

# From torrefaction to gasification

## Pilot scale studies for upgrading of biomass

**Martin Strandberg**



**Department of Applied Physics and Electronics**  
Doctoral Thesis  
Umeå University, 2015

This work is protected by the Swedish Copyright Legislation (Act 1960:729)  
ISBN: 978-91-7601-287-1  
Elektronisk version tillgänglig på <http://umu.diva-portal.org/>  
Tryck/Printed by: Print & Media, Umeå Universitet, 2015  
Umeå, Sweden 2015

*"Every time I see an adult on a bicycle, I no longer despair for the future of the human race."-H.G. Wells*



# Table of Contents

<b>Abstract</b>	<b>iii</b>
<b>Nomenclature</b>	<b>v</b>
<b>List of appended publications</b>	<b>vii</b>
<b>Additional publications and patents</b>	<b>ix</b>
<b>1. Introduction</b>	<b>1</b>
1.1. Torrefaction	1
1.2. Gasification	7
1.3. Objective	9
1.4. Thesis structure	10
<b>2. The torrefaction pilot plant</b>	<b>11</b>
2.1. General overview	11
2.2. Measurement of biomass temperature	12
2.3. Residence time distribution	13
2.4. Measurement of mass yield	14
2.5. Deposits of torrefaction gas	16
2.6. Constant fill ratio versus constant mass flow	17
2.7. Resulting upgrade to pilot plant 2.0	17
<b>3. Materials and methods</b>	<b>19</b>
3.1. Biomass	19
3.2. Torrefaction conditions	19
3.3. Characterization of different biomass materials	19
3.4. Degree of torrefaction - theory	22
3.5. Pelletizing	23
3.6. Entrained flow gasification	23
<b>4. Results and discussion</b>	<b>25</b>
4.1. Process evaluation of the torrefaction pilot plant	25
4.2. Characterization of torrefied biomass materials	26
4.3. Powder characteristics	32
4.4. Degree of torrefaction	36
4.5. Oxygen enhanced torrefaction	37
4.6. Pilot scale pelletization of torrefied biomass	38
4.7. Feasibility of using torrefied materials in entrained flow gasification	40
<b>5. Conclusions</b>	<b>45</b>
<b>6. Suggestions for future research</b>	<b>47</b>
<b>Acknowledgements</b>	<b>49</b>
<b>References</b>	<b>50</b>



# Abstract

Increasing the share of biomass, preferably by replacing fossil fuels, is one way to mitigate the present climate change. Fossil coal can be directly replaced by co-combustion of coal and biomass and fossil engine fuels (gasoline and diesel) could potentially partly be replaced by synthetic renewable fuels produced via entrained flow gasification of biomass. The use of biomass in these processes is so far limited, partly because of the fibrous and hygroscopic nature of biomass which leads to problem in storing, transportation, handling and feeding.

This thesis demonstrates how the challenging characteristics of raw biomass are mitigated by the pretreatment method torrefaction. Torrefaction is a process where biomass is heated in an oxygen deficient atmosphere to typically between 240 and 350°C for a time period of 2 minutes to 1 hour. Most of the torrefaction R&D in the literature have so far been performed with bench-scale batch reactors. For the purpose of carefully studying continuous torrefaction, a 20 kg/h torrefaction pilot plant was therefore designed, constructed and evaluated.

The overall conclusion from this thesis is that the many benefits of torrefied biomass are valid also when produced with a continuous pilot plant and for typically Swedish forest biomasses. Some of the documented improved biomass properties are increased heating value, increased energy density, higher friability (lower milling energy) and less hydrophilic biomass (less moisture uptake). Most of the improvements can be attributed to the decomposition of hemicellulose and cellulose during torrefaction.

The most common variables for describing the torrefaction degree are mass yield or anhydrous weight loss but both are challenging to determine for continuous processes. We therefore evaluated three different methods (one existing and two new suggestions) to determine degree of torrefaction that not require measurement of mass loss. The degree of torrefaction based on analyzed higher heating value of the raw and torrefied biomass ( $DTF_{HHV}$ ) predicted mass yield most accurate and had lowest combined uncertainty.

Pelletizing biomass enhance transportation and handling but results from pelletization of torrefied biomass is still very limited in the literature and mainly reported from single pellet presses. A pelletization study of torrefied spruce with a ring die in pilot scale was therefore performed. The bulk energy density was found to be 14.6 GJ/m<sup>3</sup> for pelletized torrefied spruce (mass yield 75%), a 40% increase compared to regular white pellets and therefore are torrefied pellets more favorable for long distance transports. More optimization of the torrefied biomass and the pelletization process is though needed for acquiring industrial quality pellets with lower amount of fines and higher pellet durability than attained in the present study.

Powders from milled raw biomass are generally problematic for feeding and handling and torrefied biomass has been proposed to mitigate these issues. The influence of torrefaction and pelletization on powder and particle properties after milling was therefore studied. The results show that powder from torrefied biomass were enhanced with higher bulk densities, lower angle of repose as well as smaller less elongated particles with less surface roughness. Even higher powder qualities were achieved by pelletizing the torrefied biomass before milling, i.e. another reason for commercial torrefied biomass to be pelletized.

Entrained flow gasification (EFG) is a promising option for conversion of biomass to other more convenient renewable energy carriers such as electricity, liquid biofuels and green petrochemicals. Also for EFGs are torrefied fuels very limited studied. Raw and torrefied logging residues were successfully gasified in a pilot scale pressurized entrained flow biomass gasifier at 2 bar(a) with a fuel feed corresponding to 270 kW<sub>th</sub>. Significantly lower methane content (50% decrease) in the syngas was also demonstrated for the torrefied fuel with mass yield 49%. The low milling energy consumption for the torrefied fuels compared to the raw fuel was beneficial for the gasification plant efficiency.

# Nomenclature

AWL	Anhydrous weight loss (1 - mass yield)
CGE	Cold gas efficiency
CGE <sub>fuel</sub>	CGE based on CO and H <sub>2</sub> in the syngas
CGE <sub>power</sub>	CGE based on all combustible species in the syngas
daf	dry and ash free
db	dry basis
Black pellets	Pelletized torrefied biomass
$\Delta H_f$	Enthalpy of formation
DTF <sub><math>\Delta H_f</math></sub>	Degree of torrefaction based on enthalpy of formation
DTF <sub>HHV</sub>	Degree of torrefaction based on higher heating value
DTF <sub>VM</sub>	Degree of torrefaction based on content of volatile matter
EFG	Entrained flow gasification
EMC	Equilibrium moisture content
EY	Energy yield
FC	Fixed carbon
HHV	Higher heating value (Gross calorific value)
IR	Infrared
LHV	Lower heating value (Net calorific value)
MY	Mass yield
MY <sub>pred</sub>	Predicted mass yield
MLR	Multiple linear regression
NIR	Near-infrared
OET	Oxygen enhanced torrefaction
RCG	Reed canary grass
ROC	Relative oxygen content
RTD	Residence time distribution
s	Standard deviation
SWIR	Short wave infrared
TGA	Thermogravimetric analysis
u <sub>c</sub>	Combined standard uncertainty
VM	Volatile matter
VNIR	Visible and near-infrared
White pellets	Traditional household or industrial pellets
$\lambda$	Oxygen equivalence ratio



# List of appended publications

This thesis includes the following papers, referred to in the text by their Roman numerals I-VI:

- I. Effects of temperature and residence time on continuous torrefaction of spruce wood**  
Martin Strandberg, Ingemar Olofsson, Linda Pommer, Susanne Wiklund-Lindström, Katarina Åberg, Anders Nordin  
Fuel Processing Technology 134(0): 387-398 (2015)
- II. Evaluation of existing and new approaches to determine degree of torrefaction**  
Martin Strandberg, Ingemar Olofsson, Linda Pommer, Anders Nordin  
Manuscript, to be published
- III. Oxygen enhanced torrefaction - An initial feasibility study**  
Ingemar Olofsson, Martin Strandberg, Linda Pommer, Markus Broström, Anders Nordin  
Manuscript, to be published
- IV. Effects of moisture content, torrefaction temperature, and die temperature in pilot scale pelletizing of torrefied Norway spruce**  
Sylvia Larsson, Magnus Rudolfsson, Martin Nordwaeger, Ingemar Olofsson, Robert Samuelsson  
Applied Energy 102(0): 827-832. (2013)
- V. Effects of torrefaction and compaction on resulting biomass powder characteristics**  
Martin Strandberg, Kristoffer Kollberg, Anders Nordin  
Proceedings at Impacts of Fuel Quality on Power Production, Utah, USA. (2014)
- VI. Entrained flow gasification of torrefied wood residues**  
Fredrik Weiland, Martin Nordwaeger, Ingemar Olofsson, Henrik Wiinikka, Anders Nordin  
Fuel Processing Technology 125(0): 51-58. (2014)

Nordwaeger was the author's bachelor name.

## **Authors' contributions**

**Paper I:** The authors planned the experimental work together. Strandberg and Olofsson designed and evaluated the pilot plant, and conducted the experimental work. Strandberg carried out most of the analysis, evaluated the results and wrote the paper.

**Paper II:** Strandberg and Olofsson contributed equally to the concepts of torrefaction degree. Strandberg carried out the uncertainty analysis, evaluated the results and wrote the paper.

**Paper III:** Strandberg and Olofsson planned and carried out the experimental work. Strandberg and Olofsson contributed equally to the analysis and writing of the paper.

**Paper IV:** Nordwaeger and Olofsson contributed equally to the planning and to the torrefaction experimental work. Nordwaeger contributed to evaluation of some of the results and the writing part of the paper.

**Paper V:** Strandberg and Kollberg planned and conducted the experimental work. Strandberg evaluated most of the results and wrote most of the paper.

**Paper VI:** Nordwaeger and Olofsson contributed equally to the planning and conduction of the torrefaction experimental work. Nordwaeger also participated in the gasification campaign and together with Weiland evaluated the results and wrote the paper.

# Additional publications and patents

Additional publications, reports and patents, not included in this thesis.

## Papers, technical reports and book chapters:

1. **Final report – Swedish torrefaction R&D program.**  
Linda Pommer, Ingemar Olofsson, Martin Nordwaeger, Anders Nordin  
ETPC Report 12-01. ISSN 1653-0551. (2012)
2. **Biomass conversion through torrefaction**  
Anders Nordin, Linda Pommer, Martin Nordwaeger, Ingemar Olofsson  
Book Chapter in “Technologies for converting biomass to useful energy: Combustion, Gasification, Pyrolysis, Torrefaction and Fermentation” (2013)
3. **Quality assurance of torrefied biomass using RBG, visual and near infrared (hyper) spectral image data.**  
Susanne Wiklund-Lindström, David Nilsson, Anders Nordin, Martin Nordwaeger, Ingemar Olofsson, Linda Pommer, Paul Geladi.  
Journal of Near Infrared Spectroscopy 22(2): 129-139. (2014)

## Conference proceedings

1. **Torrefaction of pelletized Reed canary grass and Norway spruce**  
Håkan Örberg, Linda Pommer, Ingemar Olofsson, Martin Nordwaeger, Markus Broström  
World Bioenergy, Jönköping, Sweden 2012
2. **Torrefaction and compaction of eucalyptus and Norway spruce**  
Ingemar Olofsson, Erik Sandström, Martin Nordwaeger, Magnus Rudolfsson, Sylvia Larsson, Torbjörn Lestander, Gunnar Kalén, Robert Samuelsson, Linda Pommer, Mattias Brännström, Anders Nordin  
19th European Biomass Conference and Exhibition 2011, Berlin
3. **Review and compilation of existing and new experimental data on torrefaction gas composition**  
Linda Pommer, Ingemar Olofsson, Eleonora Borén, Martin Nordwaeger, Anders Nordin  
21th European Biomass Conference and Exhibition, Coopenhagen 2013
4. **Process and system integration aspects on biomass torrefaction**  
Katarina Håkansson, Anders Nordin, Martin Nordwaeger, Ingemar Olofsson, Martin Svanberg  
18th European Biomass Conference and Exhibition, Lyon 2010
5. **Parametric study of pilot-scale biomass torrefaction**  
Martin Nordwaeger, Katarina Håkansson, Chenxi Li, Anders Nordin, Ingemar Olofsson, Linda Pommer, Susanne Wiklund-Lindström  
18th European Biomass Conference and Exhibition, Lyon 2010

## Patent applications

Patent applications submitted during this thesis work

1. **Torrefieringsmetod innefattande att torrefieringsreaktionen kyls för att åtminstone delvis motverka en temperaturhöjning**  
I. Olofsson, M. Nordwaeger, K. Håkansson, A. Nordin. Granted 2012
2. **Method for cooling and increasing yield of a torrefied product**  
I. Olofsson, M. Nordwaeger, K. Håkansson, A. Nordin, L. Pommer. (2011)
3. **Method and an arrangement for efficient torrefaction of biomass**  
I. Olofsson, M. Nordwaeger, K. Håkansson, A. Nordin. (2011)
4. **Method of cooling a torrefied material**  
A. Nordin, L. Pommer, K. Håkansson, I. Olofsson, M. Nordwaeger. (2011)
5. **Countercurrent oxygen enhanced torrefaction**  
I. Olofsson, M. Nordwaeger, E. Sandström, L. Pommer, A. Nordin (2011)
6. **Method for monitoring and control of torrefaction temperature**  
I. Olofsson, M. Nordwaeger. (2011)
7. **Method of torrefaction of a biomass comprising the step of cooling the torrefaction reaction**  
I. Olofsson, M. Nordwaeger, K. Håkansson, A. Nordin. (2011)
8. **Method for torrefaction with hyperspectral analysis of the torrefied material during or after torrefaction**  
A. Nordin, S. Wiklund-Lindström, M. Nordwaeger, I. Olofsson, K. Håkansson. (2011)
9. **Moisture control of a predrying step in a torrefaction process**  
I. Olofsson, M. Nordwaeger, K. Håkansson, A. Nordin. (2011)

# 1. Introduction

During the last centuries, extensive use of energy from fossil energy resources and from unsustainable biomass resources has led to increasing levels of greenhouse gases with global warming as the consequence. Fossil fuels contributed to 88% of the primary energy consumption in EU 2012, compared to biomass that contributed to only 7%. The main reasons for this extensive use of fossil fuels (coal, oil, natural gas) are related to the properties of these fuels, e.g. relatively low cost, high energy density, homogenous and available as large and concentrated resources.

By replacing fossil fuels with renewable energy carriers derived from sustainable biomass production, global warming may be significantly reduced [1, 2]. The European directive (2009/28/EC) therefore sets ambitious targets for increasing the renewables for all EU member states. By 2020, renewable sources are required to constitute 20% of the total energy used and in the transport sector, a 10% share of the used energy shall come from renewables. Increased biomass use is one measure to reach these targets, especially appealing if biomass directly replace fossil fuels [3].

Gasification, combustion and co-combustion with coal are some of the energy conversion processes that utilize biomass raw materials. A limitation of biomass fuels for coal replacement and for use in some gasification and combustion processes is that biomass generally experience a few disadvantages compared to fossil fuels: high bulk volume, usually high moisture content, hydrophilic characteristics, relatively low heating value, problematic to transport and store. Biomass also generally requires high amounts of energy for milling. The fibrous structure of biomass causes feeding issues and most feeders are not reliable, efficient or economical due to biomass bridging, blockage and rathole formation in the equipment [4].

The present thesis demonstrates how these disadvantages can be mitigated by the pretreatment method torrefaction.

## 1.1. Torrefaction

Torrefaction is a thermochemical pretreatment method for upgrading biomass to an improved energy carrier. The process has gained significant interest the last decade since several biomass properties are significantly improved such as, increased heating value, increased energy density, higher friability (lower milling energy), less hydrophilic (less water uptake), and more resistant against biological decay.

Torrefaction was used already in the late 19<sup>th</sup> century and more than 15 patents were granted until 1952 [5]. In the 1980s some new R&D were conducted and a torrefaction demonstration plant were operated by

Pechiney in France for a few years. The high interest for torrefaction in the recent years (from 2003) can largely be attributed to the dedicated work by ECN and Eindhoven University of Technology [6-8]. The history of torrefaction and the different contributions are compiled by Nordin et al. [5].

Biomass temperatures during torrefaction are typically between 240°C and 350°C and the biomass residence time vary in range from a few minutes up to several hours in the literature [5]. The torrefaction process typically operates in ambient pressure and in an inert atmosphere to avoid oxidation and combustion of the biomass. The torrefaction process is also known as roasting or mild/slow pyrolysis although pyrolysis processes usually operates at temperatures above 350°C. The word torrefaction originates from French meaning roasting, typically of coffee beans, a process relatively similar to torrefaction of biomass with the exception that roasting of coffee typically uses air instead of inert atmosphere and at a somewhat lower temperature [5]. Torrefied biomass is also known as green coal, biochar, charcoal or biocoal. However, those names should be used with care to reduce the risk of mix-up with the solid product from pyrolysis processes.

During torrefaction, the hemicellulose-cellulose-lignin matrix in the biomass is degraded. For hemicelluloses, transformation and degradation is initiated at a rather low temperature (~200°C) [9] and for cellulose, degradation starts at higher temperatures (~280°C). The thermal degradation of lignin is more complex due to the more complex structure, but results suggest that degradation occurs in the whole range from below 230°C to around 900°C [10-12].

The weakening of the mechanical strength of the hemicellulose-cellulose-lignin matrix facilitates significant reductions of required milling energy and resulting particle size, compared to corresponding data for untreated biomass (Paper I). Small particle sizes are required in some end-use processes such as entrained flow gasification and pulverized fuel burners. A lower milling energy is also beneficial as it can have significant impact on the overall energy efficiency ([13], Paper VI).

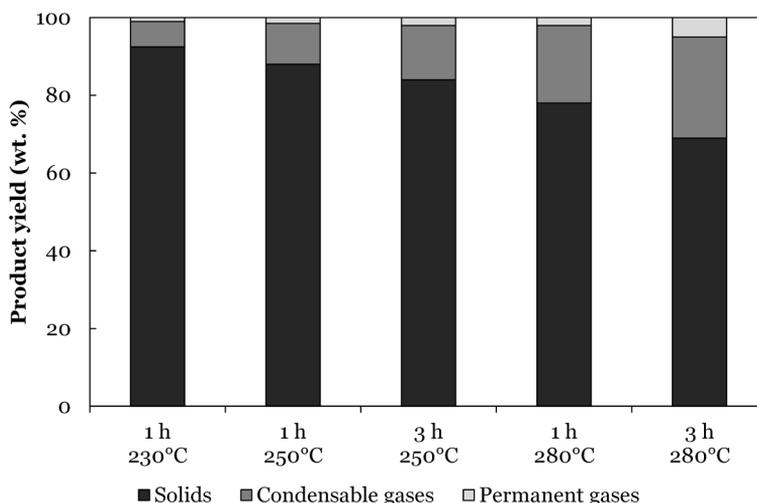
In the torrefaction process, part of the biomass volatilizes and forms a torrefaction gas. Consequently, less of the original biomass weight is retained in the torrefied product. This weight loss is here defined by mass yield:

$$MY_{daf} = \left( \frac{m_{tor}}{m_{raw}} \right)_{daf} \quad (1)$$

where  $m_{tor}$  is the weight of torrefied biomass and  $m_{raw}$  the weight of raw biomass, both on dry and ash free basis (*daf*). Mass yields of 60-95% have been reported typical for torrefaction. Sometimes the anhydrous weight loss (AWL) is presented instead of mass yield, AWL is calculated as *1-mass yield*.

The torrefaction gas is generally combusted and the heat is typically used for biomass drying and for heating of the torrefaction process. Depending on

torrefaction conditions, biomass, and moisture content, the resulting torrefaction gas acquire different heating values and combustibility, where lower biomass moisture content and increased torrefaction degree gives higher gas heating value and combustibility [14, 15]. The composition of the torrefaction gas is generally complex, consisting of a permanent gas fraction and a condensable fraction. Permanent gases are mainly CO<sub>2</sub>, between 12 and 26 wt. % of total gas, and CO at 10-30% of the CO<sub>2</sub> level [5, 14, 16]. The condensable fraction is mainly water, acetic acid, methanol, lactic acid, and formic acid, but over 100 different species have been identified in lower concentrations. More severe torrefaction conditions results in lower biomass mass yield (more weight loss) and a higher fraction of condensable gases (Figure 1). The condensable fraction could also possibly be suitable for upgrading to green chemicals or biofuels. Torrefaction increases the heating value of the biomass, a result from the release of oxygenated compounds (mainly CO<sub>2</sub>, CO, H<sub>2</sub>O) to the torrefaction gas. The energy-rich carbon and hydrogen are thus enriched in the torrefied biomass (Paper I).



**Figure 1.** Product yields of solids, condensable and permanent gases for torrefaction of pine for different residence times (1 & 3h) and torrefaction temperatures (230 to 280°C). Data extracted from [17] which used a laboratory batch reactor.

Increasing the biomass residence time or temperature in the torrefaction process results for example in decreasing content of volatile matter, hydrogen content, milling energy consumption, angle of repose, mass and energy yields, contents of cellulose and hemicellulose while heating value, hydrophobicity and carbon content increases. The effect of torrefaction, performed mainly in batch reactors, on these properties have been extensively reported during the last years [18-21]. The effect of continuous

torrefaction on these properties is further described in the appended publications and in the results section of this thesis.

Various biomass species are differently affected by the torrefaction process. For example, the mass yield for spruce was 74% but only 55% for the energy crop reed canary grass (RCG) at equal torrefaction conditions of 305°C torrefaction temperature and 16.5 minutes residence time [22]. Also the Nordic woody biomasses are differently affected by torrefaction; the mass yield was 76% for spruce and 64% for birch torrefied at 275°C with a residence time of 60 min [23]. One explanation for the differences in biomass behavior during torrefaction is related to type and composition of hemicelluloses. Di Blasi et al. [24] discussed that differences in exothermal behavior between straw and softwood pellets could be attributed to differences in hemicellulose composition. The results from Werner et al. [9] confirm this as they demonstrated that different hemicelluloses have varying exothermal effects, mass loss behaviors, and decomposition start temperatures. Another possible explanation for the different behaviors of biomasses is the content and composition of ash forming elements. Lowering the amounts of alkali metals in the biomass (mainly Na and K) have been linked to increased mass yield at the same torrefaction conditions [25]. At pyrolysis conditions on the other hand, the mass yield is lower for biomasses with lower alkali content [26, 27].

Decreasing the raw material size generally results in lower mass yield as demonstrated by Peng et al. [28], who used pine sawdust sieved into three particle sizes. Van der Stelt [29] demonstrated a decreasing mass yield with decreased particle diameter (10-28 mm diameter) for cylindrical single particles. Basu et al. [30] also used cylindrical single particles and demonstrated a lower mass yield for shorter particle lengths, but surprisingly found a lower mass yield when the diameter increased from 13 to 25 mm. The particles with increased diameter exhibited exothermal reactions *inside* the sample, with a measured core temperature of up to 18°C higher than the furnace temperature, which probably explains the lower mass yield. Bates and Ghoniem [31] recently developed a model for describing drying and torrefaction of a single particle and concluded that temperature overshoot depends on particle size, conductivity and rate of heat release from exothermal reactions.

Heat treated wood produced at slightly lower temperature than typical torrefaction temperatures are more resistant to fungus and other biological decay compared to untreated wood [32-34]. Recently this was also demonstrated for torrefied wood in laboratory but the results were not confirmed in the outdoor experiment [35]. However, very little data from outdoor experiments are published. Piles of untreated wood chips can have significant mass loss during storage that also leads to greenhouse gas emissions, due to the biological decay [36-38]. The reported average mass

loss was 0.5 to 2% per month and higher moisture content seems to increase the mass loss.

Torrefied biomass is also less hydrophilic (less water uptake) (Paper I), a great benefit since outdoor storage may be possible, compared to white pellets that require covered storages. As a reference, uncovered wood chip piles have been demonstrated to acquire moisture contents up to 62%<sub>wb</sub> during storage [39]. Covered or short time storage of the biomass before torrefaction is therefore preferred. The lower rate of biological decay and less hydrophilic nature of torrefied fuels could allow outdoor storage and longer storage times.

Torrefaction is known to change the biomass color (Figure 2); increasing residence time and torrefaction temperature results in darkening of the biomass. For heat treatment at temperatures below 200°C it has been demonstrated that also the wood density, wood specie and relative humidity affects the color [40]. Proposed explanations is caramellisation of holocellulose (cellulose and hemicellulose) components and formation of quinones [41]. González-Peña and Hale [42] proposed that color change mainly arise because of changes in acid-insoluble lignin and formation of quinones in lignin, and less due to changes in carbohydrates. The color of the torrefied biomass is correlated to mass yield but a regular RGB-camera does not adequately predict mass yield and properties as heating value, hemicellulose and carbon content [43]. Infrared based techniques such as near-infrared (NIR), short wave infrared (SWIR), and possibly also visible and near-infrared (VNIR) are more suitable for prediction of these biomass properties since those signals contain additional chemical information of the samples [43, 44].



**Figure 2.** Original spruce wood chips (A) and corresponding torrefied materials. Light brown (B) T=260°C t=25 min. Dark brown (C) T=310°C, t=8 min. Black (D) T=310°C, t=25 min.

Untreated biomass (logs, bundles or chips) is unfavorable to transport longer distances due to high moisture content and low bulk energy density. Torrefied chips are also unsuitable for transportation and handling due to possible dust formation and low bulk density. A more suitable fuel for transportation is black pellets which can be attained by combining torrefaction and densification (pelletization or briquetting) for acquiring a more energy dense and suitable energy carrier. Transport of black pellets is even favorable over traditional pelletized material, due to the higher bulk energy density (Paper IV). According to a study by Uslu et al. [45], it is economically favorable to use black pellets compared to pyrolysis oil or traditional white pellets for transatlantic supply chains (Latin America to Rotterdam). Gårdbro [46] compiled the existing supply chain studies and further found that the supply chain cost was lower for torrefied pellets compared to white pellets, both for the case with production in Sweden and transport to Denmark (7% lower cost), and for the case with production in USA and transport to Netherlands (11% lower cost). Furthermore, densified materials are favorable because of the improved fuel handling, for example when loading and unloading for transportation. Also handling the fuel on an end-users site, for example from pile to conveyors and conveying to the milling equipment is easier with densified fuels.

Other aspects of the supply chain are the location of the torrefaction plant compared to the biomass resources and the end-user. According to Svanberg and Halldórsson [47] the biomass supply distance to a torrefaction plant should be relatively short compared to the transportation distance of the refined torrefied pellets. This is because the biomass supply chain (transportation, commuting, and storage) accounts for 46% of the total production cost for a 200 kton<sub>DS</sub>/year torrefaction and pelletizing plant [48]. In contrast, the distribution system accounted to only about 9.5% of the production cost for 500 km train transport including road transport and terminal handling.

Torrefied wood is thus proposed to be a suitable fuel for various applications; gasification, co-firing and co-gasification with coal, blast furnace in steel industry, industrial oil and gas replacements, and small and medium scale pellet appliances. Torrefied wood as a gasification fuel in drop-tube reactors is described by [49-52] and as a fuel in a pilot scale entrained flow gasifier is described in Paper IV. Co-firing of regular white biomass with coal is challenging due to issues in handling, storage, and feeding, but also due to the ash issues as slagging/fouling and corrosion [53]. Experimental results on co-firing and co-gasification of coal with torrefied fuels is limited but initial results show that a higher ratio of biomass to coal is possible to attain with torrefied fuels compared to the use of white pellets, but with risk of increased dust formation during handling [54, 55].

The release of chlorine and sulfur during torrefaction is also of interest for end-use applications, and up to 90% separation of these elements during torrefaction have been reported [56-58]. Both chlorine and sulfur are unwanted as they produce acid emissions and may also cause deposits and corrosion in thermal conversion processes [59-61]. For the same reason, gasification processes should also be significantly benefitted by removing these elements in the pretreatment stage, because sulfur compounds permanently deactivate many catalysts and the presence of chlorine compounds increase the risk of fouling in heat exchangers [62]. However, the role and fate of these elements in a biomass gasification reactor is only somewhat studied [63-67]. The generally low content of nitrogen and sulfur in most biomasses compared to coal should be beneficial for combustion and gasification processes.

In a study by Li et al. [68], the flame in a pulverized fuel furnace was affected by the torrefaction degree of the fuel. The enhanced drag force on torrefied particles compared to coal particles due to lower particle density moved the flame away from the burner. Decreasing the particle size is easier after the biomass is torrefied and was beneficial for moving the flame towards the burner and also for increasing flame peak temperature. A modified design of the burner could thus be necessary for torrefied fuels.

Pelletized and torrefied spruce combusted in a pellet stove was found to give lower CO emissions, lower organic share of the PM<sub>1.0</sub> particles and reduction of unburned hydrocarbons, compared to regular pellets [69]. However, some pellet stoves may need modification of combustion air, fuel feeding rate, and chamber/burner design to be able to optimally handle torrefied pellets.

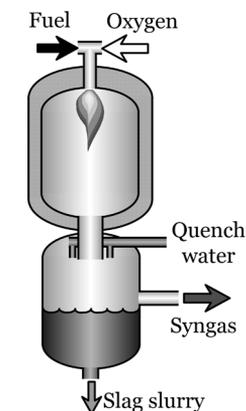
For further reading about torrefaction, several extensive review papers have compiled the present knowledge [18-21].

## **1.2. Gasification**

Gasification has been acknowledged as an option to introduce more biomass for production of more convenient energy carriers such as electricity, synthetic natural gas, liquid biofuels and green petrochemicals. Various types of gasifier technologies all have their different advantages and shortcomings but a common problem is the production of tars. Tars are very challenging to remove from the syngas and cause problems in subsequent equipment and processes. Entrained flow gasifiers, EFG, (Figure 3) operates at high process temperatures (1100-1700 °C) where methane, tars and other hydrocarbons are thermally disintegrated to a larger extent than for other gasification technologies that operate at lower temperatures. These high temperatures are achieved by using pulverized dry fuels (particle sizes of <100 µm for coal gasifiers), oxygen as oxidant, and high pressures (20-70

bar) [62]. The process conditions also allows very short residence times of only a few seconds, which enables relatively small reactor sizes.

The entrained flow gasifiers in commercial operation uses coal and pet coke as solid fuels for production of steam, electricity, chemicals (methanol, ammonia, etc.), synthetic natural gas, and liquid fuels via catalysis, e.g. Fischer-Tropsch (FT), DME, ethanol and methanol synthesis. Due to economy of scale reasons, coal entrained flow gasifiers generally have large capacities. The average installed plant size was 1000 MW<sub>th,in</sub> for coal-EFG projects finalized between 2005 and 2011, usually with two or more gasifiers in parallel operation and requiring a fuel feed of 2700 ton/day [70]. Sinopec is planning to start operation of two sites in China in 2017, each site with a capacity of 10 000 MW<sub>th</sub> syngas output with 20 gasifiers [71].



**Figure 3.** A typical entrained flow gasifier

Two of the challenges for using biomass in entrained flow gasifiers are the biomass feeding and requirement of small particles which so far is costly and energy demanding for untreated biomass. Torrefied biomass is in this perspective favorable since milling energy consumption is considerably reduced. Another challenge is the required large size of the gasifier and synthesis equipment for commercial operation. The biomass supply area must therefore be large with resulting high costs for biomass transportation. Also this issue is mitigated by torrefaction as the resulting biomass is more beneficial to transport longer distances, increasing the viable supply area by using decentralized pretreatment plants.

The high temperatures and ash composition in coal entrained flow gasifiers typically results in an ash in liquid slag form. The slag is then removed continuously by flowing along the gasifier walls. The biomass ash composition is different from coal and not prone to form the same type of slag [64]. A major challenge for biomass EFG is therefore the ash behavior, slag removal, and refractory wear [66, 72].

### **Biomass to liquids**

Biomass to liquids (BTL) is the production of liquid fuels and chemicals from biomass via thermochemical processes, e.g. via gasification. The synthetic liquid fuel can replace fossil petrol fuels (gasoline and diesel) in vehicles and thereby reduce both the oil dependency and the greenhouse gas emissions. A biomass to liquid production chain can include the following; biomass harvesting and transportation to upgrading site, biomass drying and torrefaction, size reduction and densification, transportation to end user,

further size reduction, gasification, syngas cleaning, synthesis to raw hydrocarbons and the final upgrade to liquid product (Figure 4).

Production costs for Fischer-Tropsch fuels (synthetic diesel or gasoline) via gasification in Europe and with production of the intermediate biomass fuel overseas (Latin America) could be 6 €/GJ<sub>HHV</sub> for the torrefaction case compared to 7 €/GJ for conventional pellets and 9.5 €/GJ<sub>HHV</sub> for pyrolysis oil [45]. A study by van Vliet et al. [73] concluded that BTL can be competitive when the oil price is above \$75/bbl. Greenhouse gases emitted from a vehicle could be reduced from 164 g CO<sub>2eq</sub>/km with current fossil diesel down to between 40 and -130 CO<sub>2eq</sub>/km with BTL, depending on biomass, source and if carbon capture and storage is used at the upgrading site.

### 1.3. Objective

There are many promising benefits of torrefied biomass. For example, many end-use processes could be more efficient or contribute to less greenhouse gas emissions compared to when using untreated biomass or fossil fuels. However, more research and development is required before the benefits are proved and demonstrated. Furthermore, most of the torrefaction R&D have been performed with bench-scale reactors. At the time of the present project start, studies of the continuous torrefaction process and the corresponding solid products were more or less non-existing, and are still limited to only a few recent publications [74-80]. A continuous torrefaction plant also facilitates studies on subsequent processes with pilot scale facilities that resemble large scale industrial processes. Pelletizing the torrefied biomass is important for market acceptance of the biocoal. Pelletization studies are mainly performed with small scale or with single pellet presses [81-84], except two newly published studies in pilot scale [85, 86]. The research on entrained flow gasification of torrefied biomass are also limited to small scale (for example drop-tube reactors) [49-52].

**The overall objectives** of this thesis were therefore to increase the knowledge, demonstrate production, characteristics, pelletization and gasification of torrefied biomass using continuous pilot scale facilities. Furthermore, the objective was to identify and rectify issues of technical and process nature that could be challenging or a limiting factor for a commercial plant or the solid product.

Specific objectives were to:

- Design and construct a continuous torrefaction pilot plant with good process control, mainly focusing on a narrow residence time distribution, excellent temperature control and with a possibility to

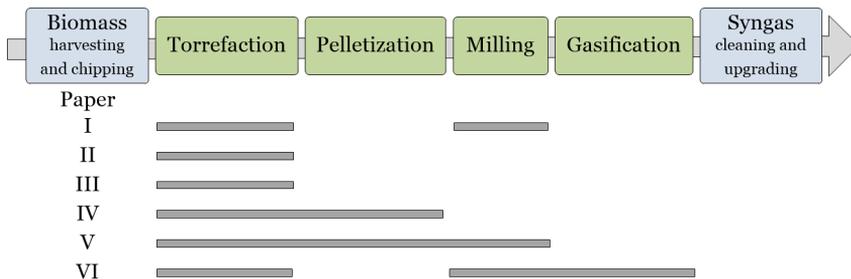
alter the reactor atmosphere, facilitating careful parametric studies (Paper I & III).

- Demonstrate and evaluate torrefaction in continuous operation and the corresponding solid product produced at various torrefaction conditions (mainly Paper I, but also II-VI).
- Develop and evaluate definitions of degree of torrefaction, useful for processes where mass yield is challenging to determine (Paper II).
- Develop an improved torrefaction process where the need for an external heat source is partly or completely eliminated by addition of oxygen, thereby also improving the scale-up potential (Paper III).
- Demonstrate ring die pelletizing in pilot scale of torrefied spruce, including influence of die temperature, biomass moisture content and torrefaction temperature (Paper IV).
- Evaluate the influence of torrefaction and pelletization on resulting powder and particle properties after milling (Paper I, IV, V, VI).
- Evaluate the influence of biomass torrefaction on entrained flow gasification (Paper VI).

#### 1.4. Thesis structure

The structure of this thesis is as follows: In chapter 1, an overview of torrefaction and gasification is presented. In chapter 2, a description of the developed torrefaction pilot plant is presented, together with some of the issues and technical solutions chosen. In chapter 3, other experimental and theoretical methods used in the thesis are described, such as characterization of torrefied biomass and description of torrefaction degree. The last two parts are a summary of the results and conclusions. The structure of the results chapter follows the objectives presented above.

The structure of the appended publications can be visualized throughout the production chain from biomass harvesting to an upgraded synthetic fuel, as visualized in Figure 4.



**Figure 4.** Schematic overview of the production chain from biomass to a liquid or gaseous fuel, together with the focus areas of the appended publications.

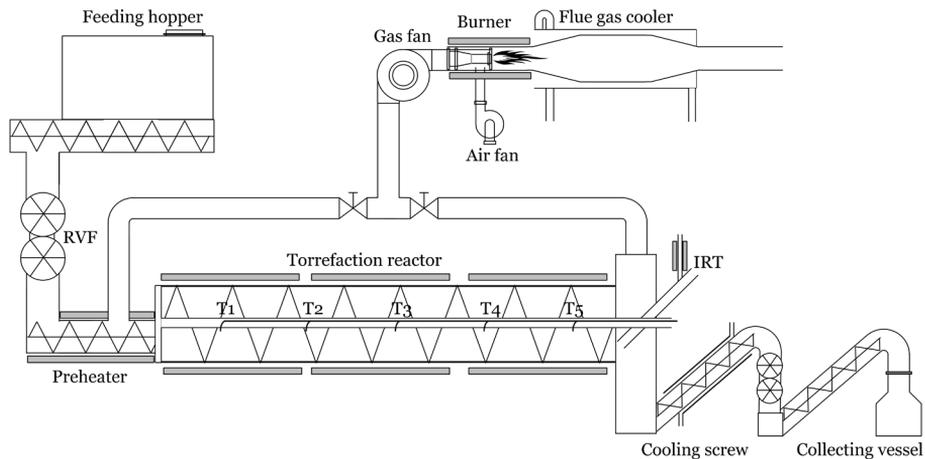
## 2. The torrefaction pilot plant

The torrefaction pilot plant (version 1) was essential for this work and it was critical during the development phase to solve the emerging technical challenges. Therefore, this description of the pilot plant is focusing on both a general overview and on some of the solved technical issues. The pilot plant was financed, designed, and constructed in collaboration between Umeå University, Swedish Agricultural University and BioEndev AB. An improved pilot plant (version 2.0) with increased capacity based on the present work is presented in the last part of this section.

### 2.1. General overview

The main parts of the torrefaction pilot plant were the preheater, the torrefaction reactor, the cooling screw and the torrefaction gas fan and burner (

Figure 5). The maximum production capacity was 14 and 20 kg/h for chips and pellets, respectively. The torrefaction reactor was a specially designed rotating drum with a dedicated internal conveying system, 1700 mm in length and an inner diameter of 270 mm. The pre-dried biomass was heated from room temperature to about 200°C by the electrical pre-heater and then the torrefaction reactor increased the biomass temperature up to the desired temperature. The torrefaction reactor was externally heated by five cylindrical and consecutively mounted electric heaters. The torrefied biomass was indirectly cooled immediately after the reactor to below 90°C by a double jacketed water-cooled transport screw.



**Figure 5.** The torrefaction pilot plant (version 1) with feeding, electrical heaters, cooling screw and gas burner. Gray sections indicate the most important electrical heaters. RVF=rotary vane feeder, IRP=infrared pyrometer.

Inert atmosphere in the reactor was ensured by; a gas tight steel shell surrounding the torrefaction reactor, by mechanically fixed sealed joints, by two rotary vane feeders before the reactor, and two rotary vane feeders after the cooling screw with small nitrogen flows in between the vane feeders. Torrefaction gases were evacuated with an in-line gas fan that withheld a small negative pressure of 0.1 mbar inside the torrefaction reactor. The torrefaction gases were then combusted in the burner located after the gas fan. The internal burner chamber surface was kept at 900°C by electrical heaters to facilitate ignition and to sustain combustion also when the heating value of the gas was too low.

The torrefaction gases could be forced to flow either concurrent or countercurrent to the biomass flow in the reactor. In Paper III, the effects of these flow patterns were evaluated together with injection of a small air flow. For the countercurrent gas flow, the air injection was positioned close to the end of the reactor and for the concurrent gas flow the air injection was positioned in the beginning of the reactor.

The gas temperatures inside the reactor were measured with five type-N thermocouples ( $T_1$  to  $T_5$ ) and in total 38 temperatures were measured. Actual biomass surface temperature was determined by an infrared thermometer as described below. The pilot plant was heated by a total of 17 electrical heaters and equipped with seven mass flow controllers for nitrogen and air flows. Oxygen content were measured with oxygen meters (Oxygen Control OC 2010, Kastrup & Genberg AB, Sweden) at four points; after the first set of rotary vane feeders, at the exit of the torrefaction reactor, after the cooling screw, and after the torrefaction gas burner. Process control and data acquisition were facilitated by a Compact FieldPoint system (National Instruments) with LabVIEW software. A total of 78 data points were logged every third second. The pilot plant is further described in Paper I.

## **2.2. Measurement of biomass temperature**

Torrefaction temperature is probably the most important variable influencing both the resulting solid product and the torrefaction gas composition. In the literature however, it is not clearly defined where it is in the process and if it is the biomass or reactor temperature that is the actual torrefaction temperature. It is also not clearly defined how the measurement of the actual torrefaction temperature should be performed. Thermocouples are typically used for batch reactors, either; in the inert gas before or next to the material bed [51, 87]; in the material bed [56, 88]; in the sample [30, 89]; and sometimes the measurement method is not stated at all [90, 91]. It is similar for the few continuous reactors presented in the literature, either the torrefaction gas temperature [74, 77, 78] or reactor wall temperature [79, 80] is chosen to represent the torrefaction temperature and in one case the

method is not at all stated [75]. Because of the various measurement methods, comparisons between torrefaction conditions/technologies are not easily performed. A torrefaction temperature of for example 280°C may denote completely different thermal conditions and temperature histories of the torrefied biomass for different reactors.

**Our solution:** Infrared thermometers (IRT) measures the thermal radiation from solids, liquids and gases within its field of view. We therefore installed an infrared thermometer with the focus on a circular measuring area of 40 mm in diameter with the center located about 30 mm upstream the exit of the torrefaction reactor. Thereby it was possible to determine the surface temperature of the exiting torrefied biomass. This technique has to our knowledge not earlier been used in the field of torrefaction. Infrared radiation emitted from the torrefied biomass can be absorbed by steam, other gases, and aerosols located in-between the biomass and the infrared thermometer. Smallest possible absorption from these gases is therefore desired. Steam have the highest absorption in the ranges 2.4-3.0  $\mu\text{m}$ , 5.8-8  $\mu\text{m}$  and 14-30  $\mu\text{m}$  and absorption maximum of  $\text{CO}_2$  is between 2.4-3.0  $\mu\text{m}$ , 4-4.8  $\mu\text{m}$  and 13-16  $\mu\text{m}$  [92]. Consequently, an infrared thermometer with bandwidth 8-14  $\mu\text{m}$  is suitable to measure the actual biomass surface temperature and a Heitronics CT09 was therefore selected for this pilot plant. Initial calibration experiments with heating of biomass in a batch reactor demonstrated good agreement between the IRT and a thermocouple measuring temperature in the top biomass layer.

As described above the torrefaction gas will deposit on cold surfaces, including the IRT lens. To prevent this, a protective gas ( $\text{N}_2$ ) was injected in front of the lens. Tests with various temperatures of the protective gas revealed that the most accurate readings were obtained at  $\text{N}_2$  temperatures. 20°C above the measured biomass surface temperature. At lower  $\text{N}_2$  temperatures we presume that due to cooling from the cold purge nitrogen, torrefaction gas compounds condensate and form aerosols that results in incorrect readings.

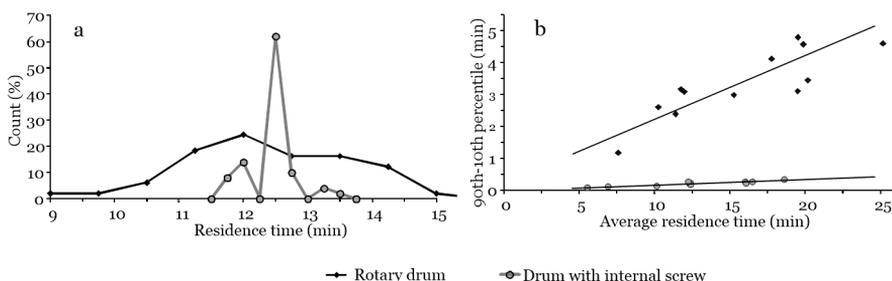
### **2.3. Residence time distribution**

The biomass residence time is the other major influencing factor during torrefaction but is more or less confounded with torrefaction temperature. In continuous processes, the temperature profile is more or less unknown and challenging to control. For parametric studies however, it is essential to vary temperature and residence time separately. Several definitions of residence time exist where the two most common are: 1) the time at which the biomass exceeds 220°C and 2) the time at which the biomass temperature is close to the final torrefaction temperature. In the present work, torrefaction residence time is defined as total time the biomass chips are inside the

torrefaction reactor, thereby including the heating time from around 200°C to final temperature.

*Residence time distribution (RTD)* is usually a non-existing problem for batch reactors and the concept has not earlier been mentioned in the literature were continuous reactors are described. We determined the residence time distribution of two torrefaction reactors by introducing a batch of 50 marked wood chips into the feed 5 cm prior to the torrefaction drum inlet and quantifying their specific residence times. The first tested reactor was an inclined rotating drum with internal lifting flights. The second improved reactor was a rotating drum with an installed shaftless screw with a screw pitch of 10 cm.

The first rotating reactor design with flights demonstrated unacceptable high variations in wood chip residence times; 9.5 to 15 min for an average of 12 min. Acceptable variation (12.3 to 13 min for an average of 12.5 min) was documented for the second improved reactor design (Figure 6). The residence time distribution of the second reactor was 12-14 times smaller compared to the first reactor. The shaftless screw reactor was thus permanently used thereafter.



**Figure 6.** Residence time distribution for the rotary drum reactor with and without internal conveying screw. Left: residence time for all 50 chips, for the experiments with average residence time of 12.5 min. Right: RTD versus average residence time.

## 2.4. Measurement of mass yield

Direct measurement and control of biomass weight loss for a continuous process is challenging. Mass flows for input and output streams can be measured with for example belt weighers but the price of the belt weigher and the many factors affecting the accuracy [93] are drawbacks for a commercial unit and for our pilot plant. Three methods for determining mass yield were therefore evaluated during a 5-day long campaign:

### 1) Mass flow of input and output streams

Input mass flows were measured nine times by filling the input silo with known amounts of biomass and record the discharge time which were about 7 h for each discharge. Similarly, mass flow out was measured 52 times and each measurement lasted for about 1.5 h. Four days of steady state operation

resulted in an average mass flow in of 9.2(0.2) kg<sub>ds</sub>/h and an average mass flow out of 8.5(0.1) kg<sub>ds</sub>/h, the numbers within parenthesis are the standard uncertainty ( $u_c$ ). Resulting mass yield was determined to be 92% with a combined standard uncertainty  $u_c=2\%$ .

### **2) Total weight of raw and torrefied biomass**

Total raw biomass weight for the steady state operation was 615(3) kg<sub>ds</sub> and weight of the torrefied biomass was 571(3) kg<sub>ds</sub>. This method determined the mass yield to be 92.9% with  $u_c=0.7\%$ .

### **3) The weight of a batch of biomass before and after torrefaction**

The third method is a variant of method 2; a batch of biomass (typically 70 kg<sub>ds</sub> during this campaign) was followed through the system, from the fuel silo to the output vessel. Further explanation is found in Paper II. We conducted five measurements of mass yield, each lasting about 5h; 89.6%, 90.9%, 93.0%, 92.3% and 91.3% with  $u_c=0.9\%$  for each mass yield. The average mass yield was thus determined to 91.4% with a standard deviation of the mean of 0.6%.

The average mass yield for the three methods can thus be considered alike, even with a conservative coverage factor of 2 for a confidence level of 95%. Method 2 is in my opinion the easiest method to carry out for determining mass yield. A sub-condition for this method should be that a selection of the process variables must be in steady state. The drawback with this method is that the average during a long period of time does not show the variation of mass yield throughout the run. Method 2 was also used in the appended publications for determining the total mass yield for the experiments. For experiments conducted for several days, also method 3 was occasionally used for verification that the process conditions were in steady state.

Again it is interesting to compare these methods to the corresponding methods for the continuous reactors presented in the literature. In a few studies neither the method nor resulting mass yield is presented [75-77]. Zhent et al. [74] and Mei et al. [80] presented the mass yield but not the measurement method. Atienza et al. [78] and Ohliger et al. [79] used the same procedure as method 2 stated above; mass loss was determined by measuring the weight of the raw and torrefied biomass. However, the weight was presumably measured during the whole experiment time, not only during steady state conditions. A side-note for these continuous reactors is that the biomass cooling after the torrefaction reactor are not presented, presumably indication of slow cooling of the biomass in the output vessel and thereby increasing residence time which gives lower mass yield.

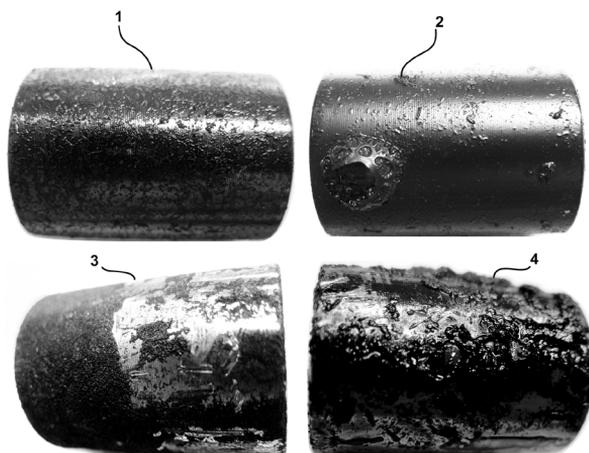
Because of the challenges to accurately determine mass yields, we developed and evaluated methods for determination of degree of torrefaction which also can predict mass yield with high accuracy (Paper II). Also other options exists for determination of mass yield, for example indirect

determination by using calibrated methods such as TGA [94] or infrared based techniques, for example near-infrared, visible and near-infrared and short wave infrared techniques. NIR and SWIR acquires the IR spectra of the torrefied product on-line or at-line and has been shown to be able to predict several properties such as mass yield, heating value, carbon content and volatile matter [43, 44]. Disadvantages with IR based techniques are the costs, the need of calibration and level of complexity.

## **2.5. Deposits of torrefaction gas**

The condensable fraction of the torrefaction gas includes components that condense already slightly below the present torrefaction temperature. Consequently, these condensable compounds will generate deposits on surfaces with lower temperature than the torrefaction gas. This characteristic is not so widely documented but will potentially cause severe operation problems. In the first version of the pilot plant, electric heaters were installed around the reactor and most torrefaction gas pipes. After a few initial experiments, the non-heated surfaces that were subjected to torrefaction gas were layered with deposits of condensed gas. The deposits were sticky at elevated temperatures and also biomass adhered to the surface and gave rise to enhanced deposit growth. At room temperature, some of the deposits were hard with a glassy surface; other deposits were porous and brittle. The countermeasure for minimizing deposit formation was to install electrical heaters on all surfaces in contact with torrefaction gas and heat the surfaces slightly above the torrefaction temperature. Most complications regarding gas condensation were related to the in-line gas fan, and several redesigns were necessary before the fan became somewhat satisfactory for several days of operation.

We also conducted a few experiments for evaluating the deposit issues for indirect cooling of the torrefaction process. Cooling of the process may be necessary for certain fuels that exhibit exothermal behavior. Heat exchangers inside the reactor were simulated by metal probes cooled to 20, 30, 50 and 100°C below the torrefaction gas temperature. The probes were inserted in the reactor and thereby exposed to torrefaction gas during 2 to 11 hours. Wood chips that fell and moved over the probe simulated wear from the biomass being torrefied. Deposits of condensed torrefaction gas were visible even when the probe was cooled to only 20 °C below the torrefaction gas temperature (Figure 7). The results demonstrate that indirect *in situ* cooling of a torrefaction reaction is not suitable because of the formation of deposits and fouling on the cold surfaces. The condensing gas issue on unheated surfaces must generally also be accounted for in designing torrefaction and material cooling processes.



**Figure 7.** Deposits of condensed torrefaction gas on a cooled probe. Torrefaction gas temperature: 300°C. Probe 1: T=280°C, t=2h. Probe 2: T=270°C, t=8h. Probe 3: T=250°C, t=11h. Probe 4: T=200°C, t=2h.

### **2.6. Constant fill ratio versus constant mass flow**

When conducting experiments at various residence times with a continuous reactor of rotary type, two possibilities exist for filling of the reactor. The first option is to fill the reactor with biomass to a constant fill ratio, for example to 15% of the total reactor volume and consequently change the input mass flow so the fill ratio remains constant. The second option is to use constant input mass flow, for example 10 kg/h and allow the reactor fill ratio to change accordingly. Constant fill ratio can be considered to simulate a large scale reactor where a maximum fill ratio is desired for high throughput regardless of the residence time.

In Paper I, we used constant fill ratio (~11%) and applied isothermal conditions on the outside surface of the reactor. In the following data evaluation logarithmic transformations were required for many of the responses. A hypothesis was that the constant mass flow could be required for more precise control of residence time and temperature when isothermal conditions are applied. In the following experiments (not presented in any of the appended publications) we therefore used constant mass flow. As expected, constant mass flow gave linear mass yield in a contour plot with residence time and temperature as factors (Figure 11, logging residues) compared to the nonlinear mass yield for constant fill ratio (Figure 11, spruce), when the reactor surface were held at isothermal conditions.

### **2.7. Resulting upgrade to pilot plant 2.0**

The low production capacity of the pilot plant described above was after some years of research a limiting factor for further pelletization and gasification studies. The capacity was also a limiting factor for some studies

regarding the torrefaction process. It was also essential to incorporate the different innovative process solutions from the work performed in the first pilot plant into an enhanced pilot plant for evaluation and demonstration purposes. Based on the results from the present work, the pilot plant was therefore upgraded from a design capacity of 20 kg/h to 200 kg/h, with use of the knowledge generated from the pilot plant 1 described above. The original torrefaction reactor was reused as a pre-drying (maximum 10% biomass moisture content allowed) and pre-heating unit in series with a new second torrefaction reactor of auger type. In the later, the biomass is heated from 220°C up to the final torrefaction temperature. Thereby it is still possible to follow one of the usual definitions of residence time; the time the biomass temperature exceeds 220°C. The upgrading also facilitates constant mass flow for a more controllable temperature profile, at higher mass flows than before. The major gas condensation issue on the torrefaction gas fan was removed by development of a novel ejector burner. This upgraded pilot plant 2.0 also has the possibility to heat the torrefaction reactor and biomass with recirculating flue gases, which is one industrial possibility for heating as well as optional incorporation of oxygen enhanced torrefaction (OET). More options for process and biomass cooling are also possible after the upgrade. Results from this upgraded pilot plant is however not included in the present thesis.

## **3. Materials and methods**

### **3.1. Biomass**

As described in the introduction, different biomass materials show somewhat different behaviors in the torrefaction process. In the appended publications we used mainly woody biomass readily available in Sweden. Stem wood Norway spruce grown in Västerbotten, Sweden were used in all studies except Paper VI. In Paper II biomasses from a wide variety of woody species and energy crops (Norway spruce, wood residues, pine, eucalyptus, and reed canary grass) were torrefied and evaluated. Both Norway spruce and wood residues were used in Paper III. In Paper VI, wood residues with known fractions of birch, pine and spruce were torrefied and gasified.

### **3.2. Torrefaction conditions**

In all of the studies except Paper III, the torrefaction reactor was indirectly heated by the electrical heaters surrounding the reactor. Reactor outer surface temperatures were held at isothermal conditions by the heaters. To maintain a constant surface temperature along the reactor, typically around 60% of the total electrical power was required in the first 1/3 of the reactor.

The atmosphere in the reactor was in situ generated torrefaction gas diluted with purge nitrogen mainly flowing from the first pair of rotary vane feeders. In Paper III, we evaluated the possibility to heat the process by in situ partial combustion of the torrefaction gas. This partial combustion was facilitated by injection of a small air flow either in the beginning or at the end of the reactor together with con- or countercurrent torrefaction gas flow.

Residence times of the biomass in the reactor were varied between 4 and 40 min. For comparison, reported residence times have previously typically been between 30 min and 3 h for batch reactors, the main reactor type used in the torrefaction literature. Torrefaction temperatures (the biomass surface temperature determined with the infrared thermometer) were varied between 260 and 340°C. For the pyrolysis experiments in Paper II, a small batch reactor was also used to reach biomass temperatures up to 606 °C.

Throughout the present thesis the torrefaction conditions are denoted as 260/8 for an experiment with a torrefaction temperature of 260°C and a residence time of eight minutes.

### **3.3. Characterization of different biomass materials**

The raw and torrefied biomass materials were characterized using more than 30 standard methods, modified standard methods, and non-standard methods. External laboratories were utilized to determine some characteristics by standard methods: lower and higher heating value,

proximate analysis (volatile matter, ash content, fixed carbon), ultimate analysis (C, H, N, S, O, Cl), ash-forming elements, Klason lignin, carbohydrates (arabinose, galactose, glucose, xylose and mannose) and acetone extractives. The standard methods are further described in the appended publications.

Non-standard and modified standard methods were used for: mass yield, energy yield, milling energy consumption, angle of repose, contact angle measurements on wood chips, equilibrium moisture content, particle size distribution (sieve analysis), image analysis (size and shape factors), and powder bulk density (tapped and loose/aerated). These methods are described below except for determination of mass yield which is described in section 2.4.

Relative milling energy consumption in Paper I and V was determined using a laboratory centrifugal mill (Retsch ZM-1) equipped with either a 0.25 or a 0.5 mm sieve. In Paper I, a clamp ampere meter measured the current which was logged 20 times per second while constant power factor and voltage were assumed. In Paper V, we updated the measuring equipment for milling energy with an active power meter (Carlo Gavazzi WM22) which determines current, voltage and power factor simultaneous and with improved accuracy. Only the energy required to mill the biomass is presented and the motor idling power was subtracted from the total milling power. The weight of the milled material was measured and used for the calculations. Typically >98% of the material was passing the mill sieve. In Paper VI, we used another milling setup. Here, the materials were first milled with a granulator with 5 mm sieve size (Rapid Granulator 15 Series) and thereafter the biomass was passed to a hammermill with 0.75 mm sieve size (MAFA EU-4B).

Angle of repose (AoR) was determined for milled materials with a dedicated AoR device (Powder Research Ltd, UK) consisting of an upper chute, a funnel, a lower chute and a baseboard with a radial scale for easy measurement of the cone diameter, the device is further described by Geldart et al [20]. About 30 gram of powder was poured on the upper chute, flowing to the baseboard until the height of the semi-cone was 96 mm (Figure 8). The upper chute was equipped with a vibrator since none of the powders were free flowing. The diameter of the semi-cone was measured at eight points and averaged, and the angle of repose was calculated.



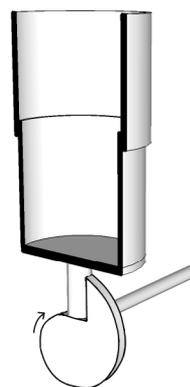
**Figure 8.** Angle of repose for mildly torrefied spruce.

Hydrophobic characteristics were determined by contact angle measurement and by measuring the equilibrium moisture content (EMC). For the contact angle method, 20  $\mu\text{l}$  water droplets were placed on the raw and torrefied wood chips and the contact angle between the chips and droplet were measured with a goniometer. A sample with an angle above  $90^\circ$  usually classifies as hydrophobic and angles closer to  $0^\circ$  indicate a hydrophilic sample. Equilibrium moisture contents for samples were determined by conditioning the samples at  $20^\circ\text{C}$  and 65% relative humidity during several weeks.

Particle size distributions (PSD) of milled materials were determined by the standard method EN15149-2 [95], modified with smaller sieve sizes: 355, 250, 180, 125, 75 and 40  $\mu\text{m}$ . We used smaller sieves compared to the standard method because of the size of the mill sieve (0.5 mm) but also to capture the particle sizes crucial for health and safety issues as well as for end use burner behavior.

Image analysis of milled powder can be used for characterization of size and shape factors of the particles in the powder. In Paper V, we used a 5 mega pixel digital camera attached to a microscope (Leica M420 Apozoom) with a zoom of 12.5x to photograph powder dispersed over microscope slides. In total, we captured 150 images of each sample and analysed between 30 000 and 130 000 particles per sample. Much effort were put on careful image pre-processing to avoid faulty detection of particle edges, otherwise particles could appear too large, small, rough or smooth. The software ImageJ was used for the particle analysis and calculation of shape factors.

Both aerated (loose) and tapped powder densities were determined by using a steel cup with a determined volume of 96.3 (0.3)  $\text{cm}^3$ . For the aerated measurements, the cup was filled with excessive amounts until the powder pored over and the excess powder was gently scraped off. For the tapped measurements, an extension tube was adapted to the cup and more powder was poured in. The cup and extension tube were tapped from a height of 18 mm (Figure 9) up to 500 times in series. After tapping, the extension was removed and excess powder was scraped off. Tapped density increased asymptotically with the number of taps up till around 500 taps where the increase was close to zero.



**Figure 9.** Equipment for determination of aerated and tapped bulk density. The top extension tube was not used for determination of aerated density.

### 3.4. Degree of torrefaction - theory

Mass yield or anhydrous weight loss is usually used to define the torrefaction severity and degree of torrefaction. For batch processes, the weight loss is easy to measure and typically with a very low measurement error, mainly depending on the accuracy of the scale used. For continuous processes on the other hand it can be very challenging as discussed in 2.4.

There is thus a demand for another method (not based on mass loss) for determining degree of torrefaction (DTF). In Paper II, we therefore developed two new methods and compared and evaluated those to one existing method proposed by Englisch in 2011 [96]. The method proposed by Englisch was based on volatile matter content (VM) in the original reference and in the torrefied biomass as:

$$DTF_{VM} = 1 - \frac{VM_{tor}}{VM_{ref}} \quad (2)$$

where the subscript *tor* stands for torrefied biomass and *ref* stands for the reference (raw) biomass.

The first new method is based on comparing the enthalpy of formation ( $\Delta H_f$ ) of the reference and torrefied biomass materials. Enthalpy of formation for a biomass material is:

$$\Delta H_f = \frac{HHV \times 100 - 32.76 \times C - 141.8 \times H - 9.26 \times S + 1.41 \times N}{100 - Ash} \quad (3)$$

where  $\Delta H_f$  is the formation enthalpy of biomass in MJ/kg<sub>daf</sub> and HHV<sub>daf</sub> is the analyzed higher heating value in MJ/kg<sub>daf</sub>. C, H and S are the mass fractions of carbon, hydrogen and sulphur in percentage on dry basis and ash is the ash content in % on dry basis. Since enthalpy of formation is higher for torrefied materials than for the reference material, we propose a torrefaction degree based on enthalpy of formation to be:

$$DTF_{\Delta H_f} = 1 - \frac{\Delta H_{f,tor}}{\Delta H_{f,ref}} \quad (4)$$

The second new method suggested is based on the higher heating values of the reference and the torrefied material related to the heating value of graphite. A higher heating value ratio of  $1 - HHV_{ref}/HHV_{tor}$  would be impractical for normal use as a maximum torrefaction degree would be about 40%. Therefore we proposed to use the theoretical heating value of graphite (32.76 MJ/kg) as a reference state and expand the simple ratio of heating values so the torrefaction degree based on heating value would be:

$$DTF_{HHV} = 1 - \frac{32.76 - HHV_{daf,tor}}{32.76 - HHV_{daf,ref}} \quad (5)$$

where  $HHV_{daf} = HHV/(1 - Ash)$ . Ash free basis were selected because the ash content decreases the heating value of a fuel which gives calculation complications. Some fuels such as untreated reed canary grass can have ash contents of more than 5% and the ash content increases with decreasing mass yield. Thus, the heating value decreases to a larger extent at lower mass yields. In the results, it is shown that the reed canary grass samples become outliers for  $DTF_{VM}$ , which is not calculated on ash free basis. The reed canary grass was not outliers for  $DTF_{HHV}$ .

The methods were evaluated by their ability to predict mass yield for five different kinds of biomass materials covering the whole extended torrefaction regime ( $MY > 40\%$ ) and by an extensive uncertainty analysis. A prediction model for each method was established from a training set: a random selection consisting of 70% of the samples within each fuel and with mass yields above 40%. A test set consisting of the remaining 30% of the samples were used to evaluate the model by calculating the predictive squared correlation coefficient  $Q^2$  (more precisely the  $Q^2_{F3}$  described and recommended by Consonni et al. [97]).

### 3.5. Pelletizing

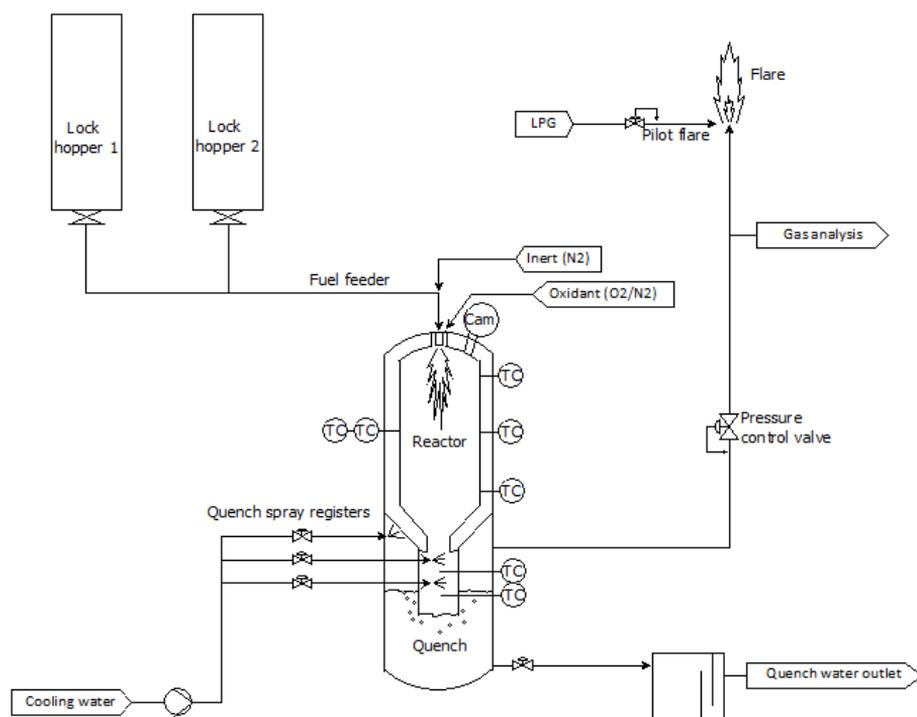
Pelletizing experiments were conducted at Biomass Technology Center (BTC) SLU (Umeå, Sweden) using a rotating die pelletizer (Bühler DPCB) with maximum softwood production capacity of 500 kg/h. Die channel diameter used was 8 mm with a channel length of 35 mm. The pelletizer motor current was continuously adjusted towards 100 A for all experiments by changing the biomass feed flow. An IR thermometer (Optris CT LT 15:1) measured the die temperature continuously and for three experiments, also the pellet temperatures were measured with a hand-held IR thermometer (Optris CT laser 75:1).

The pelletization was performed according to a factorial design and the controlled factors were: torrefaction temperature (270 and 300 °C) and material moisture content (11 and 15%). Die temperature was included as an uncontrolled factor (60-105 °C).

### 3.6. Entrained flow gasification

Gasification experiments were performed by utilizing the autothermal (not external heated) Pressurized Entrained flow Biomass Gasification (PEBG) pilot plant, situated at SP Energy Technology Centre (SP ETC) in Piteå, Sweden. The gasification reactor is ceramic lined, with inner diameter 0.52 m and inner vertical wall length 1.67 m (Figure 10). It is designed to operate

at pressures up to nine bar(a) and with process temperatures between 1200 and 1500 °C. A bubbling water sprayed quench is cooling the syngas to below 100 °C and separates the large bulk of particles from the syngas. Several thermocouples measure gas and ceramic temperatures. Process temperature was taken as the average gas temperature inside the gasifier at mid height, measured with three ceramic protected thermocouples. The oxidant was O<sub>2</sub> diluted with 10% N<sub>2</sub> in the burner, in total the ratio N<sub>2</sub>/O<sub>2</sub> was about 1/3 on mass basis. During the experiments, the system pressure was set to 2 bar(a), oxygen equivalence ratio ( $\lambda$ ) was set to 0.44 and the fuel feeding corresponded to 270 kW<sub>th</sub>. In total four different fuels were evaluated in the gasifier; raw wood residues and three torrefied wood residues with mass yields 80%, ~78% and 49%.



**Figure 10.** Schematic overview of the pressurized entrained flow biomass gasifier used in Paper VI.

## 4. Results and discussion

### 4.1. Process evaluation of the torrefaction pilot plant

In evaluating the developed torrefaction process, the performance of both the pilot plant and the characteristics of the produced torrefied biomass needs to be considered. A large part of the evaluation was performed during the design and construction phase; the pilot plant was redesigned several times before the performance was satisfactory. One of the improved mechanical parts during the design phase was the actual torrefaction reactor with respect to residence time distribution. As described in section 2.3, the first reactor without internal conveying system showed inadequately large residence time distributions. An internal conveying system of auger type with hollow center facilitating easy gas transport was therefore installed. The first reactor showed up to 14 times wider residence time distribution than the second, and the auger type reactor was therefore used in all presented experiments. The measured process temperatures (for example biomass surface temperature, reactor gas temperatures and reactor surface temperature) typically varied less than  $\pm 2.5^{\circ}\text{C}$  during steady state operation.

The repeatability of an experiment in the pilot plant was very good; mass and energy yields, heating values, and proximate and ultimate analysis differed less than 0.5% between two replicates in Paper I (285/16.5). The measured process temperatures for the replicates also deviated less than 0.5%. Other replicates not presented in the appended publications also indicate similar results. In the present thesis, two experiments were conducted during several days (80-90 h) for production of relatively large quantities of spruce for pelletization studies (Paper IV). These long runs were performed without major complications and process conditions were in steady state almost all the time. For example, thermocouple  $T_5$  in the end of the reactor measured gas temperatures of  $273 \pm 3^{\circ}\text{C}$  for all 80 h during the 270/16.5 experiment and mass yields separately determined over a five hour period were 89.6%, 90.9%, 93.0%, 92.3% and 91.3% with an total mass yield of 92.9% with a combined standard uncertainty  $u_c=0.7\%$  (section 2.4).

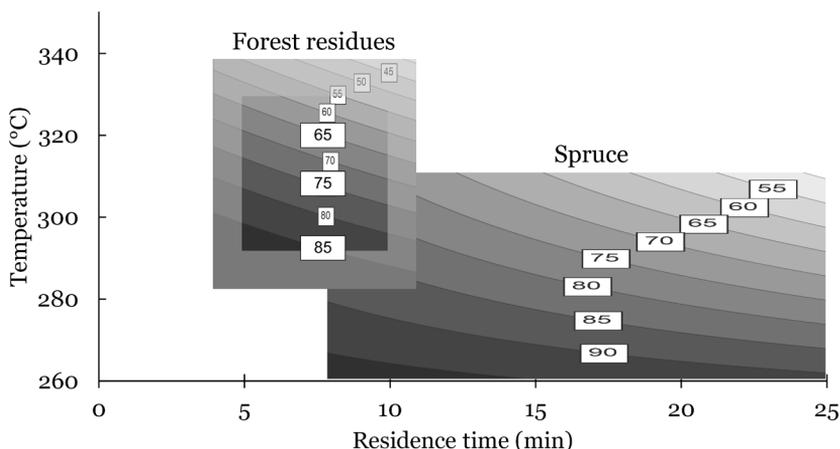
Moderate to minor exothermal reactions were evident with Norway spruce (Paper I). One or more of the measured gas temperatures then exceeded the reactor surface temperature for the experiments with residence time 16.5 and 25 min. At most, the gas temperature was  $5^{\circ}\text{C}$  above the reactor wall temperature. The small heat losses from the reactor seemed to be sufficient for somewhat moderating these minor exothermal reactions. Other biomass materials, e.g. reed canary grass and eucalyptus, exhibited considerably larger exothermal behavior and active process cooling was required to maintain the desired temperatures [22, 98].

The low residence time distributions, low variation in process temperatures and high reproducibility demonstrate good process control with reliable and predictable products as a result. In other words, the torrefaction pilot plant was found satisfactory for torrefaction research.

#### 4.2.Characterization of torrefied biomass materials

It is well known that torrefaction temperature and residence time are the main factors influencing the mass yield. In Paper I, the experimental domain was chosen such that mass yields between 97% and 46% were obtained (Figure 11 and Table 1), a large interval that covers most torrefaction degrees. The 310/25 experiment resulted in a severely torrefied material with a higher heating value of 27.8 MJ/kg, comparable to lignite. For the less severely torrefied spruce with mass yield 77% (310/8) a higher heating value of 22.4 MJ/kg was obtained, a 10% increase compared to raw spruce.

Within the temperature and residence time intervals evaluated in Paper I, the change in temperature (260 to 310°C) affected the mass yield to a higher extent than the change in residence time (8 to 25 minutes). On average, a temperature increase of 10°C decreased the mass yield by 6.4 % while a residence time increase of 10 minutes decreased the mass yield by 4.9%.



**Figure 11.** Contour plots for two mass yield models, where the model for spruce was developed in Paper I. The experimental design for forest residues was chosen such that the same mass yields as for spruce would be obtained but at lower residence times.

Further studies on torrefaction of forest residues were aiming at lowering the residence time for increasing the biomass throughput. To decrease the residence time, the experimental design was therefore chosen with higher torrefaction temperatures to obtain approximately the same mass yields as

for the spruce experiments. A multiple linear regression (MLR) model was developed from the resulting experimental mass yield for forest residues and the contour plot for the model was nicely overlapping the model for spruce (Figure 11). A short residence time of 4.5 min was thus possible to obtain with this rotating drum/auger type reactor, but requiring higher temperature. A mass yield of 75% was obtained with 4.5 min residence time at 320°C biomass surface temperature. Throughput will therefore increase considerably compared to for example the 15 min residence time required if the maximum temperature would be 300°C, for acquiring a mass yield of 75%.

Decreased mass yield, due to increased temperature or residence time, resulted in decreased oxygen and hydrogen content while carbon content increased. For spruce, 27% of the oxygen, 39% of the hydrogen, and 63% of the carbon contained in the raw material were retained in the solid biomass after torrefaction at 310°C with 25 min residence time. This is due to the formation and release of oxygenated compounds (a complex mixture of CO, CO<sub>2</sub>, H<sub>2</sub>O, and organic compounds) as torrefaction gas. Energy-rich compounds are thus retained in the solid product, explaining the increase in heating value.

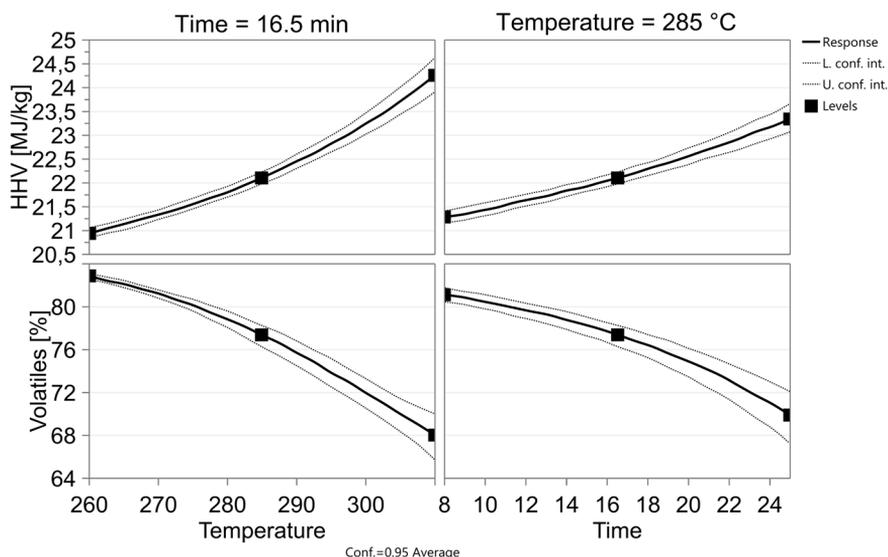
**Table 1.** Torrefaction settings and selected fuel analysis data for the raw material and torrefied products, expressed on dry basis (db) or dry and ash free basis (daf), data from Paper I.

	MY <sub>daf</sub>	EY <sub>daf</sub>	HHV <sub>daf</sub>	LHV	Ash	VM	FC	C	H	O
Temp/time	%	%	MJ/kg <sub>daf</sub>	MJ/kg <sub>db</sub>	% <sub>db</sub>					
Raw	100	100	20.37	19.01	0.4	85.0	14.6	50.4	5.9	43.2
260/8	97	99	20.65	19.31	0.3	84.0	15.7	51.4	5.9	42.3
260/25	89	94	21.51	20.14	0.4	80.3	19.3	53.6	5.9	40.0
285/16.5	80	88	22.23	20.90	0.4	77.5	22.1	55.2	5.7	38.6
285/16.5	80	87	22.28	20.97	0.4	77.3	22.3	55.2	5.6	38.7
310/8	77	84	22.42	21.07	0.4	76.2	23.4	55.8	5.8	37.9
310/25	46	62	27.78	26.51	0.7	51.5	47.8	69.2	5.0	25.0

The experimental results in Paper I were fitted to MLR models to facilitate further analysis and evaluation. The models are also used to illustrate the effects of time and temperature in contour plots (Figure 11) or in prediction plots (Figure 12). Significant interaction effects (time\*temperature) had to be included in the models for mass yield, energy yield, HHV, LHV and hydrogen content. The models for fixed carbon and volatile matter benefited by a quadratic effect but no interaction effect. However, the significant

interaction and quadratic effects may be because of the use of constant fill ratio in the reactor.

The uncertainty of the models varied, but was generally low for this type of experimental design and experimental setup. Prediction of higher heating values and volatile contents with corresponding uncertainties are shown in Figure 12. The uncertainties are somewhat larger at the more extreme conditions (long residence time or high temperature), a probable cause is the logarithmic transformation required since the 310/25 experiment were relatively extreme compared to the other experiments

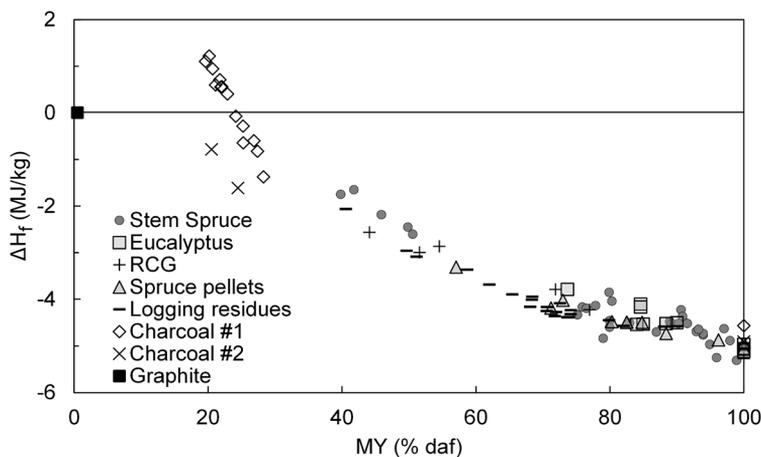


**Figure 12.** Prediction of higher heating value (HHV) and volatile matter for various torrefaction temperatures and residence times. The model used was developed for Paper I. Dotted lines show the 95% confidence intervals of the responses

The volatile matter (VM) in biomass decreases with increasing torrefaction degree, from 85% in raw spruce down to 52% in the 310/25 experiment. For comparison, the volatile content was 19% for a commercial non-smoking charcoal (severely pyrolysed at 420 °C for at least 10 h) analyzed in Paper II. The yield of volatile matter was lower than the mass yield and consequently, the yield of fixed carbon was above 100 % (Figure 4 in Paper I). Some of the volatile matter in the raw wood was thus converted to fixed carbon in the solid product. A possible explanation is that the volatiles contribute to secondary char-forming reactions by decomposition of organic vapors onto the solid [99].

In the carbonization and volatilization process occurring during torrefaction, chemical bonds in the biomass are rearranged. This results in increasing enthalpy of formation with decreasing mass yield (Figure 13).

Many raw biomass materials have enthalpy of formations close to that of raw spruce; -5.1 MJ/kg. For spruce torrefied to 46% mass yield (310/25), the enthalpy of formation was -2.2 MJ/kg. Reed canary grass and logging residues acquired similar enthalpy of formation at comparable mass yields. As can be seen for all compiled materials from the present work, enthalpy of formation increase with decreasing mass yield, although the increment is less pronounced at the highest mass yields. The small changes close to 100% mass yield are also masked by the high relative combined uncertainty of 10%. The trend is more evident by including all torrefaction degrees and additional charcoals with very low mass yields. At very low mass yields, the solids acquire positive formation enthalpies, similar to some natural coals such as anthracite, semi-coking coal and other very carbon rich coals [100, 101]. Based on the fact that torrefaction changes the formation enthalpy of the biomass, we developed a method for determination of the degree of torrefaction ( $DTF_{\Delta H_f}$ ) discussed later in this thesis.



**Figure 13.** Formation enthalpy of various biomasses as a function of mass yield. Graphite has a formation enthalpy of 0 MJ/kg by definition. (Paper II)

### Wood components

The main wood components (hemicellulose, cellulose and lignin) degrade in different temperature intervals and rates during heat-treatment. Hemicellulose degrades at lowest temperature according to experiments with both classical wet chemical methods (Paper I and [102]) and NMR analysis [10, 102]. Also within hemicellulose the different compounds (for example arabinoxylan, galactomannan, glucomannan, xyloglucan, and xylan) behave quite different during thermal treatment (Paper I and [9]) regarding for example decomposition start temperature and exothermal behavior. Cellulose consists of glucose units which seem to be more resistant

to heat than the hemicellulose carbohydrates. Amorphous cellulose originating from the raw wood is partly crystallized at temperatures of 200 to 245°C but at higher temperatures both amorphous and crystallized cellulose are degraded [10]. In Paper I, cellulose degradation was undetected at very mild torrefaction (97% mass yield, 260/8) but detected when residence time was increased to 25 min (89% mass yield).

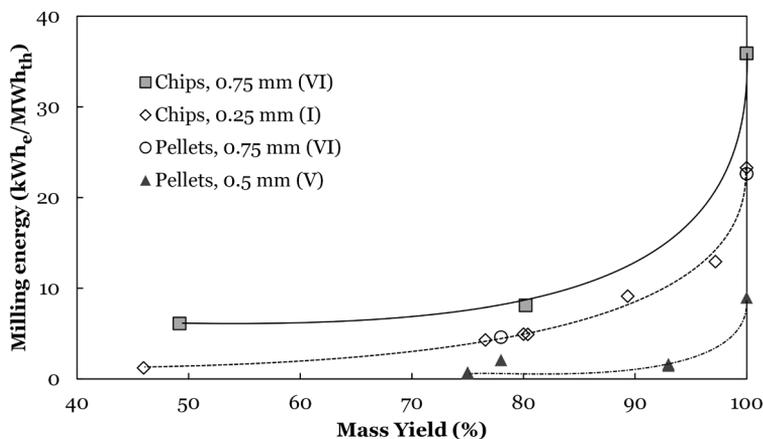
The content of wood lignin is more difficult to determine. A usual method is to determine the acid-insoluble lignin (Klason lignin). For torrefied materials, more “Klason lignin” was found than were present in the raw material, i.e. per 100g of raw material the content of acid-insoluble residue was increasing with increasing torrefaction severity (Paper I). Degraded carbohydrates combined with condensed structures originating from lignin and carbohydrates are suggested reasons [103]. Zhou et al [104] investigated isolated lignin particles and identified liquefied lignin already at 154°C. At higher temperatures, lignin were forming volatiles, but in a biomass particle the liquid lignin may be entrapped or recondensed, thus forming char. Softening of lignin is occurring at even lower temperatures and the softening temperature is reported to decrease with increasing moisture content [105, 106], a characteristic potentially important for regular white-wood pelletizing [107]. NMR-analysis of torrefied wood revealed lignin to be thermally affected at temperatures of 200°C, though not degraded or depolymerized [10].

### ***Milling energy***

Milling energy consumption during size reduction of chips and pellets to powder is substantially decreased by torrefaction. A 45% reduction in milling energy is noticeable already at 97% mass yield for spruce chips and 95% reduction for a product with 46% mass yield, compared to milling energy of raw spruce chips (Figure 14). Compared to reference white pellets, the milling energies of the black pellets were reduced by 83% and 93%, at 93% and 75% mass yield respectively. For both torrefied and untorrefied fuels, the milling energy consumption was lower when the fuel was in pelletized form, an expected result since at least one size reduction step is included in the pelletization process. For example, milling energy was 4.3 kWh<sub>e</sub>/MWh<sub>th</sub> for chips with a mass yield of 77%, compared to 0.6 kWh<sub>e</sub>/MWh<sub>th</sub> for pelletized spruce with mass yield 75%, a decrease by 86%. The difference in milling energy for chips in Paper I and VI could be related to the different milling equipment; in Paper VI we used a relatively large hammer mill compared to the bench scale centrifugal mill used in the other papers. Also, the moisture content of the chips in Paper VI was slightly higher (3-4% mc).

In Paper I, we found that the brittleness of the torrefied material to a large extent can be explained by degradation of hemicellulose (Figure 8 in Paper I). The explanation probably relates back to the main biological role of

hemicelluloses, which is to interact with cellulose and lignin and thereby contribute to the strengthening of the cell wall.



**Figure 14.** Milling energy consumption for chips and pellets for various mass yields. Fuel form prior to milling and milling screen size is shown in the legend and paper number is shown within parenthesis. Note different kinds of mills, sieves and measuring equipment were used in the three studies, but the relative trends should be comparable.

### ***Hydrophobic properties***

Torrefied chips resulted in significantly larger contact angles between chips and water droplets compared to raw spruce chips (20-30° larger), both at 1 and 5 minutes after the water droplets were placed on the chips. Only the 260/8 product was however significantly above 90° and was considered physically totally hydrophobic according to the contact angle test. However, contact angle measurement is probably not the most accurate method to determine wettability/hydrophobicity of torrefied materials due to the rough surfaces of wood chips. Also, the method does not account for the possible changes inside the samples or the hygroscopic behavior of final pellet products. Analysis of equilibrium moisture content also demonstrated a distinct difference between torrefied and raw biomass. The EMC of the torrefied biomass decreased by 50% or more compared to EMC of the raw biomass and EMC decreases as torrefaction degree increases (Figure 11 in Paper I).

There may be several explanations to the increased hydrophobic properties of torrefied biomass. During heat treatment, the presence of hydroxyl groups decreases with increasing torrefaction degree. Hydroxyl groups present in mainly hemicellulose are volatilized to a larger extent at more severe torrefaction conditions. By removal of these hydroxyl groups that form hydrogen bonds with water, less water is adsorbed by the biomass

[81, 108]. Free water can still be bound by capillary forces in micro- and macrovoids and for torrefied biomasses this is probably the main cause for water uptake as discussed by Stelte et al. [81]. There are also indications that some of the tar components present in the torrefaction gas may condensate on the surface of the solid material and thus increase the hydrophobic properties.

### ***Are time and temperature interchangeable?***

In Paper I, we made attempts to evaluate the possibility that one combination of torrefaction time and temperature could be interchanged with another time-temperature combination, i.e. if the same product could be produced for example at both 300/8 and 280/14. The evaluation was performed with the MLR-models developed for the product responses. A visualization of the evaluation could be by using the contour plots with only the selected ranges visible and then stacking layers of the contour plots. The overlapping area is the resulting area for which the time and temperature are interchangeable.

It was concluded that time and temperature potentially are interchangeable within a time-temperature area when considering only a few product properties but not with respect to several more properties (Figure 12, Paper I).

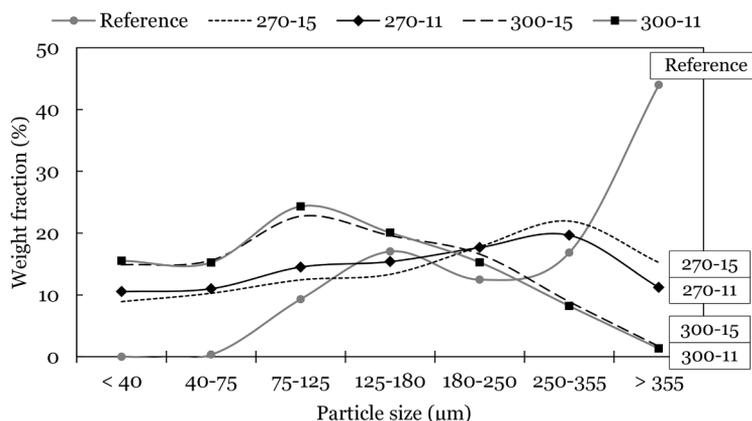
### **4.3. Powder characteristics**

The fibrous structure of biomass and resulting biomass powder are problematic in feeding equipment which can result in unreliable, inefficient and variable feeding due to bridging, blockage and rathole formation [4]. Since hemicellulose and cellulose are decomposed during torrefaction, the wood fibers become more brittle, resulting in lower milling energy. It has also been presumed, and partly previously demonstrated, that the particles from milled torrefied materials become smaller, more circular, and less problematic in feeding equipment. To elucidate this, powder characteristics were studied in Paper I, IV, V and VI, but with some differences in objectives and origin of the powder. To my knowledge, powders and particles from milled pellets from torrefied material has not earlier been carefully characterized and presented in the literature.

### ***Particle size distributions***

Analysis of particle size distributions of powders from pelletized raw and torrefied spruce reveal that even with the same mill and sieve size, powders from torrefied materials constitute of significantly smaller particles. Only about 10% of the torrefied powder (with mass yield 75%) was particles larger than 250  $\mu\text{m}$ , compared to 61 % for the reference material (Figure 15). Less than one percent of the reference powder passed through the 75  $\mu\text{m}$  sieve,

compared to between 20 and 30% for the torrefied samples. Entrained flow gasification of coal typically uses particle sizes below 100  $\mu\text{m}$ , however, during biomass gasification particle sizes of 500  $\mu\text{m}$  may be feasible due to higher reactivity [109] but any potential further reduction would be beneficial for the carbon conversion.



**Figure 15.** Particle size distribution of powders from the pelletized fuels analyzed in Paper V. 270 and 300 denotes the torrefaction temperature while 11 and 15 denotes the moisture content before pelletization.

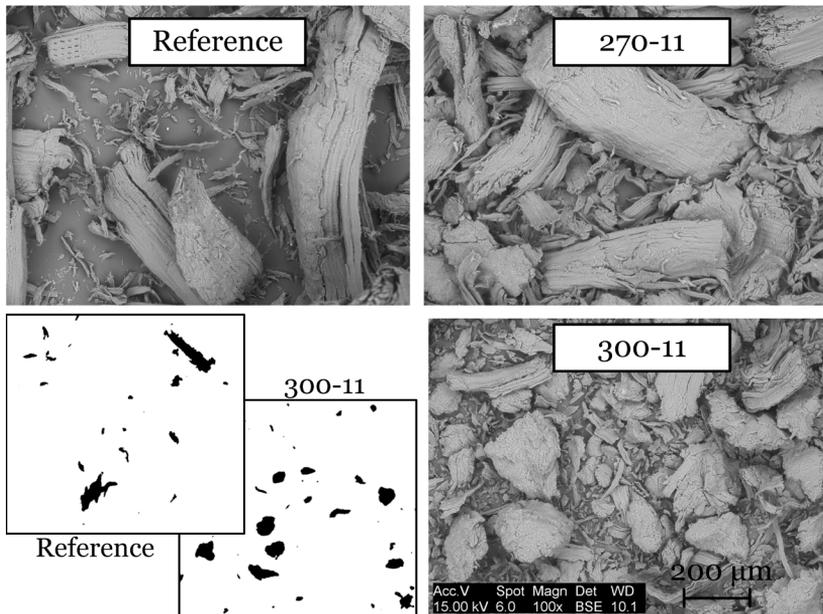
### ***Morphology***

Image analysis of milled powder, for characterization of size and shape factors, could be an important tool to explain differences in angle of repose and bulk density [110]. In Paper V, image analyses were therefore performed on powder particles from milled torrefied and pelletized spruce. The image analysis reveal that particles from torrefied materials are less elongated with up to 60% smaller aspect ratio, compared to the reference. Smaller particles were also less elongated. Elongated particles originate from the biomass fiber structure that is damaged during heat treatment as evident from the decreased content of hemicellulose and decreased milling energy consumption. Roughness of the particles was quantified by the solidity parameter. The reference had lowest solidity and hence roughest particles, more severe torrefaction gave particles with less surface roughness. SEM-images were consistent with the result from image analysis with respect to elongation, surface roughness, and particle sizes (Figure 16).

Microscopic photos of milled wood chips in Paper VI also clearly demonstrated the differences between powders from untreated wood and torrefied wood (Figure 2, Paper VI). The milled raw fuel particles were large and very elongated along the fiber structure. The powder from chips torrefied to 80% mass yield (Torr-300) contained less elongated particles of

smaller sizes, but the fibrous structure were still present. The resulting powder with 40% mass yield (Torr-340) had different characteristics compared to the less torrefied fuels; very large fraction of fine particles, and particle elongation and fiber structure were not visible at that magnification.

Size and shape of particles are important factors for example for pyrolysis fuel conversion [111], carbon burnout rate [112, 113] and particle transportation in gas flows [114].



**Figure 16.** SEM images of powder particles from pelleted reference and two torrefied fuels, produced at 270°C (MY=93%) or 300°C (MY=75%) torrefaction temperature (Paper V). Black and white images are illustrations from the image analysis in Paper V.

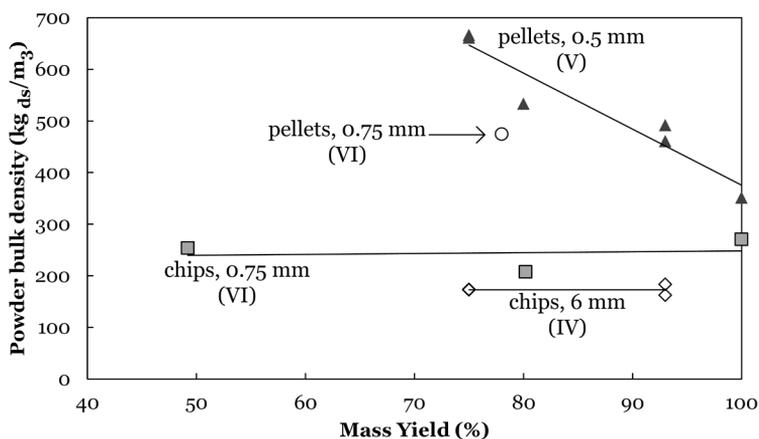
### ***Powder bulk densities***

Powder bulk densities for milled dry torrefied spruce chips were relatively low, 160-250 kg<sub>ds</sub>/m<sup>3</sup> compared 270 kg<sub>ds</sub>/m<sup>3</sup> for untreated dry spruce chips. Bulk density of milled torrefied pellets was 3-4 times higher (460 to 670 kg<sub>ds</sub>/m<sup>3</sup>) than the density of milled chips. The density of milled reference pellets (commercial white pellets) was 350 kg<sub>ds</sub>/m<sup>3</sup>, i.e. lower than for milled black pellets. Mass yield is seemingly not correlated to bulk density for milled chips. For milled pellets on the other hand, bulk density is highly correlated to mass yield; higher mass loss during torrefaction was associated with increased bulk density (Figure 17).

The lack of correlation could be explained by that single particle density is lower after torrefaction due to the weight loss, and that some elasticity of the wood fibers could be retained after torrefaction and milling, which should

contribute to lower bulk density. The elasticity and particle density possibly counteracts the effect of smaller and smoother particles, properties usually associated to higher bulk density [115].

The particles from milled pellets should be denser and less elastic, as the severe densification in the pelletization process collapses the cell walls and many cavities and hollow structures. More cavities should also collapse for the more severely torrefied biomass and thereby increasing both the particle and bulk density. Breakage of cell walls and elastic deformation of particles have previously been described for pelletization of untreated biomass materials [116, 117] so a reasonable assumption is that the similar could occur for torrefied materials, unless the elasticity already is destroyed during torrefaction.



**Figure 17.** Bulk density for powders from milled chips and pellets versus torrefaction mass yield. Fuel form prior to milling and milling screen size is shown in the legend and within parenthesis is the paper number.

### ***Angle of repose***

A low angle of repose for a powder is correlated to a low feeding variability in screw feeders and the total mass flow is highly correlated to powder bulk density [118]. Also, powders with low angle of repose are typically classified as having higher flowability in general [119-121].

Powder from untreated biomass exhibit larger angle of repose compared to powders originating from torrefied materials, although the effect is small when the powder originates from chips. AoR was 69° (standard deviation,  $s=1.5^\circ$ ) for milled raw spruce chips and 67° ( $s=0.4^\circ$ ) for milled torrefied spruce chips with 77% mass yield. Powder from pellets should be more suitable for (screw) feeding as the angle of repose is lower; 66° ( $s=1.0^\circ$ ) for milled household pellets and as low as 57° ( $s=0.5^\circ$ ) for powder from torrefied and pelletized biomass with 75% mass yield (300-15, Paper V).

A conclusion from the analysis of powder characteristics is that torrefied and pelletized biomass materials, compared to untreated materials, should be more suitable for screw feeding (higher mass flow and less variability) and possible also for other feeding technologies. The enhanced powder properties beneficial for feeding are the higher bulk density, lower angle of repose, and less elongated particles with less surface roughness.

#### 4.4. Degree of torrefaction

There is a need for a method for determination of the degree of torrefaction in addition to the traditional strenuous method to determine mass yield. We therefore developed two new methods for calculation of the torrefaction degree, one method based on higher heating value (DTF<sub>HHV</sub>) and one thermochemical method based on calculations of formation enthalpy of biomass (DTF<sub>ΔHf</sub>). Those two new and one existing method based on volatile matter (DTF<sub>VM</sub>) were compared and evaluated including a comprehensive error analysis. All three definitions (for the equations see section 3.4) were found to be highly or very highly correlated to mass yield (Table 2) although torrefaction degree based on heating value had the highest correlation to mass yield.

**Table 2.** Correlation and prediction of mass yield for the three methods evaluated for determination of torrefaction degree. Also combined standard uncertainty ( $u_c$ ) is presented. MAE=mean absolute error of the prediction.

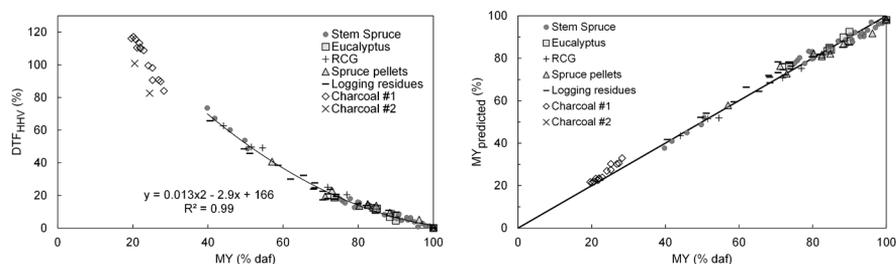
Method	R <sup>2</sup>	Q <sup>2</sup>	MAE (%)	$u_c$ (%)
DTF <sub>VM</sub>	0.97	0.97	2.4	1.6 - 2.8
DTF <sub>ΔHf</sub>	0.93	0.92	4.1	8 - 9.4
DTF <sub>HHV</sub>	0.98	0.98	1.8	1.1

Figure 18 shows the correlation between mass yield and DTF<sub>HHV</sub>. Since DTF<sub>VM</sub> is not calculated on ash free basis, ash-rich fuels as reed canary grass could be considered as slight outliers when plotting against the mass yield (Figure 1 in Paper II). Otherwise all three methods are considered valid for many types of biomasses; Norway spruce, pine, logging residues, eucalyptus, and reed canary grass were included in the evaluation. A model for predicting mass yield was developed for each torrefaction degree. The torrefaction degree based on higher heating value (DTF<sub>HHV</sub>) had the highest predicting ability of mass yield. Predictive ability was determined both by Q<sup>2</sup> and mean absolute error (MAE) of the prediction (Table 2). The prediction model developed for DTF<sub>HHV</sub> was:

$$MY_{pred} = 98e^{-0.013DTF_{HHV}} \quad (6)$$

where  $MY_{pred}$  is the predicted mass yield. Predicted mass yield with the model versus measured mass yield is demonstrated in Figure 18.

$DTF_{HHV}$  was also found to have the lowest combined standard uncertainty (1.1%) while  $DTF_{VM}$  was less accurate with an uncertainty of 2.8%. The largest combined standard uncertainty (9.4%) was obtained for torrefaction degree based on formation enthalpy ( $DTF_{\Delta H_f}$ ) due to the many analysis required (C, H, S, ash and HHV). The measurement uncertainties of hydrogen and carbon content had the highest influence on the combined uncertainty associated to  $DTF_{\Delta H_f}$ .



**Figure 18.** Left: Degree of torrefaction based on higher heating value for various biomass materials over a wide range of mass yield. Right: Mass yield versus predicted mass yield with the prediction model for  $DTF_{HHV}$ , the straight line shows  $MY = MY_{predicted}$ .

These approaches to determine the degree of torrefaction is especially useful in processes where mass yield is difficult or impossible to measure. Degree of torrefaction could also be used to validate a measured mass yield. Based on this study,  $DTF_{HHV}$  is the recommended method for determination of torrefaction degree.

#### 4.5. Oxygen enhanced torrefaction

In Paper III, we studied a potentially improved torrefaction process where small amounts of air are added to accomplish an in situ partial combustion, preferably of the torrefaction gas oxygen. The hypothesis was that the heat generated from in situ partial combustion of the gas could facilitate direct heat generation and thus improve the process economics and scale-up potential. According to the measured oxygen content in the end of the reactor, oxygen was partly consumed at about 170-180 °C and fully consumed at 225 °C, with an oxygen equivalence ratio ( $\lambda$ ; Eq. 7) of 0.008.

Several experiments with concurrent gas flow were unsuccessful, even at high  $\lambda$  of 0.03. Gas temperatures in the end of the reactor reached steady state but the gas temperatures in the beginning of the reactor declined throughout the experiments. The partial combustion of gas evolved heat too late in the reactor requiring the regular electrical heaters to heat up the biomass in the first part of the reactor. However, during the concurrent gas

flow experiments we found strong indications validating that injected oxygen mainly react with the torrefaction gas and not the solid biomass. After a step increase in air flow, the torrefaction gas temperature increased in a few seconds while the biomass surface temperature responded after some minutes.

We thereafter evaluated countercurrent gas flow in order to push the evolved heat towards the biomass inlet, thereby decreasing the need of the external heating. A biomass temperature of 305°C with a  $\lambda$  of 0.03 resulted in decreasing gas temperatures and steady state was not achievable. Increasing  $\lambda$  further as a countermeasure resulted instead in too high and alarming levels of oxygen in the reactor.

Successful steady state operation without the use of external heat (except the preheater which heated the biomass to below 204°C) was demonstrated at a biomass surface temperature of 338°C and with a  $\lambda$  of 0.014. Furthermore, the torrefaction gas burner showed no significant changes concerning the combustibility of the remaining torrefaction gas. This initial demonstration of oxygen enhanced torrefaction (OET) lasted more than three hours of steady state operation, and was also verified with a replicate run on a separate day with resulting mass yields of 69% and 66%, respectively. Another torrefaction experiment with the same biomass torrefaction temperature and residence time, but without injection of air, resulted in a mass yield of 52%. The time-temperature history for the biomass at the two types of experiments is thereby quite different. The regular torrefaction were conducted with isothermal conditions along the reactor outer surface, resulting in a relatively high heating rate and thus the biomass temperature was probably close to the final torrefaction temperature for some minutes. The biomass heating rate for the countercurrent OET experiment was lower, presumably reaching the final temperature only at the end of the reactor.

#### **4.6. Pilot scale pelletization of torrefied biomass**

Pelletization of two qualities of torrefied Norway spruce was performed in a pilot scale ring die pelletizer based on an industrial Bühler press. Torrefied chips were produced with 16.5 min residence time at 270°C and 300°C resulting in 93% and 75% mass yield, respectively. Higher torrefaction temperature was found to be correlated to better pellet quality, i.e. lower amounts of fines, increased durability and increased bulk density. Higher torrefaction temperature was also correlated to lower production rate (with constant motor power). The bulk and energy densities were 653 kg/m<sup>3</sup> and 12.9 GJ/m<sup>3</sup> on average for the 270°C-pellets and 693 kg/m<sup>3</sup> and 14.6 GJ/m<sup>3</sup> on average for the 300°C-pellets. Regular Swedish wood pellets generally have energy density of 9.7 to 11.3 GJ/m<sup>3</sup> [122]. For long distance transports are thus black pellets favorable.

Die temperatures were increasing throughout each pelletizing experiment resulting in increasing production rates but decreasing pellet bulk density. Durability and amount of fines were almost unaffected by die temperature. High die temperatures can be hazardous as the high pellet temperatures may cause a risk of fire and such indications were visible during the experiments.

Biomass moisture content is a very important factor in pelletizing of raw biomass. Too low or too high moisture content causes decreased pellet quality [117]. A higher moisture content of the torrefied spruce before pelletization decreased the amount of fines and increased durability and bulk density. However, the present black pellet quality was lower compared to commercial white softwood pellets. Torrefied biomass can bind less water as demonstrated by equilibrium moisture content measurements and this could be a reason for the lower quality compared to softwood pellets. The actual role of water is not clear but one possible explanation is that water act like bridges that bind active groups at the surface of the biomass particles together as discussed in Paper IV. Another explanation is that water is known to lower the thermal softening temperature of lignin [106] and lignin plasticization is an important bonding factor for pelletization as excellently reviewed by Stelte et al. [117].

The motor power required for pelletizing, after subtraction of the idling power, was 22 kW for torrefied materials compared to 11 kW for similar production rates of typical white softwood. This well documented [81, 82, 84] higher friction characteristics of torrefied biomass materials in terms of power consumption is probably best compensated with shorter die channel lengths but further optimization is needed to fine tune power consumption versus pellet yield and quality. Furthermore, in the present pelletizing experiments the moisture content of the newly pressed black pellets was 6 to 13 percentage points lower than for the milled input material. This corresponds to vaporization of 15 to 25 kg<sub>H<sub>2</sub>O</sub>/h, requiring 10 to 15 kW of the pelletizing motor which is comparable to the increased motor power of 11 kW. The reason for this water boiling was probably because of high temperatures either due to friction or due to the very high pressures in the pelletization process. Loosely bound water on the particle surfaces and in microvoids will possibly acquire sufficient energy at these high pressures to vaporize when the pressure releases. Whichever the reason, from an exergy perspective the pelletizing motor should not be used for vaporization of water, except if the water is needed for decreasing the friction. For a case without water vaporization the available motor power would instead be used for example to increase pellet temperature, hardness, density or the production. Therefore, in optimizing the pellet production for increasing the pellet quality, focus should also be on decreasing the vaporization.

An overall conclusion from these experiments is that the usual method to use water for enhancing bonding properties in pellet production may not be

a feasible technique. However, more degrees of freedom are available for further extensive optimization work (i.e. torrefaction temperature, torrefaction residence time, torrefaction heating by flue gases, particle size distribution, additives, die diameter, channel length, cooling and heating of the die, and biomass specie). Unpublished preliminary data demonstrated that briquetting of torrefied material also can be a successful densification method.

Here we also need to emphasize that no optimization of the materials and process were performed before these experiments. Recent extensive work and optimizations by CENER within the European SECTOR project have resulted in high quality black pellets from torrefied straw with >97% durability and bulk density exceeding 700 kg/m<sup>3</sup>. Their method for combining torrefaction and pelletization is however not published.

#### **4.7. Feasibility of using torrefied materials in entrained flow gasification**

Pretreating biomass by torrefaction could be beneficial for entrained flow gasification because of the lower milling energy consumption, smaller particle sizes which enhances fuel conversion [111], the increased heating values, and the improved powder characteristics. A possible drawback could be that the particle conversion rate may be lower for torrefied biomass materials [51, 52] presumably because of the lower volatile content. In Paper VI, we evaluated and compared the behavior of raw wood residues and three torrefied wood materials milled with a 0.75mm mill sieve during gasification at 270 kW<sub>th</sub>, 2 bar(a) with an oxygen equivalence ratio ( $\lambda$ ) of 0.44. The mass yield for the torrefied fuels were 80% (Torr-300), 49% (Torr-340) and around 78% (Torr-demo). No challenges were documented related to fuel handling, storage, milling, or feeding during these experiments.

To be able to compare the different experiments, a temperature (gas temperature inside the gasifier at mid height) range of 1210°C to 1250°C was selected. The fuels required different time for this temperature increase of 40°C with the same thermal fuel input; 34 min, 44 min, 57 min and 78 min for Torr-340, Torr-300, Raw and Torr-demo, respectively. Variances in flame structure and heat transfer are possible explanations which needs to be further investigated. Flame sizes were visually inspected with a camera and the flame of Torr-340 was considerably smaller compared to the other, an indication of higher reactivity and higher flame temperatures.

**Table 3.** Gasification results measured within process temperature range 1210-1250°C. Gas compositions as average dry and N<sub>2</sub> free.

	Unit	Raw	Torr-300	Torr-340	Torr-demo
CO	mol%	50.0	54.6	60.3	54.0
H <sub>2</sub>	mol%	26.2	27.2	26.7	28.0
CO <sub>2</sub>	mol%	23.3	18.6	12.7	16.9
CH <sub>4</sub>	mol%	1.8	1.6	0.9	1.8
H <sub>2</sub> /CO	-	0.52	0.50	0.44	0.52
Carbon conversion	-	0.89	1.10	0.84	0.97
LHV <sub>power</sub>	MJ/kg <sup>e</sup>	7.2	8.1	8.3	8.3
LHV <sub>fuel</sub>	MJ/kg <sup>e</sup>	6.6	7.6	8.0	7.7
CGE <sub>power</sub>	-	0.58	0.81	0.63	0.70
CGE <sub>fuel</sub>	-	0.54	0.76	0.61	0.65
Plant efficiency, η <sub>plant</sub>	-	0.49	0.79	0.62	0.69
Milling energy	kWh <sub>el</sub> / MWh <sub>th</sub>	35.9	8.1	6.1	4.6

<sup>e</sup> kg dry gas

An increase of the torrefaction severity resulted in a syngas with somewhat higher CO, lower CO<sub>2</sub> and CH<sub>4</sub>, and no obvious effect on H<sub>2</sub> content (Table 3). The syngas from torrefied fuels is seemingly improved as CO and H<sub>2</sub> are the desired syngas components useful for syngas synthesis whereas CO<sub>2</sub> and CH<sub>4</sub> are bulk gases in the synthesis and should be considered as energy losses. The change in syngas composition is however probably a result of the total amount of oxygen in the gasifier as explained below. Torrefied materials contain less oxygen compared to untreated materials and with the current definition of λ (Eq. 7) the fuels will therefore be differently oxidized at λ=0 and consequently also at λ=0.44. Oxygen equivalence ratio is typically defined as

$$\lambda = \frac{O_2^{gasi}}{O_2^{stoic}} = \frac{O_2^{gasi}}{C^{feed} + \frac{1}{2}H_2^{feed} - O_2^{feed}} \quad (7)$$

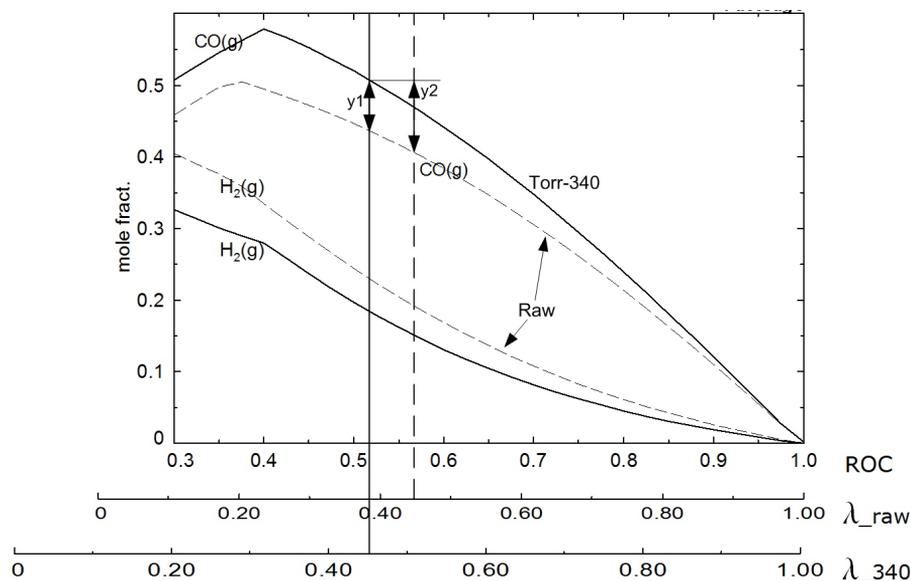
where O<sub>2</sub>, C and H<sub>2</sub> are molar flows and the superscripts are gasification agent (supplied O<sub>2</sub>), stoichiometric and feedstock.

However, another variable, Relative Oxygen Content (ROC) [123] rearranges the oxidants and reductants compared to λ so that for a given ROC the reductants (mainly carbon and hydrogen) will be exposed for the same amount of oxygen:

$$ROC = \frac{O_2^{gasi} + O_2^{feed}}{O_2^{stoic,total}} = \frac{O_2^{gasi} + O_2^{feed}}{C^{feed} + \frac{1}{2}H_2^{feed}} \quad (8)$$

Note that if the fuel has a moisture content above zero, also the oxygen and hydrogen in the water needs to be included in O<sub>2</sub><sup>feed</sup> and H<sub>2</sub><sup>feed</sup>. From these two definitions one can conclude that at constant λ, the syngas

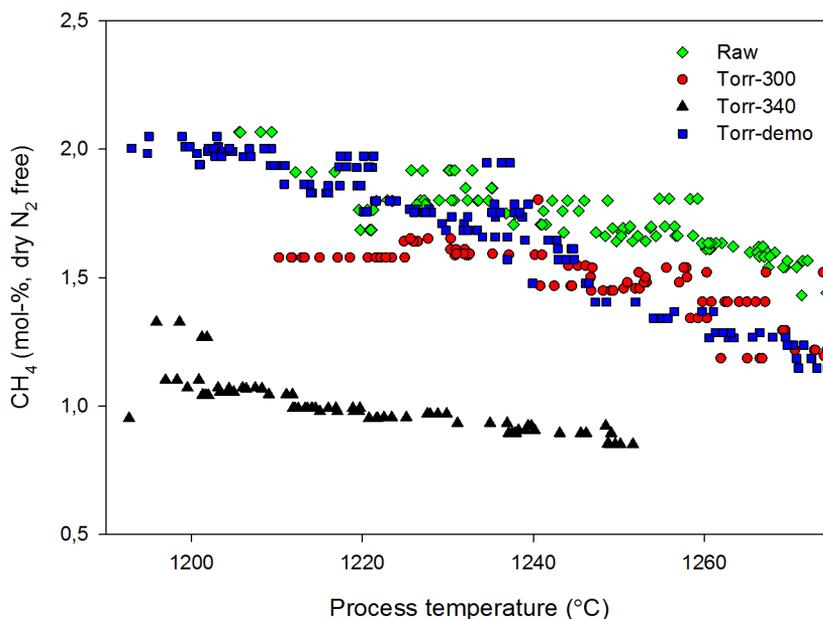
composition will shift towards more CO and less CO<sub>2</sub> with increasing torrefaction degree due to lower amount of available oxygen. Also, this is evident from equilibrium calculation of syngas composition (Figure 19). At a constant ROC of 0.53, the difference in CO content between raw and Torr-340 is represented by  $y_1$  in Figure 19. The larger  $y_2$  represents the difference at constant  $\lambda$  of 0.445. The equilibrium calculation also shows a very small difference in H<sub>2</sub> between the fuels at constant  $\lambda$ . The content of H<sub>2</sub> is expected to differ more at constant ROC.



**Figure 19.** Chemical equilibrium syngas composition from raw and torrefied (Torr-340) wood residues. Gasification equilibrium temperature was set to 1500°C. Broken lines are for raw and solid lines are for Torr-340. Upper x-axis is ROC, middle is oxygen equivalence ratio for the raw biomass and lower x-axis is oxygen equivalence ratio for Torr-340.

The methane content in the syngas was significantly lower for Torr-340 at any given process temperature (Figure 20). The raw biomass produced slightly more CH<sub>4</sub> at the higher temperatures compared to the two medium torrefied fuels. However, equilibrium calculations gives that CH<sub>4</sub> is not favorable at these high temperatures. A proposed reason for the presence of methane in gasification syngas is that it is an unconverted pyrolysis product and thus a rest from the volatile components in biomass [124, 125]. A reason for the lower CH<sub>4</sub> content in syngas for torrefied fuels could therefore be that volatile components are removed in the torrefaction process. The relationship between the biomass volatile content and the CH<sub>4</sub> yield from gasification is however not clear in the existing literature, regardless whether the volatile content were reduced by torrefaction [50, 51] or by comparing

biomasses with different volatile contents [126, 127]. Another explanation could be the finer and thus more reactive fuel powder resulting in higher flame temperature for Torr-340 that thermally decomposes  $\text{CH}_4$  to a greater extent than for the other fuels.



**Figure 20.** Measured  $\text{CH}_4$  concentration in the syngas at different gasification temperatures for raw fuel and the three torrefied fuels.

The highest carbon conversion and cold gas efficiency (CGE) were found for the two mildest torrefied fuels, Torr-300 and Torr-demo. However, there could possibly be an increased experimental error for Torr-300 due to air leakage into the gas sampling system. Several factors influence carbon conversion, for example: fuel particle size distribution, reactivity of the burning fuel particles, ROC, process temperature and char reactivity. Gasification of Torr-340 resulted in lowest carbon conversion even though this fuel had the smallest particle sizes. Lower ROC and reduced particle reactivity may be the cause but this has to be further studied. A side-note is that the feeding of the torrefied fuels worked better than for the reference fuels.

The plant efficiency,  $\eta_{\text{plant}}$ , was also compared for the different fuels both with and without including milling of the fuel. For the torrefied fuels  $\eta_{\text{plant}}$  decreased by 1-2 percentage points to between 62 and 79% when including milling. For the raw fuel,  $\eta_{\text{plant}}$  decreased by 9 percentage points to 49%. The lower milling energy consumption for torrefied fuels could therefore have a large positive impact on the total plant efficiency.



## 5. Conclusions

This chapter presents conclusions from the present thesis work together with some implications for large scale plants and for further studies.

At the start of the present project, mainly batch torrefaction processes were presented and evaluated in the literature. The present thesis shows that the benefits of torrefied biomass are valid also when produced continuously, which was demonstrated by torrefaction, pelletization and gasification experiments with continuous pilot scale facilities. Some of the documented benefits are increased heating value, increased energy density, lower milling energy consumption, and less hydrophilic biomass.

The designed and developed continuous torrefaction pilot plant showed good temperature control and narrow residence time distribution resulting in high reproducibility of experiments. The (novelty) use of an infrared thermometer made it possible to in situ measure the torrefied biomass surface temperature, a more representative torrefaction temperature compared to the typically used temperatures of the torrefaction gas or the reactor surface.

A short residence time might be desired in a large production plant due to higher biomass throughput. The developed pilot plant allowed short residence times (~4.5 min) but a trade-off is the higher temperature required. In contrast, recommendations from bench scale studies are generally 45-60 min. The pilot plant was rebuilt based on the results from the studies included in this thesis for facilitating flue gas heating instead of electric heating, thereby resembling one alternative for large scale heating.

For untreated fuels, HHV are typically 19 MJ/kg<sub>daf</sub>, but up to 27 MJ/kg<sub>daf</sub> for torrefied fuels, and up to 34 MJ/kg<sub>daf</sub> for pyrolysis solids. Pelletized torrefied fuels, compared to white pellets, also have higher bulk energy densities which should allow for smaller feeding equipment or higher biomass loads using existing equipment. The high heating values obtained after torrefaction could also be used to increase the use of fuels with high moisture content and low heating value (i.e. some wastes, residues, and sludges) by co-combustion.

Powder from milled torrefied biomass have higher bulk densities, lower angle of repose, and smaller less elongated particles with less surface roughness (compared to powder from untreated biomass). Powders from torrefied fuels should therefore be more suitable for feeding to a gasification or combustion burner. Also, the combination of torrefaction and pelletization further enhanced the powder. A recommendation is thus to densify the fuel prior to gasification and combustion R&D studies for maximum enhancement of the product and also for resembling commercial torrefied fuels that will be densified.

For continuous torrefaction processes, it is challenging to directly determine mass yield, an alternative is some kind of method to determine degree of torrefaction (DTF). Of three evaluated methods, the DTF based on higher heating value (DTF<sub>HHV</sub>) had lowest combined uncertainty and the most accurate prediction of mass yield. DTF<sub>HHV</sub> can thus also be used for verification or calibration of a measured mass yield.

The concept of oxygen enhanced torrefaction was demonstrated in an initial feasibility study. By partial combustion of the torrefaction gas inside the torrefaction reactor, more cost efficient and direct heat production can potentially be accomplished.

Pelletization of torrefied materials was more challenging than pelletizing untreated biomass. The combination of torrefaction and pelletization therefore requires further development. Also other methods for densification such as briquetting may be interesting options with additional benefits.

A feasibility study of entrained flow gasification (EFG) of torrefied materials showed no additional challenges with respect to the raw material. EFG of torrefied materials worked well with respect to fuel handling, milling, feeding, as well as concerning burner and process behavior. The total gasification plant efficiency was benefitted from the lower milling energy consumption for torrefied fuels. A recommendation for further gasification studies is to use constant ROC (relative oxygen content) instead of the usual oxygen equivalence ratio ( $\lambda$ ) that were demonstrated to be unsuitable for comparing fuels with different degrees of torrefaction.

Pelletized torrefied biomass is favorable for long distance transports due to higher bulk energy density compared to regular pellets. This should facilitate the use of remotely located, lower cost biomass which is largely unused today, for example by placing the torrefaction plants in remote inland locations.

A centralized large scale entrained flow gasification plant will be benefitted by fuel transports from decentralized torrefaction plants because the biomass supply area should increase since long distance transports are favorable and thus biomass cost decrease. Other benefits from pretreatment by torrefaction for a commercial entrained flow gasifier is the improved powder properties, increased heating value, and enhanced syngas.

By studying many aspects in the chain from biomass to a high value syngas, a desire was to identify the bottlenecks that potentially could limit the preceding or subsequent processes. As no obvious bottlenecks were found, it is possible that the main limitations are related to economy and torrefaction plant efficiency. Efficient use of the torrefaction gas, process integration and cost reduction are therefore obvious R&D suggestions.

The research regarding torrefaction and use of the solid product is however not finished. Many aspects are still not clear and extensive work still remains for a large scale implementation of torrefaction.

## 6. Suggestions for future research

Several topics would need further experimental research, for example:

### **Characteristics of the solid torrefied biomass**

Further studies are required to elucidate the possible differences between untreated and torrefied biomass regarding powder flowability; arching, silo discharge behavior, packing behavior, and fuel feeder stability and efficiency.

Hydrophobic properties of final densified products and also to identify what is needed.

Another interesting topic for a further study is if two products with the same mass yield can be considered alike when produced with different torrefaction technologies, for example a batch reactor compared to a continuous reactor.

### **Torrefaction process**

Narrow residence time distribution has been achieved for the pilot plant used in the present work and a question for further research is how wide the distribution can be for a commercial product. It would be of value to investigate if pelletization and gasification processes tolerate if the torrefied chips have residence times between 10 and 16 min in the same batch. Related to this is the need for investigating the optimum chip size and the sensitivity of the process regarding input chip size.

Recirculation of flue gases for heating of the torrefaction process requires further development and evaluation. Flue gas recirculation may facilitate improved heat transfer and thus mitigate scale-up limitations. Also, initial results indicate considerable lower volatile loss during storage of the torrefied product.

Another important question for further evaluation is whether a steady state experiment is producing a homogenous product or if the mass yield is varying more than what's observable from the temperature curves. Could the product from 1<sup>st</sup> hour be considered similar to a product from the 7<sup>th</sup> and 36<sup>th</sup> hour? The evaluation method would ideally also be used to verify operation of a commercial plant. Possible methods could be:

- Online measurement of solid product (NIR, SWIR)
- Offline measurement of solid product (TGA, py-GC/MS, DTF<sub>HHV</sub>)
- Indirect determination of flue gas composition from torrefaction gas burner by online measurement. Presumable require calibration via some of the other mentioned methods.

### **Torrefaction gas**

The torrefaction gas composition has been somewhat studied. However, the gas combustibility including heating value and adiabatic flame temperature is important aspects for designing a gas burner but results regarding these aspects are very limited. Also, reformation (gasification) of the torrefaction gas for upgrading to green chemicals or synthetic fuels is interesting topics for further studies. Since the torrefaction gas consists of high value green chemicals, extraction and separation of the green chemical products would be more beneficial than using all gas for heating the product.

### **Subsequent processes**

Further experiments with densification of the torrefied product are required in order to get a good compaction quality. Primarily this would be to improve pelletization but also study other methods such as briquetting.

Entrained flow gasification studies of torrefied fuels are still limited. For example, further experiments could determine optimum torrefaction degree and particle size via determination of carbon conversion.

Combustion tests of torrefied materials are still limited in all size ranges; large scale (co-combustion with coal or total replacement of coal), medium scale (for example conversion of oil-fired boilers), and small scale (residential pellet stoves).

# Acknowledgements

All the people whose been around me during this project have made these years wonderful and educational and all of you have helped me making this possible. Thanks for all excellent questions and remarks even though some have been frustrating from time to time.

I thank my supervisors Anders Nordin and Linda Pommer for their guidance, support and for giving me this opportunity. Thanks also to all co-authors for making this work possible.

I would like to thank my great colleagues at Applied Physics and Electronics for friendship, discussions and fun times. Thanks also to all of the people at SLU Forest Biomaterials and Technology and BTC, especially for all the support during my first years in this project.

Ingemar Olofsson, without you this journey would have not started, not been possible to finish and much less fun. Thank you!

I thank Katarina Åberg, Elenoroa Borén and Erik Steinvall for all of the discussions about life, work and everything. Erik, extra thanks for bringing me down from my “Trust me, I’m an Engineer”-pedestal once in a while.

Thanks to BioEndev AB and my colleagues there, for giving me motivation and a hope that this work and knowledge will not stay in the drawer.

Financial support from the Swedish Energy Agency (STEM) under grant agreement 31489-1, the Sector project within the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 282826, Bio4Energy - a strategic research environment appointed by the Swedish government, and TRB Sverige AB are gratefully acknowledged. Additional financing of the torrefaction pilot plant from Umeå University, Swedish Agricultural University, BioEndev AB and SP Processum are also gratefully acknowledged.

Tack till min underbara familj som har låtit mig bli den jag nu är. Anna, Tuva och Sofie, ni betyder allt för mig.

## References

- [1] Amponsah, N.Y., Troldborg, M., Kington, B., Aalders, I., Hough, R.L., Greenhouse gas emissions from renewable energy sources: A review of lifecycle considerations, *Renewable and Sustainable Energy Reviews*, 39 (2014) 461-475.
- [2] Varun, Bhat, I.K., Prakash, R., LCA of renewable energy for electricity generation systems—A review, *Renewable and Sustainable Energy Reviews*, 13 (2009) 1067-1073.
- [3] Joelsson, J.M., Gustavsson, L., Reductions in greenhouse gas emissions and oil use by DME (di-methyl ether) and FT (Fischer-Tropsch) diesel production in chemical pulp mills, *Energy*, 39 (2012) 363-374.
- [4] Dai, J., Cui, H., Grace, J.R., Biomass feeding for thermochemical reactors, *Progress in Energy and Combustion Science*, 38 (2012) 716-736.
- [5] Nordin, A., Pommer, L., Nordwaeger, M., Olofsson, I., Biomass conversion through torrefaction, E. Dahlquist (Ed.) *Technologies for converting biomass to useful energy: Combustion, Gasification, Pyrolysis, Torrefaction and Fermentation* CRC Press, 2013.
- [6] Bergman, P.C.A., Boersma, A.R., Kiel, J.H.A., Prins, M.J., Ptasinski, K.J., Janssen, F., Torrefaction for entrained flow gasification of biomass, *Proceedings of the 2nd World Conference and Technology Exhibition "Biomass for Energy, Industry and Climate Protection"*, Rome, 2004.
- [7] Bergman, P.C.A., Kiel, J.H.A., Torrefaction for Biomass Upgrading, 14th European Biomass Conference & Exhibition, Energy research Centre of the Netherlands (ECN), Paris, France, 2005.
- [8] Prins, M.J., Ptasinski, K.J., Janssen, F., Torrefaction of wood - Part 1. Weight loss kinetics, *J. Anal. Appl. Pyrolysis*, 77 (2006) 28-34.
- [9] Werner, K., Pommer, L., Broström, M., Thermal decomposition of hemicelluloses, *J. Anal. Appl. Pyrolysis*, 110 (2014) 130-137.
- [10] Melkior, T., Jacob, S., Gerbaud, G., Hediger, S., Le Pape, L., Bonnefois, L., Bardet, M., NMR analysis of the transformation of wood constituents by torrefaction, *Fuel*, 92 (2012) 271-280.
- [11] Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C., Characteristics of hemicellulose, cellulose and lignin pyrolysis, *Fuel*, 86 (2007) 1781-1788.
- [12] Liu, Q., Wang, S., Zheng, Y., Luo, Z., Cen, K., Mechanism study of wood lignin pyrolysis by using TG-FTIR analysis, *J. Anal. Appl. Pyrolysis*, 82 (2008) 170-177.
- [13] Svoboda, K., Pohorelý, M., Hartman, M., Martinec, J., Pretreatment and feeding of biomass for pressurized entrained flow gasification, *Fuel Processing Technology*, In Press, Corrected Proof (2008).
- [14] Prins, M.J., Ptasinski, K.J., Janssen, F., Torrefaction of wood - Part 2. Analysis of products, *J. Anal. Appl. Pyrolysis*, 77 (2006) 35-40.
- [15] Bergman, P.C.A., Boersma, A.R., Zwart, R.W.R., Kiel, J.H.A., Torrefaction for biomass co-firing in existing coal-fired power stations., 2005.

- [16] Nocquet, T., Dupont, C., Commandre, J.-M., Grateau, M., Thiery, S., Salvador, S., Volatile species release during torrefaction of wood and its macromolecular constituents: Part 1 – Experimental study, *Energy*, 72 (2014) 180-187.
- [17] Pach, M., Zanzi, R., Björnbom, E., Torrefied Biomass a Substitute for Wood and Charcoal, 6th Asia-Pacific International Symposium on Combustion and Energy Utilization, 2002.
- [18] Chen, W.-H., Peng, J., Bi, X.T., A state-of-the-art review of biomass torrefaction, densification and applications, *Renewable and Sustainable Energy Reviews*, 44 (2015) 847-866.
- [19] van der Stelt, M.J.C., Gerhauser, H., Kiel, J.H.A., Ptasinski, K.J., Biomass upgrading by torrefaction for the production of biofuels: A review, *Biomass and Bioenergy*, 35 (2011) 3748-3762.
- [20] Nunes, L.J.R., Matias, J.C.O., Catalão, J.P.S., A review on torrefied biomass pellets as a sustainable alternative to coal in power generation, *Renewable and Sustainable Energy Reviews*, 40 (2014) 153-160.
- [21] Koppejan, J., Sokhansanj, S., Melin, S., Madrali, S., Status overview of torrefaction technologies, IEA bioenergy task 32 report, 2012.
- [22] Örberg, H., Pommer, L., Olofsson, I., Nordwaeger, M., Broström, M., Torrefaction of pelletized Reed canary grass and Norway spruce, *World Bioenergy*, Jönköping, Sweden, 2012.
- [23] Tapasvi, D., Khalil, R., Skreiberg, Ø., Tran, K.-Q., Grønli, M., Torrefaction of Norwegian Birch and Spruce: An Experimental Study Using Macro-TGA, *Energy Fuels*, 26 (2012) 5232-5240.
- [24] Di Blasi, C., Branca, C., Sarnataro, F.E., Gallo, A., Thermal Runaway in the Pyrolysis of Some Lignocellulosic Biomasses, *Energy Fuels*, 28 (2014) 2684-2696.
- [25] Saleh, S.B., Hansen, B.B., Jensen, P.A., Dam-Johansen, K., Influence of Biomass Chemical Properties on Torrefaction Characteristics, *Energy Fuels*, 27 (2013) 7541-7548.
- [26] Saddawi, A., Jones, J.M., Williams, A., Influence of alkali metals on the kinetics of the thermal decomposition of biomass, *Fuel Processing Technology*, 104 (2012) 189-197.
- [27] Eom, I.-Y., Kim, J.-Y., Kim, T.-S., Lee, S.-M., Choi, D., Choi, I.-G., Choi, J.-W., Effect of essential inorganic metals on primary thermal degradation of lignocellulosic biomass, *Bioresource Technology*, 104 (2012) 687-694.
- [28] Peng, J.H., Bi, H.T., Sokhansanj, S., Lim, J.C., A Study of Particle Size Effect on Biomass Torrefaction and Densification, *Energy Fuels*, 26 (2012) 3826-3839.
- [29] van der Stelt, M.J.C., Chemistry and reaction kinetics of biowaste torrefaction, Doctoral degree, Department of Chemical Engineering and Chemistry, Technische Universiteit Eindhoven (2011)
- [30] Basu, P., Rao, S., Dhungana, A., An investigation into the effect of biomass particle size on its torrefaction, *The Canadian Journal of Chemical Engineering*, 91 (2013) 466-474.

- [31] Bates, R.B., Ghoniem, A.F., Modeling kinetics-transport interactions during biomass torrefaction: The effects of temperature, particle size, and moisture content, *Fuel*, 137 (2014) 216-229.
- [32] Lekounougou, S., Kocafe, D., Comparative study on the durability of heat-treated White Birch (*Betula papyrifera*) subjected to the attack of brown and white rot fungi, *Wood Material Science & Engineering*, 7 (2012) 101-106.
- [33] Hakkou, M., Petrissans, M., Gerardin, P., Zoulalian, A., Investigations of the reasons for fungal durability of heat-treated beech wood, *Polym. Degrad. Stabil.*, 91 (2006) 393-397.
- [34] Esteves, B.M., Pereira, H.M., Wood modification by heat treatment: a review, *BioResources*, 4 (2009) 370-404.
- [35] Kymäläinen, M., Havimo, M., Keriö, S., Kemell, M., Solio, J., Biological degradation of torrefied wood and charcoal, *Biomass and Bioenergy*, 71 (2014) 170-177.
- [36] Wihersaari, M., Evaluation of greenhouse gas emission risks from storage of wood residue, *Biomass and Bioenergy*, 28 (2005) 444-453.
- [37] He, X., Lau, A.K., Sokhansanj, S., Lim, C.J., Bi, X.T., Melin, S., Investigating gas emissions and dry matter loss from stored biomass residues, *Fuel*, 134 (2014) 159-165.
- [38] Eriksson, L., Gustavsson, L., Comparative analysis of wood chips and bundles – Costs, carbon dioxide emissions, dry-matter losses and allergic reactions, *Biomass and Bioenergy*, 34 (2010) 82-90.
- [39] Afzal, M.T., Bedane, A.H., Sokhansanj, S., Mahmood, W., Storage of comminuted and uncomminuted forest biomass and its effect on fuel quality, *BioResources*, 5 (2010) 55-69.
- [40] Bekhta, P., Niemz, P., Effect of High Temperature on the Change in Color, Dimensional Stability and Mechanical Properties of Spruce Wood, *Holzforschung*, 57 (2003) 539.
- [41] Boonstra, M., A two-stage thermal modification of wood, Doctoral degree, Ghent University (2008)
- [42] González-Peña Marcos, M., Hale Michael, D.C., Colour in thermally modified wood of beech, Norway spruce and Scots pine. Part 1: Colour evolution and colour changes, *Holzforschung*, 2009, pp. 385.
- [43] Lindström, S., Nilsson, D., Nordin, A., Nordwaeger, M., Olofsson, I., Pommer, L., Geladi, P., Quality assurance of torrefied biomass using RGB, visual and near infrared (hyper) spectral image data, *Journal of Near Infrared Spectroscopy*, 22 (2014) 129-139.
- [44] Lestander, T.A., Rudolfsson, M., Pommer, L., Nordin, A., NIR provides excellent predictions of properties of biocoal from torrefaction and pyrolysis of biomass, *Green Chemistry*, 16 (2014) 4906-4913.
- [45] Uslu, A., Faaij, A.P.C., Bergman, P.C.A., Pre-treatment technologies, and their effect on international bioenergy supply chain logistics. Techno-economic evaluation of torrefaction, fast pyrolysis and pelletisation, *Energy*, 33 (2008) 1206-1223.

- [46] Gårdbro, G., Techno-economic modeling of the supply chain for torrefied biomass, Masters thesis, Department of Applied Physics and Electronics, Umeå University (2014)
- [47] Svanberg, M., Halldórsson, Á., Supply chain configuration for biomass-to-energy: the case of torrefaction, *International Journal of Energy Sector Management*, 7 (2013) 65-83.
- [48] Svanberg, M., Olofsson, I., Flodén, J., Nordin, A., Analysing biomass torrefaction supply chain costs, *Bioresource Technology*, 142 (2013) 287-296.
- [49] Chen, W.-H., Du, S.-W., Tsai, C.-H., Wang, Z.-Y., Torrefied biomasses in a drop tube furnace to evaluate their utility in blast furnaces, *Bioresource Technology*, 111 (2012) 433-438.
- [50] Chen, Q., Zhou, J.S., Liu, B.J., Mei, Q.F., Luo, Z.Y., Influence of torrefaction pretreatment on biomass gasification technology, *Chin. Sci. Bull.*, 56 (2011) 1449-1456.
- [51] Couhert, C., Salvador, S., Commandré, J.M., Impact of torrefaction on syngas production from wood, *Fuel*, 88 (2009) 2286-2290.
- [52] Costa, F.F., Wang, G., Costa, M., Combustion kinetics and particle fragmentation of raw and torrefied pine shells and olive stones in a drop tube furnace, *Proceedings of the Combustion Institute*, 35 (2015) 3591-3599.
- [53] Dai, J.J., Sokhansanj, S., Grace, J.R., Bi, X.T., Lim, C.J., Melin, S., Overview and some issues related to co-firing biomass and coal, *Can. J. Chem. Eng.*, 86 (2008) 367-386.
- [54] Padban, N., Khodayari, R., Sector-project Task 7.3: Co-gasification in entrained flow gasifiers, 2014.
- [55] Eddings, E., Okerlund, R., Hanks, D., Coates, R., Bell, S., Co-firing of Pulverized Coal with Pinion Pine/Juniper Wood in Raw, Torrefied and Pyrolyzed Forms, *Impacts of Fuel Quality*, Snowbird, Utah, USA, 2014.
- [56] Keipi, T., Tolvanen, H., Kokko, L., Raiko, R., The effect of torrefaction on the chlorine content and heating value of eight woody biomass samples, *Biomass and Bioenergy*, 66 (2014) 232-239.
- [57] Saleh, S.B., Flensburg, J.P., Shoulaifar, T.K., et al., Release of Chlorine and Sulfur during Biomass Torrefaction and Pyrolysis, *Energy Fuels*, 28 (2014) 3738-3746.
- [58] Khazraie Shoulaifar, T., DeMartini, N., Zevenhoven, M., Verhoeff, F., Kiel, J., Hupa, M., Ash-Forming Matter in Torrefied Birch Wood: Changes in Chemical Association, *Energy Fuels*, 27 (2013) 5684-5690.
- [59] Khan, A.A., de Jong, W., Jansens, P.J., Spliethoff, H., Biomass combustion in fluidized bed boilers: Potential problems and remedies, *Fuel Processing Technology*, 90 (2009) 21-50.
- [60] Nielsen, H.P., Frandsen, F.J., Dam-Johansen, K., Baxter, L.L., The implications of chlorine-associated corrosion on the operation of biomass-fired boilers, *Progress in Energy and Combustion Science*, 26 (2000) 283-298.
- [61] Hupa, M., Ash-Related Issues in Fluidized-Bed Combustion of Biomasses: Recent Research Highlights, *Energy Fuels*, 26 (2012) 4-14.

- [62] Higman, C., Burt, M.v.d., Gasification, 2nd ed., Elsevier Science, Burlington, MA, 2008.
- [63] Arvelakis, S., Gehrman, H., Beckmann, M., Koukios, E.G., Agglomeration problems during fluidized bed gasification of olive-oil residue: evaluation of fractionation and leaching as pre-treatments, *Fuel*, 82 (2003) 1261-1270.
- [64] Coda, B., Cieplik, M.K., de Wild, P.J., Kiel, J.H.A., Slagging Behavior of Wood Ash under Entrained-Flow Gasification Conditions, *Energy Fuels*, 21 (2007) 3644-3652.
- [65] Carlsson, P., Ma, C., Molinder, R., Weiland, F., Wiinikka, H., Öhman, M., Öhrman, O., Slag Formation during Oxygen-Blown Entrained-Flow Gasification of Stem Wood, *Energy Fuels*, 28 (2014) 6941-6952.
- [66] Ma, C., Weiland, F., Hedman, H., Boström, D., Backman, R., Öhman, M., Characterization of Reactor Ash Deposits from Pilot-Scale Pressurized Entrained-Flow Gasification of Woody Biomass, *Energy Fuels*, 27 (2013) 6801-6814.
- [67] Leiser, S., Cieplik, M.K., Smit, R., Slagging Behavior of Straw and Corn Stover and the Fate of Potassium under Entrained-Flow Gasification Conditions, *Energy Fuels*, 27 (2013) 318-326.
- [68] Li, J., Biagini, E., Yang, W., Tognotti, L., Blasiak, W., Flame characteristics of pulverized torrefied-biomass combusted with high-temperature air, *Combustion and Flame*, 160 (2013) 2585-2594.
- [69] Khalil, R.A., Bach, Q.-V., Skreiberg, Ø., Tran, K.-Q., Performance of a Residential Pellet Combustor Operating on Raw and Torrefied Spruce and Spruce-Derived Residues, *Energy Fuels*, 27 (2013) 4760-4769.
- [70] Gasification.org, 2012.
- [71] Higman, C., State of the Gasification Industry: Worldwide Gasification Database 2014 Update Gasification Technologies Conference Washington, DC 2014.
- [72] Carlborg, M., Boström, D., Backman, R., Reactions between ash forming elements and two mullite based refractories in entrained flow gasification of wood, Impacts of Fuel Quality on Power Production, Snowbird, Utah, 2014.
- [73] van Vliet, O.P.R., Faaij, A.P.C., Turkenburg, W.C., Fischer-Tropsch diesel production in a well-to-wheel perspective: A carbon, energy flow and cost analysis, *Energy Conversion and Management*, 50 (2009) 855-876.
- [74] Zheng, A., Zhao, Z., Chang, S., Huang, Z., He, F., Li, H., Effect of Torrefaction Temperature on Product Distribution from Two-Stage Pyrolysis of Biomass, *Energy Fuels*, 26 (2012) 2968-2974.
- [75] Doassans-Carrère, N., Muller, S., Mitzkat, M., REVE — a new industrial technology for biomass torrefaction: pilot studies, *Fuel Processing Technology*, 126 (2014) 155-162.
- [76] Ratte, J., Fardet, E., Mateos, D., Hery, J.S., Mathematical modelling of a continuous biomass torrefaction reactor: TORSPYD (TM) column, *Biomass Bioenerg.*, 35 (2011) 3481-3495.

- [77] Shang, L., Ahrenfeldt, J., Holm, J.K., Bach, L.S., Stelte, W., Henriksen, U.B., Kinetic model for torrefaction of wood chips in a pilot-scale continuous reactor, *J. Anal. Appl. Pyrolysis*, 108 (2014) 109-116.
- [78] Atienza-Martínez, M., Mastral, J.F., Ábrego, J., Ceamanos, J., Gea, G., Sewage Sludge Torrefaction in an Auger Reactor, *Energy Fuels*, 29 (2014) 160-170.
- [79] Ohliger, A., Förster, M., Kneer, R., Torrefaction of beechwood: A parametric study including heat of reaction and grindability, *Fuel*, 104 (2013) 607-613.
- [80] Mei, Y., Liu, R., Yang, Q., et al., Torrefaction of cedarwood in a pilot scale rotary kiln and the influence of industrial flue gas, *Bioresource Technology*, 177 (2015) 355-360.
- [81] Stelte, W., Clemons, C., Holm, J.K., Sanadi, A.R., Ahrenfeldt, J., Shang, L., Henriksen, U.B., Pelletizing properties of torrefied spruce, *Biomass and Bioenergy*, 35 (2011) 4690-4698.
- [82] Li, H., Liu, X., Legros, R., Bi, X.T., Jim Lim, C., Sokhansanj, S., Pelletization of torrefied sawdust and properties of torrefied pellets, *Applied Energy*, 93 (2012) 680-685.
- [83] Reza, M.T., Uddin, M.H., Lynam, J.G., Coronella, C.J., Engineered pellets from dry torrefied and HTC biochar blends, *Biomass and Bioenergy*, 63 (2014) 229-238.
- [84] Rudolfsson, M., Stelte, W., Lestander, T.A., Process optimization of combined biomass torrefaction and pelletization for fuel pellet production – A parametric study, *Applied Energy*, 140 (2015) 378-384.
- [85] Järvinen, T., Agar, D., Experimentally determined storage and handling properties of fuel pellets made from torrefied whole-tree pine chips, logging residues and beech stem wood, *Fuel*, 129 (2014) 330-339.
- [86] Ghiasi, B., Kumar, L., Furubayashi, T., Lim, C.J., Bi, X., Kim, C.S., Sokhansanj, S., Densified biocoal from woodchips: Is it better to do torrefaction before or after densification?, *Applied Energy*, 134 (2014) 133-142.
- [87] Shang, L., Nielsen, N.P.K., Dahl, J., et al., Quality effects caused by torrefaction of pellets made from Scots pine, *Fuel Processing Technology*, 101 (2012) 23-28.
- [88] Fisher, E.M., Dupont, C., Darvell, L.I., et al., Combustion and gasification characteristics of chars from raw and torrefied biomass, *Bioresource Technology*, 119 (2012) 157-165.
- [89] Rodrigues, T.O., Rousset, P.L.A., Effects of torrefaction on energy properties of *Eucalyptus grandis* wood, *Cerne*, 15 (2009) 446-452.
- [90] Peng, J.H., Bi, H.T., Lim, C.J., Sokhansanj, S., Study on Density, Hardness, and Moisture Uptake of Torrefied Wood Pellets, *Energy Fuels*, 27 (2013) 967-974.
- [91] Sabil, K.M., Aziz, M.A., Lal, B., Uemura, Y., Synthetic indicator on the severity of torrefaction of oil palm biomass residues through mass loss measurement, *Applied Energy*, 111 (2013) 821-826.

- [92] Björklöf, D., Björklöf, D., Givarteknik för mätning i processer, Almqvist & Wiksell, 1991.
- [93] Aleksandrović, S., Jović, M., Analysis of Belt Weigher Accuracy Limiting Factors, *International Journal of Coal Preparation and Utilization*, 31 (2011) 223-241.
- [94] Persson, A., Holmberg, P., Broström, M., Decomposition modeling using thermogravimetry with a multivariate approach, 21st European Biomass Conference and Exhibition, Copenhagen, Denmark, 2013.
- [95] EN15149-2. Solid biofuels – Determination of particle size distribution – Part 2: Vibrating screen method using sieve apertures of 3.15 mm and below, 2012.
- [96] Englisch, M., Torrefaction: fundamentals and basic principles of torrefaction, Central European Biomass Conference (CEBC), Graz, Austria, 2011.
- [97] Consonni, V., Ballabio, D., Todeschini, R., Evaluation of model predictive ability by external validation techniques, *Journal of Chemometrics*, 24 (2010) 194-201.
- [98] Olofsson, I., Sandström, E., Nordwaeger, M., et al., Torrefaction and Compaction of Eucalyptus and Spruce Wood, 19th European Biomass Conference and Exhibition, Berlin, Germany, 2011.
- [99] Antal, M.J., Gronli, M., The Art, Science, and Technology of Charcoal Production, *Industrial & Engineering Chemistry Research*, 42 (2003) 1619-1640.
- [100] Sciazko, M., Rank-dependent formation enthalpy of coal, *Fuel*, 114 (2013) 2-9.
- [101] Bychev, M.I., Petrova, G.I., Heats (enthalpies) of formation of coals and the thermodynamic evaluation of the coal formation process, *Soil Fuel Chem.*, 45 (2011) 254-260.
- [102] Ben, H., Ragauskas, A.J., Torrefaction of Loblolly pine, *Green Chemistry*, 14 (2012).
- [103] Wen, J.-L., Sun, S.-L., Yuan, T.-Q., Xu, F., Sun, R.-C., Understanding the chemical and structural transformations of lignin macromolecule during torrefaction, *Applied Energy*, 121 (2014) 1-9.
- [104] Zhou, S., Pecha, B., van Kuppevelt, M., McDonald, A.G., Garcia-Perez, M., Slow and fast pyrolysis of Douglas-fir lignin: Importance of liquid-intermediate formation on the distribution of products, *Biomass and Bioenergy*, 66 (2014) 398-409.
- [105] Kelley, S., Rials, T., Glasser, W., Relaxation behaviour of the amorphous components of wood, *J Mater Sci*, 22 (1987) 617-624.
- [106] Bouajila, J., Dole, P., Joly, C., Limare, A., Some laws of a lignin plasticization, *Journal of Applied Polymer Science*, 102 (2006) 1445-1451.
- [107] Stelte, W., Fuel pellets from biomass - Processing, bonding, raw materials, Ph.D Thesis, Denmark, 2011, pp. 52 pages.
- [108] Khazraie Shoulaifar, T., DeMartini, N., Ivaska, A., Fardim, P., Hupa, M., Measuring the concentration of carboxylic acid groups in torrefied spruce wood, *Bioresource Technology*, 123 (2012) 338-343.

- [109] Hernández, J.J., Aranda-Almansa, G., Bula, A., Gasification of biomass wastes in an entrained flow gasifier: Effect of the particle size and the residence time, *Fuel Processing Technology*, 91 (2010) 681-692.
- [110] Paulrud, S., Mattsson, J.E., Nilsson, C., Particle and handling characteristics of wood fuel powder: effects of different mills, *Fuel Processing Technology*, 76 (2002) 23-39.
- [111] Umeki, K., Kirtania, K., Chen, L., Bhattacharya, S., Fuel Particle Conversion of Pulverized Biomass during Pyrolysis in an Entrained Flow Reactor, *Industrial & Engineering Chemistry Research*, 51 (2012) 13973-13979.
- [112] Backreedy, R.I., Fletcher, L.M., Jones, J.M., Ma, L., Pourkashanian, M., Williams, A., Co-firing pulverised coal and biomass: a modeling approach, *Proceedings of the Combustion Institute*, 30 (2005) 2955-2964.
- [113] Gera, D., Mathur, M.P., Freeman, M.C., Robinson, A., Effect of Large Aspect Ratio of Biomass Particles on Carbon Burnout in a Utility Boiler, *Energy Fuels*, 16 (2002) 1523-1532.
- [114] Black, D.L., McQuay, M.Q., Laser-based particle measurements of spherical and nonspherical particles, *International Journal of Multiphase Flow*, 27 (2001) 1333-1362.
- [115] Abdullah, E.C., Geldart, D., The use of bulk density measurements as flowability indicators, *Powder Technology*, 102 (1999) 151-165.
- [116] Holm, J.K., Henriksen, U.B., Hustad, J.E., Sørensen, L.H., Toward an Understanding of Controlling Parameters in Softwood and Hardwood Pellets Production, *Energy Fuels*, 20 (2006) 2686-2694.
- [117] Stelte, W., Sanadi, A.R., Shang, L., Holm, J.K., Ahrenfeldt, J., Henriksen, U.B., Recent developments in biomass pelletization - A review, *BioResources*, 7 (2012) 4451-4490.
- [118] Falk, J., Berry, R.J., Broström, M., Larsson, S.H., Mass flow and variability in screw feeding of biomass powders – Relations to particle and bulk properties, *Powder Technology*, 276 (2015) 80-88.
- [119] Wang, W., Zhang, J., Yang, S., Zhang, H., Yang, H., Yue, G., Experimental study on the angle of repose of pulverized coal, *Particuology*, 8 (2010) 482-485.
- [120] Santomaso, A., Lazzaro, P., Canu, P., Powder flowability and density ratios: the impact of granules packing, *Chem. Eng. Sci.*, 58 (2003) 2857-2874.
- [121] Lumay, G., Boschini, F., Traina, K., Bontempi, S., Remy, J.C., Cloots, R., Vandewalle, N., Measuring the flowing properties of powders and grains, *Powder Technology*, 224 (2012) 19-27.
- [122] Obernberger, I., Thek, G., *The pellet handbook*, 2010.
- [123] Stemmler, M., Müller, M., Theoretical Evaluation of Feedstock Gasification Using H<sub>2</sub>/C Ratio and ROC as Main Input Variables, *Industrial & Engineering Chemistry Research*, 49 (2010) 9230-9237.
- [124] Jand, N., Brandani, V., Foscolo, P.U., Thermodynamic Limits and Actual Product Yields and Compositions in Biomass Gasification Processes, *Industrial & Engineering Chemistry Research*, 45 (2006) 834-843.

- [125] Li, X.T., Grace, J.R., Lim, C.J., Watkinson, A.P., Chen, H.P., Kim, J.R., Biomass gasification in a circulating fluidized bed, *Biomass and Bioenergy*, 26 (2004) 171-193.
- [126] Qin, K., Jensen, P.A., Lin, W.G., Jensen, A.D., Biomass Gasification Behavior in an Entrained Flow Reactor: Gas Product Distribution and Soot Formation, *Energy Fuels*, 26 (2012) 5992-6002.
- [127] Qin, K., Lin, W.G., Jensen, P.A., Jensen, A.D., High-temperature entrained flow gasification of biomass, *Fuel*, 93 (2012) 589-600.