Torrefaction of biomass for power production

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Torrefaction of biomass for power production

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Ph.D Thesis
2013

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Preface

This thesis is written in partial fulfillment of the requirements to obtain the Doctor of Philosophy degree (PhD) at the Technical University of Denmark (DTU). The work has been performed between January 2010 and September 2013 at the Combustion and Harmful Emission Control (CHEC) Research Center, Department of Chemical and Biocemical Engineering (KT). The work was funded by Technical University of Denmark, Energinet.dk, Ministry of Higher Education of Malaysia and University Malaysia Pahang. The project has been supervised by Professor Kim Dam-Johansen, Associate Professor Peter Arendt Jensen and Senior Researcher Brian Brun Hansen.

I would like to express my sincere gratitude to my supervisors for giving me the opportunity to work on a very interesting project, providing the guidance and support throughout this project as well as spending a lot of their precious time for technical discussions and invaluable suggestions. A special thanks to Peter Arendt Jensen for his continuous guidance, motivation, patience and constructive suggestions on research. He has also continuously given me encouragements and carefully reading my reports and manuscripts. I am grateful to Kim Dam-Johansen for giving me a chance to study in Denmark which had opened my eyes about this wonderful and peaceful country. I also would like to thanks Brian Brun Hansen for fruitful discussions and carefully reading my manuscripts.

I owe many thanks to Nikolaj Vinterberg Nielsen and KT-Workshop for their assistance in constructing the experimental set up and also for technical support whenever needed. I would also like to thank to the CHEC technical staff, especially Lilian Beenfeldt Holgersen, Mette Larsen, and Emine Coskun for their support and help. I am thankful to all co-workers and friends at CHEC, especially Lei Shang, Zsuzsa, Anna Trubetskaya, Trung Ngoc Trinh, Vikash, Marimar, Hao Wu, Qiongxiao Wu, Ke Qin, and Kristian Nørgaard for their help, encouragement and contribution to a pleasant working environment.

Finally, I am grateful to my family members and friends in Malaysia and around the world, especially my mother, Siti Fatimah Awang and my late father, Saleh Abdul Rahman who
passed away last year when I was struggling with my PhD. I am sorry for not being there to take care of you when you were sick; I dedicate this work to you. Above all, my special thanks to my special husband for his unconditional love and constant support, and also for accompanying me during the late night and early morning’s works. Thank you for being my best friend, proof reader, and always being there when I need you. I owe you everything.

Kgs. Lyngby, October 2013

Suriyati Binti Saleh
This dissertation is dedicated to my late father, Saleh Abdul Rahman, who has been a great source of motivation, inspiration and for endless support throughout my life.

Thank you...
Summary

In order to increase the share of biomass for sustainable energy production, it will be an advantage to utilize fuels as straw, wood and waste on large suspension fired boilers. On a European scale, currently large straw resources are available that are not fully utilized for energy production. Straw can be co-fired with coal in suspension fired power plants with a maximum straw share of 10 to 20 wt%. However, 100% straw firing induced several problems that can impede both boiler availability and power efficiency. Straw is highly fibrous and tenacious in nature, therefore a relatively high amounts of energy is needed to pulverize the straw to a size where a good burn out can be obtained. Also the large alkali and chlorine content in straw often induce severe chlorine rich deposit formation on super heaters. The chlorine rich deposits are corrosive and to prevent high superheater corrosion rates, relatively low superheater temperatures have to be applied, which in turn lower the power efficiency.

The idea for this Ph.D. project is to develop a biomass pretreatment method that could provide the heating value of the fuel for the boiler, but in a way such that the fuel is easily pulverized and the superheating can be done without an exposure of alkali rich flue gas on superheaters. A potential pretreatment process is to use a ball mill with an integrated torrefaction process. The char produced is very fragile and can be easily pulverized down to a size where a high burn out is obtained. The present Ph.D. thesis focus on the following subjects: 1) the development of experimental procedures for a novel laboratory scale reactor (simultaneous torrefaction and grinding) and a study on the torrefaction of straw and wood; 2) study the influence of biomass chemical properties such as ash content, ash composition and carbohydrate composition on torrefaction characteristics by using a broader range of biomasses; and 3) quantification of chlorine and sulfur release during torrefaction.

A novel laboratory scale experimental setup which combines torrefaction and a ball mill has been constructed for studies of the influence of feedstock type, temperature and residence time on the product yields and particle size reductions. The laboratory set up was used to investigate the torrefaction properties of Danish wheat straw and spruce chips. A standard experimental procedure was developed based on initial experiments which evaluated the
influence of reactor mass loading, gas flow and grinding ball size and material. The particle size reduction capability of the torrefaction process has been evaluated by using the relative change in $d_{50}$ of the product size distribution, and this method was compared with the Hardgrove Grindability Index (HGI), showing reasonably similar results.

Significant differences in torrefaction behavior have been observed for straw and spruce chips torrefied at 270 – 330 °C. Torrefaction of straw for 90 minutes yielded a higher mass loss (27 – 60 wt %) and a larger relative size reduction (59 – 95%) compared to spruce (mass loss of 10 – 56 wt% and a size reduction of 20 – 60%). The two types of biomass investigated differ with respect to hemicellulose type, lignocellulosic composition, particle morphology and ash composition where straw has higher alkali content. Experiments with separate particle heating and grinding showed a swift grinding of the torrefied biomass which implies that the rate limiting step in the laboratory reactor is the heat transfer, and not the grinding process.

Different torrefaction characteristics are observed from straw and wood chips, therefore an improved understanding and ability to predict the torrefaction characteristic of different biomass types are desired. In this study, the influence of biomass chemical properties (carbohydrate composition and alkali content) on the torrefaction behavior with respect to mass loss and grindability is investigated. Six raw biomass samples (Danish wheat straw, miscanthus, spruce, beech, pine, and spruce bark) with different chemical and physical properties were pyrolyzed by Simultaneous Thermal Analysis (STA) and torrefied in the simultaneous torrefaction and grinding reactor. The effect of biomass alkali content on torrefaction characteristics were furthermore investigated by washing or impregnating (KCl and $K_2CO_3$) of selected biomass. The solid yields at the investigated torrefaction temperatures (270 and 300 °C) are strongly influenced by the biomass potassium content as well as to some extent the lignocelluloses composition. High biomass potassium content leads to a relatively low solid yield; however in a single case (spruce bark), a high lignin content leads to a relatively high solid yield even in the presence of relatively high potassium content. In summary both potassium content and lignocelluloses composition affect the solid yield obtained by torrefaction. A significant decrease in $d_{50}$ value of the torrefied products was
observed when the alkali content is increased from 0 to 0.2 wt% db, while no additional effect is seen for higher potassium contents.

The release of chlorine (Cl) and sulfur (S) to gas phase during biomass torrefaction has been investigated via experiments in laboratory-scale reactors by using six biomasses which cover a wide range of ash content and ash-forming elements in the temperature range of 150 – 500 °C. The relative release of chlorine and sulfur was calculated based on mass balance and analysis of the biomass before and after torrefaction. In few cases, measurement of methyl chloride (CH₃Cl) in the gas released from straw torrefaction has been conducted. Initial release of chlorine was observed at 250 °C and about sixty percent of chlorine was released from straw at 350 °C. The analysis of methyl chloride from the released gas showed that most of chlorine was released as CH₃Cl. By using a large amount of straw (40 g compared to 5 – 20 g), less Cl is released, probably due to more reactive sites available for secondary reactions. The secondary reactions can be reaction with relatively stable basic functionalities on the char surface or reaction with potassium to generate KCl. Almost complete release of chlorine was observed for woody biomass at 350 °C. This result showed an agreement with the previous studies reported that the biomass with a lower chlorine content released a higher fraction of chlorine during the pyrolysis process. Significant sulfur release (about 60%) was observed from the six biomasses investigated at 350 °C. It is seen that the initial sulfur content in biomass did not influence the fraction of sulfur release during torrefaction.
**Dansk Resume**

For at øge andelen af biomasse til bæredygtig og effektiv energiproduktion, er det en fordel at udnytte brændsler som halm, træ og affald på store suspensionsfyrede kedler. På europæisk plan er der i øjeblikket stor halm ressourcer til rådighed, som ikke udnyttes fuldt ud til energiproduktion. Halm kan samfyres med kul i suspensions fyrede kraftværker med en maksimal halm andel på 10 til 20 %. 100 % ren halmfyring giver flere problemer, der kan reducere både kedel tilgængelighed og begrænse el-produktions effektivitet. Halm er et meget fiberholdigt og sejt materiale, og pulverisering af halm ned til en størrelse hvor der opnås en god udbredning er derfor en relativt energikrævende proces. Det høje indhold af alkali og klor i halm giver desuden ofte kraftig aske belæningsdannelse i fyrrummet og kan give anledning til korrosion af kedelrør, specielt ved høje damptemperaturer. Dette medfører ofte en sænkning af overheater temperaturen er nødvendig og dermed sænkes el-virkningsgraden.


En laboratorieskala forsøgsopstilling der kombinerer torrificering og en kuglemølle er konstrueret til undersøgelser af indflydelsen af biomasse typen, temperatur og opholdstid på produkt udbytter og partikelstørrelse reduktion. Laboratorie reaktoren blev brugt til at undersøge torrificerings egenskaberne af dansk hvedehalm og gran flis. En standard
eksperimentel procedure blev udviklet baseret på indledende forsøg, hvor indflydelsen af reaktorens fyldningsgrad, gas flow og størrelse og materiale af formalingskugle blev undersøgt. Partikelstørrelsesreduktionen blev evaluert ved hjælp af den relative ændring i \(d_{50}\) af produktets størrelse fordeling, og denne fremgangsmåde blev sammenlignet med Hardgrove Index metoden (HGI). Der sås rimeligt sammenlignelige resultater af de to metoder.

Tydelige forskelle i torrificerings egenskaber er observeret for halm og gran flis behandlet ved 270-330 °C. Torrificering af halm i 90 minutter gav et højere massetab (27 – 60 vægt %) og en større relativ størrelse reduktion (59 – 95 %) sammenlignet med gran flis (massetab af 10-56 vægt\% og en størrelses reduktion på 20 – 60 %). De to typer biomasse er forskellige med hensyn til hemicellulose type, lignocellulose sammensætning, partikelmorfologi og aske sammensætning hvor halm har et højere alkaliindhold. Eksperimenter med separat partikel opvarmning og formaling viste en hurtig formaling af den opvarmede biomasse, hvilket indikerer, at det hastighedsbegrænsende trin i laboratorie torrificerings reaktoren er varmeoverførsel og ikke formalingen.

De forskellige torrificerings egenskaber observeret for halm og træflis, viser betydningen af en forbedret forståelse og evne til at forudsige torrificerings karakteristikaf forskellige biomasse typer. I denne undersøgelse er indflydelsen af biomassens kemiske egenskaber (lignocellulose sammensætning og alkaliindhold) på torrificerings opførsel med hensyn til massetab og formaling undersøgt. Seks biomasse prøver (dansk hvedehalm, elefantgræs, gran, bøg, fyr og gran bark) med forskellige kemiske og fysiske egenskaber blev pyrolyseret via Simultan Termisk Analyse (STA) og ved torrificering i den kombinerede torrificerings og formalings laboratorie reaktor. Effekten af biomasse alkali indhold på torrificerings karakteristika blev desuden undersøgt ved udvaskning eller imprægnering (med KCl og K\(_2\)CO\(_3\)) af udvalgte biomasse. Faststof udbyttet af de undersøgte biomasser ved reaktor temperaturer på 270 og 300 °C, er stærkt påvirket af biomassernes kalium indhold, samt til en vis grad lignocellulose sammensætningen. Et højt biomasse kalium indhold fører til et forholdsvis lavt faststof udbytte, men et højt ligninindhold har i et enkelt tilfælde (gran bark) ført til et relativt højt faststof udbytte selv ved et relativt højt kalium indhold. Sammenfattende påvirker både indholdet af kalium og lignocellulose sammensætning faststof udbyttet opnået ved torrificering. Et signifikant fald i \(d_{50}\) værdien af de torrificerede produkter blev observeret,
når alkali indhold øgedes fra 0 – 0,2 vægt % (tør basis), mens ingen yderligere effekt ses for højere indholdet af kalium.

Frigivelsen til af klor (Cl) og svovl (S) til gas fase under biomasse torrificering i temperaturområdet 150 – 500 °C er blevet undersøgt via forsøg i laboratorieskala reaktorer for seks biomasser, der dækker en bred vifte af askeindhold og askesammensætning. Den relative frigivelse af klor og svovl blev beregnet baseret på massebalance og analyse af biomassen før og efter opvarmning. I enkelte tilfælde er desuden målt koncentrationen af methylchlorid (CH₃Cl) i den afgivne gas fra halm. Første frigivelse af klor blev observeret ved 250 °C og omkring 60 % var frigivet fra halm ved 350 °C. Analysen af methylchlorid i den dannede gas viste, at det meste af den afgivne klor forefindes som CH₃Cl. Mindre klor blev frigivet ved brug af større prøvemængder (40g sammenlignet med 5 – 20g), sandsynligvis på grund af tilstedeværelsen af flere reaktive steder til rådighed for sekundære reaktioner. De sekundære reaktioner kan være Cls reaktion med reaktive sites på koks overflade, eller reaktion med kalium for dannelsen af KCl. Næsten fuldstændig frigivelse af klor blev observeret for træbiomasse ved 350 °C. Dette resultat viste i overensstemmelse med tidligere undersøgelser, at biomasse med et lavere klorindhold afgiver en højere fraktion af klor under pyrolyse processen. Betydelig svovl frigivelse (omkring 60 %) blev observeret fra de seks biomasser undersøgt ved 350 °C. Det ses, at det oprindelige svovlindhold i biomassen ikke påvirkede den andel af svovl der frigives.
Introduction to this thesis

A technically feasible method for converting raw biomass into a fuel similar to coal is desired in order to increase the share of biomass for sustainable energy production. As a comparison to fossil solid fuel, raw biomass has a low bulk density, hydrophilic in nature, and has a low calorific value, which makes raw biomass difficult to use on a pulverized fuel (PF) power plants. Due to its low energy density, high volumes of biomass are needed, which cause problems associated with storage, transportation, and feedstock handling at power plants. To improve properties of biomass and make it more suitable for energy applications, the material may be pretreated. The process called torrefaction is a method to preprocess biomass and produces a solid with higher energy density, hydrophobic property, improved grindability, and has a lower oxygen-to-carbon (O/C) ratio, therefore more suitable for commercial and residential combustion and gasification applications. Torrefaction involves the heating of biomass at moderate temperatures (up to 300 °C) under an inert atmosphere. A possible use of the torrefaction process is by integration of the process with a power plant and thereby a high total energy efficiency can be obtained. Possibly the gas released during the torrefaction process can be combusted in the boiler and used for steam superheating, and low temperature steam or flue gas from the boiler may be used to supply the energy needed for the torrefaction process. A possible reactor used for such a torrefaction process could be a ball mill where the biomass is simultaneously heated and milled. In the present study, there are conducted investigations that can support the development of such a torrefaction ball mill reactor.

In this thesis, most of the chapters are written as manuscripts to scientific journal. A general introduction to the field of biomass torrefaction is given through a literature study in Chapter 1. Chapter 2 presents the results on the development of experimental procedures for the newly constructed simultaneous torrefaction and grinding reactor. The main focus of Chapter 2 is on the different behaviour of straw and wood chips during torrefaction at different temperatures and residence times. Chapter 3 primarily concerns with the influence of biomass chemical properties such as alkali content and carbohydrate composition on torrefaction characteristics. Different types of biomasses with a broader range of chemical composition have been investigated and the results are presented in this chapter. The emphasis of Chapter 4 is on the
quantification of the release of chlorine and sulfur during torrefaction process. By using six different biomasses with different properties, the release behaviour at different torrefaction conditions is studied. Finally, general conclusions and suggestions for future work are given in Chapter 5.


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Chapter 1  Literature review

1.1 Introduction

Nowadays, most of the countries in the world, including Denmark are focusing on a green energy transition by investing more in renewable energy and creating a green energy supply [1]. This is due to the fact that renewable energy represents a good diversification of the energy sources and it is also preserving the equilibrium of ecosystems. Among the different energy sources, biomass holds most promising source for increasing use in the next few years. Furthermore, biomass is considered as a neutral carbon fuel because the carbon dioxide released during its utilization is an integral part of the carbon cycle [1,2].

An efficient way to reduce the greenhouse gas emissions from the energy sector is by using biomass in large power plants. In Denmark, extensive researches have been done to support the use of biomass in the power plants. [1,3-6]. In 2012, biomass such as straw, wood and biodegradable waste makes up approximately 70% of the consumption of renewable energy in Denmark [1]. However, the utilization of biomass as a fuel has to deal with several technical issues, a high alkali content of biomass that leads to ash deposit formation and corrosion of boiler coils. Also the biomass is difficult to grind, therefore relatively large particle is used in suspension fired biomass boiler, that may lead to a poor fuel conversion [3,4]. Biomass properties such as high moisture content, low bulk density and low energy density leads to relatively high transportation costs and a need for considerable storage facilities [5-8]. The tenacious and fibrous nature of biomass fuels such as straw and wood require a considerable energy input for grinding to produce the particle size needed in pulverized fuel fired power plant boilers to secure ignition and burn out [2,8,9]. Globally, there is a large demand for technology that can make the utilisation of bioenergy and biodegradable waste more efficient. One way of improving the properties of biomass is to use a torrefaction pretreatment. Torrefaction is a slow heating of biomass in an inert atmosphere in a temperature range of 200 – 320 °C producing a solid uniform product with improved properties [7-13]. Study carried out by Shang et. al. (2013) showed that the degradation of hemicelluloses (occurring at 200 – 300 °C) is the main reason for the improvement of grindability of torrefied straw [14]. The
torrefied biomass is more brittle and can be pulverized down to a small particle size without excessive energy consumption [2,9].

1.2 Suspension firing of biomass

The use of biomass in suspension fired boilers is a fairly recent development which can ensure a renewable, efficient and CO$_2$ neutral supply of electricity and heat. Biomass suspension firing has a high load flexibility and at the same time a high power efficiency is maintained [3]. In biomass suspension firing, pulverized biomass is blown into the burners, where the fuel particles are burned while suspended in the air stream [15-17]. This technology is common for coal-fired boilers and achieves high electrical efficiency, however processing biomass into the finely pulverized powder is difficult and costly. Therefore a pretreatment is desired to improve the physical and chemical properties of biomass.

A relatively higher electrical efficiency (46–48%) of suspension fired boiler makes it an attractive option for combustion of straw and/or wood compared to the traditional grate-fired systems (25–30%) [5,18]. The fuel for suspension fired boiler typically must have a particle size less than 1 mm and a moisture content less than 15% [15,17,18]. The measurements of wood particle size after milling at Avedøreværket Unit 2 during measuring campaign by Jensen et al. (2008) shows that about 90% of the wood particles entering the burners are below 1 mm [18]. In order to ensure complete burnout in only few seconds of residence time, the biomass fuel particles are normally reduced to a wide size range of 0.01–1 mm [17]. Therefore the fuel handling systems require more careful design than conventional biomass firing systems in order to be supplied to the suspension fired boiler [15]. A schematic drawing of a typical biomass suspension-fired boiler is shown in Figure 1.1 [15,19]. Suspension-fired combustion systems are generally associated with very large solid fuel boilers for power generation, and are often not fueled with biomass alone, although there are a small number of biomass fired boilers in operation in Denmark [15,18,19]. During suspension firing, fuel particle residence time is only a few seconds and peak flame temperatures are higher compared to grate firing conditions [15].
Figure 1.1 Schematic drawing of a suspension-fired boiler used for biomass firing as illustrated by Bashir (2012) [15]

1.3 Biomass composition

Biomass primarily consists of cellulose, hemicellulose, lignin and other compounds such as proteins, sugars and salts, starches, water, hydrocarbons and ash [13,20,21]. The composition of these constituents in the biomass varies with species, age, growth location and growth conditions. The plant cell wall is tough and sometimes fairly rigid layer that provides structural support and protection from mechanical and thermal stresses [13]. The major components of the plant cell wall are cellulose, hemicellulose and lignin, and the fraction of these materials in straw and woods is shown in Table 1.1 [10,13,20,21]. Cellulose which is the main cell wall component in the plant biomass generally ranging from 40-50 wt%, while hemicelluloses and lignin typically ranges from 20-30 wt% and 15-30 wt%, respectively. Softwood typically is high in lignin, compared to hardwood and straw. The main difference between softwood and hardwood is related to the hemicelluloses fraction. Softwood
predominantly consist of mannan-based hemicelluloses, meanwhile hardwood (and straw) primarily consist of xylan-based hemicelluloses.

In addition, biomass also contains, although only in minor proportions, another fraction composed of a wide variety of chemical compounds, known as extractives. Average content of extractives in biomass is 1–15%; however, some trees may have about 30% of the extractives known as tannins [13,22]. The highly heterogeneous extractive fraction includes resin acids, fats, terpenes, flavonoids, lignans, stilbenes, carbohydrates, tannins, and inorganic salts. They can have a protective role against microorganisms, while some can serve as an energy reserve [22].

Table 1.1 Typical content of cellulose, hemicellulose and lignin in straw and woods [10,13,20,21]

<table>
<thead>
<tr>
<th>Composition, wt%</th>
<th>Straw</th>
<th>Softwood</th>
<th>Hardwood</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>33-45</td>
<td>35-50</td>
<td>45-50</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>20-25</td>
<td>25-30</td>
<td>20-25</td>
</tr>
<tr>
<td>Lignin</td>
<td>15-20</td>
<td>27-30</td>
<td>20-25</td>
</tr>
</tbody>
</table>

1.3.1 Cellulose

Cellulose is a high molecular weight polymer (with molecular weight up to $10^{16}$ and higher) that makes up the fibers in biomass [13]. This complex carbohydrate consists of unbranched chains of linked glucose units as shown in Figure 1.2 [23]. Cellulose has a strong tendency to form intra- and inter-molecular hydrogen bonds by the hydroxyl groups, which stiffen the straight chain and promote aggregation into a crystalline structure, building up cellulose fibers of high mechanical strength [24]. Cellulose degradation begins at 240 – 350 °C, resulting in formation of anhydrous cellulose and levoglucosan [25]. The crystalline structure resists thermal depolymerization better than unstructured hemicelluloses [13].
1.3.2 Hemicellulose

Unlike cellulose, hemicellulose are branched polymers (also a polysaccharide) consisting of shorter chains (500 – 3000 sugars units as compared to 7000 – 15000 glucose molecules per polymer in cellulose). Specifically, hemicellulose contains xylose, arabinose, galactose, glucose, and mannose. The chemical structure of the main components in hemicellulose is shown in Figure 1.3. The most abundant hemicelluloses are xylan and glucomannan. Xylan is the major hemicellulose components of secondary cell wall constituting about 18-25 wt% of the hardwood and herbaceous biomasses [26]. Mannan-based hemicellulose such as glucomannan and galactoglucomannan are the main hemicellulose components of the secondary cell wall of softwoods. Hemicellulose thermal degradation occurs in the range of 130 – 260 °C during slow pyrolysis, with the majority of weight loss occurring above 180 °C depending on its chemical composition [25,27]. Hemicellulose generally decompose as light volatiles, producing less tars and char compared to cellulose.

![Figure 1.2 The structure of cellulose (adopted from [23])](image1)

![Figure 1.3 Chemical structures of hemicellulose components (adopted from [23])](image2)
1.3.3 Lignin

Lignin is a randomly linked, amorphous, and high molecular weight phenolic compound. Lignin fills the spaces in the cell wall between cellulose, hemicellulose and pectin components. It is covalently linked to hemicellulose and thereby cross-links different plant polysaccharides, conferring mechanical strength to the cell wall and to the plant as a whole [13]. The chemical structure of lignin is very complicated and their precursors are three aromatic alcohols namely \( p \)-coumaryl, coniferyl and sinapyl alcohols (Figure 1.4). Depending on the degree of methoxylation, the respective aromatic constituents of these alcohols in the polymer are called \( p \)-hydroxybenzyl (derived from \( p \)-coumaryl), guaiacyl (derived from coniferyl alcohol) and syringyl (derived from sinapyl alcohol) [20]. Wood lignin primarily contains guaiacyl and syringyl units, while the lignin of herbaceous biomass contains all three alcohols units. Lignin degradation begins at 280 – 500 °C producing phenols, and lignin is difficult to dehydrate thereby forms more char than cellulose and hemicellulose [21].

\[
\begin{align*}
\text{p-coumaryl alcohol} & \quad \text{coniferyl alcohol} & \quad \text{sinapyl alcohol} \\
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} \\
\text{CH} & \quad \text{CH} & \quad \text{CH} \\
\text{CH} & \quad \text{CH} & \\
\text{OH} & \quad \text{OCH}_3 & \quad \text{CH}_3\text{O} \\
\end{align*}
\]

**Figure 1.4** Chemical structures of main components of lignin (adopted from [23])

1.3.4 Decomposition mechanism during torrefaction

During torrefaction, mass loss will primarily result from the decomposition of hemicellulose and some of lignin as shown in Figure 1.5 [26,28]. Hemicellulose undergoes major decomposition reactions at torrefaction temperatures of 200 – 300 °C, resulting in different condensable and noncondensable products. Thermal degradation of hemicellulose initiates at 150 °C, with the majority of weight loss occurring above 200 °C, depending on the chemical
nature of the hemicelluloses [25,27]. Hemicellulose generally evolves as light volatiles, producing fewer tars and less char. Many researchers have noted that major hemicellulose decomposition reactions occur at temperatures between 220 and 280 °C [13]. Cellulose degradation occurs between 240 and 350 °C, resulting in anhydrous cellulose and levoglucosan [25]. Amorphous regions in the cellulose contain waters of hydration and hold free water within the plant. When heated rapidly, this water is converted to steam, which can further rupture the cellulose structure [13]. Thermal degradation of lignin takes place over a wide temperature range. At temperatures below 200 °C, some thermal softening has been observed resulting in a small weight loss of a few percent. Char formation and the release of volatiles result from a devolatilisation process in the temperature region of 240 – 600 °C [26]. However, the thermal decomposition behaviour of the individual polymers of wood (and in general biomass) may be different from their strongly interacted structure in wood itself. Indications for this can be extracted from Figure 1.5, as wood on mass basis starts to decompose at a temperature higher than 200 °C.

Figure 1.5 Thermogravimetry of cotton wood and its constituents (adopted from Shafizadeh and McGinnis 1971) [28]
1.4 Torrefaction process

Torrefaction is a feasible method for improving the properties of biomass as a fuel [7-11,29]. As defined in most of studies, torrefaction is a thermal conversion method of biomass operating in the low temperature (200 – 300 °C) under atmospheric conditions in the absence of oxygen. This process improves the physical, chemical and biochemical composition of the biomass, making it perform better for cofiring and gasification purposes [7-9]. Torrefaction is also known as roasting, slow- and mild pyrolysis, wood cooking and high temperature drying [7]. Torrefaction converts raw biomass into a solid that is suitable for combustion and gasification applications, which has a high heating value and high energy density, and are hydrophobic, compactable and grindable, and has a lower oxygen-to-carbon (O/C) ratio than the raw biomass [7-9,29,30]. Many researchers have studied the effect of torrefaction temperature and residence time on the physical and chemical composition [27,29-31]. However, knowledge on the influence of alkali content/chemical properties on torrefaction characteristics and also the release of chlorine and sulfur during torrefaction are limited.

1.4.1 Principles of torrefaction

Torrefaction is actually a low temperature (mild) pyrolysis, and is characterized by the different parameters consisting of reaction temperature, heating rate, residence time, biomass type, biomass moisture content and particle size. Understanding the composition of plant components will help in understanding the biomass degradation reaction during the thermal pretreatment process. Heating the biomass results in thermal degradation of its structure, which is often accompanied by mass loss. The degree of thermal degradation depends on the residence time and temperature, and this process was well documented by Bergman et al. (2005b) [31]. A modified version of Bergman et al.’s description of torrefaction process is illustrated in Figure 1.6 [13]. This updated figure describes the structural changes, emissions due to bond cleavage, biomass reactions, and color changes as a function of temperature (50 – 300 °C).

As can be seen in Figure 1.6, biomass loses moisture and shrinks at drying temperatures of 50–150°C (A), and most of the chemical constituents of the biomass are not yet volatilized. At
120–150 °C (B), the lignin softens and makes the material more suitable for densification, as the softened lignin acts as a binder. Temperature regime C (150–200 °C), also called the reactive drying range, initiates the breakage of hydrogen and carbon bonds and results in the emission of lipophilic extractives and compounds due to thermal degradation of biomass solids. This temperature also results in structural deformity, from which biomass loses its ability to regain its original structure if rewetted. Also, according to Bergman et al. (2005b), depolymerization of hemicelluloses results in shortened, condensed polymers with solid structures [31]. Increasing the temperature further, as shown in Regime D, also called destructive drying (200–300 °C), results in carbonization and devolatilization. These temperatures represent the torrefaction process limits, which result in the disruption of most inter- and intramolecular hydrogen bonds, C–C and C–O bonds, resulting in the formation of hydrophilic extractives, carboxylic acids, alcohols, aldehydes, ether, and gases like CO, CO₂, and CH₄. At these temperatures, cell structure is completely destroyed as the biomass loses its fibrous nature and becomes brittle. At temperatures lower than 250 °C, the mass loss is at a minimum, as main biomass decomposition results from limited devolatilization and carbonization of the hemicellulose. At temperatures greater than 250 °C, the hemicellulose decomposes extensively into volatiles and a char-like solid product. Lignin and cellulose show limited devolatilization and carbonization [13].

During torrefaction at 200–300 °C, mass loss predominantly results from the loss of moisture and decomposition (devolatilization), particularly of hemicellulose and some lignin. Xylan-based hemicellulose generally decomposes around 200–280 °C [31]. Lignin decomposition proceeds more slowly, but gradually increases and starting at about 200 °C [29]. However, the thermal decomposition behavior of individual biomass polymers may be different from the strongly integrated structure of whole biomass and the biomass ash may catalyze some reactions.
<table>
<thead>
<tr>
<th></th>
<th>Nonreactive drying (no changes in chemical composition)</th>
<th>Reactive drying (initiates changes in chemical composition)</th>
<th>Destructive drying (alters chemical composition)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water, organic emissions and gases</td>
<td>Mostly surface moisture removal</td>
<td>Insignificant organic emissions</td>
<td>Initiation of hydrogen and carbon bonds breaking. Emission of lipophylic compounds like saturated and unsaturated fatty acids, sterols, terpenes, which have no capacity to form hydrogen bonds</td>
</tr>
<tr>
<td>Cell and tissue</td>
<td>Initial disruption of cell structure</td>
<td>Maximum cell structure disruption and reduced porosity</td>
<td>Structural deformation</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>Drying (A)</td>
<td>Depolymerization and recondensation (C)</td>
<td>Limited devolatilization and carbonization (D)</td>
</tr>
<tr>
<td>Lignin</td>
<td>A Glass transition/ Softening (B)</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>Cellulose</td>
<td>A</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>Color changes in biomass</td>
<td>50 100 150 200 250 300</td>
<td>Temperature (°C)</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 1.6** Structural, chemical and color changes in biomass at different drying temperatures as adopted from Tumuluru et al. (2011). The stages include: A (drying), B (glass transition/softening), C (depolymerization and recondensation), D (limited devolatilization and carbonization), and E (extensive devolatilization and carbonization) [13]

### 1.4.2 Torrefaction product properties

During torrefaction, three different products are produced: (1) a brown to black solid biomass, which is often used for combustion in a boiler (bioenergy applications), (2) condensable volatile organic compounds comprising water, acetic acid, aldehydes, alcohols, and ketones, and (3) noncondensable gases like CO$_2$, CO, and small amounts of methane [13]. The condensables (liquid) can be further divided into four groups which are reaction water
produced from thermal decomposition, freely bound water that has been released through evaporation, organics (in liquid form) which consist of organics produced during devolatilization and carbonization, and lipids which contain compounds such as waxes and fatty acids [13]. The emissions of condensable and noncondensable products are depending on heating rate, torrefaction temperature and time, and biomass composition. The release of these condensable and noncondensable products results in the changes in terms of the physical, chemical, and storage properties of biomass. The physical and chemical properties of biomass before and after torrefaction have been analyzed for the following characteristics: (a) mass and energy yield, (b) grindability, (c) particle size and distribution, (d) chemical compositional changes, and (e) hydrophobicity.

1.4.2.1 Mass and energy yield

Torrefaction is generally characterized by the calculated mass and energy balances, which are presented in terms of mass and energy yields as shown in equations 1.1 and 1.2 [10,11,26]:

\[
Y_{mass}(\%) = \left( \frac{m_{tor}}{m_{feed}} \right)
\]

(1.1)

\[
Y_{energy}(\%) = Y_{mass} \left( \frac{HHV_{tor}}{HHV_{feed}} \right)
\]

(1.2)

where \(Y_{mass}\) = mass yield, \(Y_{energy}\) = energy yield, \(m_{tor}\) = mass of torrefied product, \(m_{feed}\) = mass of feed, and \(HHV\) = higher heating value. The data is usually provided on a dry feedstock basis.

Mass yield and energy yield of different biomasses subjected to torrefaction process from several studies are presented in Table 1.2. The mass yield of torrefied biomass can vary from 30% (herbaceous biomass torrefied at 300 °C) to 95% (woody biomass torrefied at 230 °C) depending on torrefaction temperature, residence time, and biomass physical and chemical properties. Conversion rate for herbaceous and agricultural residues is comparatively higher than woody biomass due to its chemical composition and physical properties, thus resulting in lower mass yield. Studies show that the polymeric structure of the biomass will affect the
reactivity of the torrefaction reaction, where higher xylan content will increase the rate of reaction [31-34]. In the torrefaction temperature range of 200 – 300 °C, mass loss is dominated by dehydration and devolatilization of hemicellulose components [2,8,10]. Nimlos et al (2003) through their study using mass spectrometry analysis observed that the weight loss is accompanied by degradation of hemicelluloses and primary lignin sections [35].

Table 1.2 Mass yield, energy yield and higher heating value of torrefied biomass

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Mass yield (wt%)</th>
<th>Energy yield (wt%)</th>
<th>HHV (MJ/kg)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine</td>
<td>250</td>
<td>0.5</td>
<td>82.0</td>
<td>89.2</td>
<td>20.1</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>0.5</td>
<td>73.0</td>
<td>86.3</td>
<td>21.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.5</td>
<td>52.0</td>
<td>71.5</td>
<td>25.4</td>
<td></td>
</tr>
<tr>
<td>Logging residue chip</td>
<td>250</td>
<td>0.5</td>
<td>81.0</td>
<td>91.4</td>
<td>21.2</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>0.5</td>
<td>70.0</td>
<td>82.1</td>
<td>22.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.5</td>
<td>52.0</td>
<td>73.1</td>
<td>26.4</td>
<td></td>
</tr>
<tr>
<td>Willow</td>
<td>230</td>
<td>0.5</td>
<td>95.1</td>
<td>96.1</td>
<td>20.2</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>0.5</td>
<td>79.8</td>
<td>85.4</td>
<td>21.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>0.5</td>
<td>72.0</td>
<td>78.8</td>
<td>21.9</td>
<td></td>
</tr>
<tr>
<td>Wheat straw</td>
<td>250</td>
<td>0.5</td>
<td>82.6</td>
<td>86.2</td>
<td>19.8</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>0.5</td>
<td>71.5</td>
<td>78.2</td>
<td>20.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>0.5</td>
<td>55.1</td>
<td>65.8</td>
<td>22.6</td>
<td></td>
</tr>
<tr>
<td>Reed canary grass</td>
<td>250</td>
<td>0.5</td>
<td>83.0</td>
<td>85.1</td>
<td>20.0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>0.5</td>
<td>72.0</td>
<td>76.8</td>
<td>20.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>0.5</td>
<td>61.5</td>
<td>68.8</td>
<td>21.8</td>
<td></td>
</tr>
<tr>
<td>Rice straw</td>
<td>200</td>
<td>0.5</td>
<td>59.8</td>
<td>60.0</td>
<td>17.2</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.5</td>
<td>40.3</td>
<td>42.5</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.5</td>
<td>36.6</td>
<td>39.9</td>
<td>18.7</td>
<td></td>
</tr>
<tr>
<td>Peanut husk</td>
<td>250</td>
<td>1.0</td>
<td>72.5</td>
<td>81.0</td>
<td>16.4</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>1.0</td>
<td>67.0</td>
<td>85.1</td>
<td>18.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>1.0</td>
<td>55.8</td>
<td>72.3</td>
<td>19.0</td>
<td></td>
</tr>
<tr>
<td>Straw pellets</td>
<td>230</td>
<td>1.0</td>
<td>95.0</td>
<td>95.5</td>
<td>17.9</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>1.0</td>
<td>90.0</td>
<td>92.1</td>
<td>18.21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>1.0</td>
<td>79.9</td>
<td>89.9</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>Cotton stalk</td>
<td>200</td>
<td>0.5</td>
<td>63.9</td>
<td>83.4</td>
<td>23.9</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.5</td>
<td>33.8</td>
<td>45.3</td>
<td>24.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.5</td>
<td>30.0</td>
<td>41.0</td>
<td>25.0</td>
<td></td>
</tr>
</tbody>
</table>

Torrefaction of herbaceous (reed canary grass and wheat straw) and woody biomass (willow) had been conducted by Bridgeman et al. (2008) in order to enhance the solid fuels qualities and combustion properties with temperatures varied from 230 to 290 °C [10]. Figure 1.7 shows the influence of temperature and residence time on the final mass yield of solid
residue for the three biomasses investigated. At 230 °C there was observed only a slight reduction in mass and less than the amount of moisture lost during drying (dry basis). However, increasing temperature has an obvious effect on the thermal decomposition of the herbaceous biomass; for temperatures of 290 °C mass losses of 38% - 45% were observed for the two samples [10]. The greatest mass losses at all the temperatures investigated occurred in wheat straw although they were similar to that observed in reed canary grass, whilst the lowest change in mass was observed for willow. This result may be explained by the difference in the cell wall composition. Hemicellulose is the most reactive of the three cell wall components found in biomass and during torrefaction it will undergo the most significant decomposition reactions. Wheat straw and reed canary grass have similar hemicellulose contents about (30 wt%db) whilst willow has a lower amount of hemicelluloses (14 wt%db) but higher level of lignin and cellulose. Bridgeman et al. reported that the decomposition of hemicelluloses start at temperatures above 200 °C and full devolatilisation will occur by 350 °C with the major products being H₂O, CO₂, CO and char. Pure cellulose has a comparatively slower decomposition process at 250 °C, and the rate of thermal decomposition only becomes more rapid when the temperature is above 300 °C [10].

**Figure 1.7** Solid yields (dry basis) during torrefaction of wheat straw, willow and reed canary grass at different final temperatures (for 30 minutes torrefaction) [10]
In another study, Prins et al. used hardwood (deciduous wood types) as well as softwood (coniferous wood types), and also straw to study the decomposition of lignocellulosic material in the relatively low temperature range of 225 – 300 °C [32,33]. Beech and willow are used for the sample of hardwood sample, while larch is used for softwood sample. The model compounds of wood such as cellulose and 4-O-methyl glucuronoxylan, extracted from oak spelt were also used. Figure 1.8 shows the weight loss curves of these samples at 267 °C obtained from isothermal TGA experiments [32].

![Weight loss curves](image)

**Figure 1.8** Weight loss of various biomass compounds at 267 °C; dotted line is the heating curve [32].

The weight loss observed during heating of the sample from 200 °C, the temperature at which thermal decomposition begins to occur, to the required temperature is relatively small, except for xylan. From Figure 1.8 it can be concluded that xylan, the main hemicellulose component of hardwood, is the most reactive component and starts decomposing around 200 °C and has a high weight loss after torrefaction. The cellulose decomposition rate is very low in the temperature range used. This is in agreement with results of other studies, such as Bridgeman et al. [10]. At 267 °C, limited weight loss of cellulose is found. High xylan content also explains the relatively high weight loss of wheat straw, although catalytic effects due to the presence of mineral matter could also play a role [32]. Finally, the softwood larch reacts a
lot slower than the hardwoods. Some researchers have described the lower weight loss for softwood is due to a higher lignin content, but then the differences in composition of the hemicellulose fractions in hardwood and softwood (xylan- and mannan-based, respectively) may also be the main explanation [32].

Increasing the torrefaction temperature and residence time will increase the higher heating value (HHV) of biomass. HHV increment of torrefied biomass was in the range of 1-35% for the various biomasses as shown in Table 1.2. Energy yield based on the heating value and mass yield can be viewed as a measure of the amount of energy loss during torrefaction. Energy yield for woody biomass subjected to torrefaction temperature below 250 °C is above 89%, and decrease to 71-73% as torrefaction temperature increase to 300 °C. Non-woody biomass generally has a lower energy yield compared to woody biomass with a wider spread ranging from 41% to 95% due to the higher variation in volatile matter and hemicelluloses fraction [37].

The heating value of the biomass is an important property, as it will determine its use in energy applications. An increase in the carbon content as reported from ultimate analysis lead to an increase in the heating value. At higher temperature, the content of C in the solid product increases whiles the contents of H and O decrease. Calculation of the HHV illustrates the impact that these changes have on the energy content [10]. Table 1.3 shows the heating value together with the ultimate analysis and moisture content of raw and torrefied wheat straw [10]. The energy content of wheat straw torrefied at 290 °C rose by 17% with the highest loss of hydrogen and oxygen content, and the increase in carbon content.

Table 1.3 Ultimate analysis, HHV (dry ash free basis) and moisture content of untreated and torrefied straw [10]

<table>
<thead>
<tr>
<th></th>
<th>Raw</th>
<th>Torrefaction temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>230</td>
</tr>
<tr>
<td>C (%)</td>
<td>47.3</td>
<td>48.7</td>
</tr>
<tr>
<td>H (%)</td>
<td>6.8</td>
<td>6.3</td>
</tr>
<tr>
<td>N (%)</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>O (%)</td>
<td>37.7</td>
<td>35.6</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>4.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Heating value (MJ/kg)</td>
<td>18.9</td>
<td>19.4</td>
</tr>
</tbody>
</table>
Pimchuai et al. (2010) reported that the energy density continues to increase with the increase in temperature [9]. The increase in energy density because of greater residence time, however was insignificant. Table 1.4 shows the influence of temperature and residence time on the energy density of the torrefied agriculture residue. It can be seen that the increase in energy density varied with the type of fuels investigated.

**Table 1.4** Influence of the temperature and residence time on the energy density of the torrefied agriculture residue [9]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Rice husks</th>
<th>Sawdusts</th>
<th>Peanut husks</th>
<th>Bagasse</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>1</td>
<td>1.11</td>
<td>1.08</td>
<td>1.12</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.12</td>
<td>1.11</td>
<td>1.14</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.16</td>
<td>1.06</td>
<td>1.23</td>
<td>1.42</td>
</tr>
<tr>
<td>270</td>
<td>1</td>
<td>1.12</td>
<td>1.13</td>
<td>1.27</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.14</td>
<td>1.21</td>
<td>1.27</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.2</td>
<td>1.22</td>
<td>1.28</td>
<td>1.45</td>
</tr>
<tr>
<td>300</td>
<td>1</td>
<td>1.23</td>
<td>1.31</td>
<td>1.3</td>
<td>1.58</td>
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<td></td>
<td>1.5</td>
<td>1.24</td>
<td>1.35</td>
<td>1.31</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.24</td>
<td>1.37</td>
<td>1.32</td>
<td>1.62</td>
</tr>
</tbody>
</table>

*energy density = energy yield (%) / mass yield (%)

Water is a major product released by two different mechanisms, firstly during drying when moisture evaporates and secondly during dehydration reactions between organic molecules. The experiments on the individual components of biomass showed that the cellulose particles shrink slightly as they are heated. Unlike cellulose, particles of pectin and xylan show evidences of softening or melting (at the temperatures of 150 °C and 200 °C, respectively), as well as bubble formation as they are heated. The bubbles are formed within the particles, and as the bubbles burst volatile products are released into the gas stream [40]. The torrefied sample lost most moisture and low weight organic volatile components and then the long polysaccharide chains were depolymerized, thus forming a hydrophobic bio-char with a higher energy density than the raw biomass [37].
1.4.2.2 Grindability

During torrefaction, the biomass loses its tenacious nature, producing a brittle torrefied product due to the decomposition of hemicelluloses and, to a lesser degree, lignin and cellulose. These biomass components normally comprise the fibre structure, which limits the grindability in the conventional coal pulverizer. When biomass is torrefied at 260 – 300 °C for 20 minutes, the tenacious fibre structure will be largely destroyed. Compared to the original woody biomass, milling torrefied wood in a hammer mill requires about 50-85% less energy consumption [26]. The grindability property of torrefied biomass is widely examined through the particle size distribution of milled samples after being distributed according to its size range. Generally, grindability of biomass improves after torrefaction based on the increased percentages of fine particle as torrefaction condition are raised [2,37,41]. An alternative method is the particle size distribution study coupled with grinding energy consumption in examining the grindability [36,42]. Specific energy requirement reduces dramatically when biomass is first torrefied, and Phanphanich and Mani (2009) reported that the grinding energy consumption for torrefied biomass (at 300 °C) is reduced as much as 10 times after torrefaction as shown in Figure 1.9(a). It can be observed in Figure 1.9(b) that torrefaction not only reduce the specific energy required for grinding but also decrease the mean particle size of ground biomass [36].

![Figure 1.9](image)

**Figure 1.9** Influence of torrefaction temperature on a) specific energy consumption for grinding of torrefied biomass, and b) geometric mean particle diameter of torrefied biomass ground through a screen size of 1.5 mm [36]
Repellin et al. (2010) proposed a mechanism in two steps to explain the improved grindability and reduced energy consumption in comminution for torrefied biomass [42]. The improved ease to grind biomass is attributed to the dehydration and physical transformation of lignocelluloses material at lower temperature (150 – 200 °C). Dehydration induces a shrinking of the lignocellulosic material and creates some stress in biomass fibres that can favour cracks or defect creations. The structure shrinking induces porosity and density changes. During this first step, lignin passes through its glass transition and softens [42]. After cooling, lignin is in a tightened state, which makes a plastic and viscoelastic behavior of torrefied wood decreased by comparison to natural wood. In this state, a crack can propagate easily. Thus, crack creations, density decrease and material stiffening favour energy decrease and finer particles sizes [42]. Subsequently, the second stage (200 – 300 °C) is the thermal degradation of the cell wall biomass as discussed earlier that contributes to the higher percentage of fine particle after torrefaction [42]. The second step begins with thermal decomposition of biomass which results in a progressive and general embrittlement and degradation of biomass cell walls.

The standard Hardgrove Grindability Index (HGI) that is used to analyze the grindability of coal had been studied in literature for torrefied biomass samples [11,43]. The modified HGI study adopted volumetric measurement (modified HGI) for the sample to be milled in place of mass measurement as biomass are of lower density compared to coal. The result from HGI measurement for pine chips, wheat straw and Scots pine pellets conducted by Shang (2013) is shown in Figure 1.10 [44]. Wheat straw and pine chips torrefied at 240 °C obtained similar grindability as wet coal, while for Scots pine pellets, a higher temperature (290 °C) is required. Although treated sample achieves similar grindability to the reference coal samples for extended torrefaction parameter (relatively higher temperature and longer residence time), literature indicate that modified HGI may underestimate the grinding property of biomass as a large fraction of biomass were removed in the pre-milling step. The standard HGI test requires the sample to be tested is in the particle size range of 0.6 to 1.18 mm [11]. The result obtain from modified HGI is not representative of all samples, although a general improvement in the grindability of torrefied biomass has been observed.
Figure 1.10 Hardgrove grindability index for oven dried biomass and torrefied biomass at different temperatures for 2 hour. HGI for coal also included for comparison. (adopted from Shang (2013))

1.4.2.3 Particle size distribution, sphericity and particle surface area

Raw biomass which is fibrous and tenacious and therefore difficult to grind is unfavorable for applications in pulverized fuel systems like PF-firing or entrained flow gasification. Many researchers observed that ground torrefied biomass produced narrower, more uniform particle sizes and smaller particle sizes, compared to untreated biomass due to its brittleness, which is similar to coal [2,11,36]. Phanphanich and Sudhagar (2011) studied torrefied pine chips and logging residues and found that smaller particle sizes are produced compared to untreated biomass [36]. In addition, they observed that the particle distribution curve was skewed towards smaller particle sizes with increased torrefaction temperatures. Torrefaction also significantly influences the sphericity and particle surface area. Phanphanich and Sudhagar’s (2011) results also indicated that sphericity and particle surface area increased as the torrefaction temperature was increased up to 300 °C [36]. They found that the sphericity value increased from 0.48 to 0.62 for ground, torrefied chips, concluding that an increase in particle surface area or a decrease in particle size of torrefied biomass can be desirable properties for
efficient PF-firing. Also, the bulk and particle densities of ground torrefied biomass increase because the inter- and intraparticle voids generated after milling are reduced [45,46].

1.4.2.4 Chemical compositional changes

In addition to the improvement in physical properties, torrefaction also results in considerable changes in proximate and ultimate composition of the biomass. Generally, the elemental analysis demonstrates a higher loss of oxygen and hydrogen compared to carbon which leads to a relative increase of carbon content [10,31,47]. Zanzi et al (2002) carried out torrefaction of miscanthus and have observed at 280 °C, the carbon content increased to about 52% from an initial value of 43.5%, while hydrogen and nitrogen content decreased from 6.49 to 5.54% and 0.90 to 0.65%, respectively, for 2 h of torrefaction [48]. In general, increased torrefaction temperatures result in increased carbon content and decreased hydrogen and oxygen content due to the formation of water, CO, and CO₂ [10,39]. This process also causes the hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios to decrease with increasing torrefaction temperature and time as shown by Phanphanich and Sudhagar (2011) in Figure 1.11 [36]. In torrefaction studies of reed canary grass and wheat straw torrefaction at 230, 250, 270, and 290 °C for 30 minutes residence times, Bridgeman et al (2008) found that carbon increased 48.6–54.3%, while the hydrogen and nitrogen content decreased from 6.8–6.1% and 0.3–0.1%, respectively [10]. In another study, Bridgeman et al (2010) made a Van Krevelen diagram for torrefied willow and miscanthus as shown in Figure 1.12 [11]. It is clear that at higher temperatures and residence times, the atomic O/C and H/C ratios are closer to that of coal, which suggests that torrefaction shifts the elemental ratios of biomass towards that of coal [11,36].
Figure 1.11 Chemical composition for raw and torrefied pine chips (TPC) and logging residues (TLR) at different temperatures in comparison with various solid fuels data from van Loo and Koppejan (2008). This figure is adopted from Phanphanich and Mani (2011)

Figure 1.12 van Krevelen diagram showing properties of raw and torrefied biomass in comparison with other fuels. (adopted from Bridgeman et al. 2010)
1.4.2.5 Hydrophobicity

In general, the uptake of water by the raw biomass is high due to the presence of hydroxyl groups (OH) [13]. Torrefaction yields a hydrophobic solid product by destroying the OH groups and forcing the biomass to lose the capacity to form hydrogen bonds [50]. Due to these chemical rearrangement reactions, nonpolar unsaturated structures are formed, which preserves the biomass for a long time without any biological degradation [27]. The hydrophobic property of torrefied biomass is generally examined by immersion test or by equilibrium moisture contents (EMC) studies. By using immersion test, Pimchuai et al (2010) observed a great improvement in the water-repellant or hydrophobic property of torrefied biomasses [9].

1.4.3 Torrefaction Technology

There are many established and patented potential methods for biomass torrefaction which are primarily based on different drying technologies. Kleinschmidt (2011) has summarized the international torrefaction development initiatives with the furthest in development can be found in Europe and North America [51]. A number of technologies from this overview are listed in Table 1.5. Generally these reactors can be divided into several categories: rotary drum, fluidized bed, moving bed, screw conveyor, belt conveyor and microwave reactors [51,52].
<table>
<thead>
<tr>
<th>Developer</th>
<th>Technology</th>
<th>Supplier</th>
<th>Locations</th>
<th>Production capacity (t/a)</th>
<th>Starting operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stramproy Green Investment B.V. (NL)</td>
<td>Oscillating belt conveyor</td>
<td>Stramproy Green Technology NL</td>
<td>Steenwijk (NL)</td>
<td>45,000</td>
<td>Q3 2010</td>
</tr>
<tr>
<td>Torr-Coal B.V. (NL)</td>
<td>Rotary drum</td>
<td>Unknown</td>
<td>Dilsen-Stokkem (BE)</td>
<td>35,000</td>
<td>Q3 2010</td>
</tr>
<tr>
<td>Topell Energy B.V. (NL)</td>
<td>Torbed</td>
<td>Torftech Inc (UK)</td>
<td>Duiven (NL)</td>
<td>60,000</td>
<td>Q4 2010</td>
</tr>
<tr>
<td>Integro Earth Fuels, LLC (US/NC)</td>
<td>Turbo dryer</td>
<td>Wyssmont (US/NC)</td>
<td>Roxboro, NC</td>
<td>50,000</td>
<td>2010</td>
</tr>
<tr>
<td>Agri-Tech Producers LLC (US/SC)</td>
<td>Belt reactor</td>
<td>Kusters Zima Corporation (US/SC)</td>
<td>Unknown</td>
<td>Unknown</td>
<td>2010</td>
</tr>
<tr>
<td>Thermya (FR)</td>
<td>Moving bed</td>
<td>Lantec group (SP)</td>
<td>San Sebastian (SP)</td>
<td>20,000</td>
<td>2011</td>
</tr>
<tr>
<td>ECN (NL) Vattenfall (SWE)</td>
<td>Moving bed</td>
<td>ECN</td>
<td>Unknown</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
<tr>
<td>Bio Energy Development North AB (SWE)</td>
<td>Rotary drum</td>
<td>Unknown</td>
<td>O-vik (SWE)</td>
<td>25,000-30,000</td>
<td>2011/2012</td>
</tr>
<tr>
<td>Rotawave Ltd (UK)</td>
<td>Microwave reactor</td>
<td>Group’s Vikoma</td>
<td>Terrace, British Columbia (CA)</td>
<td>110,000</td>
<td>Q4 2011</td>
</tr>
<tr>
<td>FoxCoal B.V. (NL)</td>
<td>Screw conveyor</td>
<td>Unknown</td>
<td>Winschoten (NL)</td>
<td>35,000</td>
<td>2012</td>
</tr>
<tr>
<td>Canadian Bio-coal Ltd. (CA)</td>
<td>Turbo dryer</td>
<td>Wyssmont (USA)</td>
<td>British Columbia</td>
<td>180,000</td>
<td>Q2 2012</td>
</tr>
<tr>
<td>Torrefaction System, Inc. (US)</td>
<td>Unknown</td>
<td>Bepex International (US/MN)</td>
<td>Minneapolis</td>
<td>10,000</td>
<td>2013</td>
</tr>
</tbody>
</table>

Rotary drum reactors consists of a rotating drum, which rotates about a fixed point via a rotating shaft and can either be configured in an inclined or vertical position. Most widely used type is the directly heated single-pass in which hot gas is contacted with biomass in a rotating drum. The rotating drum causes the biomass particles to tumble through the hot gas to promote heat and mass transfer [51-53].

Fluidization is one of the most commonly used techniques and found to have widespread applications for drying of solid particulates. In these reactors, the fluidizing medium (usually gas) is passed through a bed of solid, granular, inert material (sand) at high velocity, causing the solid to behave as a fluid. Fluidized bed drying offers many advantages, including fast
drying and high thermal efficiency with uniform and closely controllable bed temperature [54]. It offers good mixing and ease of combining several processes [54].

A movement of both solid and fluid phase during reaction is the main characteristic for a moving bed reactor. This operation may be countercurrent, co-current or crossflow depending upon the relative directions of fluid and solid [55]. The moving bed technique, especially on its application in agricultural dryers, has become popular owing to its lower investment, lower energy consumption, and less mechanical damage to the seeds [55]. Bergman et al. (2005a), also concluded that moving bed system has high heat transfer rate, good hold time for temperature, and low pressure drop [26].

A screw conveyor consists of 1) biomass feeding section, 2) reactor section where biomass is converted into torrefied material and a combustible gas, 3) cooling section and 4) combustor section where the produced gas and vapors are burned with an excess of oxygen and the heat generated is used to heat the process [52]. In screw conveyor torrefaction concepts, the heat required is generated by combustion of the gases that are released during the process. The hot flue gas from the combustion is forced along the wall of the reactor to indirectly heat the biomass. Screw conveyor dryer (SCD) consists of a jacketed conveyor in which material is simultaneously heated and dried through an indirectly heating contact to provide greater heat transfer area with minimum space requirements [56]. Screw conveyors dryers have been utilized in many industrial applications, including agricultural, food, chemical, pharmaceutical, and pyrolytic process of coal [57].

Microwave heating is an attractive for various chemical processes as it produces efficient internal heating for chemical reactions, even under exothermic conditions [58]. Specialized microwave chemistry reactors utilize radiation with frequency of 2.4GHz and this frequency can be used to thermally process biomass [59]. This frequency forces polar molecules of biomass to oscillate at the resonant frequency and induces friction and heating. A volumetric heating is occurred since the heating is generated the entire volume of biomass at once. The advantage of microwave torrefaction is the uniform biomass heating, provides shorter residence time, prevents undesirable secondary reactions that lead to formation of impurities and accurate control. However, some of the drawbacks of microwave heating technology are inability to process fines and allow scale up of operation, while the major drawback is the use of electricity [58].
1.4.4 Applications of torrefied biomass

Potential applications for torrefied biomass are: 1) co-firing with coal in pulverised coal fired power plants, 2) suspension firing of biomass in PF boilers, 3) dedicated combustion in small scale pellet burners, and 4) gasification in entrained flow gasifiers that normally operate on pulverized coal. Table 1.6 listed various potential applications of torrefied biomass as proposed by Kleinschmidt (2011) [51,60].

Table 1.6 Potential applications for torrefied biomass (Kleinschmidt (2011))

<table>
<thead>
<tr>
<th>Market segment</th>
<th>Conversion process</th>
<th>Conversion technology</th>
<th>State-of-the-art biofuel</th>
<th>Pretreatment requirements</th>
<th>Advantages of torrefaction</th>
<th>Market potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large scale power production</td>
<td>Co-firing (Co) gasification</td>
<td>Coal-fired boilers Entrained flow gasifiers</td>
<td>Wood pellets Wood pellets</td>
<td>High</td>
<td>Higher co-firing rates - Size reduction - Fluidization - C/H/O ratio - Very dry</td>
<td>High</td>
</tr>
<tr>
<td>Industrial heating</td>
<td>Combustion</td>
<td>Blast furnaces</td>
<td>None</td>
<td>Moderate</td>
<td>- Handling - C/H/O ratio - Energy content</td>
<td>High</td>
</tr>
<tr>
<td>Residential/ District heating</td>
<td>Combustion</td>
<td>Stoves/ boilers</td>
<td>Wood pellets</td>
<td>High</td>
<td>Transport savings</td>
<td>High</td>
</tr>
</tbody>
</table>

Torrefaction and the actual power production may be coupled through heat integration (on-site production facility). The untreated biomass is delivered to the power station and next to the production of torrefied biomass, the process may also configured to produce other products such as heat and power. This can be attractive in scattered areas to co-produce heat and power for the surroundings or district heating. One of the advantages using on-site production may be come from the possibilities to use heat from the power station for the drying and torrefaction process [26].

The advantages of torrefaction are predominantly recognized for use in an existing pulverized coal (PC) fired power plants. Since these installations have not been designed for biomass co-firing originally, significant capital costs can be saved for modification of the plant when torrefied product is co-fired instead of regular wood pellets. This is particularly the case for torrefied clean biomass resources such as clean wood, which usually meets the constraints.
of existing environmental permits of the PC fired plant. New coal fired power plants that are currently in the planning or construction phase are designed for high co-firing ratios of lignocellulosic biomass, which makes the financial advantages of a torrefied biomass fuel with similar characteristics as the main fuel less obvious [60]. Nonetheless, even in new PC boilers torrefaction might even lead to higher co-firing ratios than was originally predicted for pure biomass co-firing, as it is a much better in replacement due to the similarity in terms of grindability and combustion [60].

Torrefaction is an interesting pretreatment technology for gasification due to the relatively low moisture content, good grindability and attractive C/H/O ratios of the torrefied biomass. The heat produced in the form of steam can be recovered and be used for torrefaction process [60]. For a biomass gasifier, particle size and moisture contents are critical factors for good operation. This usually results in relatively expensive biomass feedstock. Torrefied and pelletised biomass is already uniform in particle size and has a low moisture content, therefore the incremental fuel cost is less important for gasification. Deng et al (2009) proposed a process which combines torrefaction of agricultural residues with co-gasification with coal in an entrained flow gasifier [37]. The advantages of this process are location of torrefaction plant close to the gasifier (similar milling equipment for coal can be used for torrefied biomass) and a possibility of using torrefaction gas as an energy source in the pyrolysis reactor [37]. From their study, Couhert et al (2009) confirmed that torrefaction reduces O/C ratio in biomass and the quality of syn-gas is improved where gasification of torrefied wood produces 7% more hydrogen, 20% more carbon monoxide and approximately the same amount of carbon dioxide as the original wood [47].
1.5 Conclusions

The utilization of biomass fuels such as straw and wood in suspension fired boilers is an attractive option because of the relatively high electrical efficiency is obtained (46-48%), as compared to the traditional grate-fired systems (25-30%). However the undesirable properties of biomass such as high moisture content, low bulk and energy density, and also fibrous and tenacious in nature make a limited use of biomass as a fuel for power production. In view of the drawbacks of using biomass as a fuel, pretreatment offers a promising solution to enhance the physical and chemical properties of biomass prior to the energy conversion process. Torrefaction is a pretreatment technology that requires lower temperature (200 – 300 °C) which has been reported to be highly efficient for thermochemical processing of biomass. This process improves the physical, chemical and biochemical composition of the biomass, making it perform better for further use in energy production. Torrefaction converts raw biomass into a solid which has a high heating value and high energy density, is brittle (therefore easy to grind) and hydrophobic. Torrefaction is characterized by different parameters such as temperature, residence time, heating rate, biomass type and particle size. It is important to have knowledge on the composition of plant components in order to understand the biomass degradation during torrefaction. Hemicellulose, cellulose and lignin are the main cell wall components of the biomass which undergo a decomposition process in the temperature range of torrefaction. Torrefaction produce a brown to black solid biomass, condensable volatile organic compounds and noncondensable gases.

The physical and chemical properties of biomass before and after torrefaction are described and summarized in the present literature review, which could provide some general information and knowledge on torrefaction process. The discussions are primarily based on the mass and energy yield, grindability, particle size distribution, chemical compositional changes and hydrophobicity. Most of the earliest studies on torrefaction focused on mass and energy yield, which generally relate the degradation of lignocellulosic materials to the mass loss. It is desired to further study other factors that influence the torrefaction characteristics other than lignocellulosic materials compositions.

The grindability of torrefied biomass was evaluated based on the specific grinding energy consumption and few researchers used HGI in comparison with coal. Grindability is an
important property in order to ensure the biomass can be supplied to the suspension-fired boilers which require a particle size less than 1 mm. Therefore it is desired to have a technology that can provide the heating value of the fuel and at the same time the fuel that can be easily pulverized down to a size where a high burn out can be obtained. Since there is no reported work on combining torrefaction and milling process, it is feasible to study this processes in order to produce a fuel that can be supplied to the suspension fired boilers.

1.6 References


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Chapter 2  Simultaneous torrefaction and grinding of biomass

Abstract

Combining torrefaction and grinding of biomass in one reactor may be an attractive fuel pretreatment process. A combined laboratory torrefaction and ball mill reactor has been constructed for studies of the influence of temperature and residence time on the product yields and particle size reductions of Danish wheat straw, spruce chips and pine chips. Based on initial experiments, which evaluated the influence of reactor mass loading, gas flow and grinding ball size and material, a standard experimental procedure was developed. The particle size reduction capability of the torrefaction process has been evaluated by the relative change in $d_{50}$, and this method was compared with the Hardgrove Grindability Index (HGI), showing reasonably similar results. Significant differences in torrefaction behavior have been observed for straw and spruce chips torrefied at 270 – 330 °C. Torrefaction of straw for 90 minutes yielded a higher mass loss (27 – 60 wt%) and relative size reduction (59 – 95%) compared to spruce (mass loss of 10 – 56 wt% and size reduction of 20 – 60%). The two types of biomass investigated differ with respect to hemicellulose type, lignocellulosic composition, particle morphology and ash composition where straw has a higher alkali content. This and other studies indicate that the large difference in the biomass alkali contents is the main cause for the observed difference in torrefaction characteristics. Experiments with separate particle heating and grinding showed a swift grinding of the torrefied biomass. This implies that the rate limiting step in the laboratory reactor is the heat transfer, and not the grinding process. Large pine particles (8-16 mm) showed a slightly higher mass loss than 4-8 and <4 mm particles. This could be the consequence of exothermic reactions in the particle core, thereby locally increasing temperature and conversion.
2.1 Introduction

Biomass as a renewable fuel for the production of heat and power has received considerate attention in recent years and its utilization is rapidly growing [1,2]. Biomass properties such as a high moisture content, low bulk density and low energy density may lead to high transportation costs and a need for considerable storage facilities [1-4]. The tenacious and fibrous nature of biomass fuels such as straw and wood require a considerable energy input for grinding to produce the particle size needed in pulverized fired power plant boilers to secure ignition and burn out. A torrefaction pretreatment process can improve the fuel properties of biomass thereby overcoming some of these problems [4,5]. The torrefaction process involves heating of biomass to moderate temperatures (250 – 300 °C) in a non-reactive atmosphere [1-5], thereby partially decomposing the lignocellulosic materials of the biomass [6,7]. Study carried out by Shang et. al. (2013) showed that the degradation of hemicelluloses (occurring at 200 – 300 °C) is the main reason for the improvement of grindability of torrefied straw [8]. The torrefied biomass is more brittle and can be pulverized down to a small particle size without excessive energy consumption [3,4].

Local torrefaction of biomass near the biomass production location may reduce transport and storage costs because of a higher volumetric energy density and a reduced hygroscopicity. If the torrefaction process is performed at a power plant, an integration with the power plant boiler, could greatly increase energy efficiency. A combination of the torrefaction and milling in a ball mill type reactor (as shown in Figure 2.1) could be used as part of the process [9]. The heat needed for the torrefaction process could be provided by partial combustion of the torrefaction gas or by flue gas or steam from the boiler. To minimize heat loss, the hot product streams from the torrefaction process should be directly utilized in the power plant boiler.
Figure 2.1 Illustration of a potential integration of torrefaction process and power plant

Heating of the biomass can be done by direct contact with the heat carrier (such as hot air or hot steam) or indirectly (heat transfer through the wall or by the grinding elements) [10-12]. Many commercial heating technologies can be modified to meet the specifications of a torrefaction reactor, including rotary drum dryers, screw conveyors, moving bed reactors, microwave reactors, turbo dryers and belt conveyors [13]. Most of these technologies use direct heating between gas and solids [13,14].

During torrefaction, biomass loses its tenacious and fibrous nature, mainly caused by the breakdown of the hemicelluloses matrix and depolymerization of the cellulose and lignin, resulting in a more brittle solid product with a better grindability [10,15]. In the published torrefaction studies, grindability of the torrefied biomass and thereby the improvement obtained by the torrefaction have been measured based on the Hardgrove Grindability Index (HGI) or the specific energy used for grinding in a laboratory mill [5,16,17]. However, in this study, grindability of torrefied biomass has also been evaluated by the relative change in \(d_{50}\) value (obtained from particle size distribution) and this value has been compared to the HGI. No previous work on a combined torrefaction and milling process has been found in open literature. This study investigate the properties of a combined ball mill process with simultaneous heating and grinding to obtain knowledge on the influence of biomass type, temperature, residence time and initial particle size on solid yield and grindability.
2.2 Experimental section

2.2.1 Materials

Danish wheat straw, Danish spruce chips and Spanish pine chips were used for this study and images of the samples are shown in Figure 2.2. The biomass samples were in most of the test milled to a particle size less than 4 mm, however 4-8 and 8-16 mm fractions were also made for pine wood. The ash content (determined according to CEN/TS 14775) and the elemental compositions (determined according to CEN/TS 12290/15297/15289) for wheat straw and spruce chips in Table 2.1 were analysed by Bioenergy 2020+ GmbH, Graz, Austria [9], while for pine the analysis was conducted by the analytical laboratory at DONG Energy Power A/S, Enstedvaerket. Straw has a higher content of ash (5.57 wt%), potassium (0.9 wt%) and chlorine (0.19 wt%) than the woody biomasses (0.34 – 0.5 wt% ash and less than 0.06 wt% K and Cl). The biomass carbohydrate compositions (Table 2.2) were analysed according to the ASTM E 1758-01 procedure and Kaar et. al [21,22]. The hemicelluloses in straw is mainly xylan-based as opposed to the mannan-based hemicelluloses in spruce and pine chips. All 3 biomasses have reasonably similar cellulose content while spruce and pine chips have a higher lignin content compared to straw.

![Figure 2.2 Raw materials used for torrefaction experiments](image-url)
### Table 2.1 Composition of the raw biomasses

<table>
<thead>
<tr>
<th>Component (wt% dry)</th>
<th>Wheat Straw</th>
<th>Spruce chips</th>
<th>Pine chips</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>5.57</td>
<td>0.34</td>
<td>0.5</td>
</tr>
<tr>
<td>C</td>
<td>45.93</td>
<td>48.88</td>
<td>53.2</td>
</tr>
<tr>
<td>H</td>
<td>5.86</td>
<td>6.23</td>
<td>6.2</td>
</tr>
<tr>
<td>O</td>
<td>41.87</td>
<td>44.54</td>
<td>39.95</td>
</tr>
<tr>
<td>N</td>
<td>0.64</td>
<td>0.02</td>
<td>0.1</td>
</tr>
<tr>
<td>S</td>
<td>0.13</td>
<td>0.004</td>
<td>0.05</td>
</tr>
<tr>
<td>Cl</td>
<td>0.19</td>
<td>0.003</td>
<td>0.005</td>
</tr>
<tr>
<td>K</td>
<td>0.90</td>
<td>0.03</td>
<td>0.056</td>
</tr>
<tr>
<td>Si</td>
<td>1.40</td>
<td>0.007</td>
<td>0.05</td>
</tr>
<tr>
<td>Al</td>
<td>0.006</td>
<td>0.003</td>
<td>0.01</td>
</tr>
<tr>
<td>P</td>
<td>0.095</td>
<td>0.003</td>
<td>0.007</td>
</tr>
<tr>
<td>Fe</td>
<td>0.008</td>
<td>0.002</td>
<td>0.003</td>
</tr>
<tr>
<td>Mg</td>
<td>0.079</td>
<td>0.011</td>
<td>0.029</td>
</tr>
<tr>
<td>Ca</td>
<td>0.433</td>
<td>0.104</td>
<td>0.1</td>
</tr>
<tr>
<td>Na</td>
<td>0.011</td>
<td>&lt;0.001</td>
<td>0.005</td>
</tr>
</tbody>
</table>

### Table 2.2 Carbohydrate analysis for raw biomasses

<table>
<thead>
<tr>
<th>Components (wt% db)</th>
<th>Straw</th>
<th>Spruce chips</th>
<th>Pine chips</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylan-based hemicelluloses</td>
<td>23.1</td>
<td>5.6</td>
<td>5.1</td>
</tr>
<tr>
<td>Mannan-based hemicelluloses</td>
<td>0.0</td>
<td>11.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Other hemicelluloses</td>
<td>2.3</td>
<td>1.8</td>
<td>5.4</td>
</tr>
<tr>
<td>Total hemicelluloses</td>
<td>25.4</td>
<td>18.4</td>
<td>20.5</td>
</tr>
<tr>
<td>Cellulose</td>
<td>42.7</td>
<td>45</td>
<td>38.6</td>
</tr>
<tr>
<td>Lignin</td>
<td>17.3</td>
<td>27.6</td>
<td>29.2</td>
</tr>
<tr>
<td>Ash</td>
<td>5.57</td>
<td>0.34</td>
<td>0.5</td>
</tr>
<tr>
<td>Extractives</td>
<td>3.2</td>
<td>1.0</td>
<td>4.7</td>
</tr>
<tr>
<td>Residuals</td>
<td>5.8</td>
<td>7.66</td>
<td>6.5</td>
</tr>
</tbody>
</table>
### 2.2.2 Torrefaction reactor

A novel laboratory scale experimental set up (Figure 2.3) for simultaneous torrefaction and grinding has been constructed. The set up consists of a cylindrical reactor chamber in which a biomass sample is placed together with metal balls for grinding. The reactor chamber (D = 70 mm and L = 200 mm) can be simultaneously heated and rotated thereby combining torrefaction and grinding. The set up furthermore consist of a water cooling section, an electrically heated furnace, a gas cooling section, and five thermocouples. The reactor chamber is located inside the electrically heated furnace and is rotated by an electric motor. In most of the conducted experiments, a biomass sample and 12 tungsten carbide balls were introduced into the reactor chamber and placed in the water cooled section. The reactor was then purged with 1.0 Nl/min of nitrogen to keep the system inert. After five minutes of purging, the reactor chamber was quickly pushed into the hot zone and the rotation was started. The biomass samples were simultaneously torrefied and grinded at different temperatures for 30 and 90 minutes. After torrefaction, the reactor chamber that contains solid product was cooled down to 40°C in the cooling section under inert atmosphere. The cooling time took about 20-30 minutes before the reactor chamber was taken out from the set up. Then, the torrefied product was collected and sieved in order to determine the obtained particle size distribution.

![Diagram of the experimental set up](image)

**Figure 2.3** Bench scale experimental set up for simultaneous torrefaction and grinding process
In this study, the torrefaction temperature is defined as the final reactor temperature \( T_D \) inside the reactor chamber that contains the biomass. The residence time is defined as the time from the reactor chamber that contains the biomass sample is pushed into the hot zone and the grinding is started, until the grinding and torrefaction process is stopped. This residence time includes the heating of particles from room temperature until the end of the experiment (it takes approximately 15 minutes to heat the samples to 200 °C).

### 2.2.3 Analysis equipments

A Simultaneous Thermal Analysis Netzsch STA 449 F1 Jupiter instrument (STA) was used to pyrolyze 10 – 20 mg of biomass in a nitrogen atmosphere at a heating rate of 5 K/min up to 600 °C (with 10 minutes isotherms at 120 and 600 °C). Subsequent cooling to 200 °C and heating to 650 °C in 10 vol% O\(_2\) was done to burn off the remaining char. The mass change of a fuel sample is monitored from the thermogravimetric (TG) curve, while the temperature of maximum conversion rate is obtained from the derivative thermogravimetric (DTG) curve.

A Retsch analytical sieve shaker AS 200 was used to assess the particle size distribution of raw and torrefied biomass. The samples were poured into the top sieve which has the largest screen openings. The sieve sizes used in this study ranged from 0.045 to 16 mm. After 15 minutes shaking, the material on each sieve was weighed and collected.

A bomb calorimeter IKA C200 was used to determine the higher heating value (HHV) of the torrefied biomass. Initially, the calorimeter was calibrated using benzoic acid tablets. Torrefied biomass with a particle size of less than 0.5 mm were placed in the crucible and fired inside the bomb calorimeter using an ignition wire in the presence of pure oxygen (99.95%).

A standard Hardgrove grinder (3200LB, AUBEMA, Germany) was used to determine the grindability torrefied biomass according to the ASTM D409-51 (1961) standard. HGI was developed for coals to predict the mill performance, energy requirement and the particle size distribution after milling [5]. In the standard method as described in Bridgeman et. al. (2010), the HGI value is based on the amount of sample passing through a 75 μm sieve after 60 revolutions grinding of 50 g sample [5]. Some studies have reported that the fixed mass
approach is unsatisfactory for direct comparisons of fuels with different densities [18-20]. As suggested by Joshi (1979) and Agus and Waters (1971), Bridgeman et al. (2010) used the same fixed volume (50 cm$^3$) for each coal and biomass samples as opposed to a fixed mass (50 g) [5,18,19]. The loading of the top grinding ring was 290 N and the grinding time was 3 min (377 radians of the mill at a speed of 2.09 rad s$^{-1}$). The equivalent Hardgrove Index ($HGI_{equiv}$) was determined based on the mass fraction ($x$) of the biomass samples passing through the 75 μm sieve and equation (2.1) obtained from Shang et al. (2012) [16]. A low HGI number translates into difficult grinding. For this test, straw and spruce chips were torrefied for 90 minutes (without grinding balls). In addition, biomass dried at 105 °C for 24 hours was also tested.

$$HGI_{equiv} = \frac{x + 5.2521}{0.3577}$$

(2.1)

An image analyzer CAMSIZER Retsch/Horiba, Germany/Japan was used to determine biomass particle size and shape from 30 μm to 30 mm based on dynamic imaging [23].

2.2.4 Conducted Experiments

Initially, the influence of mass loading, type and size of grinding balls, and nitrogen flow rate on biomass conversion and milling properties were investigated and a standard procedure developed. The influence of solid loading was tested in the range of 20 to 40 g for straw and 20 to 100 g for spruce in experiments with 12 tungsten carbide (TC) grinding balls. The influence of the type and size of grinding balls were tested with stainless steel and tungsten carbide balls in the diameter range 10 to 20 mm. The temperature profiles and the final temperature inside the reactor chamber ($T_D$) were compared for each test.

In order to investigate the particle loss from the reactor chamber during the grinding process, straw char that has been torrefied at 300 °C for 30 minutes (heating with rotation but without grinding balls) was used to estimate the particle loss in low temperature (100 °C grinding experiments) with nitrogen flow rates ranging from 0.2 Nl/min to 1.0 Nl/min. The standard experimental procedure developed use 20 g straw or 40 g spruce, 12 tungsten carbide balls (10 mm in diameter) and a nitrogen flow of 1.0 Nl/min (first 10 minutes) and 0.2 Nl/min.
The reactor chamber that contains biomass/char and balls were weighed before and after the grinding process to determine the char loss.

A series of experiments were furthermore conducted, with separate heating/torrefaction and grinding of straw, to identify the rate limiting step in the combined torrefaction and grinding process. The torrefaction was performed without rotation and grinding balls, and 3 grams of the torrefied biomass were subsequently grounded at room temperature with 12 tungsten carbide balls (10 mm in diameter).

Experiments were also carried out in order to study the influence of initial particle size on the torrefaction performance. Pine wood of 3 different sizes (less than 4 mm, 4-8 mm and 8-16 mm) was used for this purpose. The samples were torrefied for 90 minutes in the simultaneous torrefaction and grinding reactor, with 12 TC10 balls.

2.3 Results and discussion

2.3.1 Development of experimental procedures

As part of the development of the experimental procedures, the influence of mass loading, type and size of grinding balls, nitrogen flow rate and mass balance closure were investigated.

To investigate the influence of mass loading on the reactor temperature profile and the particle size distribution, different mass loadings of straw and wood (spruce) as illustrated in Figure 2.4 were tested. About 50% of the reactor chamber was occupied when 20 gram of straw or 40 gram of spruce was used. 40 g of straw or 80 g of spruce almost filled the reactor chamber to the maximum capacity. The obtained final temperatures inside the reactor chamber ($T_D$) and the obtained particle size distributions for torrefaction of different amounts of straw and spruce are presented in Figures 2.5 and 2.6, and the results are summarized in Table 2.3. The size distributions for the raw straw and spruce are also presented in Figure 2.6. For straw torrefaction, a high mass loading (30 g or 40 g) produced a less pulverized sample as can be seen in Figure 2.6. This may be caused by the slightly lower final temperature obtained (337 – 340 °C compared to 350 °C for the 20 g). However, the restrained movement of the grinding balls may also have a significant effect. Repeated experiments with 20 g straw show a good
reproducibility in terms of reactor temperature profile and particle size distribution, with a small standard deviation (2.5 μm) of the d_{50} value. Based on this findings, it was decided to use 20 g of sample in the further straw experiments.

For torrefaction of intermediate loadings of spruce chips (20 and 40 g), similar temperature profiles are obtained, while higher loadings (especially 100 g) resulted in decreasing temperature profile (as shown in Figure 2.5) and a larger particle size produced after the torrefaction process. The obtained particle size distribution of torrefied spruce shows a less significant influence of mass loading compared to straw torrefaction, however the d_{50} values decrease with decreasing mass loadings (Table 2.3). The influence of mass loading of straw and spruce on the torrefaction process is further discussed in the following paragraph.

![Figure 2.4 Illustration of reactor loadings for straw and wood chips (spruce)](image_url)
Figure 2.5 Reactor temperature profiles (T_D) for 7 to 40 gram straw and 20 to 100 gram spruce (30 minutes torrefaction and using 12 TC10 balls). For straw torrefaction, the oven temperature was set to 420 °C which resulted in final T_D of approximately 350 °C, while for spruce the oven was set to 450 °C which resulted in final T_D of approximately 375 °C.

Figure 2.6 Influence of mass loading on the obtained particle size distribution. For straw torrefaction, the oven temperature was set to 420 °C while for spruce the oven was set to 450 °C. The experiments were conducted for 30 minutes by using 12 TC10 balls.
Table 2.3 Summary of results from experiments with different mass loading of straw and spruce (30 minutes torrefaction)

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Mass loading, gram</th>
<th>$T_{oven}$, °C</th>
<th>Final reactor temperature $T_D$ (±std), °C</th>
<th>$D_{50}$ value (±std), μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straw</td>
<td>Untreated</td>
<td>-</td>
<td>-</td>
<td>1700</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>420</td>
<td>354</td>
<td>308</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>420</td>
<td>354</td>
<td>225</td>
</tr>
<tr>
<td></td>
<td>20 (3 runs)</td>
<td>420</td>
<td>351±1.2</td>
<td>294±2.5</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>420</td>
<td>340</td>
<td>522</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>420</td>
<td>337</td>
<td>570</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>450</td>
<td>378</td>
<td>180</td>
</tr>
<tr>
<td>Spruce</td>
<td>Untreated</td>
<td>-</td>
<td>-</td>
<td>1600</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>450</td>
<td>376</td>
<td>805</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>450</td>
<td>377</td>
<td>855</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>450</td>
<td>374</td>
<td>925</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>450</td>
<td>371</td>
<td>1010</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>450</td>
<td>368</td>
<td>1050</td>
</tr>
</tbody>
</table>

A comparison of the final reactor temperature and mean particle diameter for torrefaction of straw and spruce chips at similar temperatures (but different mass loadings) can be seen in Table 2.3. The temperature profiles for 20 g and 40 g of spruce are almost identical to the profile for 20 g of straw, while a considerable decrease of the final temperature is observed for mass loadings greater than 60 g. The particle size distribution, as shown in Figure 6, for 20 g and 40 g of spruce did not show any substantial difference, and 40 g of spruce will be used in the following torrefaction experiments.

To investigate the influence of the applied grinding balls, straw has been torrefied for 30 minutes with 12 balls of various size and material. SS10 (stainless steel, D = 10 mm), SS15 (stainless steel, D = 15 mm) and TC10 (tungsten carbide, D = 10 mm) obtain similar particle size distributions, as represented by the $d_{50}$ values in Table 2.4. However, a slight increase in the temperature profile and a small reduction of the particle size is obtained with tungsten carbide balls possibly due to a higher density and better thermal conductivity. Larger stainless steel balls (20 mm) yield a lower final reactor temperature and a larger particle size, possibly due to more heat being stored in the larger stainless steel balls.
Table 2.4 Mean particle size and reactor temperature obtained with 4 types and sizes of grinding balls from torrefaction of 20 g of straw for 30 minutes. D_{50} value of the raw straw was 1700 μm. The notations used are: TC for tungsten carbide ball, SS for stainless steel; 10, 15 and 20 are the diameter of the balls in mm

<table>
<thead>
<tr>
<th>Balls (type/size)</th>
<th>T_{oven}, °C</th>
<th>Final reactor temperature (T_D), °C</th>
<th>D_{50} value, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC10</td>
<td>380</td>
<td>312</td>
<td>520</td>
</tr>
<tr>
<td>SS10</td>
<td>380</td>
<td>307</td>
<td>540</td>
</tr>
<tr>
<td>SS15</td>
<td>380</td>
<td>308</td>
<td>550</td>
</tr>
<tr>
<td>SS20</td>
<td>380</td>
<td>284</td>
<td>940</td>
</tr>
</tbody>
</table>

Table 2.5 summarizes various tests of the precision of the char determination/mass balance. For a 15 minutes grinding experiment with a 0.2 Nl/min N_2 flow, no particle loss is observed and only 4% loss for 1.0 Nl/min N_2. For 90 minutes grinding with 10 g at a gas flow of 1.0 Nl/min (first 10 minutes) and 0.2 Nl/min a 4% particles loss was observed. As a conclusion, the simultaneous torrefaction and grinding experiments can be performed with a limited mass loss.

Table 2.5 Influence of nitrogen flow rate on particle loss during char grinding (using 12 TC10 balls) at 100 °C (straw was previously torrefied at 300 °C for 30 minutes without grinding balls)

<table>
<thead>
<tr>
<th>N_2 flow rate, Nl/min</th>
<th>Torrefaction temperature, °C</th>
<th>Weight of char used, g</th>
<th>Grinding time, minutes</th>
<th>Particle loss, g</th>
<th>Percent loss, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>300</td>
<td>5</td>
<td>15</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.0</td>
<td>300</td>
<td>5</td>
<td>15</td>
<td>0.2</td>
<td>4</td>
</tr>
<tr>
<td>1.0/0.2</td>
<td>300</td>
<td>10</td>
<td>90</td>
<td>0.4</td>
<td>4</td>
</tr>
</tbody>
</table>

The results from solid recovery tests are summarized in Table 2.6. At 120 °C, only 0.6 wt% was lost during the heating (likely moisture). Torrefaction at 200 °C resulted in 3 – 3.5 wt% of mass loss, and can be caused by the initial decomposition of carbohydrate components. Repeated experiments show a good repeatability and a limited mass loss at both temperatures.
Table 2.6 Summary of mass balance for solid product collected

<table>
<thead>
<tr>
<th>Torrefaction temperature, °C</th>
<th>Torrefaction time, min</th>
<th>Mass in, g (db)</th>
<th>Mass out, g (db)</th>
<th>Solid yield, wt% (db)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 (run1)</td>
<td>30</td>
<td>18.63</td>
<td>18.51</td>
<td>99.4</td>
</tr>
<tr>
<td>120 (run2)</td>
<td>30</td>
<td>18.63</td>
<td>18.51</td>
<td>99.4</td>
</tr>
<tr>
<td>200 (run1)</td>
<td>30</td>
<td>18.63</td>
<td>18.06</td>
<td>96.9</td>
</tr>
<tr>
<td>200 (run2)</td>
<td>30</td>
<td>18.63</td>
<td>17.97</td>
<td>96.5</td>
</tr>
</tbody>
</table>

Based on the initial tests, the following experimental conditions were used in the further work:

1. 20 g of straw or 40 g of spruce were used in the torrefaction reactor and thereby a reasonable heating rate and good grinding were obtained.
2. 12 balls of tungsten carbide (10 mm in diameter).
3. A nitrogen flow of 1.0 Nl/min (first 10 minutes) and 0.2 Nl/min subsequently.
   These conditions yield a high solid recovery as well as repeatable temperature profiles and particle size distributions.

2.3.2 Evaluation of grindability characteristics

In the present study, the grindability of torrefied biomass is evaluated based on the relative $d_{50}$ reduction. The $d_{50}$ value is obtained from the sieving analysis, and the relative $d_{50}$ reduction is evaluated based on the initial $d_{50}$ value of the raw biomass. The Hardgrove Grindbility Index (HGI) and the specific grinding energy have traditionally been used to characterize the grindability of torrefied biomass and coal [5,16,20]. The capability of the $d_{50}$ reduction and the HGI to characterize grindability has been tested.

The HGI values obtained (Figure 2.7) shows no large improvement of HGI for torrefied biomass below 250 °C, while the HGI value increases sharply above 250 °C (most distinct for straw). The HGI values obtained are similar to the values from Shang et al. (2013) [24]. For reference, the dry and wet coals HGI are also presented in the Figures 2.7 and 2.8 [16]. A good linear correlation between HGI and $d_{50}$ reduction is observed for straw and to a lesser extent for spruce as shown in Figure 2.8. It is also seen that the relation between $d_{50}$ reduction and HGI are different for the two biomass samples.
Figure 2.7 HGI values as a function of torrefaction temperature for straw and spruce chips. The biomasses were torrefied for 90 minutes in a laboratory torrefaction reactor without grinding balls before the HGI test. For comparison, HGI values for dry and wet coal has been indicated as a dotted and solid line respectively (coal data from Shang et al. (2012))

Figure 2.8 HGI value as a function of relative d$_{50}$ reduction for torrefied straw and spruce chips. For comparison, HGI values for dry and wet coal has been indicated as a dotted and solid line respectively (coal data from Shang et al. (2012))
The Hardgrove Grindability study shows that the biomass samples torrefied at low temperature (less than 250 °C) demonstrate very poor grindability. However, at higher torrefaction temperatures the biomass exhibit better pulverization properties than coals. Straw was found to have a higher HGI value than spruce at similar torrefaction condition. The d$_{50}$ reduction used in this study shows similar tendencies as the modified HGI test method.

### 2.3.3 Torrefaction of wheat straw and spruce chips

The straw and spruce chips were torrefied in the combined torrefaction and grinding reactor in order to investigate the influence of changed operation conditions (temperature and residence time) on mass yield, energy yield and particle size distribution. In Figures 2.9 and 2.10, the mass loss and energy loss at different torrefaction temperatures and residence times for straw and spruce chips are shown. The energy loss was calculated from the heating value of the torrefied biomass (Figure 2.11), the yield and the heating value of the raw biomass. The heating value of torrefied biomass increase when the temperature increase. The residence time have a large influence on the heating value of spruce, but not for straw. This may be related to the conversion of spruce which needs a longer residence time compared to straw. The increase of heating value of torrefied biomass is normally explained by a higher relative carbon content of the torrefied biomass. However no ultimate analysis was performed in this study. Torrefaction experiments by Verhoef et al. (2011), yielded similar heating values 17.85 MJ/kg for torrefied straw (270 °C, 30 minutes torrefaction) and 22.03 MJ/kg for torrefied spruce (289 °C, 30 minutes torrefaction). The carbon content in these experiments changed from 42.2 to 43.8 wt% db for straw and 50.4 to 53.3 wt% db for spruce [25].

The grindability of the torrefied biomass, evaluated as the relative d$_{50}$ reduction, are presented in Figure 2.12. A higher conversion (mass loss) is observed for the straw compared to the spruce at similar temperatures, a trend also obtained by Verhoef et al. (2011), Shang et al. (2012) and Stelte et al. (2011) [24-26]. A larger particle size reduction is observed for the straw sample, as Shang et al. also reported for straw and pine chips (torrefied at 200 – 300 °C) [24]. To obtain a 50% reduction of the d$_{50}$ value (at 90 minutes residence time), the straw has to be heated to 260 °C whereby an energy loss of 15% is observed, while for spruce the sample has to be heated to 320 °C and an energy loss of 28% is observed (Figures 2.10 and
2.12). In order to look further into the grindability of torrefied biomass, the $d_{50}$ reduction as a function of mass loss is shown in Figure 2.13. A reasonable linear relationship is observed for straw and spruce at both residence times with correlation coefficients ($r^2$) above 0.9. At a similar mass loses level, straw always obtained a higher $d_{50}$ reduction than the spruce sample.

**Figure 2.9** Influence of temperature and residence time on mass loss by torrefaction of straw and spruce chips

**Figure 2.10** Influence of temperature and residence time on energy loss by torrefaction of straw and spruce chips
Figure 2.11 Influence of temperature and residence time on solid product heating value by torrefaction of straw and spruce chips

Figure 2.12 Influence of temperature and residence time on $d_{50}$ reduction of torrefied straw and spruce chips. The initial $d_{50}$ values were 1.7 mm for straw and 1.6 mm for the spruce chips
Figure 2.13 Relation between $d_{50}$ reduction and mass loss for straw and spruce torrefied at 230 – 350 °C for 90 minutes

The results presented in figures 2.9 – 2.13 show a significant difference in the torrefaction characteristics of straw and spruce, as illustrated in Figure 2.14 (mass loss, energy loss and $d_{50}$ reduction for 90 minutes torrefaction at 300 °C). The major difference is that straw experience a greater size reduction than spruce. The differences between the torrefaction characteristics of the straw and spruce chips may be caused by several different phenomena, such as the different distribution of hemicelluloses types and lignocelluloses compositions, the alkali catalytic influence on pyrolysis, and the difference in shape, morphology and mass of the two biomasses.
Figure 2.14 Comparison of torrefaction characteristics for straw and spruce, torrefied at 300 °C for 90 minutes

To investigate the pyrolysis of spruce and straw without the heat transfer limitations that may appear in the torrefaction reactor, thermal gravimetric analysis (TGA) using a heating rate of 5 K/min were performed. The TGA curve in Figure 2.15 also shows a higher mass loss for straw than for spruce at low temperatures (below 350 °C). The TGA results indicates that the observed differences in solid yield should be related to the chemical differences between spruce and straw since the heat transfer conditions in the STA is similar for the two samples. The observed different mass loss profiles may be related to the differences in carbohydrate composition or to catalytic properties of the ash. The higher mass loss of straw at temperatures in the range 300 to 350 °C may be caused by both the higher content of hemicelluloses (see Table 2.2 for details) and its higher reactivity (xylan-based esiccatores has been reported to be more reactive compared to the mannan-based hemicelluloses in spruce) [6]. Straw and spruce have a similar amount of cellulose, however spruce has a higher lignin content than straw which may contribute to the higher solid yields below 350 °C. In addition to the carbohydrate composition, the high alkali content in straw may also influence the torrefaction process as discussed by Saleh et al. (2013) and Saddawi et al. (2012) [27,28]. Saleh et al. (2013) concluded that the solid yields from torrefaction are strongly influenced by the biomass potassium content as well as to some extent the lignocelluloses composition [27].
potassium content and xylan-based esiccators in straw leads to a relatively higher mass loss thereby a relatively larger particle size reduction was observed [27].

**Figure 2.15** Comparison of TG-DTG curves for pyrolysis of straw and spruce in nitrogen at 5K/min

When evaluating the mass loss and size reduction of torrefied biomass (Figures 2.13 and 2.14), other factors than the chemical properties of the feedstock may influence the results. The size, morphology and weight of individual particles may influence both heat transfer and particle breakup. The particle size distribution of the raw spruce and straw, and the corresponding particle weight of the particle classes are shown in Figure 2.16 (a and b). Both biomasses have similar particle size distribution with a $d_{50}$ value of 1.7 mm for straw and 1.6 mm for spruce. The straw and spruce particles also have a similar weight of particles smaller than 0.8 mm, while the weight of spruce particles above 0.8 mm increase more than straw particles.
Further particle characterizations for straw and spruce have been analyzed by using a particle size analyzer, the CAMSIZER from Retsch Technology [23]. The results are presented in Figure 2.16 (c and d) in terms of sphericity (SPHT) and width to length ratio (b/l). The sphericity calculated by equation (2.2) is a shape characteristic which is 1 for a spherical particle [23].

\[ SPHT = \frac{4\pi A}{U^2} \quad (2.2) \]

where \( A \) is the measured area of a particle projection and \( U \) is the measured circumference of a particle projection. From Figure 2.16(c), it is observed that the spruce particles are more spherical than the straw particles and data from width to length ratio in Figure 2.16(d) shows a clear shape difference between the two biomasses. Particle characterizations for straw and
spruce show that spruce have a higher mass of the single particle, a greater width to length ratio and are more spherical than the straw particle. The larger particle size reduction of the straw compared to the spruce can be caused by the higher conversion and potentially that the longer straw particles are easier to break.

2.3.4 Separate heating and grinding of straw

Previous sections have presented the results from simultaneous torrefaction and grinding experiments. This section will evaluate whether the grinding or the heating process is the limiting factor in the reactor. The results from this investigation are presented in terms of relative reduction of $d_{50}$ value as a function of grinding time. Figure 2.17 shows the result for the 30 minutes torrefaction experiments, while Figure 1.8 shows the results of the 90 minutes experiments. Selected results from simultaneous heating and grinding experiments are also presented in the figures for comparison.

A poor grindability is observed for untreated straw and straw torrefied at 240 °C (30 minutes). In the case of untreated straw, no improvement in grindability is seen even after 30 minutes grinding (Figure 2.17), while a small reduction in $d_{50}$ value is observed after 90 minutes grinding (Figure 2.18). However, torrefaction at higher temperatures (270 °C (90 minutes) or 330 °C (30 minutes), an increased particle size reduction is obtained after less than 10 minutes of grinding. The total particle size reduction obtained after 30 and 90 minutes combined torrefaction and grinding is swiftly obtained (after only 5 minutes) when grinding the torrefied straw. The results indicate that the heat transfer is the rate limiting step in this reactor while the actual grinding can be obtained swiftly.
Figure 2.17 Relative reduction of $d_{50}$ for wheat straw torrefied at 240, 300 and 330 °C for 30 minutes. 3 gram of char was used in each experiment. A solid line represent results from separate heating and grinding experiments, while open symbols represent simultaneous torrefaction and grinding experiments.

Figure 2.18 Relative reduction of $d_{50}$ for wheat straw torrefied at different temperatures for 90 minutes. 3 gram of char were ground at each grinding time. A solid line represent a result from separate heating and grinding experiments, while a one point marker represent a result from simultaneous torrefaction and grinding experiment.
2.3.5 Influence of particle size on torrefaction of pine wood

Table 2.7 summarizes the results obtained from torrefaction of different particle sizes of pine wood. The solid yields from the 300 °C experiments are similar for the three size classes, while a decreasing trend with increasing particle size is observed for the torrefaction at 320 °C (90 minutes experiments). A similar result was obtained by Basu et al. (2013) for poplar wood cylinder where the mass yield decreased with increasing particle diameter (in the range of 4.76 to 25.4 mm) [29]. This somewhat surprising result was explained by exothermic reactions taking place during the torrefaction process, because of an increased wall thickness that offer a higher thermal resistance, thereby increasing the particle core temperature of large particles [29]. A higher relative particle size reduction (d50) is observed for the larger particle size for torrefaction at 320 °C as compared to torrefaction at 300 °C, while the smallest size class (less than 4 mm) shows only a small increment. The solid yields decreased with increasing torrefaction time and the size reductions are significantly increased.

Table 2.7 Summary of investigations of different initial particle size of pine wood used in the torrefaction process. The solid yield data from TGA measurement of 8-16 mm pine wood were also listed

<table>
<thead>
<tr>
<th>Particle size, mm</th>
<th>T_{D,final}, °C</th>
<th>Residence time, min</th>
<th>Solid yield, wt% db</th>
<th>d_{50} reduction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 4</td>
<td>300</td>
<td>90</td>
<td>65.7</td>
<td>43.97</td>
</tr>
<tr>
<td>4 – 8</td>
<td>300</td>
<td>90</td>
<td>65.9</td>
<td>40.78</td>
</tr>
<tr>
<td>8 – 16</td>
<td>300</td>
<td>90</td>
<td>64.6</td>
<td>39.81</td>
</tr>
<tr>
<td>&lt; 4</td>
<td>320</td>
<td>90</td>
<td>50.4</td>
<td>48.20</td>
</tr>
<tr>
<td>4 – 8</td>
<td>320</td>
<td>90</td>
<td>48.4</td>
<td>60.64</td>
</tr>
<tr>
<td>8 – 16</td>
<td>320</td>
<td>30</td>
<td>64.3</td>
<td>21.20</td>
</tr>
<tr>
<td>8 – 16</td>
<td>320</td>
<td>90</td>
<td>45.6</td>
<td>53.46</td>
</tr>
<tr>
<td>8 – 16</td>
<td>320</td>
<td>180</td>
<td>39.8</td>
<td>85.01</td>
</tr>
<tr>
<td>&lt; 1 (TGA 0.5K/min)</td>
<td>300</td>
<td>-</td>
<td>66.5</td>
<td>-</td>
</tr>
<tr>
<td>&lt; 1 (TGA 5K/min)</td>
<td>300</td>
<td>-</td>
<td>83.2</td>
<td>-</td>
</tr>
<tr>
<td>&lt; 1 (TGA 0.5K/min)</td>
<td>320</td>
<td>-</td>
<td>46.0</td>
<td>-</td>
</tr>
<tr>
<td>&lt; 1 (TGA 5K/min)</td>
<td>320</td>
<td>-</td>
<td>73.0</td>
<td>-</td>
</tr>
</tbody>
</table>
A comparison of the \(d_{50}\) reductions for different sizes of pine wood, spruce and straw is shown in Figure 2.19. Straw experiences the highest size reduction at all temperatures investigated. The woody biomass (spruce and pine) shows almost similar trend of size reduction, regardless of the difference in initial particle size. As discussed by Saleh et al., spruce and pine chips have a similar potassium content (0.036 and 0.056 wt%, respectively), and also relatively similar carbohydrate composition [27]. These similar chemical properties may explain a relatively similar size reduction for spruce and pine chips as shown in Figure 2.19.

![Figure 2.19 Influence of temperature on \(d_{50}\) reduction of pine, spruce and straw for 90 minutes torrefaction](image)

\[\text{Figure 2.19 Influence of temperature on } d_{50} \text{ reduction of pine, spruce and straw for 90 minutes torrefaction}\]

### 2.4 Conclusions

In this study, a combined torrefaction and grinding process was investigated in an electrically heated laboratory ball mill. Wheat straw and wood chips (spruce) were used to investigate the influence of operation conditions on solid yield, energy loss and obtained particle size distribution. Initial tests were conducted and experimental procedures with a good repeatability were developed. Tests on the solid recovery in the reactor showed a limited loss of solid material (maximum of 4%) during experiments. To evaluate the grinding efficiency,
the relative reduction of the $d_{50}$ value was used. A comparison of this method with the modified HGI test was performed and similar tendencies were observed.

A significant difference between the torrefaction characteristic of straw and spruce was observed. Straw experienced a larger mass loss at lower temperature than spruce, resulting in larger size reduction of the straw compared to the spruce. This means that at the same temperature straw yields a higher mass loss and size reduction than spruce. Straw do also obtain a higher size reduction at a given mass loss level. The observed different mass loss profiles of straw and spruce can be related to differences of hemicelluloses type, lignocelluloses compositions, catalytic properties of the ash or to the difference in shape and mass of the biomass particle. TGA analysis shows that the observed differences in solid yield should be related to the chemical differences between spruce and straw since the heat transfer conditions in the STA is similar for the two samples. This study and our study on the comparison of different biomass types indicate that the main cause of the observed difference in mass loss can be related to catalytic properties of ash, more specifically to the high straw alkali content. The larger particle size reduction of straw than spruce wood at similar mass loss level is also related to the high straw alkali content as showed in the next chapter. This work has shown that straw particles are more elongated than spruce particles, which also could contribute to the swifter grinding of straw particles.

Experiments with separate heating and grinding of straw showed a swift grinding of biomass pre-exposed to torrefaction temperatures in a fixed bed. The particle size reduction obtained after 30 and 90 minutes combined torrefaction and grinding experiments was obtained in only 5 minutes by separate grinding of torrefied char. This result implies that the heat transfer is the rate limiting step in this reactor.

The results from particle size influence on pine wood torrefaction showed that the mass yield decreased with increasing particle diameter for torrefaction at 320 °C (90 minutes). This is possibly related to exothermic reactions taking place during torrefaction of larger particles (8 – 16 mm), where the larger wall thickness offer a higher thermal resistance resulting in a higher particle core temperature, thus increasing the mass loss of solid product.
2.5 References

Chapter 3  Influence of biomass chemical properties

Abstract

The torrefaction process (low temperature pyrolysis) can be used as a pretreatment method to overcome the problems associated with the handling, storage and grinding of biomass. Different biomasses have different torrefaction characteristics and an improved understanding and ability to predict the torrefaction characteristic of different biomass types is therefore desired. In this study, the influence of biomass chemical properties (lignocelluloses composition and alkali content) on the torrefaction behavior with respect to mass loss and grindability is investigated. Six raw biomass samples (Danish wheat straw, miscanthus, spruce, beech, pine, and spruce bark) with different chemical and physical properties were pyrolyzed by Simultaneous Thermal Analysis (STA) or torrefied in a combined torrefaction reactor and ball mill. The effect of biomass alkali content on torrefaction characteristics were furthermore investigated by washing or impregnating (KCl and K$_2$CO$_3$) of selected biomass. The investigated biomasses have reasonably similar carbohydrate compositions (hemicelluloses 18 – 25 wt% db; cellulose 38 – 48 wt% db; lignin 17 – 29 wt% db) with the exception of spruce bark which is lower in esiccators es content (12.9 wt% db) and cellulose content (24 wt% db), and higher in lignin content (36.8 wt% db). An increasing biomass potassium (K) content decreases the temperature of maximal conversion, thus decreasing the solid product yield at 270 and 300 °C. A steep decline of the solid yield was observed when the biomass potassium content increased from 0 to 0.2 wt%. Generally it is observed for both pure biomass and alkali impregnated biomass that the solid yield decrease with increasing alkali content. However, the higher lignin content in bark causes a higher solid yield than what would be expected from the alkali content. In summary both potassium content and lignocelluloses composition affect the solid yield obtained by torrefaction. The grindability of the torrefied products was evaluated by determining the $d_{50}$ value of the particle size distribution of the biomass before and after torrefaction in the combined torrefaction and mill reactor. A significant decrease in $d_{50}$ value was observed when the alkali content is
increased from 0 to 0.2 wt% db, while no additional effect is seen for higher potassium contents.

3.1 Introduction

Biomass in the form of wood and straw can be utilized for CO$_2$ neutral production of power and heat on suspension fired power plants. However, the utilization of biomass in suspension fired-boilers have to deal with several technical issues, such as fuel storage and grinding, ash deposit formation and fuel conversion [1,2]. One of the major problems when using biomass in suspension fired boiler systems is the difficult and energy consuming grinding down to the small particle sizes used. Large biomass particles may induce problems with ignition, flame stability and burn out [2]. One way of improving the properties of biomass is to use a torrefaction pretreatment [3,4]. Torrefaction involves heating of biomass at moderate temperatures (200 – 300 °C) under an inert atmosphere. This process releases both moisture and carbon dioxide, both of which remove oxygen from the biomass, resulting in a fuel with a lower O/C ratio [5,6]. Torrefaction also partially decomposes the organic constituents of the biomass whereby less energy is required to grind the torrefied biomass [7,8]. The torrefied biomass is brittle and can be pulverized down to a small particle size without excessive energy consumption [6,9]. Most of the earliest research studies have focused on torrefaction of woody biomasses [4,7,10]. In the recent years, more works on utilization of herbaceous biomass and agro-forestry residue have also been done [5,8,11]. Biomass decomposition during pyrolysis and torrefaction are influenced by the ash composition and the contents of the three main biomass components; hemicelluloses, cellulose, and lignin [12].

Most of the published torrefaction studies focused on the mass loss, carbon content, and energy distribution as a function of time and temperature for a selected biomass sample. Only few studies have paid attention to the influence of biomass physical and chemical properties on torrefaction. However, several Simultaneous Thermal Analysis (STA) based studies on the influence of biomass alkali content and organic composition on biomass pyrolysis behavior have been conducted [12-17]. Alkali metals have been found to catalyze the pyrolysis process and have a strong influence on the products distribution [12-14]. Most of the potassium (K) in
herbaceous biomass probably appears as KCl and K₂CO₃ as can be seen from the ionic composition of leachates from leaching of straw and straw char with water [15,16]. The highest concentration of positive ions was in both cases K⁺ and the largest concentrations of negative ions were found to be Cl⁻, CO₃²⁻ and HCO₃⁻. To investigate the influence of potassium on biomass pyrolysis, several STA studies have been done where alkali is removed by washing with water or added to samples by doping with KCl and K₂CO₃ [12,15-17]. The STA studies have generally focused on the complete pyrolysis process but some relevant data at the torrefaction temperature range (270 – 300 °C) can be extracted. In Table 3.1 data with respect to initial decomposition temperature of the main organic biomass constituents, straw and wood, and samples doped with KCl and K₂CO₃ are shown. It is seen that the lowest initial decomposition temperature for biomass constituents with no alkali addition is seen for lignin (approximately 230 °C) then comes esiccators (approximately 240 °C) and the highest initial decomposition temperature is observed for cellulose (320 °C). However, the relative conversion at 300 °C is 40 wt% for xylan (xylan is a hemicelluloses constituent) and only 10 wt% for lignin [12]. A FTIR measurement on torrefied wheat straw has shown that the main decomposition below 270 °C can be attributed to decomposition of hemicelluloses [11]. Even TGA measurements of pure cellulose shows a mass loss above 320 °C, analysis of wheat straw (that typically has a K content of 1.0 wt%) torrefied at 300 °C showed in most cases that all esiccators and most cellulose have been destructed [18]. The influence of adding KCl and K₂CO₃ to the biomass organic main constituents can be seen in Table 3.1. The addition of KCl seems to decrease the initial decomposition temperature of cellulose, but do not influence the initial decomposition temperature of esiccators and lignin. The addition of K₂CO₃ strongly decreases the initial decomposition temperature of cellulose (down to 225 °C), but do not influence the initial decomposition temperature of lignin and only slightly change the initial decomposition temperature of esiccators.
Table 3.1 Initial decomposition temperatures of biomass and biomass constituents found by TGA. The initial decomposition temperature is defined as the temperature that corresponds to an approximate weight loss of 5% with respect to the total weight loss.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Initial decomposition temperature, °C</th>
<th>Heating rate in TGA, °C/min</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw sample</td>
<td>Sample doped with KCl</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hemicellulose</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>242 (xylan)</td>
<td>242 (xylan)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>253 (xylan)</td>
<td>212</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Cellulose</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>327</td>
<td>277</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>319</td>
<td>327</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>310</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>300</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Lignin</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>227</td>
<td>227</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>259</td>
<td>227</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>210</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Wheat straw</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>247</td>
<td>247</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Washed wheat straw</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>287</td>
<td>247</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Pine wood</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>261</td>
<td>261</td>
<td>20</td>
</tr>
</tbody>
</table>

In most cases the torrefaction process will aim at obtaining a minimum mass loss (a minimum loss of the solid product heating value) and obtaining a high grindability (a fragile product that is easily grinded). However, different types of biomass have different torrefaction behavior and therefore an improved understanding and ability to predict the torrefaction behavior is desired. The objective of the present study were to determine the influence of biomass type, carbohydrate composition and alkali content on the weight loss and the grindability of biomass exposed to heating at torrefaction temperatures of 250 – 300 °C. In this study, six different biomasses were pyrolyzed in a Simultaneous Thermal Analysis (STA) and were torrefied in a simultaneous torrefaction and grinding reactor; and the obtained results were discussed with respect to the influence of biomass alkali content and carbohydrate compositions. To further investigate the influence of alkali metals on torrefaction characteristics, some washed biomass samples (to remove alkali) and some impregnated
samples (with addition of KCl and K$_2$CO$_3$) were included in the study. The grindability of the torrefied biomass is investigated by measuring the particle size distributions of the chars produced.

### 3.2 Experimental section

#### 3.2.1 Materials

The investigated biomass samples used in this study were two herbaceous biomasses (Danish wheat straw and miscanthus) and four woody biomasses (spruce wood chips, beech wood chips, pine wood chips and spruce bark). All the samples were ground to a particle size less than 4 mm. The ash content (determined according to CEN/TS 14775) and the elemental compositions (determined according to CEN/TS 12290/15297/15289) were analysed by Bioenergy 2020+ GmbH, Graz, Austria [19] and the results are shown in Table 3.2. The biomass samples cover a wide range of ash contents (0.34 – 5.57 wt%), carbon contents (45 – 53 wt%), chlorine contents (0.003 – 0.19 wt%) and potassium contents (0.036 – 0.904 wt%). The herbaceous biomass has a higher ash content compared to the woody biomass, except the spruce bark (4.98 wt%). The woody biomass have a low potassium content (less than 0.2 wt%), while miscanthus and straw contains 0.49 wt% and 0.9 wt% (potassium), respectively. The biomass carbohydrate compositions were analysed according to the ASTM E 1758-01 and Kaar et al. [20,21]. First, the sample was dissolved in strong acid (72% H$_2$SO$_4$) at room temperature and then hydrolyzed in dilute acid (4% H$_2$SO$_4$) at 121 °C by autoclavation. Hemicelluloses and cellulose contents were determined by HPLC of the liberated sugar monomers. The lignin content was determined based on the filter cake, subtracting the ash content determined by incinerating the residues from the strong acid hydrolysis at 550 °C for 3 h. The result from the carbohydrate analysis is presented in Table 3.3. The six investigated biomasses have a reasonably similar carbohydrate compositions with the exception of the spruce bark, which is lower in hemicelluloses content (12 wt% db) compared to the other biomasses (approximately 20 wt% db). The spruce bark is also lower in cellulose content with 22 wt% db compared to 34 – 44 wt% db for the other biomasses, and has a higher lignin content of 35 wt% db compared to 17 – 29 wt% db of the other biomasses.
Straw and miscanthus have reasonably higher xylan-based hemicelluloses, while the woody biomasses have a significant amount of mannan-based hemicelluloses.

Straw and spruce wood chips were chosen for alkali impregnation because straw has the highest potassium and chlorine content, while spruce has the lowest content of potassium. To partly remove the minerals from the straw sample, a hot water wash method was applied [12]. 2 g of straw were stirred in a beaker with 150 mL of deionized water at 80 °C for 2 h. The suspension was then filtered, washed with 300 mL H₂O, and then dried in a desiccators under vacuum at room temperature. A previous study has shown that almost 90% of the potassium is removed by this washing process [12]. For alkali impregnation, 5 g of KCl or K₂CO₃ were dissolved in 250 mL of deionized H₂O and 1 mL of this solution was added to 1 g of sample to provide 2 wt% KCl/K₂CO₃ in the sample. The mixture was thoroughly mixed to give as uniform distribution of the salt as possible. After that the sample was dried in a desiccators under vacuum at room temperature.

<table>
<thead>
<tr>
<th>Component (wt% dry)</th>
<th>Wheat Straw</th>
<th>Miscanthus</th>
<th>Bark (Spruce)</th>
<th>Wood chips (Spruce)</th>
<th>Wood Chips (Beech)</th>
<th>Wood chips (Pine)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>5.57</td>
<td>2.26</td>
<td>4.98</td>
<td>0.34</td>
<td>0.64</td>
<td>0.5</td>
</tr>
<tr>
<td>C</td>
<td>45.93</td>
<td>47.97</td>
<td>49.66</td>
<td>48.88</td>
<td>48.50</td>
<td>53.2</td>
</tr>
<tr>
<td>H</td>
<td>5.86</td>
<td>5.92</td>
<td>5.63</td>
<td>6.23</td>
<td>6.05</td>
<td>6.2</td>
</tr>
<tr>
<td>O</td>
<td>41.87</td>
<td>43.54</td>
<td>39.36</td>
<td>44.54</td>
<td>44.74</td>
<td>39.95</td>
</tr>
<tr>
<td>N</td>
<td>0.64</td>
<td>0.28</td>
<td>0.34</td>
<td>0.02</td>
<td>0.06</td>
<td>0.1</td>
</tr>
<tr>
<td>S</td>
<td>0.13</td>
<td>0.03</td>
<td>0.03</td>
<td>0.004</td>
<td>0.009</td>
<td>0.05</td>
</tr>
<tr>
<td>Cl</td>
<td>0.19</td>
<td>0.15</td>
<td>0.01</td>
<td>0.003</td>
<td>0.004</td>
<td>0.005</td>
</tr>
<tr>
<td>K</td>
<td>0.90</td>
<td>0.485</td>
<td>0.184</td>
<td>0.036</td>
<td>0.128</td>
<td>0.056</td>
</tr>
<tr>
<td>Si</td>
<td>1.400</td>
<td>0.450</td>
<td>0.318</td>
<td>0.007</td>
<td>0.005</td>
<td>0.050</td>
</tr>
<tr>
<td>Al</td>
<td>0.006</td>
<td>0.008</td>
<td>0.073</td>
<td>0.003</td>
<td>0.002</td>
<td>0.010</td>
</tr>
<tr>
<td>P</td>
<td>0.095</td>
<td>0.020</td>
<td>0.034</td>
<td>0.003</td>
<td>0.005</td>
<td>0.007</td>
</tr>
<tr>
<td>Fe</td>
<td>0.008</td>
<td>0.008</td>
<td>0.053</td>
<td>0.002</td>
<td>0.002</td>
<td>0.003</td>
</tr>
<tr>
<td>Mg</td>
<td>0.079</td>
<td>0.055</td>
<td>0.081</td>
<td>0.011</td>
<td>0.028</td>
<td>0.029</td>
</tr>
<tr>
<td>Ca</td>
<td>0.433</td>
<td>0.130</td>
<td>1.290</td>
<td>0.104</td>
<td>0.134</td>
<td>0.100</td>
</tr>
<tr>
<td>Na</td>
<td>0.011</td>
<td>0.003</td>
<td>0.010</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>0.005</td>
</tr>
</tbody>
</table>
Table 3.3 Carbohydrate analysis for raw biomasses

<table>
<thead>
<tr>
<th>Components (wt% dry)</th>
<th>Straw</th>
<th>Miscanthus</th>
<th>Spruce chips</th>
<th>Beech chips</th>
<th>Pine chips</th>
<th>Spruce bark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylan-based hemicelluloses</td>
<td>23.1</td>
<td>18.1</td>
<td>5.6</td>
<td>16.2</td>
<td>5.1</td>
<td>3.9</td>
</tr>
<tr>
<td>Mannan-based hemicelluloses</td>
<td>0</td>
<td>0</td>
<td>11.0</td>
<td>2.3</td>
<td>10.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Other hemicelluloses</td>
<td>2.3</td>
<td>2.0</td>
<td>1.8</td>
<td>2.7</td>
<td>5.4</td>
<td>5.0</td>
</tr>
<tr>
<td>Total hemicelluloses</td>
<td>25.4</td>
<td>20.1</td>
<td>18.4</td>
<td>21.2</td>
<td>20.5</td>
<td>12.9</td>
</tr>
<tr>
<td>Cellulose</td>
<td>42.7</td>
<td>48.5</td>
<td>45</td>
<td>40.8</td>
<td>38.6</td>
<td>24.1</td>
</tr>
<tr>
<td>Lignin</td>
<td>17.3</td>
<td>22.4</td>
<td>27.6</td>
<td>23.8</td>
<td>29.2</td>
<td>36.8</td>
</tr>
<tr>
<td>Ash</td>
<td>5.57</td>
<td>2.26</td>
<td>0.34</td>
<td>0.64</td>
<td>0.5</td>
<td>4.98</td>
</tr>
<tr>
<td>Extractives</td>
<td>3.2</td>
<td>4.3</td>
<td>1.0</td>
<td>1.0</td>
<td>4.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Residuals</td>
<td>5.8</td>
<td>2.4</td>
<td>7.66</td>
<td>12.56</td>
<td>6.5</td>
<td>15.52</td>
</tr>
</tbody>
</table>

3.2.2 Torrefaction reactor

The laboratory reactor for simultaneous torrefaction and grinding is shown in Figures 3.1 and 3.2. The set up includes a reactor chamber (inner diameter = 70 mm and length = 200 mm) in which a biomass sample is placed together with metal balls for grinding (as can be seen in Figure 3.2). The reactor chamber can be simultaneously heated and rotated whereby torrefaction and grinding takes place. In addition the set up consists of a water cooling section, an electrically heated furnace, a gas cooling section, and five thermocouples as shown in Figure 3.1. The reactor chamber is located inside the electrically heated furnace and a motor is used to rotate the reactor chamber (120 rpm). In the conducted experiments, a biomass sample and 12 metal balls (10 mm in diameter) were introduced into the reactor chamber and placed in the water cooled part of the set up. The reactor was then purged with nitrogen (1.0 Nl/min) to avoid combustion. After five minutes of purging, the reactor chamber was quickly pushed into the hot zone and the rotation was started (120 rpm). The biomass samples were simultaneously torrefied and grinded at different temperatures (270 and 300 °C) for 90 minutes. During this processes, the nitrogen flow was 1.0 Nl/min for the first ten minutes and
then reduced to 0.2 Nl/min until the end of experiments. After the torrefaction process the solid product was cooled down in the cooling section under nitrogen atmosphere. Then, the char was collected and weighed to determine the mass loss. The treated samples were sieved in order to determine the obtained particle size distribution. The torrefaction temperature used in this work is defined as the final reactor temperature inside the reactor chamber. The residence time is defined as the time from the reactor chamber that contains the biomass sample is pushed into the hot zone, until the grinding and torrefaction process is stopped. This residence time includes the heating of particles from room temperature until the end of the experiment (it takes approximately 15 minutes to heat the samples to 200 °C). A more detailed explanation of the applied experimental procedure can be found in Saleh et al. (2013) [22].

**Figure 3.1** Bench scale experimental set up for simultaneous torrefaction and grinding

**Figure 3.2** Reactor chamber equipped with rotating pins and thermocouple
3.2.3 Thermogravimetric analysis (TGA)

All the investigated biomass samples were pyrolyzed (separate test) in a Simultaneous Thermal Analysis Netzsch STA 449 F1 Jupiter instrument (STA). Pyrolysis of 10 – 20 mg of biomass was carried out in a nitrogen atmosphere at a heating rate of 5 K/min up to 600 °C (with 10 minutes isotherms at 120 and 600 °C). The sample was then cooled to 200 °C, and heated to 650 °C in the presence of 10 vol% O₂ to burn off the remaining char. The temperature of maximal conversion is obtained from the derivative thermogravimetric (DTG) curve.

3.2.4 Sieving analysis

A Retsch analytical sieve shaker AS 200 was used to assess the particle size distribution of raw and torrefied biomass. The samples were poured into the top sieve which has the largest screen openings. Each lower sieve in the column has smaller openings and at the base is a round pan called the receiver. The sieve sizes used in this study were ranges from 0.045 to 4 mm. The sieves column was placed in a sieve shaker, and the shaker shakes the column for 15 minutes. After the shaking was completed, the material on each sieve was weighed and then the cumulative weight was calculated.

3.3 Results and discussion

3.3.1 Thermal decomposition characteristics (TGA)

As an example, Figure 3.3 shows the thermogravimetric mass loss (TG) and its derivative (DTG) for straw, washed straw and KCl-impregnated washed straw. The DTG profile for raw straw has one broad peak from 200 to 350 °C with a maximum at 320 °C. This peak represents the thermal decomposition of the lignocelluloses components. The initial thermal degradation is mainly attributed to the decomposition of hemicelluloses [23]. Upon removing alkali from the straw, two peaks appeared at 290 and 354 °C [12]. An addition of KCl to the washed straw
moves the peaks to lower temperature (254 °C and 319 °C respectively). As discussed by Antal and Varhegyi (1995), the low temperature peak is mainly due to the decomposition of hemicellulose, whereas the high temperature peak was associated with cellulose/lignin decomposition [24]. A further explanation for the results obtained from pyrolysis of all biomass samples in STA are discussed in the following section.

![Figure 3.3 TG-DTG curves for pyrolysis of straw, washed straw and KCl-impregnated washed straw](image)

**3.3.2 Influence of alkali content on thermal decomposition of biomass samples**

The influence of biomass alkali content on the maximal conversion rate temperature and the solid yield obtained from the STA measurements are shown in Figures 3.4 and 3.5 respectively. The maximum conversion rate temperature is determined as the temperature at which the maximum DTG value is obtained (see Figure 3.3). In Figure 3.4, a simple nearly linear relation between the maximum conversion rate temperature and the biomass potassium (K) content can be observed. The raw biomass with the lowest K content (spruce chips) shows the highest conversion rate temperature (354 °C) and straw with the highest K content has the lowest peak temperature (at 322 °C). As seen in Figure 3.4, all data shows a similar trend including the K₂CO₃ impregnated samples indicating that alkali is catalyzing the pyrolysis process. This is in agreement with the work conducted by Fahmi et al. (2007) which shows the
alkali metals present in biomass has the ability to reduce the degradation temperatures [25]. As shown in Figure 3.5, the solid yield is significantly decreased at 270 and 300 °C when the biomass potassium (K) content increase from 0 to 0.2 wt%. However, at K contents above 0.2 wt% a less pronounced influence on the solid yield is observed. A similar behavior is observed for most of the washed and impregnated samples. However, bark spruce and three impregnated samples (spruce+K_2CO_3, washed straw+KCl, washed straw+K_2CO_3) deviate from the general trend of solid yield at 300 °C. The reason for the higher solid yield from torrefaction of bark spruce at 300 °C is mainly because of the higher lignin content in the bark, where lignin has a low degree of gas release at 300 °C [26]. The lowest yield obtained at 300 °C from torrefaction of the three impregnated samples could be caused by the distribution of the added potassium being different than the ash distribution. In addition, not all potassium in straw and spruce samples are present as KCl and K_2CO_3 [12]. Subsequently, the results obtained from STA measurement can be compared with the measured solid yield from the simultaneous torrefaction reactor as shown in Figure 3.6 for experiments conducted at 270 and 300 °C. Similar to the STA data, the solid yields from the torrefaction reactor are decreasing when the alkali content is increased. The most significant influence is observed when the biomass potassium content is increased from 0 to 0.2 wt%.

Repeatability of the results obtained from torrefaction experiments were tested for miscanthus at 270 and 300 °C and for spruce bark at 270 °C. As shown in Figure 3.6, the results obtained from the repeated measurements show a good agreement. The standard deviations for the solid yield for three cases were relatively small (0.4 wt%).
**Figure 3.4** Influence of biomass K content on maximum conversion rate temperature in TGA

**Figure 3.5** Influence of biomass K content on solid yields obtained at 270 and 300 °C in TGA
Figure 3.6 The solid yields obtained from the torrefaction reactor as a function of the biomass potassium contents (torrefaction at 270 and 300 °C for 90 minutes)

A slightly different behavior of KCl- and K$_2$CO$_3$-impregnated biomass samples as compared to the raw biomasses is observed in Figures 3.4 – 3.6. The TGA results for raw, washed and impregnated straw and spruce chips are summarized in Table 3.4. The maximal conversion rate temperature is slightly lower for the KCl-impregnated washed straw compared to the raw straw, resulting in a moderate decline of solid yield from 75.3 to 71 wt% db. However, the decrease of solid yield is larger for the K$_2$CO$_3$-impregnated washed straw (68.6 wt% db). An even larger difference is seen for the impregnated spruce samples with a solid yield of 76 wt% for the KCl-impregnated and a solid yield of 66 wt% for the K$_2$CO$_3$-impregnated sample. The derivative thermogravimetric curves for KCl- and K$_2$CO$_3$-impregnated washed straw (as shown in Figure 3.7) demonstrates that by adding KCl to washed straw, the lower and main DTG peaks are moves towards lower temperatures. However, the lower peak disappear when K$_2$CO$_3$ was added to the washed straw, resulting in a broad peak similar to raw straw but with a higher mass loss rate, yielding a lower solid fraction at 300 °C. Previous studies have discussed the influence of inorganic salts on pyrolysis products in the temperature range of 400 – 600 °C [17,27,28]. Wang et. al. (2010) reported that in the presence of K$_2$CO$_3$ the crystalline structure of cellulose in wood
completely disappeared at a pyrolysis temperature of 350 °C, while for the raw wood, this cellulose structure remained unimpaired at a similar temperature [27]. The result shows that K$_2$CO$_3$ facilitated the destruction of cellulose. In their study, Shimada et. al. (2008) also observed that the addition of KCl lowered the temperature at which weight loss started (as can be seen in Figure 3.7), however the presence of a large DTG peak at 319 °C corresponding to the bulk cellulose pyrolysis, indicates that the cellulose structure was not altered with this salt [17]. Patwardhan et. al. (2010) observed that the presence of small quantities of KCl reduced the formation of levoglucosan, which is the primary product of pure cellulose pyrolysis at 500 °C [28]. In summary, the addition of K$_2$CO$_3$ completely destroys the cellulose structure at temperature of 350 °C, while the addition of KCl do not alter the cellulose structure, but only reduce the formation of levoglucosan (affecting the distribution of pyrolysis products). This difference may be caused by the stronger alkalinity of carbonate. In conjunction with the reduction of levoglucosan formation, these studies also reported that the addition of K$_2$CO$_3$ or KCl led to an increase in the char yield during pyrolysis at 400 °C (Shimada et. al. 2008) and 500 °C (Patwardhan et. al. 2010). A decreasing solid yield with increasing biomass alkali content at typical torrefaction temperatures have been observed in this study, however results in several studies have shown that higher alkali content leads to high char yields at high temperatures [12,17,23,28]. The solid yield at 300 and 600 °C obtained from TGA data is shown in Figure 3.8, and it is seen that similar results as previous studies are obtained from our TGA measurements [12,17,23,28].

**Table 3.4** Maximal conversion rate temperatures and solid yields for raw, washed and impregnated straw and spruce chips samples, determined by TGA measurement

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum conversion rate temperature, °C</th>
<th>Solid yield at 300 °C, wt%db</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Straw</td>
<td>Spruce chips</td>
</tr>
<tr>
<td>Washed sample</td>
<td>354</td>
<td>359</td>
</tr>
<tr>
<td>Raw sample</td>
<td>322</td>
<td>354</td>
</tr>
<tr>
<td>KCl-impregnated (2wt%)</td>
<td>319</td>
<td>319</td>
</tr>
<tr>
<td>K$_2$CO$_3$-impregnated (2wt%)</td>
<td>309</td>
<td>309</td>
</tr>
</tbody>
</table>
Figure 3.7 DTG profiles for straw, washed straw, KCl and K$_2$CO$_3$–impregnated wash straw

Figure 3.8 Comparison of solid yields at 300 and 600 °C from TGA measurement

Generally, most of the samples as shown in Figure 3.8 demonstrate a linear trend as the potassium content increases, except for spruce bark at 600 °C. Spruce bark shows the highest solid yield at 600 °C, despite its relatively lower potassium content. The explanation may be the high lignin content of the bark which contributed to the higher char formation. Apart from
the influence of biomass alkali content, the biomass lignocelluloses composition also influence the torrefaction process as has been reported in the previous studies [5,8]. A comparison of the raw biomass lignocelluloses compositions, the potassium contents and the solid yields obtained from the torrefaction reactor and the STA is shown in Figure 3.9. The six investigated biomasses have a reasonably similar lignocelluloses compositions with the exception of the spruce bark, which is lower in hemicelluloses content (12 wt% db) compared to the other biomasses (approximately 20 wt% db hemicellulose). The spruce bark is also lower in cellulose content which is 22 wt% db (as compared to 34 – 44 wt% db in other biomasses), and has a higher lignin content of 35 wt% db (as compared to 17 – 29 wt% db in other biomasses). Generally it is observed that the solid yield decrease with increasing alkali content. However, the higher lignin content in bark causes a higher solid yield than what would be expected from the alkali content. It can be concluded that the solid yield is mainly determined by the biomass potassium content and to some degree also the lignocelluloses compositions of the biomass.
Figure 3.9 Comparison of the carbohydrate compositions, the potassium contents and the solid yields obtained from thermogravimetric analysis (TGA) and the torrefaction reactor. The bar graph shows the lignocelluloses composition and the potassium contents of the biomass samples (Note that the potassium content is multiplied by 100). The cross markers represents the solid yield obtained from the torrefaction reactor (final temperature 270 °C, 90 minutes residence time) and the STA (temperature 300 °C, heating rate of 5 °C/min).

3.3.3 Influence of alkali content on the grindability of torrefied biomass

The grindability of torrefied biomass is an important parameter with respect to obtaining a high burn out of the fuel supplied to a suspension fired boiler. Thus, it is also the aim of this work to study the influence of biomass properties on the grindability of the produced torrefied solid. As documented in the literature, different methods have been used to characterize the grindability of torrefied biomass, such as Hardgrove Grindability Index (HGI) used by Bridgeman et al. (2010) and Shang et al. (2012), Hybrid Work Index (HWI) introduced by Essendelft et al. (2013) and specific grinding energy measured by Phanpanich and Mani (2011). In most cases, the influences of torrefaction temperature and particle size on
grindability have been discussed. Presently, no discussion of the influence of biomass alkali content on the torrefied biomass grindability is available in literature. In this study, the grindability of biomass is evaluated based on the relative d₅₀ reduction. The d₅₀ value is the particle size at which 50 wt% of the particles in a sample are smaller than that size, while the relative d₅₀ reduction is evaluated with respect to the initial d₅₀ value of the raw biomass. The d₅₀ value is obtained from sieving the raw and torrefied samples, and an example of particle size distributions are shown in Figure 3.10. The relative reduction of d₅₀ by torrefaction can then be used as a measure of the grindability of a torrefied biomass.

![Particle size distributions of raw straw and torrefied straw at 270 and 300 °C](image)

**Figure 3.10** Particle size distributions of raw straw and torrefied straw at 270 and 300 °C obtained from 90 minutes torrefaction

The particle size reduction (expressed as the relative d₅₀ reduction) obtained from the torrefaction reactor at 270 and 300 °C as a function of biomass potassium content is shown in Figure 3.11. When the K content is increased up to 0.2 wt% db, the relative d₅₀ reduction is increased significantly. However, the higher K contents (>0.2 wt%db) do not further influence the particle size reduction. Increasing the reactor temperature from 270 to 300 °C does in all cases increase the particle size reduction. It is important to note that the samples with addition of KCl or K₂CO₃ show a somewhat different behavior compared to the non-impregnated
samples. The samples with KCl generally show a higher particle size reduction than samples impregnated with K$_2$CO$_3$.

The relationship between mass loss and the obtained particle size reduction in the torrefaction reactor at 270 and 300 °C with respect to the biomass potassium content are shown in Figure 3.12. At a given reactor temperature a reasonable linear relation between mass loss and particle size reduction is observed. At 270 °C, spruce with the lowest potassium content experienced the lowest mass loss and particle size reduction. As the biomass potassium content increases, the mass loss increases, and a relatively linear increase in particle size reduction is observed in Figure 3.12. Biomasses that experience a high mass loss during the torrefaction process do also experience a relatively high particle size reduction. However, a different behavior is observed for spruce bark torrefied at 300 °C. A high $d_{50}$ reduction (80%) is obtained with an intermediate mass loss (34 wt%). A possible reason may be that a high fraction of the relatively low content of hemicelluloses (12.9 wt%) in the bark has been converted, making the biomass more brittle. It is observed that the biomasses impregnated with KCl shows a similar trend to the raw biomasses, while the K$_2$CO$_3$ impregnated biomasses cause a relatively high mass loss without a corresponding high particle size reduction.
**Figure 3.11** Relative reduction of particle size ($d_{50}$ reduction) as a function of biomass potassium (K) content. The simultaneous torrefaction and grinding experiments were conducted at 270 and 300 °C for 90 minutes.

**Figure 3.12** Relationship between $d_{50}$ reduction and mass loss of torrefied biomass with different K content. The two trendlines are based on the biomass potassium content with respect to their mass loss after torrefaction.
3.4 Conclusions

To study the influence of biomass composition on torrefaction characteristics, six raw biomasses were torrefied both in a STA and a simultaneous torrefaction and grinding reactor. In addition, washed samples and alkali-impregnated samples were included to further investigate the influence of alkali content on torrefaction behavior. The solid yields at the investigated torrefaction temperatures (270 and 300 °C) are strongly influenced by the biomass potassium content as well as to some extent the lignocelluloses composition. High biomass potassium content leads to a relatively low solid yield; however, in a single case a high lignin content leads to a relatively high solid yield even in the presence of relatively high potassium content. K$_2$CO$_3$-impregnated samples resulted in the lowest maximum conversion rate temperature, thus yielding the lowest solid product as compared to the KCl-impregnated samples at 300 °C. The addition of K$_2$CO$_3$ is expected to destroy the cellulose structure at temperatures less than 350 °C, while the addition of KCl only reduce the formation of levoglucosan (affecting the distribution of pyrolysis product) and do not affect the cellulose structure. Lower solid yield is obtained for biomass with high hemicellulose contents. Biomass that shows a high mass loss during torrefaction also obtains a relatively large particle size reduction. A significant decrease in d$_{50}$ value is observed when the alkali content is increased from 0 to 0.2 wt% db, while no additional effect is seen for higher potassium contents. The results from this study show that the torrefaction characteristics were highly influenced by the biomass alkali content.
3.5 References

changes of 3 biomass fuels caused by torrefaction. Submitted to *Biomass and Bioenergy* 2013.


Chapter 4 Chlorine and sulfur release during low temperature pyrolysis

Abstract

The release of chlorine (Cl) and sulfur (S) during biomass torrefaction and pyrolysis has been investigated via experiments in two laboratory-scale reactors: a rotating reactor and a fixed bed reactor. Six biomasses with different chemical compositions covering a wide range of ash content and ash-forming elements were torrefied/pyrolyzed in the temperature range of 150 – 500 °C. The relative release of chlorine and sulfur was calculated based on mass balance and analysis of the biomass before and after torrefaction. In selected cases, measurement of methyl chloride (CH$_3$Cl) in the gas from straw torrefaction has furthermore been conducted. The release of chlorine from straw was first observed at 250 °C and peaked with about sixty to seventy percent at 350 °C. Analysis of the released gas showed that most of the chlorine was released as methyl chloride. Increasing the straw content in the reactor resulted in a lower fractional release of Cl, probably due to more reactive sites being available for secondary reactions, such as relative stable basic functionalities on the char surface or potassium particles (forming KCl). Almost complete release of chlorine was observed for woody biomass at 350 °C. This result is in agreement with previous studies reporting that biomass with a lower chlorine content release a higher fraction of chlorine during the devolatilization process. A significant sulfur release (about 60%) was observed from the six biomasses investigated at 350 °C. The initial sulfur content in the biomass did not influence the fraction of sulfur release during torrefaction, and the influence of organic or inorganic binding of sulfur was not investigated.

4.1 Introduction

Torrefaction is used to produce a fuel with increased energy density and improved grindability, and thereby reduced costs of transportation, milling and storage [1,2]. These
improved properties make torrefied biomass an attractive fuel for combustion and gasification processes [1,3]. Torrefaction is typically conducted in an inert atmosphere at temperature from 250 – 320 °C and yields are typically 40 – 90 wt% solids and 10 – 60 wt% released gases [3-9]. However, the use of biomass which has a relatively high content of chlorine (Cl), sulfur (S), potassium (K), calcium (Ca), silicon (Si) and some other elements may cause problems with deposition and corrosion in thermal fuel conversion systems [10,11]. The solid torrefied product is often used as a fuel in boilers, while the released gases can be combusted and used to supply energy for the torrefaction process [1,5,6,8]. To evaluate the influence of the torrefaction products on combustion equipments, it is important to obtain knowledge on how the inorganic fuel elements (Cl, S, K, Ca, Si, Na, Mg) are distributed between the gas and solid [10-12]. Chlorine and sulfur are known to play an important role in boiler deposit formation, deposit induced corrosion and at the same time Cl and S facilitate the mobility of many inorganic compounds, particularly potassium [10-14]. Therefore both an improved understanding of the fate of Cl and S and a quantification of the release at torrefaction conditions are desired.

The release of Cl and S and other ash-forming elements during combustion of biomass has been investigated in a number of publications, however only a few studies have measured the fate of ash forming elements, including Cl and S at temperatures relevant to torrefaction and low temperature pyrolysis. It is documented in previous studies that chlorine and sulfur to some extent are released to the gas phase by heating of biomass to temperatures below 500 °C, while elements such as K, Na, Ca, Si and Mg are nearly completely retained in the solid product at these temperatures [15-23]. A recent study has found that torrefaction of birch wood at 240 °C resulted in an approximately 25% decrease in Cl and 40% decrease in S; while torrefaction of birch at 280 °C resulted in an 85% and 55% decrease in Cl and S contents, respectively [15]. In this same study with birch wood, there was not observed a release of K at torrefaction conditions [15]. Similarly, it has been found that the torrefaction of corn stover at 250 and 280 °C resulted in sulfur release [16]. Jensen et al. (2000) pyrolyzed straw in a nitrogen atmosphere in the temperature range from 200 – 1050 °C. They observed that the Cl was released in two steps. Approximately 60% of the Cl was released between 200 – 400 °C, and the residual Cl was released between 700 and 900 °C. They also observed that no significant amount of K was volatilized below 700 °C [17]. Björkman & Strömberg (1997)
showed that 20 – 50% of the Cl was released during pyrolysis of some biomasses (sugarcane trash, switch grass, lucerne and rape straw) below 400 °C [18]. Knudsen et al. (2004) suggested Cl to be released as HCl gas during pyrolysis at temperatures below 500 °C. They found that biomass with a higher content of Cl, released a lower fraction of the Cl than biomass with a lower content of Cl. They proposed that the release of Cl is probably caused by a reaction between KCl and the organic part of the biomass [13]. Zintl et al. (1998) performed experiments with mixtures of KCl and wood in the temperature range of 200 – 700 °C, and proposed that the initial low temperature release of Cl originate from a reaction between KCl and carboxylic groups as shown in reaction (4.1) [19].

\[ R - COOH(s) + KCl(s) \rightarrow R - COOK(s) + HCl(g) \]  

(4.1)

The release of methyl chloride (CH$_3$Cl) from leaves and woody biomass has been studied by Hamilton et al. (2003). In that work, CH$_3$Cl emission was observed at the initial temperature of 150 °C, and significantly increased as the temperature increased to 300 °C [20]. They proposed that pectin, a major component of the primary cell wall, could be contributing to the evaporation of methyl chloride, and suggested that the pectin could be instrumental in the release of CH$_3$Cl by acting as CH$_3$ donor [20]. An analytical method for the determination of CH$_3$Cl in producer gas from biomass gasification has been developed by Egsgaard et al. [2010]. They found by analysis of released gases from straw that pectin can react with chloride ions to form methyl chloride (as shown in Figure 4.1), and the gas phase release of the methyl chloride has already been completed at a temperature of 300 °C [21].

![Figure 4.1 Reaction for the formation of methyl chloride (CH$_3$Cl) as illustrated by Egsgaard et al. (2010)](image)

In another study, Knudsen et al. (2004) investigated sulfur transformation during thermal conversion of two straw samples. They measured that 35 and 50% of the total straw sulfur was released during pyrolysis up to 400 °C, and suggested that the initial release of S is related to
the degradation of organic sulfur compounds (proteins) [22]. Knudsen et al. (2004) made a comparison of sulfur release from two straws with different contents of organic and inorganic sulfur. The straw with the highest inorganic sulfate content showed the lowest sulfur release during devolatilization, supporting the hypothesis that the initial sulfur release originates from decomposition of organic sulfur [22]. Dayton et al. (1999) who investigated the sulfur release from straw by using a molecular beam mass spectrometer (MBMS) technique on combustion products, made a similar conclusion as no alkali release apparently accompanied the initial sulfur release [23].

It is important to have some knowledge on how sulfur is associated in the biomass structure in order to understand the release behavior of sulfur. Sulfur forms a wide variety of compounds in biomass, both organic and inorganic, and it can exist in oxidation states ranging from (-II) to (+VI) [22]. Rennenberg et al. (1990) proposed a reductive sulfur assimilation mechanism during growth, in which sulfur (as sulfate) is absorbed by the plant roots and transported to the leaves where a reduction process occurs [24]. A gradual reduction results in the incorporation of S into the organic structure of the plant via the transformation into the amino acids cysteine and methionine from which plant protein are synthesized [24]. This mechanism does provide a qualitative description of the occurrence and distribution of the different sulfur forms in biomass. In straw, sulfate is transported from the roots, through the stem, and up to the leaves, while organically bound sulfur such as protein and sulfur lipids are also found throughout the plant tissue [24]. Since the S content in biomass is distributed between organic and inorganic compounds, a two step release mechanism for S can be observed. A few studies suggested that the organically associated S is released at low temperatures, while inorganic S is retained in the ash up to combustion temperatures of 900 °C [13,25-27]. Johansen et al. (2011) assumed that the S release started at 200 °C as the decomposition of cysteine and methionine (the two main S-containing precursors for plant protein) occur at 178 and 183 °C, respectively [25,28]. Lang et al. (2005) observed significant differences in S release, even within the biomass fuel subclasses, and they did not see any clear trend related to the difference between woody and herbaceous biomasses [29]. The fraction of sulfur released during biomass pyrolysis to the gas phase at temperatures above 400 °C was greater than 50%, while only a small amount of additional S was released at temperature above 500 °C. They also showed an enrichment of sulfur in the char when the
Pyrolysis is performed at a temperature above 325 °C, showing the possibility of the produced char to recapture the devolatilized S [29].

As mentioned above, some Cl and S are released to the gas phase at torrefaction temperatures, but quantitative data of the amount of Cl and S released at low pyrolysis temperature from different biomass is limited. Also the degree to which Cl is released as HCl or CH₃Cl is uncertain. If the gas is used in a combustion unit, the Cl and S species may cause corrosion of heat transfer surfaces. Therefore it is desirable to have more knowledge on the amount of Cl and S released during torrefaction. The main objective of this study is to quantify the release of Cl and S from different biomasses pyrolyzed in the temperature range of 150 – 500 °C in a nitrogen atmosphere. These conditions are relevant to torrefaction and pyrolysis conditions.

### 4.2 Experimental Section

#### 4.2.1 Fuel analysis

The investigated biomass samples used in this study were two herbaceous biomasses (Danish wheat straw and miscanthus) and four woody biomasses (spruce chips, spruce bark, waste wood, and short rotation coppice (SRC) poplar). All the samples were ground to a particle size less than 4 mm. The chemical analyses of the biomass were performed by Bioenergy 2020+ GmbH, Graz, Austria [30]. The ash content was determined according to CEN/TS 14775 by determination of the residue on ignition at 550 °C. The elemental compositions were determined according to CEN/TS 12290/15297 by pressure decomposition in acid and detected by inductively coupled plasma-optical emission spectroscopy (ICP-OES), while Cl was quantified by ion chromatography following CEN/TS 15289. An additional spruce sample was prepared by impregnation with 2 wt% of KCl in order to investigate the release from woody biomass with a higher Cl content. To add KCl to the spruce, 5 g of KCl was dissolved in 250 mL of deionized H₂O and 1 mL of this solution was added to 1 g of sample to provide 2 wt% KCl in the sample [31]. The wood and solution were thoroughly mixed to give as uniform distribution of the salt as possible. After that the sample was dried in
a desiccator under vacuum at room temperature. The biomass carbohydrate compositions for four biomasses were analysed according to the ASTM E 1758-01 and Kaar et al. (1991), and the details about the analysis can be found elsewhere [32-34].

The uronic acid contents (pectin measurement) of the raw biomass samples were analyzed using acid methanolysis combined with gas chromatography-mass spectrometry (GC-MS) analysis. Approximately 15 mg biomass was weighed in and $^{13}$C labeled glucose was added and was used as internal standard. The samples were then freeze dried and subjected to acid methanolysis and acetylation. The methanolysis and acetylation procedure is described elsewhere [35]. The samples were analyzed by GC-MS using a Hewlett Packard HP 6890 gas chromatograph interfaced to a HP5973 Mass Selective Detector (Agilent, Denmark). Samples (1 μl) were injected in split mode (1:20) using an HP 7683 autosampler (Agilent, Denmark). The source and rod temperatures were 230 °C and 150 °C, respectively. The products were separated using a 0.32-mm i.d.$\times$30 m WCOT-fused silica column coated with VF-23ms at a thickness of 0.25 μm (Analytical, Denmark). The carrier gas was He at a flow rate of 1.2 ml/min. Separation of products was achieved using a temperature program from 70 to 250 °C at 10 °C/min. The applied ionization energy was 70 eV. Full mass spectra were recorded every 0.3 s (mass range m/z 40–450). Products were identified using the NIST search engine version 2.0 f. (Agilent, Denmark) and retention times of a standard monosaccharide and sugar acid mixture.

4.2.2 Lab-scale release experiments

4.2.2.1 Rotating kiln reactor

Experiments were conducted in a rotating kiln reactor which included a reactor chamber (inner diameter = 70 mm and length = 200 mm), a water cooling section, an electrically heated furnace, and a gas cooling section. The details regarding the experimental setup can be found in Saleh et al. (2013).

Batch experiments with 20 g of biomass were conducted at temperatures in the range of 150 – 500 °C. The reactor chamber is located inside the electrically heated furnace and a motor is used to rotate the reactor chamber. In the conducted experiments, a biomass sample was introduced into the reactor chamber and placed in the water cooled part of the set up. The
reactor was then purged with nitrogen to avoid combustion. After five minutes of purging, the reactor chamber was quickly pushed into the hot zone and the rotation was started (120 rpm). The biomass sample was heated for 60 minutes in nitrogen atmosphere (flow rate of 0.2 Nl/min) until the desired temperature was reached, and the torrefaction was continued for 15 minutes at the final temperature. The reactor chamber was then cooled in the cooling section and the char was collected and analyzed with respect to Cl and S content. The release of Cl and S was calculated based on the Cl and S analysis of the raw biomass and solid product, and solid yield. In selected experiments, the gas from straw torrefaction was collected in gasbags to analyze methyl chloride content by using GC-MS [21].

4.2.2.2 Fixed bed tube reactor

A horizontal tube reactor was furthermore used for the release studies. A small sample size (2–4g) was applied in this reactor compared to the rotating kiln (20 g) as mentioned previously. The setup consists of a gas mixing system, a horizontal tube reactor, a gas conditioning system, gas analyzers, a thermocouple and a data acquisition system. The details regarding the experimental setup can be found in Johansen et al. (2011) and Knudsen et al. (2004) [25,36]. Torrefaction was performed in the temperature range of 200 – 500 °C with a gas flow of 2 Nl/min of N₂. In the experiments, the tube reactor was preheated to a desired temperature, and an alumina boat with 3 g of sample was then inserted into the reactor. The residence time was 90 minutes from when the sample was inserted into the reactor until the sample was pulled out to the cooling section. After cooling, the char was collected and analyzed.

4.2.3 Analysis of residues

The raw and torrefied biomasses were analyzed by two different laboratories using different methods, as shown in Table 4.1. Firstly, some torrefaction and pyrolysis experiments were conducted and the samples were analyzed by DONG Energy Power A/S at Enstedværket, Denmark. The contents of Cl and S were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) after pressure decomposition in an acid following standard
DS/EN 15290 (2011). However, a few samples which had relatively low initial Cl and S contents (most of the woody biomass) could not be detected using this method. Therefore another set of experiments were performed and the samples were analyzed at Åbo Akademi University, Turku, Finland by using the following method. To measure chloride, the chloride was first leached with water and then the solution was analyzed for chloride by ion chromatography (IC). The samples were ground to less than 1 mm and then 2 g of sample was added to 30 ml of water and shaken for one day, after which the whole suspension was filtered. Ion chromatography with conductivity detection was used to quantify the concentration of Cl⁻ in the leachate. A Metrosep A SUPP-5 column was used with an eluent of 1.0 mM NaHCO₃ and 3.2 mM Na₂CO₃ in ultra-pure water. The leachate was analyzed 6 times for each sample to get the standard deviations for the IC analysis. For calibration, standards were prepared from high purity (p.a.) sodium chloride. To analyze total sulfur, the sample was first decomposed, and then analyzed by ICP-OES by the following procedure. A sample of 0.2 g of the oven dried sample was placed into a Teflon bomb and 5 ml of HNO₃ (65%) + 1 ml H₂O₂ (30%) + 1 ml HClO₄ (70%) were added to the sample. For the samples pyrolyzed at temperatures higher than 250 °C, HBF₄ was also added to successfully digest the chars. The sample was digested in a microwave oven (Anton Paar, Multiwave 3000) and then diluted to 100 ml by deionized water. Finally, the amount of sulfur was quantified with ICP-OES. Sulfur was analyzed at 181.975 nm and a commercial standard (ICP-016) from Ultra Scientific (RI, USA) was used for calibration. The used acids were of high purity (suprapur®, Merck).

The collected gas samples, stored in gasbags, were analyzed for methyl chloride using GC-MS. A 100 µl gas sample was taken out from each gasbag sample using a gas syringe and was directly injected into the GC-MS system. Standards of methyl chloride were volumetrically prepared by injecting known volumes (50 to 500 µl) of 1000 ppm of methyl chloride in nitrogen and a standard curve was generated and used for methyl chloride quantification. The gas analyses were performed using a Varian 3400 gas chromatograph, interfaced to a Saturn II ion trap mass spectrometer (Varian Inc., USA). Samples were injected manually using a Pressure-Lok® syringe (VICI Precision Sampling, Inc, USA), and introduced in split mode (approximately 1:50) at a temperature of 150 °C. Both the GC to MS transfer line and the manifold of the mass spectrometer were kept at 200 °C. Separation was established using a 0.32 mm i.d. x 25 m fused silica column coated with 10 µm PoraPLOT U (Analytical,
Denmark). Appropriate separations were achieved isothermally at 80 °C. Full mass spectra were recorded every 0.5 s (mass range m/z 35 - m/z 100).

**Table 4.1** List of samples analyzed by Dong Energy and ÅAU

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Temperature, °C</th>
<th>Sample size, g</th>
<th>Analyzed by</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dong Energy</td>
</tr>
<tr>
<td>Straw</td>
<td>150</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Straw</td>
<td>250</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Straw</td>
<td>350</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Straw</td>
<td>500</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Straw</td>
<td>350</td>
<td>5</td>
<td>√</td>
</tr>
<tr>
<td>Straw</td>
<td>350</td>
<td>10</td>
<td>√</td>
</tr>
<tr>
<td>Straw</td>
<td>350</td>
<td>40</td>
<td>√</td>
</tr>
<tr>
<td>Straw (with grinding)</td>
<td>250</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Straw (with grinding)</td>
<td>350</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Spruce Wood+KCl</td>
<td>250</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Spruce Wood+KCl</td>
<td>350</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Spruce Bark</td>
<td>250</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Spruce Bark</td>
<td>350</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>SRC Poplar</td>
<td>250</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>SRC Poplar</td>
<td>350</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Waste Wood</td>
<td>250</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Waste Wood</td>
<td>350</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>250</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>350</td>
<td>20</td>
<td>√</td>
</tr>
<tr>
<td>Bark (spruce)</td>
<td>250</td>
<td>3</td>
<td>√ (S only)</td>
</tr>
<tr>
<td>Bark (spruce)</td>
<td>350</td>
<td>3</td>
<td>√ (S only)</td>
</tr>
<tr>
<td>Wastewood</td>
<td>350</td>
<td>3</td>
<td>√ (S only)</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>250</td>
<td>3</td>
<td>√</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>350</td>
<td>3</td>
<td>√</td>
</tr>
<tr>
<td>SRC (Poplar)</td>
<td>250</td>
<td>3</td>
<td>√ (S only)</td>
</tr>
<tr>
<td>SRC (Poplar)</td>
<td>350</td>
<td>3</td>
<td>√ (S only)</td>
</tr>
<tr>
<td>Straw</td>
<td>200</td>
<td>3</td>
<td>√</td>
</tr>
<tr>
<td>Straw</td>
<td>350</td>
<td>3</td>
<td>√</td>
</tr>
<tr>
<td>Straw</td>
<td>450</td>
<td>3</td>
<td>√</td>
</tr>
<tr>
<td>Spruce+2wt%KCl</td>
<td>350</td>
<td>3</td>
<td>√ (Cl only)</td>
</tr>
</tbody>
</table>

Notes: Double check marks (✓✓) represent two samples from different experimental runs
4.3 Results and Discussion

4.3.1 Fuel analysis

The chemical compositions of the six biomasses used in this study are listed in Table 4.2. Significant differences in the Cl and S contents are observed in the fuels investigated. As shown in Table 4.2, the Cl and K contents in straw and miscanthus (herbaceous biomasses) are significantly higher than in the other fuels. The woody biomasses have lower contents of Cl, S and K, however bark has a moderate content of K. Ca is the dominating ash-forming element for the wood fuels, while the straw ash is rich especially in Si. Straw has the highest contents of P and Na, followed by bark and miscanthus and the other wood fuels. It is observed that the biomasses used in this study cover a wide range of ash content and ash-forming elements.

Table 4.2 Composition of the raw biomasses

<table>
<thead>
<tr>
<th>Component (wt% dry)</th>
<th>Wheat Straw</th>
<th>Miscanthus</th>
<th>Bark (Spruce)</th>
<th>Spruce</th>
<th>Waste wood</th>
<th>SRC(poplar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>5.57</td>
<td>2.26</td>
<td>4.98</td>
<td>0.34</td>
<td>1.70</td>
<td>1.75</td>
</tr>
<tr>
<td>C</td>
<td>45.93</td>
<td>47.97</td>
<td>49.66</td>
<td>48.88</td>
<td>49.01</td>
<td>48.48</td>
</tr>
<tr>
<td>H</td>
<td>5.86</td>
<td>5.92</td>
<td>5.63</td>
<td>6.23</td>
<td>6.13</td>
<td>6.06</td>
</tr>
<tr>
<td>O</td>
<td>41.87</td>
<td>43.54</td>
<td>39.36</td>
<td>44.54</td>
<td>41.77</td>
<td>43.32</td>
</tr>
<tr>
<td>N</td>
<td>0.64</td>
<td>0.28</td>
<td>0.34</td>
<td>0.02</td>
<td>1.33</td>
<td>0.36</td>
</tr>
<tr>
<td>S</td>
<td>0.13</td>
<td>0.027</td>
<td>0.03</td>
<td>0.004</td>
<td>0.061</td>
<td>0.03</td>
</tr>
<tr>
<td>Cl</td>
<td>0.19</td>
<td>0.152</td>
<td>0.01</td>
<td>0.003</td>
<td>0.034</td>
<td>0.005</td>
</tr>
<tr>
<td>K</td>
<td>0.90</td>
<td>0.49</td>
<td>0.18</td>
<td>0.03</td>
<td>0.07</td>
<td>0.29</td>
</tr>
<tr>
<td>Si</td>
<td>1.40</td>
<td>0.45</td>
<td>0.32</td>
<td>0.007</td>
<td>0.17</td>
<td>0.04</td>
</tr>
<tr>
<td>Al</td>
<td>0.006</td>
<td>0.008</td>
<td>0.073</td>
<td>0.003</td>
<td>0.045</td>
<td>0.009</td>
</tr>
<tr>
<td>P</td>
<td>0.095</td>
<td>0.020</td>
<td>0.034</td>
<td>0.003</td>
<td>0.009</td>
<td>0.073</td>
</tr>
<tr>
<td>Fe</td>
<td>0.008</td>
<td>0.008</td>
<td>0.053</td>
<td>0.002</td>
<td>0.036</td>
<td>0.014</td>
</tr>
<tr>
<td>Mg</td>
<td>0.079</td>
<td>0.055</td>
<td>0.081</td>
<td>0.011</td>
<td>0.044</td>
<td>0.046</td>
</tr>
<tr>
<td>Ca</td>
<td>0.433</td>
<td>0.130</td>
<td>1.290</td>
<td>0.104</td>
<td>0.320</td>
<td>0.412</td>
</tr>
<tr>
<td>Na</td>
<td>0.011</td>
<td>0.003</td>
<td>0.01</td>
<td>&lt;0.001</td>
<td>0.033</td>
<td>0.004</td>
</tr>
</tbody>
</table>
The results from the carbohydrate analyses are presented in Table 4.3. These biomasses have a reasonably similar carbohydrate composition with the exception of the spruce bark, which is lower in hemicelluloses content (12 wt% db) compared to the other biomasses (18 – 25 wt% db). The spruce bark is also lower in cellulose content with 22 wt% db compared to 43 – 48 wt% db for the other biomasses, and has a higher lignin content of 35 wt% db compared to 17 – 27 wt% db of the other biomasses. Straw and miscanthus have reasonably higher xylan-based hemicelluloses content, while spruce chips has a significant amount of mannan-based hemicelluloses content.

Table 4.3 Carbohydrate composition of the raw biomasses

<table>
<thead>
<tr>
<th>Components (wt% dry)</th>
<th>Straw</th>
<th>Miscanthus</th>
<th>Spruce chips</th>
<th>Spruce bark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylan-based hemicelluloses</td>
<td>23.1</td>
<td>18.1</td>
<td>5.6</td>
<td>3.9</td>
</tr>
<tr>
<td>Mannan-based hemicelluloses</td>
<td>0</td>
<td>0</td>
<td>11.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Other hemicelluloses</td>
<td>2.3</td>
<td>2.0</td>
<td>1.8</td>
<td>5.0</td>
</tr>
<tr>
<td>Total hemicelluloses</td>
<td>25.4</td>
<td>20.1</td>
<td>18.4</td>
<td>12.9</td>
</tr>
<tr>
<td>Cellulose</td>
<td>42.7</td>
<td>48.5</td>
<td>45</td>
<td>24.1</td>
</tr>
<tr>
<td>Lignin</td>
<td>17.3</td>
<td>22.4</td>
<td>27.6</td>
<td>36.8</td>
</tr>
<tr>
<td>Ash</td>
<td>5.57</td>
<td>2.26</td>
<td>0.34</td>
<td>4.98</td>
</tr>
<tr>
<td>Extractives</td>
<td>3.2</td>
<td>4.3</td>
<td>1.0</td>
<td>5.7</td>
</tr>
<tr>
<td>Residuals</td>
<td>5.8</td>
<td>2.4</td>
<td>7.7</td>
<td>15.5</td>
</tr>
</tbody>
</table>
4.3.2 Chlorine release

4.3.2.1 Torrefaction of straw

The relative release of chlorine was calculated by use of mass balance and analysis of the biomass before and after torrefaction. The results from torrefaction of straw in the rotating kiln reactor are presented in Figure 4.2. The replicated data points shown in Figure 4.2 represent the separate runs with single analysis for each run. The samples were analyzed by different laboratories, which were Dong Energy (Lab_1) and ÅAU (Lab_2), using different methods as shown in Figure 4.2. Some difference in Cl release between the two methods used is observed in Figure 4.2, mainly for the samples at 250 and 500 °C. However, for most of the replicated samples analyzed at both laboratories, it is observed that the Cl measurements could be repeated within 10%, while the result in Figure 4.2d shows a good repeatability. Repeated measurements of methyl chloride (CH$_3$Cl) shown in Figure 4.2b deviates up to 17%. It is not expected that significant amounts of Cl are released to the gas phase at temperatures below 200 °C which indicates that the Cl release at 150 °C (as can be seen in Figure 4.2a,b) probably is related to the uncertainty on the experimental procedure [17,18].

The released chlorine during straw torrefaction at different temperatures is shown in Figure 4.2a. The initial Cl release is somewhat uncertain because of the uncertainty of the mass balance measurements, however approximately 20% of the Cl was released at 250 °C. The release increased to 64% when the temperature was increased to 350 °C, while further increasing the temperature up to 500 °C did not significantly increase the Cl release. The amounts released were similar to those seen by Khazraie et al. (2013) for the torrefaction of birch wood at 240 and 280 °C [15]. Jensen et al. (2000) found that chlorine was released from straw in two steps during pyrolysis: 60% was released between 200 – 400 °C and the residual Cl was released between 700 and 900 °C [17]. According to most studies, the major form of chloride released during pyrolysis has been proposed to be HCl in the temperature range of 250 and 500 °C [13,18]. However, studies conducted by Hamilton et al. (2003) and Egsgaard et al. (2010) show that volatilization of chloride as methyl chloride (CH$_3$Cl) occurs during biomass pyrolysis at temperatures below 350 °C. In this study, the amount of CH$_3$Cl released was measured at different temperatures by collecting pyrolysis gas in a gasbag and the results are presented in Figure 4.2b. As can be seen in Figure 4.2b, a major part of the released Cl
appeared as CH$_3$Cl. At 350 °C, about 50% of the fuel Cl content was released as CH$_3$Cl and a similar level was seen at 500 °C. This result is in agreement with Hamilton et al. (2003) where they found that CH$_3$Cl release had terminated by the time 300 °C was reached.

Figure 4.2c shows the influence of grinding the biomass sample with metal balls (tungsten) during torrefaction on the chlorine release at 250 and 350 °C. During the process, the reactor was heated and the sample was ground to a small particle size. No influence of grinding is seen at 250 °C, while at 350 °C, grinding seems to increase the chlorine release. The release increased up to 20% when the grinding process was simultaneously conducted with torrefaction at 350 °C. Different sample sizes (from 5 to 40 g) of straw were torrefied at 350 °C in order to investigate the influence of the sample size in the reactor on the chlorine release. The result is presented in Figure 4.2d, where about 80% of the chlorine was released when a small amount of sample (5-10 g) was used. By applying a large amount of sample (40 g), the fraction of the Cl released was reduced to 54%. As discussed by Jensen et al. (2000), secondary reactions may take place if a large amount of sample is used [17]. The secondary reactions can be reaction with relatively stable basic functionalities on the char surface or reaction with potassium to generate KCl [17]. Knudsen et al. (2005) studied the ability of biomass char to capture HCl from a gas stream in the temperature range of 400 – 800 °C. They observed that 87% of the added HCl (0.16 mmol/g straw) in a gas stream was captured in the char at 600 °C, while increasing the HCl to 0.52 mmol/g straw reduced the capture efficiency to 67% [37]. They proposed that the capture efficiency will decrease as a function of load, because the reactive sites in the char are gradually occupied, and they discovered that the capture of HCl was entirely governed by the inorganic metal species (mainly potassium) of the biomass [36]. In the present study, pyrolysis at 350 °C in the rotating kiln reactor of 40 grams of straw produced about 15 g of torrefied solid, while 20 grams of straw produced 7 grams of torrefied solid. In the case of 40 g of straw, more char is produced, thus the gas to solid ratio changes and the capture efficiency is increased, resulting in lower release of Cl compared to the 20 gram straw torrefaction case. The N$_2$ gas flow during torrefaction was fixed to 0.2 Nl/min.
Figure 4.2 Cl release from straw torrefaction in rotating kiln reactor; a) influence of temperature, b) mass balance results compared with CH₃Cl formation, c) influence of grinding on Cl release, and d) influence of sample size with the experiment at 350 °C. Error bars represent a standard deviation of six replicate analysis of each sample analyzed by ÅAU. (Lab_1 = analyzed by Dong Energy, Lab_2 = analyzed by ÅAU)

4.3.2.2 The influence of biomass type

Figure 4.3 shows the release of chlorine during torrefaction of several biomasses at 250 and 350 °C (for straw in the temperature range of 150 to 500 °C). The biomasses can be classified into herbaceous biomass (straw and miscanthus) and woody biomass (bark, waste wood, SRC poplar, and spruce impregnated with KCl). In Figure 4.3a, the chlorine release from
miscanthus was slightly higher than from straw at 250 °C, while significantly higher at 350 °C. Figure 4.3a also showed a comparison of chlorine release from 3 g (fixed bed) and 20 g (rotating kiln reactor) of straw and miscanthus. The results of the 3 and 20 g experiments are similar. From the results on the influence of sample size as discussed in torrefaction of straw, it was observed that a higher fraction of Cl is released from a smaller sample size. In this work, though, we have used two different reactors even that a small sample size is used in the fixed bed reactor the released gases pass through the bed material and this may cause the similar release levels.

The chlorine release for different wood samples is shown in Figure 4.3b. Chlorine release was between 40 and 60% at 250 °C and between 85 and 98% at 350 °C for the undoped wood samples, but about 20% lower for the wood with KCl added. Most of the chlorine was released at 350 °C from waste wood, bark and SRC (poplar), whereas only 58% was released from the KCl-impregnated spruce.

![Figure 4.3 Influence of temperature on Cl release from a) herbaceous and b) woody biomasses](image)

To further analyze the results, the released chlorine as a function of initial chlorine content in the biomass samples is plotted in Figure 4.4a. It is seen that a higher Cl fraction is released from the samples with the lower chlorine content (bark, waste wood and SRC poplar). About 85 – 95% of chlorine is released from these biomasses at 350 °C. There is generally observed a decreased fraction of Cl release with an increased biomass Cl content, the only exception is
for miscanthus pyrolyzed at 350 °C. This result agrees with a previous study that also showed the Cl release during devolatilization is dependent on the biomass initial Cl content [13]. Adding KCl to the low-chlorine content spruce, resulted in a lower release fraction of Cl, as also observed by Björkman and Strömberg (1997). They suggested that by adding inorganic salt to wood, the chlorine atoms have a possibility to interact with the organic material [18]. In Figure 4.4b, the fraction of chlorine released is plotted as a function of biomass potassium (K) content. A relatively linear decreasing trend is observed for the chlorine released when the biomass K content is increased for both temperatures. It is seen that the release was almost complete at 350 °C for the waste wood and bark which have K content less than 0.2 wt%. Straw with a relatively higher K content released the lowest amount of Cl at both temperatures for the untreated biomass. KCl-impregnated spruce which has the highest K content shows the lowest fraction of Cl released.

Hamilton et al. (2003) proposed that pectin, a major component of the primary cell wall, could contribute to the release of methyl chloride. They suggested that the pectin could be instrumental in the release of CH$_3$Cl as a CH$_3$ donor [20]. In this study, the pectin content in each biomass was measured, and the chlorine release is plotted as a function of pectin content and Cl-to-pectin ratio (dry weight basis) in Figures 4.4c and 4.4d, respectively. Minor (<1.0 wt%) pectin contents were found in the miscanthus, spruce chips and waste wood samples. The highest pectin content appeared in the spruce bark and in the wheat straw samples. Spruce bark showed a significantly higher pectin content than spruce chips. The pectin levels are higher in the spruce bark than in the internal parts of the wood samples, for example in spruce wood chips [38,39]. It has been proposed that the Cl release is controlled by the reaction of KCl with pectin [20]. However in Figure 4.4c, there is no significant correlation between Cl release and biomass pectin contents observed at either temperature. The results are scattered without any significant trend. While in Figure 4.4d, it is seen that the release was almost complete at 350 °C for the woody biomass which have the Cl-to-pectin ratio less than 0.1. However, a different result is observed for straw even though straw has a Cl to pectin of ratio less than 0.08. A lower Cl release at 250 and 350 °C are seen for straw compared to the woody samples. Miscanthus has a Cl to pectin ratio of 0.4 and shows almost similar release as the woody biomasses.
Generally there is seen a reasonable clear tendency, that an increased Cl and K contents leads to a decreased fraction of Cl gas phase release. This could indicate that the Cl release is controlled by a reaction between KCl and organic constituents. However, the pectin concentration in the biomass does not seem to be rate limiting and the measuring data indicates that other organic species than pectin also acts as CH$_3$ donors. The Cl release up to 350 °C (as seen in Figure 4.2b) is dominated by release of CH$_3$Cl, however minor amounts of other Cl-species seems to be recaptured on char and contained as KCl [37]. While most of the measuring data in this study can be explained by a primary release of CH$_3$Cl and some recapture of Cl by the K contained in the char, there are some of the data (miscanthus release in Figures 4.4a and 4.4b) that cannot be completely explained by these mechanisms.

![Figure 4.4](image_url)

**Figure 4.4** Release of Cl as a function of biomass a) chlorine (Cl) content, b) potassium (K) content, c) pectin content; and d) Cl to pectin ratio
4.3.3 Sulfur release

The release of sulfur from straw torrefaction is shown in Figure 4.5. A considerable deviation between the two measurements (from different laboratories) at each condition is observed in Figure 4.5. This difference probably resulted from the different analysis methods used to measure the release. It is seen in Figure 4.5a that the release of sulfur gradually increases from 200 to 500 °C, and approximately 60% of the straw sulfur content is released to the gas phase at 500 °C. As mentioned by Johansen et al. (2011), the initial S release is expected to begin as the cysteine and methionine (two main S-containing precursors for plant protein) start to decompose at 178 and 183 °C, respectively [25]. A similar result was obtained by Knudsen et al. (2004) and they demonstrated that 35 to 50% of the total biomass sulfur was released during the devolatilization process (200 – 400 °C), and assumed that the initial release of S is related to the degradation of the organic structure [22]. In experiments with different amounts of straw at 350 °C (Figure 4.5b), there was a gradual decrease of S release when the sample amount was increased, as observed in Cl release. In Figure 4.5c, a higher release of S is observed when grinding was applied during torrefaction at 350 °C. Simultaneous torrefaction and grinding possibly provide less contact between gas phase S and char, thus reducing the possibility of secondary capture of S in char matrix, resulting in a higher release of S.
Figure 4.5 S release from straw torrefaction; a) influence of temperature, b) influence of sample amount at 350 °C, and c) influence of grinding on S release. (Lab_1 = analyzed by Dong Energy, Lab_2 = analyzed by ÅAU)
Figure 4.6 shows the release of sulfur from herbaceous and woody biomasses during pyrolysis. The release of S from straw and miscanthus are similar (Figure 4.6a), where some S is released at 250 °C, and gradually increased to approximately 50% at 350 °C. About 20 – 35% of S is released at 250 °C from the woody biomasses, and the release increases to approximately 60% for all samples at 350 °C (Figure 4.6b). Literature data indicated that the release of S at 200 – 400 °C could originate from the decomposition of organically-associated S in the proteins [22,23]. Therefore the fraction of S released during devolatilization was related to the distribution between organic and inorganic S forms in biomass [22]. There is no observed relationship between the biomass sulfur content and the fraction of S released during pyrolysis as illustrated in Figure 4.7. Lang et al. (2005) also did not observed any clear relationship between the fraction of sulfur release and the biomass type (woody or herbaceous fuels). As mentioned above, the release of S is probably dependent on the content of organic and inorganic S in biomass and that was not measured in the study.

**Figure 4.6** Influence of temperature on S release for a) herbaceous and b) woody biomasses
4.4 Conclusions

In this study, the release of chlorine and sulfur from six different biomasses at torrefaction conditions was investigated. Release of chlorine is already observed at 250 °C and about 64% of the chlorine in straw is released at 350 °C. Analysis of the released gas showed that the CH₃Cl is the main Cl compound in the gas phase. Regarding the influence of biomass amount in a reactor, the results from this study were consistent with earlier findings that a larger sample size resulted in a lower Cl release. The practical implication of these results is that chloride release from torrefaction will depend on both temperature and the contact between the off gas from torrefaction and the biomass being torrefied. For woody biomass, most of the chlorine is released at 350 °C. The woody biomasses have a lower chlorine content (less than 0.04 wt %) compared to the herbaceous biomasses (0.15 – 0.19 wt%). A higher fraction of chlorine was released from the samples with the lower Cl and K contents. The fraction of Cl release may be controlled by a reaction between KCl and organic constituents of the biomass. It has been shown that a mixture of KCl and pectin can release CH₃Cl when heated in N₂ [21], but the results in this study showed that there was no correlation between Cl release and
biomass pectin concentration, indicating that the pectin concentration in the biomass is not the rate limiting for the chlorine release.

The fraction of S release from straw and miscanthus is similar, with about $50 - 60\%$ of S released at 350 °C. For the four wood samples investigated, a sulfur release fraction of $20 - 50\%$ was observed at 250 °C and a release fraction of $40 - 70\%$ at 350 °C. When comparing the S release with the initial S content in biomass, there is no clear trend at the investigated temperatures. These results clearly show that torrefaction and pyrolysis at temperature below 500 °C reduce the concentration of both Cl and S in biomass. This can be an added benefit of torrefaction for the solid fuel produced, though these results indicates that high Cl biomass fuels will release a lower proportion of the Cl. Additionally, this work shows that the major gaseous chlorine containing species released is CH$_3$Cl in low temperature processes. More research is needed to clarify the controlling mechanism for the Cl and S release at torrefaction and pyrolysis temperatures.

4.5 References


Chapter 5  Conclusions and future works

5.1 Conclusions

A potential utilization of a torrefaction process is by integration with a power plant, thereby a high total energy efficiency can be obtained. The gas released during the torrefaction process can be used to supply the energy needed for torrefaction or by supplied to the boiler. The main idea for this project was to develop biomass pretreatment method that could provide the heating value of the fuel for a boiler, and at the same time the solid fuel product can be easily grinded. Therefore, a novel laboratory scale experimental set up for simultaneous torrefaction and grinding was constructed. The investigations conducted in this study were mainly focused on: 1) the development of experimental procedures for a new laboratory scale experimental setup (simultaneous torrefaction and grinding reactor); 2) a broader range of biomasses have been tested to study the influence of biomass chemical properties such as ash content, ash composition and carbohydrate composition on torrefaction characteristics; and 3) quantification of chlorine and sulfur gas phase release during torrefaction.

The main findings obtained from this work are summarized as follows:

1. The influence of operation conditions such as reactor temperature and residence time on mass loss, energy loss and particle size reduction have been established for wood and straw. A significant difference between the torrefaction characteristic of straw and spruce was observed. Straw experienced a larger mass loss at lower temperature than spruce, resulting in larger size reduction of the straw compared to the spruce. This means that at the same temperature, straw yields a higher mass loss and size reduction than spruce. The observed different mass loss profiles of straw and spruce can be related to differences of hemicelluloses type, lignocelluloses compositions, catalytic properties of the ash or to the difference in shape and mass of the biomass particle. TGA analysis shows that the observed differences in solid yield should be related to the chemical differences between spruce and straw since the heat transfer conditions in the STA is similar for the two samples.
Experiments with separate heating and grinding of straw showed a swift grinding of biomass pre-exposed to torrefaction temperatures in a fixed bed. The particle size reduction obtained after 30 and 90 minutes combined torrefaction and grinding experiments was obtained in only 5 minutes of grinding in the separate grinding and torrefaction experiments. This result implies that the heat transfer is the rate limiting step and not the grinding process. The results of experiments to study the particle size influence on pine wood torrefaction showed that the mass yield decreased with increasing particle diameter for torrefaction at 320 °C (90 minutes). This is possibly related to exothermic reactions taking place during torrefaction of larger particles (8 – 16 mm), where the larger wall thickness offer a higher thermal resistance resulting in a higher particle core temperature, thus increasing the mass loss of the solid product.

2. The influence of biomass composition on the torrefaction process was investigated by treating six different biomasses and some biomasses impregnated with KCl or K$_2$CO$_3$ on a TGA and in the laboratory torrefaction reactor. It was observed that the solid yield at typical torrefaction temperatures (270 to 300 °C) is strongly influenced by the biomass potassium content. High biomass potassium content leads to a relatively lower solid yield; however, in a single case a high lignin content leads to a relatively high solid yield even in the presence of relatively high potassium content. The carbohydrate composition also influences the solid yield, such that higher hemicelluloses content leads to a relatively low solid yield. It was also seen that biomasses that experiences a high mass loss during torrefaction also obtains a relatively large particle size reduction. A significant decrease in d$_{50}$ value is observed when the alkali content is increased from 0 to 0.2 wt% db, while no additional effect is seen for higher potassium contents. The results from this study show that the torrefaction characteristics were highly influenced by the biomass alkali content.

3. The gas phase release of Cl and S from six different biomasses at torrefaction/pyrolysis conditions was investigated by using the rotating kiln and fixed bed reactors. Release of chlorine is already observed at 250 °C and about 64% of the chlorine in straw is released at 350 °C. CH$_3$Cl is found to be a major Cl compound from the analysis of the gas released. Regarding the influence of biomass hold-up in a reactor, the results from this study were
consistent with earlier findings that a larger sample size resulted in less complete Cl release, at least for a reactor with good solids/gas mixing. The practical implication of these results is that chloride release in torrefaction will depend on both temperature and the contact between the off gas from torrefaction and the biomass being torrefied. For woody biomass, most of the chlorine is released at 350 °C. The woody biomasses have a lower chlorine content (less than 0.04 wt %) compared to the herbaceous biomasses (0.15 – 0.19 wt%). A higher fraction of chlorine was released from the samples with the lower Cl and K contents. The fraction of Cl release may be controlled by a reaction between KCl and organic constituents of the biomass. It has been shown that mixture of KCl and pectin can release CH₃Cl when heated in N₂ [21], but the results in this study showed that there was no correlation between Cl release and pectin concentration, indicating that the pectin concentration in the biomass is not the rate limiting for the chlorine release. In the case of sulfur release, about 60% of sulfur in biomasses is released at 350 °C from torrefaction of all investigated biomasses. There is no clear trend observed when comparing the S release with the initial S content in biomass at the investigated temperatures. Generally the results from this study clearly indicate that torrefaction and pyrolysis can reduce the concentration of both Cl and S in biomass. This can be an added benefit of torrefaction for the solid fuel produced, though these results tend to indicate that very high Cl biomass fuels will release a lower proportion of the Cl. More research is needed to clarify the controlling mechanism for Cl and S release at torrefaction and pyrolysis temperatures.
5.2 Future works

Besides the research conducted in the present study, following are the areas where more detailed investigations can further help to understand the torrefaction characteristics:

1. Evaluation on how the breakage of particles is occurred during simultaneous torrefaction and grinding.
2. Accurate evaluation on particle morphology of torrefied biomass produced and make a comparison to the raw biomass.
3. A predictive model for the particle size development during torrefaction and grinding processes.
4. Investigation on the combustion properties of torrefied biomass produced from torrefaction of different biomasses. Study the possibility to use the mixture of different torrefied biomass (from different type of raw biomass) in combustion system.
5. Evaluation on the possibility to scale up the simultaneous torrefaction and grinding reactor.
Appendix A: Simultaneous torrefaction and grinding experimental set-up

The drawings for the experimental set-up are shown in the following figures. Basically the set-up consists of an electrically heated furnace, a reactor chamber (rotating device in Figure A.1), a water cooling section, a gas cooling section, and five thermocouples. The reactor chamber is located inside the electrically heated furnace and a motor is used to rotate the reactor chamber (120 rpm).

Figure A.1 Bench scale experimental set up for simultaneous torrefaction and grinding
Figure A.2 The set-up in CHEC laboratory

Figure A.3 The reactor chamber (rotating device) is mounted to the set-up
A schematic drawing for the reactor chamber (rotating device) is shown in the following figure:

**Figure A.4** Reactor chamber equipped with rotating pins
Appendix B: Experimental procedure for simultaneous torrefaction and grinding set-up

B1: General experimental procedure

1. Turn on the ventilation in the fume cabinet.
2. Check for water in tar-glass for flue gas exhaust.
3. Close the reactor with nuts and bolts. Place the nitrogen tube at position 2 (as shown in Figure B.1). Open the nitrogen bottle and turn on the nitrogen flow at 0.2 Nl/min (set the flowmeter at ~12.5. Note: the flowmeter has a scale of 0-150, which the maximum flowrate is equal to 2.4 Nl/min at 150 flowmeter scale).
4. Turn on the oven and set the temperature on the wanted temperature. Note the time.
5. Turn on the cooling water.
6. Weigh approximately 20 grams of straw and note the weight.
7. Weigh the loader and note the weight.
8. Pour the biomass sample and metal balls into the loader, and note the weight (loader, sample and metal balls).
9. After 60 minutes heating up the oven (in order to reach the stable oven temperature profile), open the reactor. Remember to take off the nitrogen tube from position 2.
10. Place the loader to the right side of the reactor (cooling zone) and close the reactor.
11. Place the nitrogen tube at position 1 and turn on the nitrogen flow at 1.0 Nl/min (set the flowmeter at ~62.5. At this position, nitrogen is supplied directly into the loader that contains biomass sample). Close the opening part for nitrogen tube at position 2 using the closed nut.
12. After 5 minutes, turn off the nitrogen flow and take off the nitrogen tube from position 1. Take off the closed nut from position 2.
13. Push the loader into the central part of the oven.
14. Immediately place the nitrogen tube to a position 2, and turn on the nitrogen flow at 1.0 Nl/min.
15. Start the rotation by pressing start button on the oven controller panel and note the time. Note all the temperatures and pressure.
16. After 10 minutes, reduce the nitrogen flow to 0.2 Nl/min.
17. After a given time, stop the rotation by pushing the rotation button (red button near to the motor), and pull the loader to the cooling zone. Adjust the nitrogen flow to 1.0 Nl/min.
18. Let the reactor cool down to 40 °C.
19. When a temperature of 40 °C is reached, turn off the nitrogen flow (0.0 Nl/min), and close the nitrogen bottle.
20. Open the reactor and take out the loader.
21. Weigh out the loader that contains char and metal balls, and transfer the char into a suitable container and close the container quickly. Weigh the char. Make sure the loader is completely empty.
22. Turn off the oven, unless another experiment is being conducted.

![Diagram](image)

**Figure B.1** Bench scale experimental set up for simultaneous torrefaction and grinding
B2: Procedure for separate heating and grinding experiments

1. Turn on the ventilation in the fume cabinet.
2. Check for water in tar-glass for flue gas exhaust.
3. Close the reactor with nuts and bolts. Place the nitrogen tube at position 2 (as shown in Figure B1). Open the nitrogen bottle and turn on the nitrogen flow at 0.2 Nl/min (set the flowmeter at ~12.5. Note: the flowmeter has a scale of 0-150, which the maximum flowrate is equal to 2.4 Nl/min at 150 flowmeter scale).
4. Turn on the oven and set the temperature on the wanted temperature. Note the time.
5. Turn on the cooling water.
6. Weigh approximately 20 grams of straw and note the weight.
7. Weigh the loader and note the weight.
8. Pour the biomass sample into the loader, and note the weight (loader and biomass sample).
9. After 60 minutes heating up the oven (in order to reach the stable oven temperature profile), open the reactor. Remember to take off the nitrogen tube from position 2.
10. Place the loader to the right side of the reactor (cooling zone) and close the reactor.
11. Place the nitrogen tube at position 1 and turn on the nitrogen flow at 1.0 Nl/min (set the flowmeter at ~62.5. At this position, nitrogen is supplied directly into the loader that contains biomass sample). Close the opening part for nitrogen tube at position 2 using the closed nut.
12. After 5 minutes, turn off the nitrogen flow and take off the nitrogen tube from position 1. Take off the closed nut from position 2.
13. Push the loader into the central part of the oven.
14. Place the nitrogen tube to a position 2, and turn on the nitrogen flow at 1.0 Nl/min. Note the time and all the temperatures and pressure.
15. After 10 minutes, reduce the nitrogen flow to 0.2 Nl/min.
16. After a given time pull the loader to the cooling zone. Adjust the nitrogen flow to 1.0 Nl/min.
17. Let the reactor cool down to 40 °C.
18. When a temperature of 40 °C is reached, turn off the nitrogen flow (0.0 Nl/min), and close the nitrogen bottle.
19. Open the reactor and take out the loader.
20. Weigh out the loader that contains torrefied biomass, and transfer the char into a suitable container and close the container quickly. Weigh the char. Make sure the loader is completely empty.
21. Divide the torrefied biomass to several portions with 3 gram each.
22. Put the 3 g torrefied biomass into the loader and 12 metal balls, and weigh the loader. Note the weight.
23. Make sure the oven temperature is at room temperature (normally the grinding experiment is conducted after 12-24hrs of heating the biomass in the oven, in order to cool down the oven to room temperature). During the grinding experiment, the oven temperature is set to 25 °C.
24. Place the loader inside the reactor, and close the reactor.
25. Push the loader into the central part of the oven, and start the rotation by pressing start button on the oven controller panel. Note the time.
26. After grinding the sample for desired duration, stop the rotation by pushing the rotation button (red button near to the motor).
27. Pull the loader to the right side of the oven (cooling zone).
28. Open the reactor and take out the loader.
29. Weigh out the loader that contains sample and metal balls, and transfer the sample into a suitable container and close the container quickly. Make sure the loader is completely empty.
30. Turn off the oven, unless another experiment is being conducted.