union (EU) Commission has set as target to reduce greenhouse gas emissions by 40 % for 2030 compared with 1990, where at least 32 % of the total energy consumption should be renewable energy [1]. Different technical solutions are needed to cover the multidisciplinary reliance on fossil resources. For the transportation sector, the EU Commission has proposed to incorporate obligations for fuel supply and consumption. The fraction of feed and food-based biofuels, i.e. 1st generation biofuels, should be reduced to 3.8 % until 2030. Also, requirements on fuel suppliers should result in blending 6.8 % of renewable fuels into their products by 2030. These obligations aim to encourage the development of alternative fuels, such as advanced biofuels and renewable electricity [2]. Regarding the production of renewable fuels and chemicals, biomass serves as an obvious alternative being a carbon-containing renewable resource. Additionally, its diverse chemical composition makes it an interesting material to be converted into a wide range of products. Therefore, technical conversion routes for efficient utilization of biomass are under development.

Despite an increasing demand for electric vehicles, their penetration of the EU market is slow where only 1.5 % of newly registered passenger vehicles in 2017 were battery electric vehicles or plug-in hybrid electric vehicles [3]. Therefore, renewable alternatives to fossil-based transportation fuels are needed to promote short-term decarbonisation of the transportation sector. Thermochemical processes such as pyrolysis allows the liquefaction of biomass and can play an important role in the petrochemical industry and in the transition to bio-based refineries. Fluids produced from renewable feedstocks have the potential to be used in the petrochemical industry as, for example: (1) blended with fossil resources as a drop-in fuel, (2) a direct substitute to fossil supplies, or (3) as feedstocks in new conversion routes. By stimulating the exploitation of bio-based feedstocks in the petrochemical industry, main parts of the existing infrastructure for production, supply and utilization of chemicals and transportation fuels can remain while reducing the global reliance on fossil feedstocks. However, liquids derived from thermochemical conversion of biomass present complex and unfavourable characteristics for direct implementation in the infrastructure. Biomass-based liquids derived through pyrolysis present thermal instabilities and high acidity, mainly associated with their high oxygen
content as well as their wide diversity of chemical compounds and reactivity. Therefore, the biomass-to-liquid process needs further development, for example, by enhancing the selectivity of certain compounds. Such process development could include, for example, biomass pre-treatment, optimization of the biomass devolatilization step, and/or downstream vapor reforming.

Biomass is a complex and heterogeneous material that requires further investigations in order to exploit its full potential. A few examples of valuable biomass resources are woody biomass, energy crops, horse manure, and agricultural waste. Its composition of the constituents cellulose, hemicellulose, and lignin provide a wide range of compounds in the derived liquids which can be utilized for production of chemicals and transportation fuels. Therefore, careful process development for the biomass-to-liquid conversion based on both the biomass chemistry and industrial demands is of high concern.

This work investigates the selective conversion of biomass into targeted liquid compounds by extending the liquefaction through pyrolysis with additional process units integrated to the biomass-to-liquid route. More specifically, the influence of biomass characteristics and pyrolysis conditions are investigated as well as the utilization of catalytic upgrading. The layout of the thesis is stated in the following section.
1.2 Objectives

The overall aim of this thesis is to selectively derive targeted liquid feedstocks from biomass to be used as sustainable precursors for producing renewable chemicals and fuels. Different technical aspects of utilizing pyrolysis in combination with additional process units to enhance the liquid composition for end-users are investigated based on the following objectives:

- Investigate the influence of leaching pre-treatment of biomass to remove intrinsic ash and to alter the composition of pyrolysis liquids
- Evaluate a stepwise pyrolysis process concept to produce fractionated pyrolysis liquids
- Investigate catalytic pyrolysis of biomass by comparing the catalyst activity and deactivation for producing aromatic hydrocarbons
- Investigate how the composition of pyrolysis liquids influence their catalytic conversion to aromatic hydrocarbons
- Study the performance of a continuous ex-situ catalytic pyrolysis process in lab-scale for producing renewable liquids

The objectives are further specified in Table 1.
<table>
<thead>
<tr>
<th>Supplement</th>
<th>Supplement title</th>
<th>Objectives</th>
</tr>
</thead>
</table>
| 1          | Wood-derived acid leaching of biomass for enhanced production of sugars and sugar derivatives during pyrolysis: influence of acidity and treatment time | • Study the effect of the inorganic content of biomass on the composition of primary pyrolysis products  
• Investigate the leaching pre-treatment using wood-derived acids to remove inorganic elements in biomass  
• Investigate the influence of leaching pre-treatment based on the composition of primary pyrolysis products |
| 2          | Fractionation of liquid products from pyrolysis of lignocellulosic biomass by stepwise thermal treatment | • Evaluate the performance of a stepwise pyrolysis concept to derive fractionated liquids  
• Investigate the thermal decomposition of lignocellulosic biomass at different temperatures  
• Compare the chemical characteristics of liquids derived at one and several temperatures respectively |
| 3          | Catalytic pyrolysis over transition metal-modified zeolites: a comparative study between catalyst activity and deactivation | • Investigate the influence of a catalyst metal-doping based on catalyst activity and deactivation  
• Compare the composition of liquid and coke from catalytic pyrolysis |
| 4          | Catalytic pyrolysis of demineralized lignocellulosic biomass                       | • Investigate the effect on upgraded products when combining leaching pre-treatment with catalytic pyrolysis  
• Study the performance of in-bed and ex-bed catalytic pyrolysis of pre-treated and raw biomass |
| 5          | Production of renewable aromatic hydrocarbons by ex-situ catalytic fast pyrolysis of biomass in a combined fluidized bed and fixed bed system | • Study the performance of a continuous ex-situ catalytic pyrolysis setup  
• Investigate the performance of catalytic upgrading at varying biomass-to-catalyst ratios |
1.3 Structure of the dissertation

This thesis is a compendium of five Supplements formulated during a doctoral thesis study. The individual Supplements are categorized into two different groups based on their main objectives. Firstly, the influence of the biomass characteristics and the pyrolysis process design on the formation of condensable compounds during biomass devolatilization are investigated. Thereafter, the study is extended towards catalytic upgrading of pyrolysis liquid on the basis of previous findings.

- Supplements I & II: Fundamentals of how the composition and chemical structure of biomass influence the composition of pyrolysis liquid
- Supplements III, IV & V: Catalytic pyrolysis of biomass for targeted production of aromatic hydrocarbons

Chapter 2 provides a brief overview of the process of pyrolysis of biomass for producing pyrolysis liquid. Fundamentals of pyrolysis, the characteristics of derived liquids, catalytic pyrolysis as well as the composition of biomass are discussed. Specific background to each Supplement is stated in the corresponding sub-chapters in Chapters 4 and 5.

Chapter 3 presents the materials and methods used in the experimental studies. In this chapter, the experimental facilities and procedures are further explained.

Chapter 4 is based on the work conducted for Supplements I and II where the chemical structure and composition of biomass are related to the characteristics of derived pyrolysis liquids. Supplement I discusses the effect of demineralizing biomass through leaching prior to pyrolysis. Supplement II investigates the concept of stepwise pyrolysis and the thermochemical decomposition properties of biomass correspondingly.

Chapter 5 focuses on the work conducted for Supplements III, IV and V. The different studies investigate catalytic pyrolysis of biomass from different aspects and in different experimental scale with the aim to reform raw pyrolysis liquids into aromatic hydrocarbons. Supplement III investigates the different catalysts based on their activity and deactivation characteristics during vapor upgrading. In Supplement IV, the combination of biomass pre-treatment through leaching and catalytic upgrading of vapors was investigated, studying the influence of the vapor composition for catalytic conversion. Lastly, Supplement V studies ex-situ catalytic pyrolysis of biomass in a continuous lab-scale facility. In this study, the performance
of a catalytic upgrading unit for vapor conversion was investigated for upgrading different feeding rates of pyrolysis products.

**Chapter 6** presents the general conclusions based on the Supplements.

**Chapter 7** states suggested future works based on the research findings in this doctoral thesis.

The five individual studies performed are summarized in Figure 1 with respect to the research areas of study in the conversion of biomass to targeted liquid feedstocks.

![Figure 1: Graphical overview of the thesis work](image-url)
1.4 Sustainability aspects of the thesis

This thesis investigates a process to convert biomass into renewable liquids that can be used as feedstock to produce materials and energy that today are produced from fossil resources. Liquids derived from this process could serve as a renewable alternative resource to fossil crude oil in the depletion of fossil feedstocks without counteracting the global reliance on chemicals, fuels, materials and energy. In this way, the main parts of the existing petrochemical industry as well as sectors that directly rely on refined products could remain while implementing a drastic decrease in the global reliance on fossil resources. As one of multiple technical concepts to reduce greenhouse gas emissions from the transportation sector, this process concept also enables the utilization of the existing transport that uses internal combustion engines, e.g. land vehicles, watercraft ships, and aircraft. An overview of the shift from fossil resources to renewable feedstocks derived from pyrolysis of biomass is illustrated in Figure 2. Based on the perspectives stated above, the investigated process concept is in accordance with UN Sustainable Development Goals (SDG) 7, 9, 12, and 13 [4].

Another sustainability aspect of the work conducted in this thesis is the use of non-edible biomass. By using, for example, non-edible lignocellulosic biomass, this work aims to promote a reduced feedstock competition between food and fuel production in a future bioeconomy by securing food supply. This is in accordance with SDG 2 [4].

The conduction of experimental investigations to evaluate the performance of precursors with low environmental impact is an important aspect in the development of future industrial processes. Therefore, careful selection was made in this thesis regarding the choice of, for example, chemicals and materials used in the experimental work. Some examples are the chemicals and metals used in biomass pre-treatment and catalytic pyrolysis, respectively. This action is in accordance with SDG 12 [4].
Figure 2: Illustration of implementing renewable feedstocks in the petrochemical industry
2. Background

Chapter 2 provides a brief overview of topics relevant for production of liquids by pyrolysis of biomass. Fundamentals of the composition of biomass, the production of renewable feedstocks, fundamentals of pyrolysis, the characteristics of pyrolysis liquids, and catalytic pyrolysis are discussed. Specific background for each Supplement is stated in the background of Chapter 4 and 5.

2.1 Lignocellulosic biomass

The term biomass covers natural material found in any kind of organic matter that recently originate from photosynthesis, e.g. wood, grass, sewage, manure, and vegetables [5]. However, not all biomass feedstocks might be suitable for producing chemicals and 2nd generation biofuels since they might be used in food production or negatively affect the biodiversity. Therefore, lignocellulosic biomass is considered as a suitable alternative for energy and material purposes. The feedstock can be found as, for example, wood and forestry residues, but also as agricultural residues and certain industrial waste streams related to the mentioned feedstocks [6].

The organic structure of lignocellulosic biomass consists of three main constituents: cellulose, hemicellulose, and lignin.

Cellulose is a linear polymer of β-D-glucopyranose units and covers approximately 35-50 wt% of dry wood biomass. Its polymeric structure is linked by hydrogen bonds and includes crystalline and amorphous regions [7, 8]. Based on its chemical properties, it provides mechanical strength to the biomass structure as well as an increased thermal stability and resistance to biological degradation [9, 10].

Hemicellulose is a polysaccharide made of different monosaccharaides such as pentoses (e.g. D-xylene, L-arabinose), hexoses (e.g. D-glucose, D-mannose), and acidified sugars (e.g. D-galacturonic acid). In comparison to cellulose, hemicellulose is amorphous and has a lower degree of polymerization, which makes it less resistant to thermal and biological degradation. Its chemical composition, physical properties and content varies between different biomass feedstocks, where the hemicellulose content varies between 15-35 wt%. In softwood biomass, hemicellulose is mainly present as galactoglucomannans and arabinoglucoronoxylan [7, 9, 11].

Lignin is the third most abundant polymer in lignocellulosic biomass. Its polymeric structure is a three-dimensional highly cross-linked amorphous structure and is built based on p-coumaryl, coniferyl, and sinapyl alcohols linked by mainly carbon-carbon and ether bonds. Softwood biomass mainly contains coniferyl alcohols. In the
biomass structure, lignin serves as a binder for cellulose and hemicellulose components. Among the biomass constituents, lignin has the highest thermal stability. The lignin content in biomass can vary from between 15 to 45 wt% determined on a dry basis (d.b.) [9, 11-14].

Additionally to the organic components of biomass, the material also contains inorganic matter. The inorganic content and composition varies between different biomass types and can originate from, for example, nutrients or local conditions related to the ecosystem. Wood typically has an inorganic content of <1 wt% whereas algae and grass may have 25 wt% [15, 16]. The inorganic matter in biomass is present in different chemical states, for example as: (1) minerals such as SiO$_2$, (2) metal ions ionically bonded to the biomass structure such as alkali and alkaline earth metals (AAEMs), and (3) covalently bonded in the organic structure such as P and S [17]. Intrinsic inorganic elements in biomass are known to influence the thermal stability of biomass [18, 19].

### 2.2 Production of renewable liquid feedstocks

Today’s society strongly relies on carbon-based fossil resources for production of chemicals, fuels, materials and electricity/heat. However, such resources are finite and associated with economic and political instabilities in the global market. Also, the exploitation of carbon-based fossil resources contributes to global warming in terms of emitting greenhouse gases to the atmosphere which also cause significant perturbation to the carbon cycle [20]. Therefore, the replacement of fossil resources with renewable alternatives to satisfy the societal demands of today is necessary to secure the human living standards associated with fossil carbon for future generations. Sustainable solutions for generating electricity and heat have already been integrated in different parts of the world based on utilizing, for example, geothermal, solar, wind, and hydropower energy sources. Additionally, renewable heat and electricity can be generated by combustion of biomass. However, being the only solid carbonaceous renewable feedstock in nature, it is the author’s opinion that biomass should be considered as a resource primary for producing renewable chemicals and transportation fuels which today are derived from fossil crude oil. To utilize the full potential of biomass for producing renewable chemicals and liquid fuels, reliable and sustainable processes need to be developed. Figure 3 presents primary chemical differences between lignocellulosic biomass, chemicals, and transportation fuels to be considered in the design of such processes.
There are many different technical routes for converting biomass into chemicals and fuels. The depolymerization of its organic structure can be performed by, for example, an enzymatic treatment, a chemical treatment, and a thermochemical conversion. A major difference between these processes is the biomass depolymerization procedure. In biological and chemical treatments, the biomass constituents are generally separated prior to depolymerization, whereas in thermochemical conversion the complete biomass matrix is depolymerized instantaneously [23, 24]. Therefore, thermochemical conversion processes are relatively time and cost efficient routes for the biomass-to-liquid conversion [25]. Examples of thermochemical conversion routes are gasification and pyrolysis. Gasification of biomass generates a syngas which can be converted into liquid chemicals in downstream processing. Pyrolysis is performed at lower temperatures than gasification, and can directly generate a liquid feedstock from the biomass.
depolymerization step. However, the simultaneous depolymerization of the biomass constituents results in a low selectivity towards specific chemical compounds and a highly complex composition of the derived liquid.

As of today, based on the multiple conversion routes existing in non-commercial scale for converting biomass into liquids, it is difficult to distinguish which technologies that will exist in future industrial processes. However, this thesis focuses on pyrolysis and how to overcome unfavorable characteristics of conventional pyrolysis liquid to promote its applicability as a precursor for production of chemicals and transportation fuels.

2.2.1 Pyrolysis

Pyrolysis is the thermal decomposition of organic matter in a non-oxidizing atmosphere. The word originates from the Greek words "πῦρ" (pyr) and "λύσις" (lysis) which means fire and breakdown, respectively, and describes the separation of matter because of the addition of heat. Pyrolysis is a thermochemical process and can occur both as a standalone process and as one of multiple reaction steps in combustion and gasification processes. The concept of pyrolysis is also known by other technical terms such as dry distillation, thermal cracking, thermolysis etc. During pyrolysis, chemical bonds in organic matter, e.g. polymers or macromolecules, break because of the addition of heat which produce three main products:

- A carbonaceous solid residue known as char, mainly consisting of carbon and ash
- Permanent gases, e.g. CH₄, CO, CO₂, H₂, and light hydrocarbons
- Condensable vapors known as, for example, pyrolysis liquid, bio-oil, bio-crude, mainly consisting of oxygenated compounds, aromatic hydrocarbons, water, and tar

The thermal decomposition of the chemical structure of organic matter is an endothermic process. Depending on the properties of an organic feedstock, different temperatures and amount of heat are needed to crack its chemical bonds and generate volatile compounds. However, the volatile compounds formed during pyrolysis can react in the hot vapor phase by, for example, thermal cracking or interactions with other compounds, known as secondary pyrolysis reactions. Therefore, the proportion of stated pyrolysis products and their compositions are dependent on process parameters such as temperature, heating rate, vapor residence time, and pressure. To promote the production of liquid from pyrolysis, a high sample heating rate, and a short vapor residence time is preferable, commonly known as fast pyrolysis. In fast pyrolysis, the generation of a high yield of condensable
primary pyrolysis products is promoted while suppressing the influence of secondary pyrolysis reactions in the vapor phase known to reduce the yield of condensed liquid. Based on the multiple chemical reactions occurring during pyrolysis as well as the significant influence of process parameters on the composition of derived products, it is difficult to model or simulate specific parameter studies of a pyrolysis process in-depth without direct support of experimental investigations.

Pyrolysis of biomass has been extensively studied for over hundred years. Historically, pyrolysis liquid such as wood tar was used by the ancient Egyptians. In the 19th century, biomass was pyrolyzed to produce charcoal for combustion purposes, performed by the “wood distillation industry”, which is considered as a forerunner to today’s petrochemical industry [26-28].

2.2.2 Composition of pyrolysis liquid

Liquids derived from pyrolysis of biomass are usually dark-brown and contain organic compounds derived during the depolymerisation of biomass. Therefore, the elemental composition of the liquid resembles the elemental composition of biomass. One major difference between pyrolysis liquid and petroleum-based fuels is its high oxygen content, which is distributed in more than 200 compounds. Water is typically the most abundant compound in pyrolysis liquids and also contributes with the highest fraction of oxygen [29, 30]. Fuel properties of pyrolysis liquids and commercial heavy fuel oil are presented in Table 2. As seen in the table, the nature of pyrolysis liquids varies depending on the choice of biomass feedstock. Depending on the choice of feedstock, the structure and composition of the biomass constituents’ vary, which play a vital role for the composition of the derived liquid [31]. The composition of pyrolysis liquids can vary based on, for example: (1) the type of biomass, (2) the geographical origin of biomass, and (3) different parts of wood, e.g. stem wood and bark [32]. Additionally, inorganic matter in biomass can influence the composition of derived pyrolysis liquids, e.g. AAEMs [33-36].

Examples of potential applications of pyrolysis liquids are direct production of heat and power by combustion or as precursors for producing chemicals and fuels. However, the liquid presents a poor fuel quality relative to fossil alternatives which reduces the demand for the liquid in the energy sector. Additionally, its wide diversity of oxygenated compounds and its high water content results in a high polarity. This makes it immiscible with fossil carbon-based liquids which complicates its applicability as a drop-in feedstock in existing petrochemical industry [9, 37].

Liquids derived from pyrolysis of biomass can be present as one homogeneous phase or two individual phases according to its composition of water-soluble and non-water-soluble compounds. General reasons for the occurrence of phase separation
are: (1) a high water content (>30 wt%) and (2) a high fraction of high molecular mass compounds. The separation of pyrolysis liquid into two phases might complicate its applicability in downstream processing [38-40].

Table 2: Properties of liquids from different feedstocks. Data are adapted from [30, 41]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Biomass feedstock</th>
<th>Heavy fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Birch</td>
<td>Pine</td>
</tr>
<tr>
<td>Solids (wt%)</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Water (wt%)</td>
<td>18.9</td>
<td>17</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>1.25</td>
<td>1.24</td>
</tr>
<tr>
<td>LHV (MJ/kg)</td>
<td>16.5</td>
<td>17.2</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>0.004</td>
<td>0.03</td>
</tr>
<tr>
<td>C (wt%)</td>
<td>44</td>
<td>45.7</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>3.9</td>
<td>7</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>S (wt%)</td>
<td>0</td>
<td>0.02</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>49</td>
<td>47</td>
</tr>
<tr>
<td>N + K (ppm)</td>
<td>29</td>
<td>22</td>
</tr>
<tr>
<td>Ca (ppm)</td>
<td>50</td>
<td>23</td>
</tr>
<tr>
<td>Mg (ppm)</td>
<td>12</td>
<td>5</td>
</tr>
</tbody>
</table>

*Calculated based on [42]

The elemental composition of pyrolysis liquids is not the only property which resembles the biomass composition. Overall, the organic compounds of the liquids reflect the polymeric structures in biomass, which can exist as a complex composition of more than 400 compounds. The chemical composition of a pyrolysis liquid is of significant importance, especially in terms of its suitability for downstream applications. Major organic compound groups found in pyrolysis liquid from biomass are hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, phenolic compounds, and oligomers which can be correlated to the polymeric structures in biomass [41, 43, 44]. Examples are acetic acid which is mainly derived from hemicellulose, and levoglucosan (LGA) mainly derived from cellulose [9]. A typical composition of a pyrolysis liquid is presented in Table 3, where also the biomass constituents from which the compounds are derived is presented. Pyrolysis liquids contain significant amounts of organic acids, mainly present as acetic acid and formic acid. This results in pH in the range of 2-3 and total acid numbers (TAN) of 50–100 mg KOH/g. This makes pyrolysis liquids corrosive to, for example, carbon steel and aluminium, commonly used as construction materials [45, 46].

Pyrolysis is not a process at thermodynamic equilibrium and hence the derived liquid composition is not at chemical equilibrium. The liquid contains compounds that react with each other during storage by, for example, polymerization, etherification, and esterification reactions, commonly known as aging. Aging does not only change
the liquid’s chemical composition but also its physical properties, e.g. density, viscosity, and volatility. Also, aging reactions are exothermic which increases the temperature in insulated storage units [47-49]. Main compounds responsible for aging include carbonyl, carboxyl, and hydroxyl groups, for example, acids and phenols [22, 35, 36, 46]. The technical issue of aging reactions also complicates the distillation of pyrolysis liquids, where heating of the liquid enhances the aging reaction rates [30].

Table 3: Typical chemical composition of pyrolysis liquid. Data are adapted from [41, 50]

<table>
<thead>
<tr>
<th>Compound groups</th>
<th>Concentrations (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>20-30</td>
</tr>
<tr>
<td>Acids&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5</td>
</tr>
<tr>
<td>Furans&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3</td>
</tr>
<tr>
<td>Aldehydes&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10</td>
</tr>
<tr>
<td>Pyrans</td>
<td>1</td>
</tr>
<tr>
<td>Monophenolics&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2</td>
</tr>
<tr>
<td>Anhydrosugars&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5</td>
</tr>
<tr>
<td>Water insolubles (e.g. oligomeric phenolics)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>16</td>
</tr>
<tr>
<td>Extractives</td>
<td>5</td>
</tr>
</tbody>
</table>

<sup>a</sup>Derived from cellulose and hemicellulose  
<sup>b</sup>Derived from lignin

The composition of pyrolysis liquids does not only depend on the biomass characteristics, but also on the process conditions for biomass-to-liquid conversion. One critical parameter for the composition of a derived liquid is the pyrolysis temperature. This can be explained by the variation in thermal stability among the biomass constituents as well as their different chemical structures [51-53]. The complex characteristics of pyrolysis liquid overall suppress its applicability on commercial scale. Liquid upgrading as a part of the biomass-to-liquid conversion process could be an alternative to enhance its properties to be directly used as a fuel in combustion engines, for production of chemicals and upgraded fuels etc. Therefore, the concept of catalytic pyrolysis as an upgrading route is discussed in the next section.

### 2.2.3 Catalytic pyrolysis

The direct application of pyrolysis liquid in downstream applications is unfavourable due to its chemical and physical properties. By catalytically upgrading the liquid it can be converted into a more attractive carbon-based liquid feedstock for industrial use with a higher economic value. However, the unstable chemical nature of pyrolysis liquids complicates its processing in downstream treatment. Instead, one option
could be to introduce a catalytic upgrading step within the biomass-to-liquid conversion process between the biomass devolatilization step and the vapor condensation unit, commonly known as catalytic pyrolysis [54]. In catalytic pyrolysis, pyrolysis vapors are upgraded by heterogeneous catalysis over a solid material. Popular catalysts used in catalytic pyrolysis of biomass are zeolites. These zeolites are silica-alumina based structures well-known from the refining industry for promoting, for example, deoxygenation and aromatization of crude oil feedstocks. Aromatic hydrocarbons are vital in the petrochemical industry and are essential precursors for the production of chemicals and fuels [9]. Therefore, zeolites could be used for catalytic upgrading of pyrolysis vapors from biomass into aromatic hydrocarbons which could serve as a renewable substitute to fossil crude oil – either as drop-in feedstocks or by complete feedstock substitution in existing refineries [55-57].

The most promising commercial catalyst used in catalytic pyrolysis of biomass is the zeolite HZSM-5. The reasons are its narrow pore diameter distribution and its shape selectivity, which is suitable for biomass-derived vapors [58-62]. The catalyst promotes reactions such as aromatization, deoxygenation, and oligomerization. A crucial parameter for the choice of catalyst used in catalytic pyrolysis is the catalyst’s density of acid sites, such as the concentration of Brønsted acid sites which influences the production of aromatic hydrocarbons [63]. Also, the density of acid sites may influence the rate of catalyst deactivation caused by coke formation on the catalyst surface [64]. In previous studies, HZSM-5 catalysts of varying acidity have been screened in catalytic pyrolysis of biomass, where a SiO$_2$:Al$_2$O$_3$ ratio of 30:1 was found to be optimal for a high conversion of vapors into aromatic hydrocarbons with a relatively low rate of catalyst deactivation [65].

One important technical parameter in the development of catalytic pyrolysis on commercial scale is the process design. The design of catalytic pyrolysis systems is typically defined into two different setups:

- **In-situ catalytic pyrolysis**, which refers to process setups where the catalyst is positioned in the pyrolyzer itself. Thereby, the temperature of pyrolysis and catalytic upgrading is essentially the same. Such systems are categorized into two sub-groups: *in-bed* and *ex-bed*. In-bed setups refer to when the catalyst is positioned in the same bed as where the biomass devolatilization occurs. Examples of such systems are fluidized beds where the catalyst is mixed with biomass in the fluidizing bed [66], and fixed bed reactors where biomass and catalyst are pre-mixed prior to biomass devolatilization [67]. Ex-bed setups refer to when the catalyst and the biomass devolatilization is separated into different beds. Examples are fixed bed pyrolyzers where a catalyst bed is
positioned downstream the bed where biomass devolatilization occurs, as illustrated in Figure 5. A main difference between *in-bed* and *ex-bed* in-situ catalytic pyrolysis is the residence time of pyrolysis vapors from when diffusing from the biomass structure until being upgraded over the catalyst surface. The instantaneous catalytic upgrading of pyrolysis vapors after biomass devolatilization in *in-bed* setups allows catalytic upgrading of primary pyrolysis vapors. The longer residence time of pyrolysis vapors in *ex-bed* setups allows secondary reactions of pyrolysis vapors prior to catalytic upgrading [68]. Another significant difference between the setups is the physical contact between a catalyst and biomass/char, which can influence the transfer of biomass ash to the catalyst and lead to catalyst poisoning [69].

- *Ex-situ catalytic pyrolysis*, which refers to process setups where the catalytic upgrading is positioned downstream the pyrolyzer itself. In such systems, the temperature of the pyrolyzer and the catalytic reactor can be individually optimized. Also, the setup allows continuous operation with separation of biomass/char, biomass ash, and catalyst, by introducing separation stages between the pyrolyzer and the catalytic reactor such as cyclone and particle filter [70, 71]. One example of an *ex-situ catalytic pyrolysis* setup is a fluidized bed pyrolyzer combined with a fixed/fluidized bed catalytic reactor, illustrated in Figure 6.
3. Experimental procedures, materials and methods

3.1 Pyrolysis experimental facilities and procedures

In this study, different experimental setups were used to study pyrolysis of biomass as well as catalytic pyrolysis. All experiments were conducted at KTH Royal Institute of Technology in Stockholm, Sweden. In this sub-chapter, each experimental facility is further described.

3.1.1 Py-GC/MS

To study the composition of primary pyrolysis vapors as well as their catalytic upgrading, a pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) setup was used. The setup consisted of a filament pyrolyzer (Pyrola2000), which was coupled with an Agilent 7890A GC and an Agilent 5975C MS. The pyrolyzer can be used to study the composition of polymeric materials by thermal decomposition of their chemical structure. It consists of a platina (Pt) filament which acts as a sample holder for treating samples in the amounts of milligrams. The filament is positioned inside a closed chamber which was kept at 175 °C. A constant flow of He was used as carrier gas to transport produced pyrolysis vapors to the GC/MS. Heat for pyrolysis is provided by applying an electrical current through the filament that is rapidly heated up by electrical resistance. The filament is calibrated based on a time-temperature profile, which is generated by adjusting the magnitude of the electrical current and the corresponding heating time. In this study, the heat-up time was set to 8 ms followed by keeping constant temperature for 2 s. The temperature of the filament is measured by a resistance temperature detector for temperatures below 500 °C, whereas an optical temperature detector is used to monitor temperatures higher than 500 °C. The Py-GC/MS setup is illustrated in Figure 4.

![Figure 4: Illustration of the Py-GC/MS setup](image)

For catalytic pyrolysis experiments conducted in the Pyrola2000 unit, catalyst and biomass powders were pre-mixed before applied on the Pt filament. Also, the particle size range of all samples analyzed in the Pyrola2000 unit was 63-125 μm.
In the conducted studies using Py-GC/MS, the GC column was equipped with one of the columns VF-1701ms or HP5-ms, both being 60 m long with 0.25 μm film thickness, respectively. Also, the identification and integration of peaks in derived chromatograms and their corresponding chemical compounds were performed with NIST11 library and Chemstation software.

The Py-GC/MS setup was used in Supplements I and IV. Further details regarding the experimental studies are stated in the Supplements, respectively.

### 3.1.2 Fixed bed pyrolyzer

A fixed bed bench-scale setup was used to study pyrolysis and catalytic pyrolysis in the sample amounts of grams. The setup is illustrated in Figure 5. The reactor consisted of a tubular stainless steel pipe with an inner diameter of 5 cm mantled with a water-cooled (1) and an electrically heated (2) section. A sample holder of fine stainless steel mesh was used to hold biomass and the solid residue produced during pyrolysis. The sample holder was manually transported between the cooled and heated sections by a metallic rod. The pyrolyzer was heated by a 2.52 kW three-zone furnace with a heated length of 60 cm (Carbolite EVZ 12/600). Above the heated zone, a water-cooled section was positioned where the sample was placed prior to and after pyrolysis. N₂ was used as carrier gas. Downstream the furnace, vapors were quenched in a condensation system consisting of cold traps positioned in-series and placed in a cooling bath operating at -15 to -17 °C. Non-condensable gases were collected and/or analysed downstream the condensation step.

For catalytic pyrolysis performed in the bench-scale pyrolyzer, a catalyst fixed bed was positioned on a fine stainless steel mesh below the position of the sample holder in the heated zone. This is illustrated in Figure 5.
The fixed-bed pyrolyzer setup was used in Supplements II, III, & IV. Further details on the experimental procedures of the specific studies are stated in the Supplements, respectively.

### 3.1.3 Ex-situ catalytic fast pyrolysis

An experimental setup for lab-scale ex-situ catalytic fast pyrolysis was used as part of the experimental work of this thesis. The experimental process scheme is illustrated in Figure 6. The setup consisted of a biomass hopper, a feeding system, a gas preheater, a bubbling fluidized bed (BFB) reactor, a cyclone for char separation, a filter for separation of fine char particles, a catalytic reactor for vapor upgrading, a filter for separation of fine catalyst particles, a condensation system, and a gas analyzer.
Figure 6: Illustration of the ex-situ catalytic fast pyrolysis setup

The biomass feeding system consisted of two stages of screw feeders. The first screw was used for controlling the biomass feed rate and was positioned below the hopper. The second screw feeder was used for injection of biomass to the pyrolysis reactor with a constant speed of 900 rpm. The pressure of the feeding system was kept higher than the pressure of the pyrolyzer in order to avoid back-flow of pyrolysis vapors. The particle size range of biomass used was 1.0 to 1.4 mm.

The pyrolysis reactor consisted of a stainless steel reactor with a height of 95 cm and an inner diameter of 7.2 cm. A sand bed with a particle size range of 0.25 to 0.355 mm was positioned on a perforated plate that also served as gas distributor. The fluidization agent and carrier gas used was N$_2$. The sand bed was heated by the pre-heated gas as well as by electrical heating elements that surrounded the reactor body up to 60 cm from the perforated plate. The temperature inside the reactor, including the wind box and inside the sand bed, was measured by six K-type thermocouples.

A cyclone was used for centrifugal separation of char from the gas-vapour stream. Separated char was stored in a steel container positioned below the cyclone while the gas-vapor stream was transported by the N$_2$ flow downstream the experimental process.
After the cyclone, the pyrolysis gas-vapor stream passed through a stainless steel mesh filter in order to separate fine char particles. Thereafter, the gas-vapor stream was catalytically upgraded in a vertical fixed bed reactor with an inner diameter 11.4 cm and a height 18 cm. The catalytic reactor is illustrated in Figure 7. A catalyst pellet bed was held by a perforated plate. The temperature of the catalyst bed and the void space of the reactor were measured with K-type thermocouples. The reactor was mantled with electrical heaters. Downstream the catalyst bed, a fine stainless steel mesh filter was placed to trap fine catalyst particles. The two filters surrounding the catalyst bed are illustrated as lined in Figure 7.

Pyrolysis vapors were condensed in a condensation system consisting of a water-cooled metal condenser followed by glass condenser tubes. A cooling liquid of -17 °C was pumped through the condensation system in co-current direction to the gas flow.

Remaining pyrolysis gas was analyzed on-line downstream the experimental process. The ex-situ catalytic fast pyrolysis setup was used in Supplement V. Further details on the experimental setup and the experiments conducted can be found in the Supplement and in previous works [72].
3.2 Biomass raw materials

3.2.1 Softwood sawdust

For the major part of the experimental studies conducted in this thesis, softwood sawdust was used as biomass feedstock. The biomass was a mixture of spruce and pine provided by SCA BioNorr in Härnösand, Sweden. For the pyrolysis experiments, biomass was shredded and sieved to different particle size ranges according to the requirements of the different experimental facilities. The particle size ranges used in this thesis are stated in Table 4 according to their corresponding Supplement.

Table 4: Particle size ranges in the corresponding Supplements and experimental facilities

<table>
<thead>
<tr>
<th>Experimental facility</th>
<th>Supplement no.</th>
<th>Particle size range (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Py-GC/MS</td>
<td>I\textsuperscript{a}, IV\textsuperscript{b}</td>
<td>\leq0.125\textsuperscript{a}</td>
</tr>
<tr>
<td>Fixed bed-pyrolyzer</td>
<td>III</td>
<td>0.35-0.50</td>
</tr>
<tr>
<td>Fluidized bed-pyrolyzer</td>
<td>V</td>
<td>1-1.4</td>
</tr>
</tbody>
</table>

\textsuperscript{a,b}Different particle size ranges used for studies including non-catalytic (a) and catalytic pyrolysis (b).

The ultimate and proximate analysis of the softwood biomass is presented in Table 5. The fraction used for the presented sample analysis was used in Supplement III. Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) of the sample performed in inert atmosphere are presented in Figure 8.
Table 5: Composition of softwood sawdust (d.b.)

<table>
<thead>
<tr>
<th></th>
<th>Proximate analysis (wt%, d.b.)</th>
<th>Ultimate analysis (wt%, d.b.)</th>
<th>Inorganic composition (mg/kg, d.b.)</th>
<th>Organic composition (g/kg, d.b.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volatile matter</td>
<td>Ash content</td>
<td>Si</td>
<td>Glucose</td>
</tr>
<tr>
<td></td>
<td>84.4</td>
<td>0.21</td>
<td>14.8 Pb</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al</td>
<td>Mannose</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.24 Ba</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ca</td>
<td>Galactose</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>349 Cd</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe</td>
<td>Arabinose</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.97 Co</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>K</td>
<td>Lignin (wt%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>242 Cu</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mg</td>
<td></td>
</tr>
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<td></td>
<td>51.6 Cr</td>
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<td>Mn</td>
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<td>42.4 Hg</td>
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<td>Na</td>
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<td></td>
<td>11.9 Mo</td>
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<td></td>
<td>P</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13.5 Ni</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ti</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.24 Va</td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td>As</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&lt;0.09 Zn</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ba</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.72</td>
<td></td>
</tr>
</tbody>
</table>

*Calculated by difference
3.2.2 Palm kernel shells

For experiments performed in Supplement II, palm kernel shells (PKS) were used. The particle size distribution was 2-3 mm. Ultimate and proximate analysis of PKS is presented in Table 6. Also, TGA and DTG analysis of PKS performed in inert atmosphere are presented in Figure 9.

Table 6: Composition of PKS used for pyrolysis experiments (d.b.)

<table>
<thead>
<tr>
<th></th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate analysis</strong></td>
<td></td>
</tr>
<tr>
<td>Volatile matter</td>
<td>64.4</td>
</tr>
<tr>
<td>Ash content</td>
<td>8.5</td>
</tr>
<tr>
<td><strong>Ultimate analysis</strong></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>51.7</td>
</tr>
<tr>
<td>O*</td>
<td>33.8</td>
</tr>
<tr>
<td>H</td>
<td>5.6</td>
</tr>
<tr>
<td>S</td>
<td>0.03</td>
</tr>
<tr>
<td>N</td>
<td>0.4</td>
</tr>
</tbody>
</table>

*Calculated by difference
Figure 9: TGA and DTG results of PKS

### 3.3 Biomass pre-treatment procedure

In the experimental works summarized in Supplements I and IV, softwood sawdust was pre-treated for reducing its ash content prior to pyrolysis. This was performed by treating biomass in a heated aqueous solution of de-ionized water and acetic acid. Acetic acid was chosen since it is the main acid found in pyrolysis liquid from where it could be extracted [35, 73]. For the biomass pre-treatment performed in Supplements I and IV, two different experimental setups with capacities to treat 25 g and 100 g dry biomass, respectively, were used. The setups are illustrated in Figure 10 and 11. The design of pre-treatment facilities and the magnitude of pre-treatment operational conditions were inspired by previous works [35]. The biomass pre-treatment was based on pre-heating the acidic aqueous solution in a closed vessel to the desired treatment temperature. Thereafter, pre-dried biomass was mixed with the aqueous solution and kept under constant heating and stirring for the desired time of pre-treatment. The biomass and the solution were then separated by filtration. Biomass was thereafter washed with de-ionized water in order to remove any organic and inorganic residues [34, 35].

Specific pre-treatment conditions are described in the corresponding Supplements. The results of biomass pre-treatment and the corresponding pyrolysis experiments from Supplement I served as basis for the biomass pre-treatment performed in Supplement IV.
Figure 10: Illustration of experimental pre-treatment setup used in Supplement I

Figure 11: Illustration of the experimental pre-treatment setup used in Supplement IV
3.4 Catalysts and catalyst preparations

The catalysts used in the thesis were HZSM-5 with a SiO₂:Al₂O₃ ratio of 30:1. The SiO₂:Al₂O₃ ratio has been found to be optimal for producing aromatic hydrocarbons from biomass with a relatively low rate of deactivation by coke formation [65].

For catalytic pyrolysis experiments performed in the Py-GC/MS and in the fixed bed-pyrolyzer, catalyst in powder form supplied by Alfa Aesar was used. For catalytic pyrolysis performed in the fluidized bed setup with continuous vapor upgrading in a fixed bed reactor, catalyst pellets were used and supplied by Nankai University in China. The catalyst preparations performed in the different studies are presented below.

3.4.1 Preparation of powder-formed catalyst

For the study presented in Supplement III, HZSM-5 was doped with Fe and/or Ni by the wet-impregnation method. The following catalysts were compared in the study: HZSM-5, Fe/ZSM-5, Ni/ZSM-5, and FeNi/ZSM-5. For metal impregnation, HZSM-5 was mixed with Fe(NO₃)₃(H₂O)₉ and Ni(NO₃)₂(H₂O)₆ dissolved in de-ionized water. The impregnation was performed for 24 h under constant stirring at 50 °C, followed by drying at 105 °C for 12 h and calcination in air. The elemental composition of the catalysts and BET surface area is presented in Table 7. X-ray Diffraction (XRD) results are presented in Figure 12. NH₃-TPD results are presented in Figure 13. The characterization results are further explained in Supplement III.

Table 7: Elemental composition of the catalysts and BET surface area

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Ni</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>BET m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>340000</td>
<td>21200</td>
<td>&lt;700</td>
<td>62</td>
<td>5000</td>
<td>3000</td>
<td>&lt;0.1</td>
<td>403</td>
</tr>
<tr>
<td>Ni/ZSM-5</td>
<td>331000</td>
<td>21300</td>
<td>&lt;700</td>
<td>45700</td>
<td>4000</td>
<td>3000</td>
<td>&lt;0.1</td>
<td>382</td>
</tr>
<tr>
<td>Fe/ZSM-5</td>
<td>321000</td>
<td>20500</td>
<td>39200</td>
<td>995</td>
<td>4000</td>
<td>2000</td>
<td>&lt;0.1</td>
<td>369</td>
</tr>
<tr>
<td>FeNi/ZSM-5</td>
<td>334000</td>
<td>21100</td>
<td>42800</td>
<td>41700</td>
<td>4000</td>
<td>3000</td>
<td>&lt;0.1</td>
<td>348</td>
</tr>
</tbody>
</table>
Figure 12: XRD results of investigated catalysts: (1) HZSM-5, (2) Ni/ZSM-5, (3) Fe/ZSM-5, and (4) FeNi/ZSM-5. * refers to NiO whereas ◊ refers to Fe₂O₃ (hematite).

Figure 13: NH₃-TPD of investigated catalysts: (1) HZSM-5, (2) Ni/ZSM-5, (3) Fe/ZSM-5, and (4) FeNi/ZSM-5.

All catalysts based on powder-formed HZSM-5 were calcined in air accordingly followed by preparation to suitable particle size ranges for the different experimental facilities. Calcination temperatures for each study are stated in the corresponding Supplement. For particle size preparation, the catalysts were pelletized, crushed and sieved to specific particle size ranges which are stated in Table 8.
Table 8: Catalyst particle size ranges used in the different experimental facilities

<table>
<thead>
<tr>
<th>Experimental facility</th>
<th>Supplement no.</th>
<th>Particle size range (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Py-GC/MS</td>
<td>IV</td>
<td>0.063-0.90</td>
</tr>
<tr>
<td>Fixed bed</td>
<td>III, IV</td>
<td>0.125-180</td>
</tr>
</tbody>
</table>

3.4.2 Catalyst preparation for fluidized bed-pyrolyzer experiments

HZSM-5 in pellet form supplied by Nankai University in China was used for the investigation of ex-situ catalytic fast pyrolysis presented in Supplement V. Catalyst was calcined in air by heating the sample with 10 °C/min to 650 °C followed by dwelling for 15 h. Thereafter, the catalyst was cooled to room temperature by 10 °C/min prior to being placed in the catalytic reactor.

3.5 Analysis instruments and methods

In this section, the analysis instruments and methods used for characterization of liquids, gases, solids products and biomass are presented. Additional characterization methods stated in the Supplements were provided by external partners and research labs.

3.5.1 Liquid characterization

Liquids derived from the fixed bed and fluidized bed-pyrolyzers were analyzed based on their organic composition, water content and TAN.

The organic composition was qualitatively analyzed by GC/MS. The instrument used was an Agilent 7890A/5975C setup, similar to the one previously presented for the Py-GC/MS setup. Columns used in the thesis were VF-1701ms and HP5-ms, both with a length of 60 m and a coating thickness of 0.25 μm. Liquids were injected to the column by an Agilent G4513A autosampler. Peaks in the derived chromatograms were integrated by Chemstation software and the corresponding MS results were identified by comparison to a NIST11 library. Prior to the analysis, liquid samples were prepared by solvent dissolution in methanol and/or dichloromethane (DCM). Further details on the analysis method is stated in the corresponding Supplements.

Water content and TAN were analyzed based on Karl Fischer (KF) and TAN-titration using a Mettler Toledo Excellence Titrator T5. Standard methods used were ASTM E203 and ASTM D664, respectively.
3.5.2 Gas characterization

Non-condensable gases derived from the fixed bed-setup and the fluidized bed-setup were analyzed by an Agilent 490 micro-GC with four different columns and equipped with TCD-detectors calibrated for H₂, CH₄, CO, CO₂, N₂, O₂, C₂H₂-C₄, and C₃H₆. The different columns use Ar and He as carrier gases. For gas collection and quantification, the water-displacement method was used.

3.5.3 Catalyst characterization

Catalyst characterization performed in this thesis involves elemental composition, BET surface area, micropore volume, XRD, and NH₃-TPD. The analysis instruments used for catalyst characterization are specified in Table 9. Further specifications can be seen in the corresponding Supplements.

Table 9: Summary of different catalyst characterization performed

<table>
<thead>
<tr>
<th>Catalyst characteristics</th>
<th>Analysis instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental composition*</td>
<td>ICP/MS</td>
</tr>
<tr>
<td>BET surface area</td>
<td>Micromeritics ASAP2010</td>
</tr>
<tr>
<td>Micropore volume</td>
<td>Micromeritics ASAP2010</td>
</tr>
<tr>
<td>NH₃-TPD</td>
<td>Micromeritics Autochem 2910</td>
</tr>
<tr>
<td>X-ray diffraction</td>
<td>Bruker D8 Discover</td>
</tr>
</tbody>
</table>

*Performed by external analysis lab

3.5.4 Catalyst coke characterization

Coke deposited on catalysts during upgrading of pyrolysis vapors was analyzed based on the coke content, composition and the thermal properties during coke oxidation. The coke content and its thermal properties were analyzed by TGA in an oxygen atmosphere by heating up deactivated catalysts to 850 °C. The results were compared to a reference of a fresh catalyst. The TGA instrument used was a Mettler Toledo TGA/DSC 1.

In order to study the coke composition, coke was extracted from the catalyst structure for analysis in GC/MS and Fourier-Transform Infrared Spectroscopy (FTIR). Similar coke extraction procedure was performed for both analysis instruments by dissolving the catalyst in concentrated hydrofluoric acid (HF) followed by solvent extraction using DCM, inspired by previous works [74, 75]. 500 mg of coked catalyst was dissolved in 10 cm³ of concentrated HF and kept under stirring for 60 min. Thereafter, dissolved organic coke compounds were extracted for 30 min using 3 cm³ of DCM. After separating the two immiscible liquid phases, the composition of the DCM fraction was analyzed by GC/MS and FTIR. Prior to GC/MS analysis, the extracted fraction was filtrated. Further details on the coke analysis can be found in Supplement III.
3.5.5 Biomass characterization

The thermal degradation of biomass was analyzed by using TGA, namely a Netsch TGA-DSC STA 449 F3 Jupiter. TGA was also used to investigate the thermal degradation of demineralized pre-treated biomass in comparison to raw feedstock.

The biomass structure was studied by scanning electron microscopy (SEM) in Supplement I. The instrument used was a Hitachi S3700N. The samples were studied by secondary electron imaging.
4. Influence of biomass characteristics and pyrolysis conditions on the liquid composition

4.1 Introduction

This chapter is a compilation of the work conducted for Supplements I and II. The performed works investigate how the composition of the derived liquid from pyrolysis of biomass is influenced by the biomass characteristics (Supplement I) as well as the pyrolysis conditions and the design of the pyrolysis process (Supplement II).

Pyrolysis liquids are known for their poor characteristics for direct utilizations in industrial applications [9]. The work conducted in Supplement I studies the effect of the intrinsic inorganic content in biomass in terms of the composition of pyrolysis vapors. The study was performed by experimentally demineralizing biomass by using a leaching pre-treatment prior to pyrolysis. The influence of leaching inorganic elements from biomass on the overall biomass characteristics as well as the composition of derived pyrolysis liquid were investigated.

In conventional pyrolysis processes for liquid production, the temperature of thermal treatment is high enough to devolatilize the main part of the volatile matter of the different biomass constituents. This results in highly complex liquid compositions that needs advanced downstream treatments for liquid fractionation to exploit their full economic potential as chemicals and fuels. However, the composition of liquids derived from pyrolysis could be controlled by adapting the treatment temperature according to the thermal decomposition of biomass pyrolysis. In Supplement II, a concept of utilizing the pyrolysis process itself to produce fractionated liquids is investigated. The work presented investigates a concept of stepwise pyrolysis in several units where the temperature is increased downstreams.

In this chapter, these two studies are further presented in sub-chapters 4.2 and 4.3, respectively.
4.2 Influence of leaching pre-treatment and demineralization on the pyrolysis liquid composition (Supplement I)

4.2.1 Introduction

Inorganic matter in biomass influences the composition of derived pyrolysis liquids. Examples of groups of elements well-known for influencing the liquid composition are alkali and alkaline earth metals (AAEMs) [33-36]. These have been reported to promote cracking and dehydration reactions during pyrolysis of biomass, which lead to increased production of gas, water, and char, as well as decreased organic liquid yield [10, 35, 76]. Previous works have suggested that the thermal decomposition of cellulose can take two different pathways depending on the presence of AAEMs. The presence of AAEMs promotes the formation of several lower molecular weight compounds such as carboxyls and suppresses the formation of sugar derivatives such as levoglucosan (LGA). Also, AAEMs catalyze the fragmentation of ring-structures [76]. The formation of lower molecular weight compounds caused by AAEMs leads to reduction of the overall molecular weight of derived organic compounds as well as reduced yield of pyrolysis liquid by secondary cracking reactions [77, 78]. The effect of AAEMs on the thermochemical decomposition of lignin is still under investigation, based on contradictory results of previous studies.

One important technical parameter in the development of processes for converting biomass into renewable liquids is the carbon-conversion from raw feedstocks into derived products to enhance a mass efficient utilization of the feedstocks. Additionally, the ash content and composition in different biomass feedstocks may vary based on their chemical structure and their geographical origin [79]. One example is the concentrations of alkali metals, which can vary from around 500 mg/kg in pine sawdust to 12 000 mg/kg in straw [80]. High concentrations of AAEMs result in low organic liquid yields and increased water production, which can lead to liquid phase separation [38].

Except from affecting the production of pyrolysis liquids, inorganic matter in biomass can also contribute to damage to the pyrolysis process and its equipment, such as corrosion and reduced heat transfer rates over heat exchange surfaces [81]. Also, inorganic elements in biomass may poison catalysts in downstream treatment of pyrolysis liquids [69].

Based on stated issues of inorganic matter in biomass for liquid production through pyrolysis, it could be of interest to study the removal of such elements prior to pyrolysis as well as its effect on the pyrolysis products. Inorganic matter in biomass can be partially removed by leaching in water and/or acidic aqueous solutions [76,
82]. By integrating biomass demineralization pre-treatment in a pyrolysis-based process, its sensitivity to fluctuations in the product composition due to variations in the composition of inorganics could be reduced. Additionally, pyrolysis of biomass with lower AAEM concentrations would increase the production of anhydrosugars and phenolic compounds, which are promising precursors in the biochemical and petrochemical industries [83]. One example is for production of 1st generation biofuels, where edible feedstocks are converted into, for example, ethanol which counteracts the SDGs specified by the United Nations [4, 84]. Furthermore, leaching pre-treatment could promote the utilization of biomass feedstocks with higher inorganic content as raw materials for pyrolysis processes, which today mainly focuses on low-ash feedstocks.

Previous works investigating the pyrolysis characteristics of demineralized biomass have observed significant differences in the liquid compositions. Inorganic acids such as HCl, HNO₃, and H₂SO₄ have been used as leaching agents in aqueous solutions in biomass pre-treatments. Leaching with acidic solutions promotes the removal of AAEMs. AAEMs are ionically bonded to the biomass structure and can be removed by ion-exchange reactions with protons [85]. However, the use of strongly acidic solutions may not only remove the inorganic matter but also dissolve organic volatile matter in biomass, e.g. dissolution of hemicellulose by acidolysis [34, 86]. Also, volatile matter in terms of hemicellulose can be dissolved by hydrolysis when treating biomass in water or aqueous solutions at higher temperatures requiring pressurized vessels [87]. Losses of volatile matter in biomass during leaching pre-treatment may lead to a reduced liquid yield from the pyrolysis process, which contradicts the efficient utilization of biomass resources and mass efficient conversion of biomass to organic liquids. Preferably, biomass pre-treatment should be performed by leaching of inorganic matter without dissolving significant amounts of volatile matter. Therefore, one option could be to use weak acids such as organic acids as leaching agents in biomass pre-treatment, which would reduce the magnitude of acidolysis. Also, by using organic acids the risk of biomass contamination with, for example, Cl and S caused by inorganic acids (HCl and H₂SO₄, respectively) is suppressed. One alternative could be to utilize acids existing in derived pyrolysis liquids as leaching agents in biomass pre-treatments by an internal process recycling. The conceptual design of such a process is illustrated in Figure 14.
Previous works have shown that acids can be separated from the pyrolysis vapors by utilizing fractional condensation [88]. The concept of using wood-derived acids for leaching pre-treatment was recently investigated by others, observing increased liquid yields and concentration of LGA in comparison to non-treated biomass [35, 89, 90]. Furthermore, previous studies have identified the combination of leaching pre-treatment and pyrolysis as a cost-efficient process to produce sugars and organic liquids from lignocellulosic biomass [91]. As a continuation of these observations, further investigations are performed in this work in order to understand the influence of mild organic acid leaching in terms of:

- The effect on biomass characteristics
- The effect on liquid composition

The work performed in this study focused on leaching of inorganic elements from the biomass structure using aqueous solutions of wood-derived acids present in the pyrolysis liquid. The influence of treatment conditions in terms of acidity and treatment time, the composition of derived pyrolysis liquids, and the mechanism for leaching of different inorganic elements were investigated. Acetic acid was chosen as a model compound for the experimental investigation, as it is the main acid found in pyrolysis liquids derived from biomass [35, 73]. Demineralization of biomass by leaching was performed in the experimental setup illustrated in Figure 10. Investigation of the effect of pre-treatment on the composition of pyrolysis vapours was performed by studying primary pyrolysis vapours in the Py-GC/MS setup illustrated in Figure 4. Ultimate and proximate analysis as well as the thermal decomposition by TGA was performed for non-treated and pre-treated biomass.
4.2.2 Results and discussion

The biomass used for the study was softwood sawdust ground and sieved to the particle size range < 125 µm. Ultimate and proximate analysis of the raw biomass sample which was also used as reference to pre-treated samples is presented in Table 10.

Table 10: Ultimate and proximate analysis of the biomass sample (d.b.)

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash content</td>
<td>3.5</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>81.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate analysis</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>50.8</td>
</tr>
<tr>
<td>O*</td>
<td>39.4</td>
</tr>
<tr>
<td>H</td>
<td>6.1</td>
</tr>
<tr>
<td>N</td>
<td>0.3</td>
</tr>
</tbody>
</table>

*Calculated by difference

Leaching pre-treatment was performed at 85 °C for 30, 60, and 90 min in acidic aqueous solutions consisting of 5 and 10 wt% acetic acid and de-ionized water. The temperature was based on parameter studies performed in previous works, while acid concentrations were chosen based on acetic acid concentrations found in pyrolysis liquids in previous works [35, 73, 88]. The ash content in pre-treated biomass is presented in Figure 15. For leaching of inorganic matter in 5 wt% acetic acid solution, the demineralization is positively correlated with the treatment time. For pre-treatment performed in 10 wt% acetic acid solution, no influence of treatment time could be observed within 30 to 90 min.
Concentrations of inorganic elements (Si and the main AAEMs) in raw biomass as well as from the different pre-treatment conditions are presented in Figure 16. The trends of demineralization is similar for individual elements as for the overall ash content reduction seen in Figure 15. This includes elements present both as minerals (e.g. Si as SiO$_2$), as well as covalently bonded to the organic structure and present as metal salts (e.g. AAEMs). The non-complete removal of inorganic matter in biomass in any of the performed pre-treatment cases is speculated to be due to the mild treatment conditions relative to other studies [34, 86].
Concentrations of Si and main AAEMs in raw and pre-treated biomass

The proton concentration in the leaching liquid was measured by a pH-meter before and after each pre-treatment case. The difference in the reduction of proton concentration for the different pre-treatment cases is presented in Figure 17. By correlating this data to the removal of AAEMs seen in Figure 16, the removal of AAEMs in different acid concentrations and treatment times can be studied. For the pre-treatment cases performed using a 5 % acetic acid solution, a positive correlation over time between the AAEM removal in biomass and the reduction of protons in the liquid can be seen. Firstly, these results present the chemical state of AAEMs in biomass that is mainly present as ion-exchangeable metals covalently bonded to the biomass structure. Secondly, these results indicate that the ion-exchange reaction is the rate limiting step for leaching of ion-exchangeable AAEMs in 5 wt% acid solution.

Overall, the performed leaching experiments show that removal of inorganic matter in biomass is enhanced by treatment in liquids with higher acidities.

Figure 16: Concentrations of Si and main AAEMs in raw and pre-treated biomass
Results of volatile matter in biomass after different pre-treatment conditions is presented in Figure 18 on a dry ash free (DAF) basis. The results show that no significant amounts of volatile matter was dissolved during the pre-treatment, which has been observed in studies using leaching solutions with higher acidity [86]. This confirms that the leaching pre-treatment was performed under relatively mild conditions, where the total amount of pyrolysis liquid and gas is not negatively affected by the pre-treatment, on the basis of the volatile matter in biomass.

SEM analysis of raw and pre-treated biomass (10% acid, 90 min) was performed in order to study the sample topography and investigate if the biomass structure is
visually affected by the treatment in acidic aqueous solutions. Raw biomass was compared to biomass pre-treated at the most severe conditions. SEM images are presented in Figure 19 and 20 with magnification x150 and x1000, respectively. No significant difference on the biomass structure between raw and pre-treated biomass could visually be observed.

![Figure 19: SEM images of raw (left) and pre-treated biomass (right) (magnification x150)](image)

![Figure 20: SEM images of raw (left) and pre-treated biomass (right) (magnification x1000)](image)

The composition of primary pyrolysis products of raw and pre-treated biomass were qualitatively analyzed by using Py-GC/MS. The results are presented in Figure 21 as the relative peak area distribution of different compound groups. All pre-treated samples present a significantly different compositions of pyrolysis products compared to raw biomass. Derivatives originating from cellulose and hemicellulose presents a clear shift towards sugars and anhydrosugars (e.g. LGA) for pre-treated biomass at the same time as smaller compounds such as carbonyls (e.g. aldehydes and ketones), acids, furans, and alcohols are suppressed. This observation correlates well with previous observations on the influence of AAEMs during the thermal decomposition of biomass [76], where cellulose was synthetically impregnated with metal salts prior to pyrolysis. However, the relative area of sugars and sugar derivatives in this study increased with the treatment time for pre-treatment
performed in 10 wt% acetic acid solutions, where no clear reduction in AAEM concentration could be observed over time during 30 to 90 minutes of treatment. Therefore, the differences observed regarding the influence of AAEMs might depend on the chemical state of AAEMs when comparing raw biomass after demineralization with biomass constituents synthetically impregnated with metals.

Figure 21: Relative peak area of different compound groups derived from Py-GC/MS

Further details on the experimental study is available in Supplement I.
4.2.3 Summary

- Significant amounts of inorganic matter in biomass can be removed by mild leaching using organic acids at similar concentrations as in the pyrolysis liquid.
- Correlations between AAEM removal from biomass and ion-exchange reactions with protons was identified.
- No significant effect of the leaching pre-treatment on the biomass structure and its volatile matter was observed, which confirms mild conditions of pre-treatment.
- Demineralized biomass results in significantly higher production of sugars and sugar derivatives such as LGA and suppresses the formation of smaller molecular compounds such as carbonyls.
- The results suggest that the chemical state of inorganics plays an important role in the formation of pyrolysis products, e.g. AAEMs present as metal salts or covalently bonded to the organic structure.
4.3 Influence of stepwise pyrolysis and treatment temperatures on the liquid composition (Supplement II)

4.3.1 Introduction

The liquid derived from conventional pyrolysis of biomass is known as a complex mixture of hundreds of organic compounds and water. Its diverse composition of chemicals complicates downstream separation and upgrading of the liquid to maximize its economic value as a feedstock for producing chemicals and fuels [46]. One way to separate pyrolysis liquids is to introduce multiple condensers downstream the pyrolyzer, where chemical compounds are quenched based on their boiling points [88]. Another approach is to exploit the thermochemical properties of the biomass constituents, i.e. the devolatilization of polymeric fractions generating certain chemical compounds at specific temperatures. This could be performed by using several pyrolysis units in-series, where the treatment temperature increases downstream the process. Very few works have been published that report stepwise pyrolysis results. However, the concept was proven in previous works based on thermogravimetry and a two-staged thermal degradation process of different biomass feedstocks: coniferous, deciduous, and herbaceous [92]. The findings and overall concept of the work is illustrated in Figure 22.

![Figure 22: Example of a stepwise pyrolysis concept adapted from [92]](image)

One of the main reasons for the complex composition of liquids derived from conventional pyrolysis is the process design and the choice of pyrolysis temperature, usually within 450 to 600 °C [93]. At such temperatures, the main part of the volatile matter of the biomass constituents are devolatilized into condensable vapours and non-condensable gases. Based on the different polymeric structures of the biomass constituents, they contribute to a wide range of compounds. However, the polymeric structures of the biomass constituents have different thermal decomposition properties. This provides an opportunity to use pyrolysis for fractionation of less complex liquids. Hemicellulose is the least stable constituent and commonly decomposes in the range 220 to 315 °C, and is also the main contributor of acids and carbonyls. Cellulose decomposes within 315 to 400 °C, while the amorphous structure of lignin decomposes within 160 to 900 °C [51-53]. The thermal
decomposition of the biomass constituents is illustrated in Figure 23. Hemicellulose and cellulose contribute to sugar derivatives such as LGA, but also furans and carbonyls [94]. Lignin mainly contributes to oxygenated aromatic hydrocarbons such as phenols and guaiacols [41]. Further details on chemicals derived from different biomass constituents are presented in Table 3. By exploiting the thermal properties of the biomass constituents and their corresponding chemical structure, the composition of pyrolysis liquids could be controlled by varying the treatment temperature. The concept is illustrated in Figure 24. This could result in the production of fractionated liquids with lower complexities and suppressed rates of aging reactions compared to liquid derived from one-step pyrolysis. In this way, value-added chemicals could be extracted from biomass through a dry distillation process based on pyrolysis.

One drawback of a stepwise pyrolysis process could be a reduced total liquid yield in a setup of several pyrolyzers in comparison to conventional pyrolysis in one unit. The reason is competing reactions of char formation and depolymerisation during the thermal treatment of biomass. This was investigated in previous studies of stepwise pyrolysis, where one-step and two-step pyrolysis processes where compared based on the total organic liquid yield derived from each process. They found that treating biomass at maximum 290 °C prior to the final thermal treatment stage does not negatively affect the liquid yield derived from a stepwise treatment procedure [95].

The behaviour of a wide range of biomass feedstocks have not been addressed in previous studies of stepwise pyrolysis processes. The aim of this work is to evaluate the stepwise pyrolysis concept to produce fractionated condensable liquids with temperature-dependent compositions. PKS was used as biomass feedstock since it is a lignin-rich material, which could be beneficial for producing renewable aromatic hydrocarbons for the petrochemical industry [96, 97]. The study was performed in the fixed-bed reactor illustrated in Figure 5. The process concept and investigated treatment temperatures are illustrated in Figure 24.
Figure 24: Illustration of the investigated process concept in the experimental work

4.3.2 Results and discussion

The experimental cases presented in Table 11 were performed on the basis of the TGA and DTG results of PKS presented in Figure 9, including a reference case of one-step pyrolysis at the highest temperature of 550 °C.

Table 11: Experimental cases investigated in the study

<table>
<thead>
<tr>
<th></th>
<th>1st step (°C)</th>
<th>2nd step (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 0</td>
<td>-</td>
<td>550</td>
</tr>
<tr>
<td>Case 1</td>
<td>200</td>
<td>550</td>
</tr>
<tr>
<td>Case 2</td>
<td>250</td>
<td>550</td>
</tr>
<tr>
<td>Case 3</td>
<td>275</td>
<td>550</td>
</tr>
<tr>
<td>Case 4</td>
<td>300</td>
<td>550</td>
</tr>
</tbody>
</table>

The product yields of the liquid and solid products from the different experimental cases and individual pyrolysis steps are presented in Figure 25. Yields are based on the solid treated in each case. Results show an increasing liquid yield and reducing yield of solid residue as the pyrolysis temperature increases from 200 to 300 °C. The yield of solid residue derived from each case at 550 °C is positively correlated with the temperature of the first step, explained by its reduced content of volatile matter by previous devolatilization in the first pyrolysis step. The sum of the yields of liquids and solid residues in each case is similar to the reference test of one-step pyrolysis at 550 °C. This observation is coherent with previous works claiming that no irreversible char forming reactions occurred in the polymeric structure at temperatures lower than 290 °C [95].
The distribution of organic liquid and pyrolytic water in the liquid derived at each pyrolysis step was calculated based on Karl-Fischer titration. The results are presented in Figure 26 relative to the total liquid yield of each experimental case. Based on these results it can be seen that both the production of organic liquid and water increase gradually with pyrolysis temperature in the first pyrolyzer. The main fraction of organic liquid is derived in the temperature range 250 to 300 °C. Also, at temperatures higher than 300 °C, the production of pyrolytic water is higher relative to the production of organic liquid.
Figure 26 also presents relatively high yields (up to 22.6 wt%) of pyrolytic water compared to, for example, studies using a fluidized bed pyrolyzer. This could be explained by a lower heating rate of biomass as well as longer residence time of vapors both in the hot gas phase of the pyrolyzer and in the fixed bed of biomass/char [77]. Because of the relatively high water content of liquids from each pyrolysis step, they naturally separated into two immiscible phases: aqueous phase and non-aqueous phase [30]. In Figure 27, the yield of each phase from the different pyrolysis steps and cases are presented. Results show that the main part of the derived liquids is derived between 250 to 275 °C. Also, the overall results show that the main part of the total liquid derived from PKS in the process (both in one and two-step pyrolysis) exist as an aqueous solution of water and water-soluble organic compounds. After treating PKS at 300 °C, only a negligible fraction of the non-aqueous phase was produced (0.3 wt% of raw PKS).
The composition of pyrolysis liquids were qualitatively analyzed by GC/MS. The results are presented in Table 12 for each liquid phase, experimental case and pyrolysis step. Overall, these results show the temperature dependency for the evolution of different compound groups from the biomass structure during thermal treatment. Also, it can be seen that the formation of compounds in the first step reflects a reduced relative composition in the second step treatment. Regarding compounds found in the aqueous phase, it is seen that furan production is initiated at 250 °C at the same time as its relative composition in the second treatment is decreased. Similar observations can be seen for ketones and sugars where an increased temperature of the first step reduces their relative composition in the liquid from the second treatment. These observations indicate that the summarized chemical composition of liquids derived from the two steps might not be significantly different compared to liquids derived from one step pyrolysis. Similar observations has been seen in previous studies [95]. Regarding the analysis of the chemical composition of the non-aqueous phase, lignin derivatives such as phenolics was the dominating group of compounds.

Based on the GC/MS of pyrolysis liquids, the advantage of two-step pyrolysis to fractionate and concentrate chemical groups is clearly seen, especially for water-soluble chemicals. However, the process concept and conducted experiments do not favour a complete fractionation of chemical groups, which could be explained by the overlap of thermal decomposition temperature ranges for the different biomass constituents.
Table 12: Distribution of peak area from GC/MS analysis of liquids from first and second step of pyrolysis.

‘550(200)’ represents treatment at 550 °C after treatment at 200 °C.

<table>
<thead>
<tr>
<th>Aqueous phase</th>
<th>200</th>
<th>250</th>
<th>275</th>
<th>300</th>
<th>550</th>
<th>550(200)</th>
<th>550(250)</th>
<th>550(275)</th>
<th>550(300)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acids</td>
<td>27.1</td>
<td>25.1</td>
<td>11.9</td>
<td>12.8</td>
<td>16.0</td>
<td>15.4</td>
<td>14.2</td>
<td>14.1</td>
<td>5.7</td>
</tr>
<tr>
<td>Alcohol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>-</td>
<td>-</td>
<td>0.8</td>
<td>0.8</td>
<td>0.6</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Alkanes</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
<td>0.7</td>
<td>1.1</td>
<td>1.1</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Furans</td>
<td>-</td>
<td>18.8</td>
<td>8.3</td>
<td>7.5</td>
<td>6.3</td>
<td>6.7</td>
<td>4.6</td>
<td>0.9</td>
<td>4.8</td>
</tr>
<tr>
<td>Ketones</td>
<td>-</td>
<td>1.8</td>
<td>3.5</td>
<td>4.0</td>
<td>2.4</td>
<td>3.5</td>
<td>2.9</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>N compounds</td>
<td>0.0</td>
<td>7.0</td>
<td>2.3</td>
<td>2.1</td>
<td>1.3</td>
<td>1.3</td>
<td>1.0</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>Phenolic compounds</td>
<td>72.9</td>
<td>47.3</td>
<td>70.8</td>
<td>65.9</td>
<td>58.0</td>
<td>58.1</td>
<td>60.2</td>
<td>66.8</td>
<td>89.5</td>
</tr>
<tr>
<td>Sugar compounds</td>
<td>-</td>
<td>-</td>
<td>1.1</td>
<td>6.0</td>
<td>13.5</td>
<td>12.5</td>
<td>15.4</td>
<td>15.8</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Acids</td>
<td>-</td>
<td>-</td>
<td>2.1</td>
<td>-</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Furans</td>
<td>-</td>
<td>-</td>
<td>2.6</td>
<td>-</td>
<td>3.2</td>
<td>3.6</td>
<td>1.5</td>
<td>4.5</td>
<td>2.7</td>
</tr>
<tr>
<td>Phenolic compounds</td>
<td>-</td>
<td>100</td>
<td>95.3</td>
<td>100</td>
<td>94.5</td>
<td>96.4</td>
<td>98.5</td>
<td>95.5</td>
<td>97.3</td>
</tr>
</tbody>
</table>

Liquids were also analyzed based on their concentration of acids, performed by TAN titration. Results are presented in Table 13. Thermally treating biomass in the first step results in lower acid concentrations in liquids derived in the second step at 550 °C. Also, the acid concentration in liquids derived in the second step is negatively correlated with the temperature of the first step. The results are reflected by higher acid concentrations in the first step, where the main part of acids are derived around 250 °C compared to the evolution of other compounds. A reduced concentration of acids in liquids from the second step indicates that these liquids should present reduced rate of aging reactions [47-49]. However, the derived liquids were not experimentally evaluated based on their aging characteristics.
Table 13: TAN values (mg KOH/g) of liquid phases from each pyrolysis step

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous phase 1st step</td>
<td>-</td>
<td>n.d.</td>
<td>172</td>
<td>171</td>
<td>148</td>
</tr>
<tr>
<td>Non-aqueous phase 1st step</td>
<td>-</td>
<td>n.d.</td>
<td>201</td>
<td>200</td>
<td>131</td>
</tr>
<tr>
<td>Aqueous phase 2nd step</td>
<td>125</td>
<td>129</td>
<td>96</td>
<td>21</td>
<td>15</td>
</tr>
<tr>
<td>Non-aqueous phase 2nd step</td>
<td>112</td>
<td>113</td>
<td>87</td>
<td>38</td>
<td>-</td>
</tr>
</tbody>
</table>

Further details on the experimental study is available in Supplement II.

4.3.3 Summary

- Stepwise pyrolysis can be used to understand the thermal decomposition properties of biomass feedstocks and the temperature dependency regarding the evolution of different compounds.
- The summarized liquid yield derived in two-step pyrolysis does not significantly differ from the liquid yield derived from one-step pyrolysis.
- The main part of the organic liquid derived from PKS is derived between 250 to 300 °C.
- The evolution of certain compounds in the first step reduces their concentration in the second step, reflecting the decomposition of the polymeric structure of PKS.
- Thermally treating biomass in two separated pyrolysis units connected in-series is a promising approach to fractionate and concentrate chemical groups, especially water-soluble compounds. However, a complete separation of chemicals by the two-step process design is more complicated, which could be explained by overlapping temperature ranges of decomposition for the different biomass constituents.
5. Catalytic pyrolysis of biomass

5.1 Introduction

This chapter is a compilation of the work conducted in Supplements III, IV, and V. The performed works investigate different aspects of catalytic pyrolysis of biomass in the spectra of fundamental studies of catalyst activity and deactivation (Supplement III), influence of the vapor composition for catalytic upgrading (Supplement IV), and the performance of a continuous catalytic pyrolysis process (Supplement V).

Catalytic pyrolysis of biomass can be used to enhance the technical properties of pyrolysis liquid and to increase its economic value [54]. By letting pyrolysis vapors pass through a heterogeneous catalyst upstream vapor quenching, their chemical composition can be significantly reformed. However, commonly used zeolite-based catalysts tend to rapidly deactivate due to coke formation. Metal-doping of zeolites is a well-known approach to promote the formation of certain compounds. Little is known about the influence of metal-doping on the catalyst deactivation, for example, the rate of deactivation and the coke composition. Therefore, the work conducted in Supplement III focused on identifying correlations between the catalyst activity and the catalyst deactivation during upgrading of pyrolysis vapors from biomass.

As mentioned above, the performance of catalytic pyrolysis and the product selectivity can be affected by changing the properties of the catalyst. Another approach could be to adjust the process conditions of catalytic vapor reforming, e.g. temperature, vapor residence time and gaseous atmosphere in the pyrolyzer. In the work conducted in Supplement IV, the influence of adjusting the composition of pyrolysis vapors from biomass for catalytic upgrading was investigated by comparing pre-treated and non-treated biomass. Also, the influence of reactor temperature as well as the process design for in-situ catalytic pyrolysis were investigated, comparing in-bed and ex-bed setups.

In the final Supplement of this thesis, an experimental lab-scale setup for catalytic fast pyrolysis and continuous production of pyrolysis liquid was evaluated. The setup included a fluidized bed-pyrolyzer and a catalytic fixed bed-reactor. The work conducted in Supplement V investigated the capacity and performance of the setup for producing upgraded pyrolysis liquid.

In this chapter, these three individual studies are further presented in sub-chapters 5.2, 5.3, and 5.4, respectively.
5.2 Influence of metal-doping on catalyst activity and catalyst deactivation (Supplement III)

5.2.1 Introduction
Catalytic pyrolysis is a promising route to produce high-value liquid products from biomass. One drawback of using zeolite-based catalysts in catalytic pyrolysis of biomass is their severe deactivation characteristics in terms of coke formation during vapor upgrading. Catalyst coke typically consists of large compounds formed within the porous structure that due to the shape selectivity of the catalyst cause pore blockage. The outer surface of the catalyst can be coked by, for example, accumulation of heavy compounds. Coke formation on the catalyst surface can occur through, for example, aromatization and polymerization reactions. Overall, catalyst deactivation by coking leads to a decrease of the reactive surface area which reduces the catalytic activity in terms of upgrading capacity and the catalyst’s lifetime [98-101]. However, the catalyst can be regenerated by combustion of the coke [102]. Unfavourably, the generation of local higher temperatures in the catalyst bed during regeneration, known as ‘hot spots’, may permanently damage the catalyst by, for example, sintering and dealumination [98, 103, 104]. The coke characteristics such as its composition and content on the catalyst may therefore influence the magnitude of such irreversible catalyst deactivations. Therefore, catalyst deactivation by coking is an important parameter to consider when developing catalysts for industrial processes, where the catalyst should present an adequate performance for upgrading pyrolysis vapors but also a low deactivation rate. The study of catalytic properties both in terms of vapor upgrading and deactivation characteristics are considered as interesting approaches when evaluating different materials to be used as catalysts in future processes for producing renewable feedstocks through catalytic pyrolysis.

By impregnating zeolites with different elements, e.g. transition metals, the catalyst’s selectivity towards certain compounds can be promoted [105-107]. However, research on the dopants’ effects on coke formation on catalysts during catalytic pyrolysis of biomass has been sparsely published, e.g. the rate of coking and the coke composition. Therefore, this work focused on comparing the properties of different catalysts to study the catalyst activity and the catalyst deactivation in parallel. HZSM-5 was used as a supporting catalyst structure and compared as a reference material to metal-doped zeolites. The metals used for doping of HZSM-5 were Fe and Ni, investigated as single and co-doped zeolite catalysts. Fe and Ni were chosen based on their interesting characteristics seen in previous works, but also for their
availability, relatively low cost, and relatively low environmental impact compared to other metals commonly used in heterogeneous catalysis [55, 108-112]. In this experimental study, the characteristics of upgraded vapors and catalyst coke were investigated aiming to identify connections between catalyst activity and deactivation in the upgrading of pyrolysis vapors over different catalysts. This is illustrated in Figure 28.

![Figure 28: Illustration of catalytic pyrolysis, its products and the focus of this study](image)

In previous studies, impregnation of Ni has resulted in several advantages such as promoting the aromatization reactions and the formation of phenolic compounds, but also to suppress the production of polycyclic aromatic hydrocarbons (PAHs) as well as water. Ni is also known for promoting hydrogen transfer reactions, e.g. the water gas shift reaction [60, 64, 113, 114].

Metal-impregnation of Fe in the HZSM-5 structure has been found to promote the formation of monocyclic aromatic hydrocarbons (MAHs) and naphthalenes but also to suppress the production of PAHs and phenolic compounds [55, 108, 115, 116].

In the experimental work performed, the catalysts were prepared, characterized and experimentally evaluated in the fixed-bed pyrolyzer illustrated in Figure 5. Thereafter, the pyrolysis products were characterized, including the coke formed on the catalysts.

### 5.2.2 Results and discussion

The mass balance results for catalytic pyrolysis over the different catalysts are presented in Figure 29, varying between 98.1-101.3 wt%. HZSM-5 presents higher organic liquid yield and lower gas yield compared to metal-doped catalysts, i.e. a lower cracking performance of the catalyst. Ni-doping results in the highest catalytic cracking performance, whereas Fe/ZSM-5 gives the highest organic liquid yield of metal-doped catalysts. FeNi/ZSM-5, with the highest metal loading, does not present any clear difference on yield basis compared to Fe/ZSM-5 and Ni/ZSM-5. The reduced liquid yields for metal-impregnated catalysts can be explained by their
catalytic properties but also on the increased surface acidity of the catalysts, seen in Figure 13 [65]. Additionally, the increased catalytic activity of metal-doped catalysts can be correlated to their increased catalyst coke yield.

![Mass balance of investigated catalysts relative to biomass input mass](image)

Figure 29: Mass balance of investigated catalysts relative to biomass input mass (d.b.)

Results from KF-titration as well as TAN-titration of derived liquids are presented in Table 14, and show a significant increase in the water concentration when using metal-doped catalysts. Also, metal-doping results in reduced concentrations of acids in derived liquids. Interestingly, Fe-doping gives the lowest TAN value as well as the lowest water content.

<table>
<thead>
<tr>
<th>Liquid characteristics</th>
<th>HZSM-5</th>
<th>Ni/ZSM-5</th>
<th>Fe/ZSM-5</th>
<th>FeNi/ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAN (d.b.)</td>
<td>130.0±2.1</td>
<td>115.9±3.9</td>
<td>88.0±1.0</td>
<td>90.0±0.9</td>
</tr>
<tr>
<td>Water content (wt%)</td>
<td>67.8±0.2</td>
<td>81.2±0.1</td>
<td>73.5±0.3</td>
<td>82.3±0.2</td>
</tr>
</tbody>
</table>

Results of GC/MS analysis of derived liquids are presented in Table 15, and show a significant impact of metal-doping for the promoting of certain chemical reaction pathways during catalytic upgradings of pyrolysis vapors. As expected based on previous works, impregnation of Fe and Ni promotes the selectivity towards aromatic hydrocarbons [55, 60]. Fluorenes and PAHs (hereby defined as polycyclic
aromatic hydrocarbons with more than two aromatic rings) are suppressed for all metal-doped catalysts whereas MAHs and naphthalenes are promoted. Fe mainly promotes the formation of MAHs but limits their polymerization reactions, reflecting previous observations [108]. Ni however promotes MAHs and naphthalenes, i.e. enhances aromatization reactions. FeNi/ZSM-5 reflects the combined effects of both metals where the promotion of MAHs and naphthalenes are further enhanced.

Table 15: GC/MS analysis results of liquids (peak area %)

<table>
<thead>
<tr>
<th></th>
<th>HZSM-5</th>
<th>Ni/ZSM-5</th>
<th>Fe/ZSM-5</th>
<th>FeNi/ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAHs</td>
<td>6.5</td>
<td>15.3</td>
<td>27.0</td>
<td>28.5</td>
</tr>
<tr>
<td>Fluorenes</td>
<td>3.4</td>
<td>1.3</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>Naphthalenes</td>
<td>36.8</td>
<td>46.3</td>
<td>39.5</td>
<td>48.3</td>
</tr>
<tr>
<td>PAHs</td>
<td>12.3</td>
<td>4.5</td>
<td>2.7</td>
<td>4.2</td>
</tr>
<tr>
<td><strong>Aromatic hydrocarbons</strong></td>
<td><strong>59.0</strong></td>
<td><strong>67.4</strong></td>
<td><strong>70.9</strong></td>
<td><strong>82.8</strong></td>
</tr>
<tr>
<td>Acids</td>
<td>2.7</td>
<td>1.0</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Alcohols</td>
<td>1.5</td>
<td>0.9</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>3.2</td>
<td>0.8</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Ester</td>
<td>0.2</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Furans</td>
<td>1.1</td>
<td>2.8</td>
<td>1.9</td>
<td>1.3</td>
</tr>
<tr>
<td>Ketones</td>
<td>2.3</td>
<td>2.6</td>
<td>1.7</td>
<td>0.5</td>
</tr>
<tr>
<td>N compounds</td>
<td>1.5</td>
<td>0.6</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Phenols</td>
<td>22.8</td>
<td>20.9</td>
<td>21.9</td>
<td>12.4</td>
</tr>
<tr>
<td>Unknowns</td>
<td>5.8</td>
<td>3.0</td>
<td>1.9</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Other Compounds</strong></td>
<td><strong>41.0</strong></td>
<td><strong>32.6</strong></td>
<td><strong>29.1</strong></td>
<td><strong>17.2</strong></td>
</tr>
</tbody>
</table>

Moving on to the analysis of compounds found in the catalyst coke, presented in Table 16, the results can be seen to overall correlate with the trends of catalytic activities seen in the GC/MS analysis of upgraded liquids. Some examples are: (1) Fe/ZSM-5 presenting an increased concentration of MAHs in both fractions, (2) Ni/ZSM-5 presenting increased concentration of naphthalenes, and (3) a reduced concentration of fluorenes for all metal-doped zeolites. These observations indicate that the composition of coke is influenced by the choice of catalyst.

Metal-doped catalysts present higher concentrations of aromatic hydrocarbons in the coke. Also, they present an increased selectivity towards PAHs which is consistent with their increased coke yield compared to HZSM-5 [115]. However, metal-doped catalysts show a suppression in the concentration of fluorenes in derived coke. Ni and FeNi-doping give higher concentrations of MAHs, naphthalenes, and PAHs in the coke compared to HZSM-5, while Fe results in higher concentrations of MAHs and naphthalenes. Except for the results presenting direct similarities between coke and liquid compositions, the results also indicate a chemical reaction pathway influenced by metal-doping. The increased concentration of naphthalenes and
suppression of fluorenes in both liquids and coke for metal-doped catalysts suggests that polymerization reactions of MAHs are affected by the presence of metals, i.e. metal-doping promotes polymerization of MAHs via sp² hybridized carbon atoms. This is illustrated in Figure 30 in terms of a suggested overall reaction pathway. Investigations of more complex reaction mechanisms for the polymerization of MAHs over metal-doped zeolites are left for future studies.

Table 16: GC/MS analysis of extracted coke (peak area %)

<table>
<thead>
<tr>
<th></th>
<th>HZSM-5</th>
<th>Ni/ZSM-5</th>
<th>Fe/ZSM-5</th>
<th>FeNi/ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAHs</td>
<td>0.4</td>
<td>1.3</td>
<td>1.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Fluorenes</td>
<td>11.2</td>
<td>6.9</td>
<td>6.5</td>
<td>7.1</td>
</tr>
<tr>
<td>Naphthalenes</td>
<td>8.9</td>
<td>16.0</td>
<td>21.1</td>
<td>13.6</td>
</tr>
<tr>
<td>PAHs</td>
<td>34.5</td>
<td>44.8</td>
<td>33.9</td>
<td>40.5</td>
</tr>
<tr>
<td><strong>Aromatic hydrocarbons</strong></td>
<td><strong>55.0</strong></td>
<td><strong>69.0</strong></td>
<td><strong>63.3</strong></td>
<td><strong>62.1</strong></td>
</tr>
<tr>
<td>Acids</td>
<td>8.7</td>
<td>6.1</td>
<td>6.8</td>
<td>8.0</td>
</tr>
<tr>
<td>Alcohols</td>
<td>10.3</td>
<td>4.8</td>
<td>5.6</td>
<td>4.3</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>0.3</td>
<td>0.9</td>
<td>1.6</td>
<td>1.1</td>
</tr>
<tr>
<td>Alkanes</td>
<td>4.8</td>
<td>3.3</td>
<td>4.8</td>
<td>6.9</td>
</tr>
<tr>
<td>Alkenes</td>
<td>0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Ester</td>
<td>1.7</td>
<td>0.8</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Furans</td>
<td>2.2</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Ketones</td>
<td>7.8</td>
<td>4.3</td>
<td>4.5</td>
<td>5.4</td>
</tr>
<tr>
<td>N compound</td>
<td>2.7</td>
<td>2.7</td>
<td>2.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Phenols</td>
<td>4.9</td>
<td>3.8</td>
<td>4.8</td>
<td>4.8</td>
</tr>
<tr>
<td>Unknowns</td>
<td>1.5</td>
<td>2.8</td>
<td>3.0</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>Other Compounds</strong></td>
<td><strong>45.0</strong></td>
<td><strong>31.0</strong></td>
<td><strong>36.7</strong></td>
<td><strong>37.9</strong></td>
</tr>
</tbody>
</table>

Results of TGA of spent catalysts are presented in Figure 31 and show an increased coke formation on metal-doped catalysts which can be associated with their
increased acid site concentration presented in Figure 13 [64, 117]. Among investigated catalysts, Fe-doping results in the highest coke yield followed by the FeNi-doped catalyst. Interestingly, the strength of acid sites (seen in Figure 13) correlates with the coke yield for the different catalysts.

The co-doped catalyst gives the highest concentration of aromatic hydrocarbons followed by Fe/ZSM-5. However, co-doping gives a lower coke yield than Fe-doping. Additionally, no trends between the promotion of certain compounds and the magnitude of coke formation could be observed. Based on this, the results indicate that a catalyst’s high activity for aromatization of pyrolysis vapors does not result in a high coke formation. Instead, catalyst coking seems to depend on the acid site strength and the characteristics of metals impregnated in the zeolitic structure.

TGA results also show the effect of regeneration temperature for the different catalysts. This could be explained by a catalytic effect of metals during the combustion of the carbonaceous solid coke [118]. A lower temperature needed for catalyst regeneration could reduce the strain on the catalyst and the risk of irreversible deactivation during regeneration [119]. However, this investigation is left for further studies.

![TGA results of spent catalysts](image)

Figure 31: TGA results of spent catalysts

*Further details on the experimental study is available in Supplement III.*
5.2.3 Summary

- The composition of coke formed on zeolite catalysts during upgrading of pyrolysis vapors overall reflect the catalysts’ activity.
- Metal-doping promotes the aromatization of biomass vapors as well as increased catalyst deactivation in catalytic pyrolysis.
- The deactivation rate of metal-doped catalysts is correlated with the concentration and strength of acid sites. The coke yield was seen to depend on the strength of acid sites.
- Co-doped FeNi/ZSM-5 presents multifunctional characteristics reflecting the activity of Fe and Ni-doped catalysts, respectively.
- Metal-doping influences the temperature for catalyst regeneration.
Figure 32: Graphical abstract and summary of results from the conducted study.
5.3 Catalytic pyrolysis of demineralized biomass
(Supplement IV)

This study is a continuation of the work presented in Supplement I and section 4.2.

5.3.1 Introduction

As presented and discussed in Supplement I and section 4.2, demineralization of biomass has a significant impact on the composition of primary pyrolysis vapors. Pre-treating biomass in organic acids existing in the pyrolysis liquid can significantly reduce the ash content without reducing the volatile matter of biomass. The lower concentration of AAEMs in biomass increases the formation of larger organic compounds such as sugars and anhydrosugars, e.g. LGA [33]. Liquid derived from pyrolysis of biomass is commonly known for its complex organic composition and high content of oxygen, resulting in a complicated feedstock for downstream refining, a low heating value etc. Catalytic pyrolysis can be used to homogenize the liquid composition and promote its similarities to fossil crude oil. The concept of catalytically upgrading pyrolysis vapors prior to quenching has been widely studied, mainly by screening different catalysts used in the petrochemical industry for cracking, aromatization, deoxygenation etc. HZSM-5 has gained much attention for its suitable properties for converting lignocellulosic biomass and biomass model compounds, e.g. glucose, into aromatic hydrocarbons [59, 61]. Different technical pathways has been investigated to increase the conversion of biomass into aromatic hydrocarbons, e.g. temperature of catalytic pyrolysis, and metal-doping of catalysts [58, 107, 120]. However, research on the influence of the composition of the vapor stream prior to catalytic upgrading has been sparsely published. Pyrolysis of demineralized biomass results in enhanced concentrations of anhydrosugars among derived products. This means that vapors from demineralized biomass are more similar to vapors from pyrolysis of glucose, which has been used as a model compound for biomass when screening different catalytic materials [121]. The theoretical shift of vapor composition due to biomass pre-treatment is illustrated in Figure 33.
Additionally, the composition of vapors derived from demineralized biomass is less complex compared to raw biomass, which should be preferable in the upgrading over one catalyst. Biomass demineralization could also reduce catalyst poisoning caused by alkali metals during catalytic upgrading of biomass vapors [69]. This study combines biomass demineralization pre-treatment and catalytic pyrolysis, which is illustrated in a conceptual process scheme in Figure 34.

This work investigates catalytic and non-catalytic pyrolysis of demineralized biomass in comparison to raw biomass. Softwood sawdust was experimentally demineralized based on findings in Supplement I. Pre-treatment was performed in the setup illustrated in Figure 11. Pyrolysis and catalytic pyrolysis were performed by Py-GC/MS and in the bench-scale pyrolyzer illustrated in Figure 4 and 5. This allowed studying the influence of pyrolysis temperature, the composition of primary and secondary vapors and their upgrading characteristics over HZSM-5. Thermal treatment was conducted at 400, 500, and 600 °C.

Figure 33: Illustration of the theoretical shift of the pyrolysis vapor composition from pre-treated biomass

Figure 34: Illustration of a conceptual process for combined biomass pre-treatment and catalytic pyrolysis
5.3.2 Results and discussion

Biomass was pre-treated according to findings in Supplement I. A 10 wt% acetic acid aqueous solution was used for leaching at 85 °C for 30 min. Results of biomass pre-treatment are presented in Table 17 and show a 76 % ash content removal without any loss of volatile matter. The pre-treatment mainly removed AAEMs in comparison to transition metals. Further discussion of leaching pre-treatment is presented in section 4.2 and in Supplement I.

<table>
<thead>
<tr>
<th></th>
<th>Raw</th>
<th>Pre-treated</th>
<th>Raw</th>
<th>Pre-treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash content (wt%)</td>
<td>0.21</td>
<td>0.05</td>
<td>Ca (mg/kg)</td>
<td>349</td>
</tr>
<tr>
<td>Volatile matter (wt%)</td>
<td>84.4</td>
<td>86.3</td>
<td>K (mg/kg)</td>
<td>242</td>
</tr>
<tr>
<td>C (wt%)</td>
<td>50.7</td>
<td>50.9</td>
<td>Mg (mg/kg)</td>
<td>51.6</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>6.0</td>
<td>6.5</td>
<td>Mn (mg/kg)</td>
<td>42.4</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>Fe (mg/kg)</td>
<td>7.97</td>
</tr>
<tr>
<td>O* (wt%)</td>
<td>43.0</td>
<td>42.5*</td>
<td>Al (mg/kg)</td>
<td>5.24</td>
</tr>
</tbody>
</table>

*Calculated by difference

The mass balance of the catalytic and non-catalytic pyrolysis experiments performed in the bench-scale setup are presented in Figure 35. Overall, pre-treated biomass presents significantly different pyrolysis characteristics compared to raw biomass. In non-catalytic pyrolysis, pre-treated biomass results in higher organic liquid yield at the higher pyrolysis temperatures. Largest difference in liquid yield between pre-treated and raw biomass is observed at 600 °C, where the organic liquid yield is 33 % higher for pre-treated biomass. The higher liquid yields observed for pre-treated biomass can be explained by its lower AAEM concentration resulting in suppressed cracking of pyrolysis vapors into gas and water [122]. Pre-treated biomass also presents a lower char yield at higher temperatures, which also correlates with the reduced AAEM concentration by the suppression of char-forming reactions [123]. Also, the increased organic liquid yield and lower char yields at higher pyrolysis temperatures could be associated with the increased temperature gradients during biomass heating.

In catalytic pyrolysis, a reduced catalyst coking was observed with increasing temperature which is in accordance with previous studies [120]. The slightly higher catalyst coking for pre-treated biomass is associated with its increased catalytic conversion of pyrolysis vapors, which is further discussed below together with Figure 39.
Moving on to the composition of pyrolysis vapors derived from raw and pre-treated biomass, characteristic organic compounds from the different biomass samples were chosen for comparison. Acetic acid, furfural, and LGA are the main acid, aldehyde, and anhydrosugar found in pyrolysis liquids and are derived from the holocellulosic structure [46]. Furan was also chosen since it is a known derivative from decomposition of LGA and commonly used as a model compound in catalytic pyrolysis studies [124, 125]. Guaiacol is one of the main phenolic compounds derived from lignin [126].

Figure 36 presents the results of Py-GC/MS analysis at 400, 500, and 600 °C. In accordance with observations in previous studies and in Supplement I, pre-treated biomass gives a significantly reduced production of acetic acid and an increased production of LGA at higher temperatures. The concentration of furfural does not present any significant difference between raw and pre-treated biomass. However, the production of guaiacol is significantly reduced for pre-treated biomass which confirms the influence of leaching on the lignin decomposition [35].

The overall increase in product concentrations with pyrolysis temperature should be attributed to the short time of heating and exposure to the pyrolysis temperature in the Py-GC/MS setup. Therefore, the results presented in Figure 36 also reflects the thermal stability of the biomass constituents under different temperature conditions.
The results of GC/MS analysis of liquids derived from non-catalytic pyrolysis in the bench-scale pyrolyzer are presented in Figure 37. Firstly, the DCM (internal standard) results present uniform peak area results for the different liquids analyzed, which confirms an even dilution and sample injection in the GC/MS analysis. Compared to Py-GC/MS results, the bench-scale tests are performed at a lower heating rate and longer treatment time, allowing complete biomass devolatilization. Similar to Py-GC/MS results, pre-treated biomass gives a reduced concentration of acetic acid between 26 to 63 % compared to raw biomass at all temperatures investigated. Pre-treated biomass also shows a suppression of furan, which can be linked with a reduced decomposition of anhydrosugars in the biomass structure with a lower AAEM concentration in biomass [127, 128]. Similar observations of a reduced guaiacol concentration in derived vapors was observed as for Py-GC/MS results and in previous studies performed in a fluidized bed [35]. The concentration of LGA was between 173 to 208 % higher for pre-treated biomass at all temperatures. When the pyrolysis temperature increases, the rate of secondary reactions among pyrolysis
vapors is increased where LGA decompose/reacts, e.g. by thermal cracking or repolymerization [129]. This can explain the reduced concentration of LGA at 600 °C for pre-treated biomass. By comparing the results from bench-scale experiments and Py-GC/MS the significance of such secondary reactions is seen. In Py-GC/MS, primary pyrolysis vapors can be studied whereas the bench-scale pyrolysis includes secondary vapors. Additionally, the results overall indicate the influence of AAEMs in the biomass structure in terms of the composition of derived liquids.

Figure 37: GC/MS results from non-catalytic pyrolysis in bench-scale setup
For the composition of liquids from catalytic pyrolysis of biomass, characteristic one and two-ringed aromatic hydrocarbons were chosen since they are the main products of interest when upgrading pyrolysis vapors over HZSM-5 [59, 130]. Examples are benzene, toluene and xylenes (BTX), and 2-methylnaphthalene.

The results of catalytic pyrolysis in Py-GC/MS, i.e. in-bed catalytic pyrolysis, are presented in Figure 38. In these experiments, biomass and catalyst were pre-mixed followed by thermal treatment in the Pyrola2000 unit. At all temperatures, raw biomass gives higher yields of aromatic hydrocarbons compared to pre-treated biomass, especially at higher temperatures. The influence of temperature on the catalytic pyrolysis of raw biomass shows similar trends as seen in previous studies [120]. Reasons why pre-treated biomass results in lower selectivity towards aromatic hydrocarbons can be studied by correlating the results to observations from non-catalytic pyrolysis in the Py-GC/MS setup. Primary pyrolysis vapors from demineralized biomass includes significantly higher fractions of anhydrosugars compared to raw biomass, especially LGA. The kinetic diameter of LGA is 6.7 Å, which does not match the shape selectivity of the narrow porous structure of HZSM-5 with a pore diameter range 5.5-5.6 Å. This limits the catalytic upgrading of primary pyrolysis vapors from pre-treated biomass. However, the primary pyrolysis vapors from raw biomass present higher concentrations of smaller organic compounds due to its higher concentration of AAEMs, which are suitable to enter the porous structure of HZSM-5 and can therefore undergo catalytic reactions such as aromatization and deoxygenation [59].
Results of catalytic pyrolysis performed in the bench-scale facility, i.e. ex-bed catalytic pyrolysis, are presented in Figure 39. As for the comparison of the results from bench-scale and Py-GC/MS analysis of non-catalytic pyrolysis, the results are significantly different from catalytic pyrolysis in Py-GC/MS. At lower pyrolysis temperatures, raw biomass gives higher concentrations of BTX compounds compared to pre-treated biomass. However, as the temperature increases the production of such compounds is enhanced for upgrading of vapors from the pre-treated biomass. For catalytic pyrolysis at 600 °C, pre-treated biomass gives a higher...
selectivity towards BTX and two-ringed aromatic hydrocarbons than raw biomass. By comparing these results to in-bed catalytic pyrolysis experiments performed in Py-GC/MS, it can be clearly seen that the pyrolysis vapors’ exposure to a hot vapor phase and the occurrence of secondary vapor reactions prior to catalytic upgrading over HZSM-5 play a significant role in the performance of catalytic pyrolysis. A higher pyrolysis temperature increases the heating rate of biomass in the experimental facility as well as the rates of secondary vapor-phase reactions. At 600 °C, the vapor composition of biomass from pre-treated biomass gives higher concentrations of aromatic hydrocarbons compared to raw biomass when upgraded over HZSM-5. Also, an increased catalytic conversion is indicated by a higher magnitude of catalyst coking presented in Figure 35.

Based on the results of catalytic pyrolysis of biomass over zeolites, the composition of vapors prior to catalytic upgrading has a significant impact on the performance of catalytic conversion into aromatic hydrocarbons. Furthermore, both the presence of AAEMs and the occurrence of secondary reactions in the vapor phase significantly influence the catalytic upgrading of pyrolysis vapors and the biomass-to-aromatics conversion. Therefore, derivatives originating from secondary reactions of anhydrosugars should have a significant role in the conversion of biomass pyrolysis vapors over HZSM-5.
Figure 39: GC/MS results from catalytic pyrolysis in bench-scale setup

TAN results of pyrolysis liquids from bench-scale experiments are presented in Table 18. The reduced TAN values with increasing temperature of non-catalytic pyrolysis can be explained by the thermal decomposition properties of biomass, further discussed in Chapter 5.3 and Supplement II. Also, pre-treated biomass presents lower TAN values than raw biomass, which correlates with previous observations in the analysis of the organic vapor compositions.
Catalytic pyrolysis of vapors significantly influences the magnitude of TAN values for the derived products, where the most significant reduction is observed at 600 °C for pre-treated biomass. However, no clear trend based on pyrolysis temperature was observed.

Table 18: TAN results of liquids from tests performed in fixed-bed pyrolyzer

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Raw</th>
<th>Pre-treated</th>
<th>Raw</th>
<th>Pre-treated</th>
<th>Raw</th>
<th>Pre-treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>139.6 ± 1.1</td>
<td>109.2 ± 1.9</td>
<td>112.5 ± 1.1</td>
<td>80.8 ± 2.1</td>
<td>91.6 ± 0.9</td>
<td>70.4 ± 0.6</td>
</tr>
<tr>
<td>500</td>
<td>182.4 ± 1.7</td>
<td>140.0 ± 2.7</td>
<td>96.8 ± 1.7</td>
<td>83.7 ± 0.3</td>
<td>104.8 ± 2.4</td>
<td>41.9 ± 2.5</td>
</tr>
<tr>
<td>600</td>
<td>139.6 ± 1.1</td>
<td>109.2 ± 1.9</td>
<td>112.5 ± 1.1</td>
<td>80.8 ± 2.1</td>
<td>91.6 ± 0.9</td>
<td>70.4 ± 0.6</td>
</tr>
</tbody>
</table>

Further details on the experimental study is available in Supplement IV.

5.3.3 Summary

- Pre-treated biomass with lower concentration of AAEMs presents increased organic liquid yield with altering organic composition compared to raw biomass, as well as a decreased char yield
- In-bed catalytic pyrolysis in Py-GC/MS of pre-treated biomass presents limited performance which is explained by the small and narrow pore size-distribution of HZSM-5 compared to the kinetic diameters of pyrolysis vapors
- Ex-bed catalytic pyrolysis of pre-treated biomass in a bench-scale pyrolyzer gives an increased production of aromatic hydrocarbons at higher temperatures in comparison to raw biomass. This is explained by a favorable composition of organic vapors after secondary reactions in the vapor phase
5.4 Ex-situ catalytic fast pyrolysis of biomass (Supplement V)

5.4.1 Introduction
Catalytic fast pyrolysis (CFP) is a promising technical route to convert biomass into renewable substitutes for utilization on an industrial scale. By rapidly heating biomass in inert atmosphere, known as fast pyrolysis, the liquid yield derived from biomass can be enhanced. The unfavourable characteristics of raw pyrolysis liquid for utilization as precursor in industrial applications are suppressed by catalytic upgrading. In the development of large-scale catalytic pyrolysis systems, the biomass-to-catalyst ratio is a critical parameter, since the vapor loading on a catalyst can reflect both the degree of vapor conversion as well as the degree of catalyst deactivation [131]. In continuous processes, the parameter is often defined as the weight hourly space velocity (WHSV), presented in Equation 1.

Equation 1: \[ WHSV = \frac{m (\text{biomass feeding rate})}{m (\text{catalyst})} [h^{-1}] \]

Regarding the choice of reactor type for rapid heating of biomass, a fluidized bed-pyrolyzer can provide the heat transfer criteria required for continuous fast pyrolysis. The catalytic upgrading of pyrolysis vapors can either be performed in-situ or ex-situ. Studies comparing the two different setups have found in-situ catalytic pyrolysis to favour the production of naphthalenes and other PAHs, while ex-situ catalytic pyrolysis setup favors the production of MAHs [132, 133]. In-situ catalytic pyrolysis has been the focus of studies since it results in higher yields of both liquid and aromatic hydrocarbons explicitly. However, in-situ catalytic pyrolysis setups have also been found to results in higher degree of catalyst deactivation [70, 133, 134]. Another drawback of in-situ catalytic pyrolysis in a fluidized bed is that the integration of the catalyst material in the fluidized bed requires pyrolysis and catalytic upgrading to be performed at the same temperature, which might not be the optimal temperature for both conversion processes individually [135]. The optimization of the temperature for pyrolysis and catalytic vapor upgrading can be performed in an ex-situ setup. Also, by separating the catalyst and the biomass in ex-situ setups, the risk of irreversible catalyst deactivation by ash poisoning can be suppressed [69]. Ex-situ catalytic fast pyrolysis could also allow, for example: (1) a more economic use of precious catalysts, (2) utilization of a cascade of different catalyst placed in-series, and (3) direct separation of char to be used as a by-product [71, 134]. Furthermore, ex-situ catalytic pyrolysis has presented lower techno-economic uncertainty compared to in-situ catalytic pyrolysis [136]. However, limited amount of works in
lab-scale ex-situ catalytic fast pyrolysis performed in a fluidized bed-pyrolyzer and a catalytic fixed bed-reactor have been published [71].

In this study, the catalytic performance of HZSM-5 was investigated in a continuous ex-situ catalytic fast pyrolysis setup, illustrated in Figure 6. The experimental process consisted of a fluidized bed-pyrolyzer followed by char separation and vapor upgrading in an ex-situ fixed-bed catalytic reactor. The catalytic reactor is illustrated in Figure 7. The catalyst was supplied in pellet form by Nankai University, China. In order to study the catalyst lifetime and its upgrading capacity, the WHSV was varied by adjusting the biomass feeding rate up to 0.5 kg/h followed by downstream vapor upgrading over a fixed amount of catalyst. Experiments was performed for 260 min. As reference, catalytic pyrolysis was compared to non-catalytic pyrolysis performed in the same setup. Based on online gas analysis and liquid analysis, the catalyst’s deactivation and upgrading performance over time was evaluated, revealing the catalytic performance for deoxygenation and aromatization under varying vapor pressures and time of operation.

5.4.2 Results and discussion

The experimental cases investigated are presented in Table 19.

<table>
<thead>
<tr>
<th>Biomass feed rate (kg/h)</th>
<th>WHSV (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-catalytic pyrolysis</td>
<td>0.23</td>
</tr>
<tr>
<td>Non-catalytic pyrolysis</td>
<td>0.50</td>
</tr>
<tr>
<td>Catalytic pyrolysis</td>
<td>0.23</td>
</tr>
<tr>
<td>Catalytic pyrolysis</td>
<td>0.38</td>
</tr>
<tr>
<td>Catalytic pyrolysis</td>
<td>0.50</td>
</tr>
</tbody>
</table>

The yield of organic liquid and char collected in the catalytic pyrolysis experiments are presented in Figure 40. The yield of permanent gases is presented as the average composition of permanent gases. The relatively low organic liquid yield can be attributed to the relatively high zeolite content per biomass feeding rate, as well as a strong cracking capacity of HZSM-5 according to the biomass-to-catalyst ratio [66].
Derived liquids were analyzed based on elemental composition, TAN value, and semi-quantitative analysis of the organic composition. The elemental composition of collected organic liquids presented in Table 20 shows different elemental compositions between the liquids derived at the different biomass feeding rates in non-catalytic pyrolysis. The organic liquids collected from catalytic pyrolysis presents the deoxygenating activity of HZSM-5 with a reduced oxygen content compared to non-catalytic pyrolysis. A lower WHSV, i.e. higher amount of catalyst per biomass feeding rate, results in higher deoxygenation of pyrolysis liquids as well as a higher concentration of carbon in upgraded liquids [137].

Table 20: Elemental composition of liquids from pyrolysis and catalytic pyrolysis (d.b.)

<table>
<thead>
<tr>
<th>Pyrolysis 0.23 kg/h</th>
<th>Catalytic pyrolysis 0.35 h⁻¹ 0.58 h⁻¹ 0.77 h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 56.9</td>
<td>79.5 77.0 71.0</td>
</tr>
<tr>
<td>H 6.9</td>
<td>6.9 6.6 6.8</td>
</tr>
<tr>
<td>N &lt;0.1</td>
<td>&lt;0.1 &lt;0.1 &lt;0.1</td>
</tr>
<tr>
<td>S &lt;0.05</td>
<td>&lt;0.05 &lt;0.05 &lt;0.05</td>
</tr>
<tr>
<td>O* 36.2</td>
<td>13.6 16.3 22.0</td>
</tr>
</tbody>
</table>

*Calculated by difference

Table 21 presents the TAN values of collected liquids, where a significant reduction in the liquids’ acid numbers is observed after being catalytically upgraded over HZSM-5. This correlates with the decreased oxygen content in HZSM-5 and presents the affinity for carboxylic acids to react over the zeolite structure by decarboxylation reactions [113].
Table 21: TAN values (mg KOH/g) of liquids from pyrolysis and catalytic pyrolysis

<table>
<thead>
<tr>
<th>Feed rate (kg/h)</th>
<th>Pyrolysis TAN</th>
<th>Catalytic pyrolysis WHSV (h⁻¹)</th>
<th>TAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23</td>
<td>51.2 ± 0.2</td>
<td>0.35</td>
<td>6.2 ± 0.2</td>
</tr>
<tr>
<td>0.5</td>
<td>52.7 ± 0.3</td>
<td>0.58</td>
<td>9.2 ± 0.4</td>
</tr>
</tbody>
</table>

Semi-quantitative analysis of the organic composition of catalytically upgraded liquids is presented in Figure 41 in terms of representative aromatic hydrocarbon products. The uniform concentration of dichloromethane (DCM) for the liquid analysis, used as internal standard in the GC/MS samples, presents an even dilution and sample injection of the liquids to the GC/MS. These results present the catalytic activity in terms of vapor aromatization for producing MAHs and PAHs. Also, the results show the influence of the partial pressure of pyrolysis vapors in the catalytic reactor. Liquids derived from higher biomass feeding rates give reduced concentrations of aromatics, which correlates with previous observations [128, 138]. Therefore, lower production of aromatic hydrocarbons at higher biomass feed rates and higher WHSV could be due to a limitation in active sites of the catalytic bed and a reduced residence time of vapors in the catalytic bed at higher biomass feeding rates. The concentrations of aromatic hydrocarbons in non-catalytic pyrolysis was below detection limit, due to the absence of HZSM-5 [139].
In order to study the carbon efficiency of the experimental process for converting biomass to liquids, Figure 42 presents the carbon conversion from dry biomass to organic liquid. Overall, the results show that the ratio between biomass feeding rate and the catalyst amount influences the carbon concentration found in the derived liquid. The carbon concentration in liquids increase with the conversion of pyrolysis liquids to aromatic hydrocarbons. However, this simultaneously results in a lower carbon conversion from biomass to liquid. This observation can be explained by the catalyst’s activity for vapor cracking, deoxygenation, and aromatization. Therefore, the carbon conversion can be seen to be negatively correlated with the aromatic concentrations in derived upgraded liquids.
In order to study the influence of vapor loading in terms of catalyst activity and deactivation over time, the permanent gases were analyzed online and compared to a reference case of a non-catalytic pyrolysis process. The ratio between CO and CO$_2$ are presented in Figure 43 in order to study the catalyst activity for deoxygenation reactions. Results present an enhanced selectivity towards CO$_2$ for lower vapor loadings over the catalyst surface, indicating a higher conversion of carboxylic acids. Previous studies have compared the relative reactivity of carbonyls such as aldehydes and ketones to acids for conversion over HZSM-5, and have found acids to be significantly more reactive [106]. Additionally, the results of increased selectivity towards CO$_2$ for lower vapor loadings reflect an increased carbon efficiency during vapor deoxygenation. However, no significant influence of catalyst deactivation could be observed over the time of experiment. Therefore, the difference in the composition of upgraded vapors seen in Figure 41 is explained by technical limitations during catalytic upgrading, which become evident when increasing the concentrations of pyrolysis vapors in the gas stream.

Figure 42: Carbon conversion of biomass to upgraded organic liquid
The coke formed on the catalyst at different WHSVs is presented in Figure 44. An increased vapor feed in terms of the partial pressure of individual compounds per catalytic active site results in a slight increase in the rate of coke formation during the time of experimental investigation. The coke formed on the catalyst could be caused by polymerization reactions within its porous structure which may lead to pore blockage of the narrow pore size distribution of HZSM-5 and a reduction of the available reactive surface area [106, 140].

Further details on the experimental study is available in Supplement V.
5.4.3 Summary

- A lower WHSV per amount of catalyst results in higher concentrations of aromatic hydrocarbons in the collected liquid products after the vapor upgrading step
- An increased catalytic conversion of pyrolysis vapors results in a reduced carbon conversion from biomass to upgraded liquid
- A higher WHSV increases the formation of coke on the catalytic surface
- No variation in catalyst activity in terms of deoxygenation is observed over the time of operation
- The results indicate that a low WHSV has a major influence on the conversion of biomass to aromatic hydrocarbons using HZSM-5, where the catalyst deactivation has a neglectable influence during the time of operation
6. Conclusions

6.1 Concluding summary

The efforts of this thesis were dedicated to increase the understanding of how to selectively convert lignocellulosic biomass into targeted liquid feedstocks by using pyrolysis-based process concepts. Different technical aspects were investigated separately as well as interconnected to gain fundamental and applied understanding of their influence on the derived products in a biomass-to-liquid conversion process. The complete work is summarized in Figure 1.

The work conducted for the formulation of Supplements I and II investigated the influence of the biomass characteristics on the composition of pyrolysis liquids. Supplement I focused on the influence of intrinsic ash by demineralizing biomass prior to pyrolysis and studying both the biomass characteristics as well as the composition of derived liquids. Supplement II focused on the influence of the pyrolysis temperature and the design of the biomass liquefaction step on the composition of pyrolysis liquids. The results of biomass demineralization presented a significant reduction of ash content without significant loss of volatile matter, i.e. the liquid yield from pyrolysis should not be lower compared to that of raw biomass. Investigation of the pyrolysis products from demineralized biomass present a significantly higher formation of sugars and anhydrosugars such as LGA as well as a suppressed formation of smaller compounds such as carbonyls compared to raw biomass. Also, demineralized biomass results in less complex liquid compositions. In order to study the influence of pyrolysis temperature and design of the pyrolysis unit for the composition of pyrolysis liquids, a stepwise pyrolysis concept was investigated where biomass was thermally treated in two steps. The results show that the main part of organic liquid is derived between 250 to 300 °C, together with the main part of acids. Stepwise pyrolysis as a process setup to convert biomass to fractionated liquids is a promising approach to concentrate chemical compounds found in conventional pyrolysis liquid. However, a complete separation of chemicals in two separated pyrolysis units is complicated, mainly due to the overlapping temperature ranges of decomposition of the biomass polymers.

Due to the chemical nature of the biomass polymers, the derived liquids have a highly complex composition and a high oxygen content, making the direct application of pyrolysis liquids unfavorable in end-user applications. Catalytic pyrolysis is a widely studied topic to enhance the properties of derived liquids. Therefore, the three remaining Supplements (III, IV, and V) focused on the conversion of pyrolysis
vapors into aromatic hydrocarbons utilizing findings from previous works. The catalytic conversion of pyrolysis vapors was studied based on the influence of the catalyst itself (Supplement III) as well as the influence of the pyrolysis vapor composition on the catalytic reforming step (Supplement IV). Results from the work presented in Supplement III show that the impregnation of metals (Fe and/or Ni) to a zeolite-based catalyst increases the selectivity towards aromatic hydrocarbons but also promotes the rate of catalyst deactivation. Results from Supplement IV show that the vapor composition from demineralized biomass (from Supplement I) can result in increased aromatization of pyrolysis vapors as well as higher organic liquid yields compared to raw biomass when using zeolitic catalysts.

In Supplement V, the concept of catalytic pyrolysis of biomass was studied in a continuous lab-scale process. In this work, the performance of catalytic upgrading during continuous operation was investigated by varying the biomass feeding rate to the pyrolyzer followed by upgrading over a fixed amount of zeolitic catalyst. Results show that the vapor upgrading capacity is dependent on the partial pressures of pyrolysis vapors in the catalyst bed, where lower vapor pressures result in higher conversion to BTXs and PAHs.

Overall, the work conducted in this thesis presents the potential of producing renewable liquid feedstocks from biomass in pyrolysis-based applications. The understanding of the biomass characteristics for pyrolysis as well as their modification prior to pyrolysis by pre-treatment can significantly alter the composition of derived liquids towards targeted end-user applications. Also, the composition of pyrolysis vapors plays a significant role in performance of catalytic pyrolysis processes together with the choice of catalyst.
6.2 Main conclusions

The main conclusions can be summarized based on the objectives and the corresponding Supplements as follows:

**Investigate the influence of leaching pre-treatment of biomass to remove intrinsic ash and to alter the composition of pyrolysis liquids (Supplement I):**

- Biomass treated in aqueous solutions of acetic acid presents a significant reduction of ash, especially AAEMs. Leaching performance was higher when using 10 wt% acetic acid solution compared to 5 wt% during similar treatment time, which indicates that inorganic matter is removed by ion-exchange reactions with protons.
- Biomass with lower concentration of AAEMs results in increased concentrations of sugars and anhydrosugars in the pyrolysis products, and a suppressed selectivity towards smaller compounds.
- The results suggest that the chemical state of inorganics in biomass has a vital role during biomass devolatilization in terms of the composition of derived liquids.

**Evaluate a stepwise pyrolysis process concept to produce fractionated pyrolysis liquids (Supplement II):**

- The main part of organic liquid from PKS is derived between 250 to 300 °C.
- The evolution of certain compounds in the first pyrolysis step results in lower concentrations in the second step, reflecting the polymeric structure of biomass.
- Stepwise pyrolysis is a promising approach to fractionate and concentrate chemical groups, especially water-soluble compounds. However, a complete separation of chemical groups is complicated in the two-step process design, which could be explained by overlapping temperature ranges for the decomposition of the biomass polymers.
Investigate catalytic pyrolysis of biomass by comparing the catalyst activity and deactivation for producing aromatic hydrocarbons (Supplement III):

- Impregnation of Fe and/or Ni to HZSM-5 results in higher rate of aromatization and formation of catalyst coke
- The composition of catalyst coke reflects the overall catalyst activity observed in the composition of upgraded liquids
- The rate of catalyst deactivation of metal-doped catalyst is influenced by the concentration of acid sites on the catalyst. Also, the coke yield was correlated to the strength of acid sites
- Co-doping of Fe and Ni presents multifunctional characteristics in catalytic pyrolysis reflecting the activity of the individual metals
- Metal-doping influences the temperature of catalyst regeneration

Investigate how the composition of pyrolysis liquids influence their catalytic conversion to aromatic hydrocarbons (Supplement IV):

- Pre-treated biomass presents higher organic liquid yield with altering chemical composition compared to raw biomass, explained by its reduced concentration of AAEMs
- In-bed catalytic pyrolysis of pre-treated biomass presents limited performance due to its increased concentration of LGA and the shape selectivity of HZSM-5
- In ex-bed catalytic pyrolysis, pre-treated biomass results in an increased selectivity towards aromatic hydrocarbons at higher temperatures compared to raw biomass
- The results show the significance of biomass pre-treatment and secondary vapor phase reactions to produce a favorable composition of vapors for catalytic upgrading into aromatic hydrocarbons
Study the performance of a continuous ex-situ catalytic pyrolysis process in lab-scale for producing renewable liquids (Supplement V):

- An increasing WHSV results in reduced biomass-to-aromatics conversion, explained by increased partial pressures of pyrolysis vapors
- A higher conversion towards aromatic hydrocarbons results in a lower carbon conversion of biomass to upgraded liquids
- An increased WHSV results in higher coke yield on the catalyst. However, significant catalyst deactivation was not observed during the time of operation
7. **Recommendations of future works**

Research for development of technologies requires continuous development and investigation of innovative and promising concept. Based on the performed experimental studies, several aspects can be considered for further investigations:

- Scale-up of promising technical concepts is needed to evaluate their performance on larger scale in order to bring the biomass liquefaction processes to the market.
- Techno-economic analysis of process concepts based on energy and mass balances derived from experiments and literature is needed to evaluate their feasibility in commercial scale.
- Design and construct continuous processes for experimental concept evaluation.
- Evaluate the performance of developed processes by conducting experimental investigations in continuous production.
- Develop process models for computational investigations to further explore and evaluate technical routes for converting biomass into demanded products.
8. References


A perspective on oxygenated species in the refinery integration of pyrolysis oil, Green Chemistry 16(2) (2014) 407-453.


E. Kantarelis, Catalytic steam pyrolysis of biomass for production of liquid feedstock, KTH Royal Institute of Technology, 2014.


[86] A. Saddawi, J.M. Jones, A. Williams, C. Le Coeur, Commodity fuels from biomass through pretreatment and torrefaction: effects of mineral


M. Müller, G. Harvey, R. Prins, Comparison of the dealumination of zeolites beta, mordenite, ZSM-5 and ferrierite by thermal treatment, leaching with oxalic acid and treatment with SiCl4 by 1H, 29Si and 27Al MAS NMR, Microporous and Mesoporous Materials 34(2) (2000) 135-147.


