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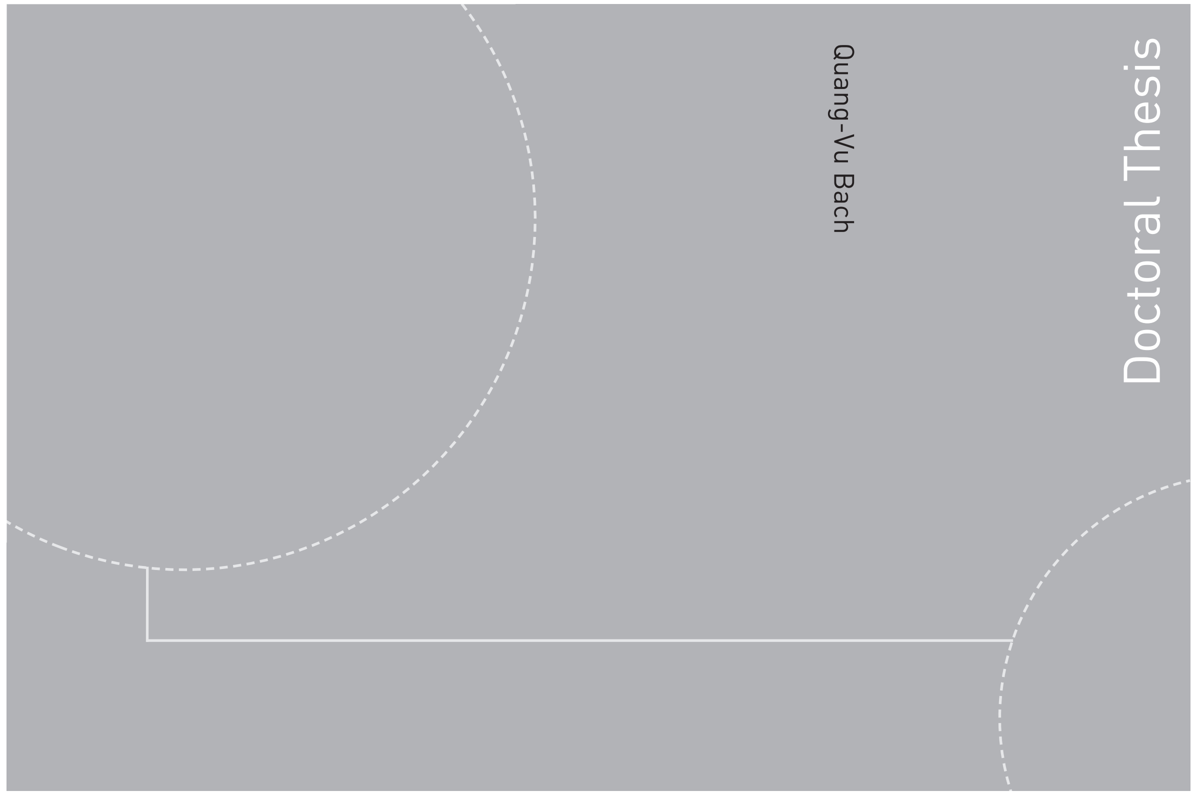
Quang-Vu Bach

Wet Torrefaction of Biomass – Production and Conversion of Hydrochar

NTNU – Trondheim
Norwegian University of
Science and Technology



Doctoral Thesis

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NTNU
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Faculty of Engineering
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Department of Energy and
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Thesis for the degree of Philosophiae Doctor

Trondheim, January 2015

Norwegian University of Science and Technology
Faculty of Engineering Science and Technology
Department of Energy and Process Engineering

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After the rain, the sun shines.

Executive Summary

Biomass is a renewable and carbon neutral energy resource which has a high potential for replacing fossil fuels. However, the use of biomass for energy applications is not straightforward. It is because native solid biomass fuels are highly bulky and inhomogeneous. They normally have higher moisture content, inferior heating value, and poorer grindability, compared to coal. These drawbacks limit the use of biomass as fuel. Pretreatment of biomass via chipping and/or pelletizing for example is therefore a common practice in order to overcome the drawbacks. This operation adds more costs to biomass fuels, but improvements in the fuel properties are limited.

Wet torrefaction (WT) is a promising method for pretreatment of biomass for use as fuel. The method involves the use of hot compressed water, within 180–260 °C approximately, as reaction medium. Like dry torrefaction (DT), which may be defined as mild thermal treatment of biomass within 200–300 °C, WT improves significantly the fuel properties of biomass. In addition, due to the use of water as reaction medium, WT is highly suitable for low cost biomass sources such as forest residues, agricultural wastes, and aquatic energy crops, which normally have very high moisture content.

This PhD was carried out to technically assess the WT process as a pretreatment method for production of advanced solid biofuel, *hydrochar*, from forest residues, a low cost biomass resource in Norway.

As the first step, stem woods from Norway spruce (softwood) and birch (hardwood) were tested as feedstocks. This choice made it possible to compare with the results from previous studies on DT of biomass using identical feedstocks. WT experiments were carried out using a bench-top autoclave reactor of 250 ml in volume from Parr Instrument, with nitrogen as purge gas. Effects of various WT

process parameters on the yield and the fuel properties of hydrochar (solid fuel obtained from biomass WT) were examined. The pyrolysis and combustion reactivity of hydrochar, produced under various WT conditions, was studied thermogravimetrically by means of a Mettler Toledo TGA/SDTA 815e. Multi-pseudo-component models with different reaction orders were adopted for kinetic modelling and extraction of the kinetic parameters from these thermochemical conversion processes of hydrochars. Effects of WT on the kinetics were also discussed.

In the second step, forest residues were used as feedstock, employing similar approaches as in the first step. In addition, carbon dioxide was tested as purge gas and compared with nitrogen for evaluating the possibility to use and recover heat of the flue gas from combustion plants.

Finally, the pelletability of hydrochar from forest residues was investigated and compared with that of untreated feedstock. The pelletization was performed using a single pellet press. Different compressing pressures (20, 40, 80, 160, 240 MPa) and temperatures (120, 180 °C) were applied to produce pellets. The pellet strength was then tested via diametric compression test, employing a 60 mm diameter probe connected to a Lloyd LR 5K texture analyzer. Effects of WT on the mass density, energy density and mechanical strength of the pellet were investigated.

The major findings from the studies reported in this PhD are:

- Both reaction temperature and holding time have significant effects on the mass yield, energy yield, and fuel properties of the hydrochar.
- Pressure also enhances the torrefaction rate; however, the effect becomes marginal above a certain pressure.
- Feedstock particle size slightly affects the yield and fuel properties of the hydrochar.
- Ash content of biomass fuel is significantly reduced by WT.

- Given the same solid yields, WT requires significantly lower torrefaction temperatures and shorter holding times than DT.
- Given the same solid yields, solid biomass fuels upgraded via WT have greater heating values than via DT.
- Hardwood is more reactive and produces less hydrochar than softwood in identical WT conditions.
- Forest residues are more reactive than stem woods in identical WT conditions.
- WT in CO_2 enhances the torrefaction process, but reduces the heating value of hydrochar, compare to WT in N_2.
- The pellets made from wet-torrefied forest residues are more compressible and mechanically stronger than the pellets made from raw forest residues.
- Overall, WT has positive effects on the fuel properties of biomass.

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Preface

This doctoral work was carried out at the Department of Energy and Process Engineering, NTNU, under the supervision of Associate Professor Khanh-Quang Tran (NTNU) and Dr. Øyvind Skreiberg (SINTEF Energy Research). The work is part of the STOP (*STable OPerating conditions for biomass combustion plants*) project, financed by the Research Council of Norway and industry partners through the FME CenBio (*Bioenergy Innovation Centre*).

This thesis consists of the following papers, which are referred to in the text by their Roman numerals:

I. Quang-Vu Bach, Khanh-Quang Tran, Roger A. Khalil, Øyvind Skreiberg, Gulaim Seisenbaeva. C*omparative assessment of wet torrefaction*. Energy & Fuels **2013**, *27*, 6743-6753.

II. Quang-Vu Bach, Khanh-Quang Tran, Øyvind Skreiberg, Roger A. Khalil, Anh N. Phan. *Effects of wet torrefaction on reactivity and kinetics of wood in air combustion*. Fuel **2014**, *137*, 375-383.

III. Quang-Vu Bach, Khanh-Quang Tran, Øyvind Skreiberg, Thuat T. Trinh. *Effects of wet torrefaction on pyrolysis of woody biomass fuels*. **Submitted** to Energy.

IV. Quang-Vu Bach, Khanh-Quang Tran, Øyvind Skreiberg. *Torrefaction of forest residues in subcritical water*. **Submitted** to Applied Energy.

V. Quang-Vu Bach, Khanh-Quang Tran, Roger A. Khalil, Øyvind Skreiberg. *Effects of CO_2 on wet torrefaction of biomass*. Energy Procedia, **accepted**.

VI. Quang-Vu Bach, Nevena Mišljenović, Khanh-Quang Tran, Carlos Salas-Bringas, Øyvind Skreiberg. *Influences of wet torrefaction on pelletability and pellet properties of Norwegian forest residues*. Annual Transactions - The Nordic Rheology Society **2014**, *22*, 61-68.

Other publications related to the topic, but not included in this thesis:

1. Quang-Vu Bach, Miguel Valcuende Sillero, Khanh-Quang Tran, Jorunn Skjermo. *Fast hydrothermal liquefaction of a Norwegian macro-alga: Screening Tests*. Algal Research **2014**, *6, Part B(0)*, 271-276.

2. Quang-Vu Bach, Khanh-Quang Tran, Roger A. Khalil, Øyvind Skreiberg. *Wet torrefaction of forest residues*. Energy Procedia, **accepted**.

3. Quang-Vu Bach, Roger A. Khalil, Khanh-Quang Tran, Øyvind Skreiberg. *Torrefaction kinetics of Norwegian biomass fuels*. Chemical Engineering Transactions **2014**, *37*, 49-54.

4. Khanh-Quang Tran, Quang-Vu Bach, Thuat T. Trinh; Gulaim Seisenbaeva. *Non-isothermal pyrolysis of torrefied stump – A comparative kinetics evaluation*. Applied Energy **2014**, *136(0)*, 759-766.

5. Nevena Mišljenović, Quang-Vu Bach, Khanh-Quang Tran, Carlos Salas-Bringas, Øyvind Skreiberg. *Torrefaction influence on pelletability and pellet quality of Norwegian forest residues*. Energy & Fuels **2014**, *28*, 2554-2561.

6. Roger A. Khalil, Quang-Vu Bach, Øyvind Skreiberg, Khanh-Quang Tran (2013). *The performance of a residential pellets combustor operating on raw and torrefied spruce and spruce derived residues*. Energy & Fuels **2013**, *27*, 4760-4769.

Acknowledgements

I would like express my gratitude to my supervisors, Professor Khanh-Quang Tran and Dr. Øyvind Skreiberg, for introducing me to the field of bioenergy and for their valuable guidance, supports and advices during my PhD period.

I would also like to thank Dr. Roger A. Khalil, for his contributions to my publications. I really appreciate practical supports from the Thermal lab, especially Dr. Morten Grønli, the lab manager, and Erik Langørgen.

Special thanks should be given to my colleagues and friends, who shared the friendly environment and coffee times with me during the last three years of high working pressure.

Trondheim, October 2014.

Quang-Vu Bach

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Nomenclature

Abbreviations

ASTM	American Society for Testing and Materials
DAEM	Distributed activation energy model
daf	Dry and ash free basis
db	Dry basis
DT	Dry torrefaction
DTG	Differential thermogravimetric
EMC	Equilibrium moisture content
GHV	Gross heating value
GKM	Global kinetic model
HHV	Higher heating value
HTC	Hydrothermal carbonization
LHV	Lower heating value
MC	Moisture content
NHV	Net heating value
NLSM	Non-linear least squares method
SEM	Scanning electron microscope
TG	Thermogravimetric
TGA	Thermogravimetric analysis
vol	Volume
wt	Weight
WT	Wet torrefaction

Symbols

A	Pre-exponential factor
C	Char

E_0	Mean activation energy
E_a	Activation energy
$f(\alpha)$	Conversion function
$f(E)$	Distribution function of activation energy
$k(T)$ or k	Rate constant
m	Sample mass at any time
m_0	Initial sample mass
m_f	Final residual mass
n	Reaction order
OF	Objective funtion
R	Universal gas constant, 8.314 $J.mol^{-1}.K^{-1}$
S	Solid
S^*	Intermediate solid
T	Absolute temperature
t	Time of conversion
V	Volatiles
v	Volatile released at any time
v_f	Volatile released in total
α	Degree of conversion
σ	Standard deviation of activation energy
β	Heating rate

Subscript

i	i^{th} component

Chapter I

INTRODUCTION

I.1 Problems identification

Biomass is currently the major renewable energy source in use and has a high potential for replacing fossil fuels. While other renewable energy sources can produce only heat and power, biomass can also be converted to chemicals and materials. The use of biomass as an energy source contributes to reduce CO_2 emission, increase energy security, and support sustainable development. However, using biomass for energy applications is not straightforward due to some inherent disadvantages of this fuel including its heterogeneity, low bulk density, high moisture content, low heating value, and poor grindability. These drawbacks make the conversion of biomass to produce heat and power challenging. In addition, they increase the cost for handling, transport, and storage of the fuel.

One way to overcome the aforementioned disadvantages of using biomass as fuel is to pretreat the fuel via torrefaction. There are two torrefaction techniques, dry and wet torrefaction. Dry torrefaction (DT) is thermal treatment of biomass in an inert environment at atmospheric pressure and at temperatures of 200–300 °C. Wet torrefaction (WT) may be defined as treatment of biomass in a hydrothermal media, or hot compressed water, at temperatures of 180–260 °C. Both torrefaction technologies produce hydrophobic solid fuels with much better grindability, more homogeneity and superior heating value, compared with original biomass.

During the last decade, research and development activities on DT for energy applications have been very active. However, similar studies for WT are still limited. Consequently, the understanding of the WT process (effects of temperature, holding time, pressure, feedstock particle size, feedstock type, and feedstock moisture content) as well as the characterizations of wet-torrefied fuels (fuel properties, reactivity, and pelletability) are very limited.

I.2 Research objectives

This study is part of the STOP project (*STable OPerating conditions for biomass and biomass residues combustion plants*) funded by the Research Council of Norway, research partners and industry partners through FME CenBio. The STOP project aims at developing new strategies for improved operating conditions control in biomass and biomass residues combustion plants through the utilisation of more homogenous fuel with minimised season variation and optimised fuel in terms of pollutant emissions.

The first objective of this study is to investigate the effects of wet torrefaction conditions (temperature, holding time, pressure, feedstock particle size, feedstock type, and drying method) on the yield, fuel properties, and pelletability of the solid product. The outcome from this investigation would be helpful to establish mass and energy balances for wet torrefaction and fundamental knowledge for further process optimization.

Examining the reactivity and kinetics of hydrochar in subsequent thermal conversion processes (pyrolysis and combustion) is the second objective of this work. Results from this examination help understanding the thermal behaviour and kinetics of the hydrochar for the design, modification and optimization of thermal conversion units.

The third objective of the study is to identify opportunities for WT process integration, considering that hot flue gas from thermal power plants can be utilized for WT continuous processes at industrial scales to reduce the cost.

I.3 Thesis structure

The thesis is organized in four chapters:

- **Chapter I** gives a brief introduction to the thesis, which includes problem identification and core objectives of the thesis.
- **Chapter II** introduces a background for the study, which includes the main thermochemical conversion processes of biomass fuel for heat and power generation. Challenges and pretreatment needs in utilization of biomass fuels for energy applications are then discussed.
- **Chapter III** presents the methods of study, which include methods for studying hydrochar production, characterization and conversion kinetics.
- **Chapter IV** summarizes the papers included in this thesis and recommends further works.

I.4 List of publications included in this thesis

1. Quang-Vu Bach, Khanh-Quang Tran, Roger A. Khalil, Øyvind Skreiberg, Gulaim Seisenbaeva. C*omparative assessment of wet torrefaction*. Energy & Fuels **2013**, *27*, 6743-6753.

2. Quang-Vu Bach, Khanh-Quang Tran, Øyvind Skreiberg, Roger A. Khalil, Anh N. Phan. *Effects of wet torrefaction on reactivity and kinetics of wood in air combustion*. Fuel **2014**, *137*, 375-383.

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Chapter II

BACKGROUND

II.1 Biomass as solid fuel for heat and power generation

Biomass is organic matter derived from plants or animals available on a renewable basis [1]. It is available in many forms and from various sources: forestry products, agricultural crops, herbaceous and woody energy crops, municipal organic wastes as well as manure [1, 2]. In 2013, biomass supplied approximately 56 EJ [1] globally, accounting for roughly 10% of global annual energy consumption [3]. Biomass can either be converted directly via combustion to produce heat, or indirectly to different forms of biofuel (e.g. bioethanol, biodiesel) for further conversion processes.

Biomass stores energy from the sun via photosynthesis during its growth. In other words, energy from biomass is indirect solar energy. In addition, biomass is considered as a carbon neutral energy source. This is because carbon dioxide is captured during biomass growth and released the same amount when biomass or biofuel is burned. Unlike fossil fuels and other alternative energy sources such as

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[1] 1 EJ = 10^{18} Joules (J) = 10^{15} kilojoules (kJ) = 24 million tonnes of oil equivalent (Mtoe).

wind, geothermal and tidal power, biomass is a distributed source of energy [4], i.e. it is available all over the world and near the point of use. Hence, it reduces the dependence on other energy sources in many countries. Therefore, the use of biomass as an energy source is believed to contribute to reduce CO_2 emission, increase energy security, and support sustainable development.

II.1.1 Plant biomass composition

Plant biomass mainly consists of cellulose, hemicellulose and lignin, which together construct the plant cell wall, shown in Figure II-1. Apart from those, extractives and ash are also present in biomass in small fractions. The structure and the role of these components are introduced in this section.

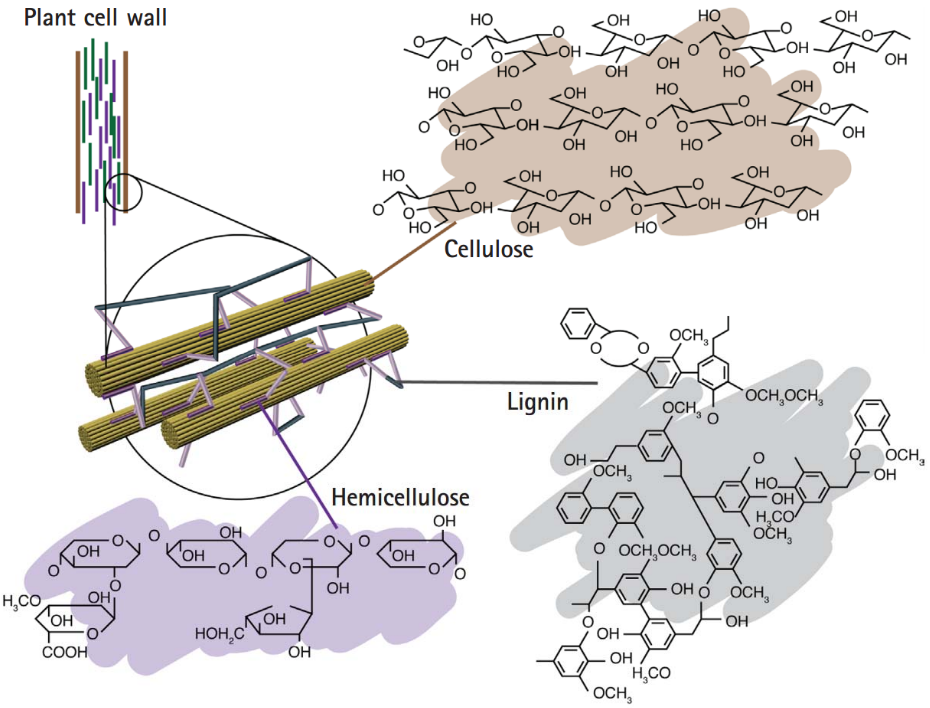

Figure II-1. Biomass constituents in plant cell wall (adopted from [5]).

II.1.1.1 Cellulose

Cellulose is a homopolysaccharide composed of D-glucopyranose units which are linked together by β–(1→4)–glycosidic bonds with the degree of polymerization (DP) from 10,000 to 150,000. Cellulose molecules are virtually linear and have a strong tendency to form intra- and inter-molecular hydrogen bonds. These properties result in an easy aggregation between cellulose molecules to form a crystalline fibrous structure. Therefore, cellulose has high mechanical strength, high thermal resistance and is insoluble in most solvents. Usually, hardwood contains more cellulose than softwood (38.3–51.3 wt% versus 33.0–41.7 wt%).

II.1.1.2 Hemicellulose

Unlike cellulose, **hemicellulose** is a heteropolysaccharide with lower DP, only 150–200, and has different side groups on the chain molecule. It is essentially amorphous polymer made of various monomers including glucose, galactose, mannose, xylose, arabinose and glucoronic acid. Hemicellulose contributes to strengthening the cell wall by interaction with cellulose and/or lignin. The structure and composition of hemicellulose varies for different wood species and cell types. The main hemicelluloses of softwood are galactoglucomannans and arabinoglucuronoxylan, while in hardwood, glucuronoxylan is the major hemicellulose. The differences in the composition lead to different thermal behaviors of hardwood and softwood hemicelluloses, which are caused by the different reactivity of xylan-based and mannan-based compounds to temperature.

II.1.1.3 Lignin

Lignin is an amorphous, highly complex, mainly aromatic polymer made of phenylpropane units. There is a wide variation of lignin structures within different wood species. The lignin content of hardwood is usually in the range of 20.8–31.3%, whereas the lignin content of softwood varies between 26.8 and 32.1%. Softwood lignin contains mainly guaiacyl and a smaller fraction of p-hydroxyphenyl residues. The lignin content of hardwood is composed primarily of syringyl and guaiacyl residues, with fewer amounts of phydroxyphenyl residuals.

II.1.1.4 Extractives and ash

Besides three main components above making up 95–98% of plant biomass, a small portion of low-molecular-weight organic compounds (known as extractives) and inorganic mineral contents (known as ash) can also be found in biomass.

Extractives are highly heterogeneous and can be divided into three subgroups: aliphatic compounds (mainly fats and waxes), terpenes and terpenoids, and phenolic compounds [6]. These components can be extracted from the wood by either organic solvent or water. Particularly, some biomass species may contain up to 30 wt% tannins.

Ash is the inorganic part left after combustion of biomass fuel. The inorganic materials in the plant are absorbed from the water or the soil during its growth. Normally, ash content in wood is less than 1%. The composition of ash will be presented later in section II.1.2.3.

II.1.2 Fuel properties of solid biomass fuel

II.1.2.1 Heating value

Heating value is the most important indicator for the fuel properties of biomass. It is defined as the amount of heat produced by complete combustion of a unit quantity of biomass fuel, normally expressed in MJ/kg. Heating value presents the energy contained in the fuel. There are two common types of heating value:

- Gross or higher heating values (GHV or HHV) is determined when assuming that the combustion products are cooled down to the initial temperature, which takes into account the latent heat of water vaporization in the combustion products.

- Net or lower heating values (NHV or LHV) is calculated by subtracting the latent heat of vaporization of the water vapor formed in the combustion.

Biomass heating value is greatly affected by its chemical composition, moisture and ash content. The heating value can be measured directly employing a bomb calorimeter or estimated from elemental analysis data via empirical formulas. For comparison, the heating vale of biomass fuels is generally reported on a “dry basis” (db) or “dry and ash free basis” (daf).

II.1.2.2 Moisture content

Moisture content (MC) is defined as the mass percentage of the water in wet biomass. Water in woody biomass exists in two main forms: free water found in the lumens or voids of the wood and bound water held between micro-fibrils in the cell wall [7]. Most raw woods contain approximately 40–70% of water.

MC has a significant effect on the engineering of the thermochemical conversion process. The heating value of woody fuel decreases with increasing MC. High moisture fuel burns less readily and produces less useful heat because energy is wasted to vaporize the water. For correct and efficient operations of boilers or stoves, a strict range of feedstock MC may be required. Moreover, the presence of moisture increases the risk of fungal development and biodegradation of biomass during storage. Also, transportation and handling costs rise with increasing MC in fuel.

II.1.2.3 Proximate composition

A typical method to categorize the composition of biomass fuel is the **proximate analysis**, in which the percentages of volatile matter, fixed carbon and ash in dry solid biomass fuel are determined. This analysis is normally carried out in a laboratory furnace, where the temperature is precisely controlled and the analysis is following the relevant international standards, e.g. ASTM.

Proximate analysis shows the ratio of volatile matter and fixed carbon in biomass fuel, an important ratio for the combustion behavior of a fuel. The ash content influences the energy content and determines the cleanness of a fuel. Raw biomass fuel contains more volatile matter but less fixed carbon than coal.

II.1.2.4 Elemental composition - Ultimate analysis

Another method to present the composition of biomass is to determine the mass fraction of elements present in the fuel. For major elements (C, H, N, S, O), an **ultimate** or **elemental analysis** is commonly used and referred to as CHNS analysis, for which a CHNS analyzer normally employed. Based on this analysis, the heating value of biomass fuel can be calculated from the elemental composition via empirical correlations. However, it should be noted that the presences of other minor elements and ash forming elements are also important. The ash forming elements have negative effects on the heating value of biomass fuel. They also influent the reactivity of the fuel during the combustion; and cause problems in the combustion systems, as well as environmental and health impacts. Ash forming elements include major (Si, Ca, Mg, Na, K, P), minor (Fe, Al, Mn, Cu, Zn, Co, Mo, As, Ni, Cr, Pb, Cd, V, Hg) and inorganically bound (Cl, S) [8]. Due to very small fractions in the fuel, both qualitatively and quantitatively measurements of the minor and trace metal elements require high sensitive analysis equipment such as ICP (Inductively Coupled Plasma), AAS (Atomic Absorption Spectroscopy), EDX/EDS (Energy Dispersive X-Ray Spectroscopy), etc. On the other hand, the presences of Cl and S can be detected by ion chromatography (IC).

Carbon (C) is the most important element not only for biomass but also for any organic material. It has a major contribution to the overall heating value of biomass fuel. Carbon comes from the atmospheric CO_2 and becomes part of the plants during photosynthesis. It is mainly released back to the atmosphere in form of CO_2 during the combustion of biofuels. Typical carbon content in woody biomass is between 48–57 wt% (daf), while the value for herbaceous biomass is slightly lower [9].

Hydrogen (H) is another important element of biomass, and can be found in the carbohydrates and phenolic polymers. It contributes significantly to the heating value of biomass. During combustion, hydrogen is converted to H_2O. The content of hydrogen in woody biomass is around 6–8% (daf) [9].

Oxygen (O) is a major element in biomass fuels, present in all biomass chemical compositions. However, oxygen has a negative effect to reduce the heating value of biomass. The content of oxygen in woody biomass is about 32–45 wt% (daf). Its content is usually not measured directly, but calculated by subtracting the fractions of all other elements in the fuel from 100%.

Nitrogen (N) is the most important nutrient for plants but its contribution to the heating value of biomass is almost zero. It is absorbed via the soil or the fertilizers by the plant during its growth. The total nitrogen content in woody biomass is normally 0.1–0.7 wt% (daf). During combustion, nitrogen is partly emitted in oxide forms (NO, NO_2, N_2O), which have negative effects on the global climate and human health.

Sulfur (S) has only a small fraction (less than 0.1%) in woody biomass and presents in some organic structures like amino-acids, proteins and enzymes. Like nitrogen, it is an important nutrient for plant growth but has very small contribution to the heating value of biomass. During combustion, sulfur is mainly transformed to SO_2, which contributes to aerosol and smog formation, acid rain and corrosion problems.

Potassium (K) and **Sodium** (Na): these alkaline metals have very low melting points, which can reduce ash melting temperature and cause problems in combustion systems such as agglomeration, deposition, corrosion, slagging and fouling. The combination of these elements with chlorine makes the problems more critical. Moreover, the vaporization and subsequent condensation of volatile metals in general lead to the formation of sub-micron fly ash particles, which are more difficult to precipitate in dust filters, and hence cause health problems [8].

Calcium (Ca) and **Magnesium** (Mg) have relatively high melting point, which helps increase the melting temperature of ashes and reduces ash sintering on the grate or in the furnace.

Silicon (Si) is one of the main ash forming elements. Its combination with K and Na can lead to the formation of alkali silicates in fly ash particles, which melts at low temperatures and results in deposition problem.

Chlorine (Cl) is almost completely vaporized, forming HCl, Cl_2 and alkali chlorides during biomass combustion. This element is associated with many problematic issues including emissions (dioxins, acid rain, and aerosol formation) and operation problems (fouling and corrosion). However, chlorine is not solely responsible for these issues. Together with the presence of alkali metals, it forms alkali chlorides which reduce the overall ash melting temperature to 700–800 °C or even lower for high alkali content biomass such as straw. This causes deposition and corrosion problems for the combustion system. Generally, chlorine content higher than 0.1 wt% (db) is problematic.

Heavy metals (Hg, Sb, As, Cd, Cr, Co, Pb, Ni, and Se) are present in trace levels in biomass, but they are toxic and cause risks to human health [10]. Ash treatment or dust precipitation can be applied to reduce the emissions of these metals.

II.1.2.5 Grindability

Prior to conversion processes, biomass needs to be pulverized to obtain a more homogeneous feedstock as well as to improve the heat and mass transfer during the processes and the combustion stability. **Grindability** presents qualitatively how easy a biomass sample can be pulverized. Generally, fuel with good grindability consumes less energy to comminute, and vice versa. However, raw biomass possesses very poor grindability due to its fibrous structure compared to coal, and therefore consumes much more energy than coal in the pulverization step.

In the literature, there are two methods that can be adopted for evaluation the grindability of biomass fuel. The first method estimates the grindability by measuring the portion of ground materials passing through a 75 μm sieve and comparing it with that of standard coals [11, 12]. This assessment is somehow similar to the determination of HGI (Hardgrove Grindability Index) for coal. Although this method can show how fine the fuel particles are, it does not explicitly show the grinding energy. In the second method, the power consumption of a mill to pulverize an amount of biomass sample is recorded and regarded as the specific grinding energy (SGE) [13, 14]. This method gives information on the energy requirement, but not the particle size distribution of the samples. Therefore, the particle size distribution should be analyzed in a separate step.

II.1.2.6 Hydrophobicity

Hydrophobicity is the water repellant property of biomass fuel. Biomass constituents (hemicellulose, cellulose and lignin) contain hydroxyl (–OH) groups, which are likely to form hydrogen bonds with free water. This gives biomass a hygroscopic nature, i.e. it has poor hydrophobicity. During storage, biomass fuel tends to absorb water even if it is already dried, until equilibrium is reached with the humidity in the surrounding atmosphere. The presence of water in biomass is undesired, as mentioned in section II.1.2.2. Therefore, poor hydrophobicity is a drawback of biomass fuel compared to coal.

There exists no standard method for assessment of the hydrophobicity of biomass fuel so far. Researchers have had to develop or adopt methods on their own for such investigations. However, it can be found in the literature two groups of methods for evaluation the hydrophobicity of biomass fuel. In the first group, biomass bulk samples or pellets were immersed in water for some hours and then the amount of absorbed water was recorded and compared [15-17]. In the other assessments, the moisture uptake rates of biomass powder were measured using a controlled humidity cabinet [18-21]. Methods in the second group are preferable because it can minimize the interferences of water trapped in pores, and more importantly, it gives the information of the equilibrium moisture content (EMC) of the fuel as well as how long time needed to reach this level.

II.1.2.7 Bulk density and energy density

Bulk density (kg/m^3) and **energy density** (GJ/m^3) are defined respectively as the mass and energy per unit volume of biomass. Compared to coal, these two densities of biomass is much lower. For example in [22], bulk density of raw biomass is 350–680 kg/m^3 versus 1100–1350 kg/m^3 for coal, whereas energy density values are about 5.8 for raw biomass and 30–40 GJ/m^3 for coal, respectively. The low bulk and energy densities limit the use of biomass for heat and power production, as well as increase the cost of biomass logistics and storage.

II.1.2.8 Pelletability

Pelletization is a mechanical process that converts bulky solid biomass fuels into pellets with both increased bulk and energy densities. In addition, biomass pellets have more homogeneous shape and structure than bulky biomass, which is advantageous for automated feeding into boiler systems [23]. **Pelletability** is a qualitative indicator, which can be evaluated via some factors such as pelleting pressure and temperature, durability or mechanical strength of the pellets. Generally, biomass with good pelletability requires low pelleting pressure and temperature to produce high durable pellets.

II.2 Thermochemical conversions of biomass

Thermochemical conversion is the main pathway to produce heat and power from biomass fuels. They include pyrolysis, gasification and combustion, of which the main products and applications are summarized in Figure II-2. More details for each process will be introduced in the next sub-sections.

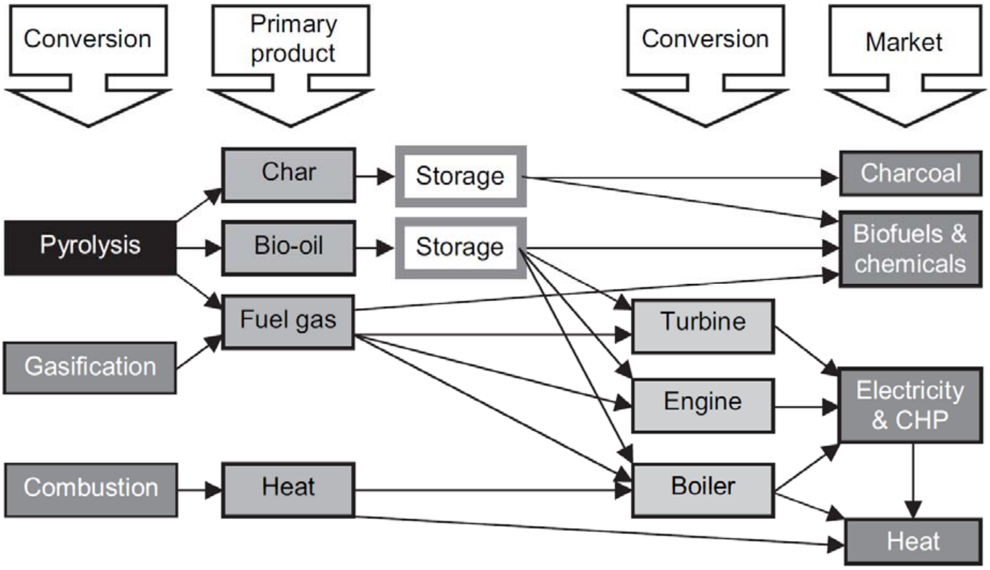

Figure II-2. Thermochemcial conversion routes for biomass fuels (adopted from [24]).

II.2.1 Pyrolysis

Pyrolysis is the thermal degradation of biomass at elevated temperatures and in the absence of oxygen. The process involves simultaneous and successive reactions when biomass is heated in an inert atmosphere. The main operating parameters in pyrolysis are temperature, residence time, heating rate, pressure, reactor configuration, feedstock, etc. In addition, biomass properties including chemical composition, ash content and composition, particle size, moisture content, etc. also play an important role in a pyrolysis process [25]. The products from biomass pyrolysis include a solid (biochar), a viscous liquid mixture (bio-oils) and some non-condensable gases. The products distribution strongly depends on the operating parameters [24]. Low temperatures and long residence times favor the production of biochar. High temperatures and long residence times increase the gas yield. Moderate temperatures and short vapor residence times promote the bio-oil production.

Generally, pyrolysis is divided into three categories based on the heating rate of the process: slow (or conventional), fast, and flash pyrolysis. Slow pyrolysis tends to produce more biochar than fast and flash pyrolysis, while the two latters aim at bio-oil production. Some important operating parameters for different types of pyrolysis are presented in Table II-1. On the other hand, pyrolysis is also first in two consecutive steps in both gasification and combustion processes.

Table II-1. Main operating parameters for different pyrolysis processes (adopted from [26]).

	Slow pyrolysis	**Fast pyrolysis**	**Flash pyrolysis**
Heating rate (°C/s)	0.1 – 1	10 – 200	> 1000
Pyrolysis temperature (°C)	300 – 700	600 – 1000	800 – 1000
Solid residence time (s)	300 – 500	0.5 – 10	< 0.5
Feedstock particle size (mm)	5 – 50	< 1	< 0.2

Slow pyrolysis is a conventional process, known for thousands of years, in which biomass is heated with a low heating rate to a final temperature. It takes up to hours to complete and results in biochar as the main product.

Fast pyrolysis employs much faster heating rates (about 10–200 °C/s) and yields more than 60% of bio-oil. Typically, fast pyrolysis can produce 60–75 wt% of bio-oil, 15–25 wt% of biochar, and 10–20 wt% of gases.

Flash pyrolysis is an upgraded version of fast pyrolysis, where the biomass is heated up extremely fast (> 1000 °C/s), and the residence time is only part of second. Up to 80% bio-oil can be obtained via this technology. Due to very high heating rates and short reaction times, fine particles are required to minimize the heat and mass transfer limitation in flash pyrolysis.

While the charcoal production technologies are mature, the bio-oil production technologies are still being developed. Moreover, for fuel application, bio-oil has some drawbacks, compared to petroleum oil, which include: high viscosity, high oxygen content, high corrosiveness, high water content, etc. An extensive upgrading and/or refining step is required before pyrolysis bio-oil can be used directly or blended with other petroleum-based fuels.

II.2.2 Gasification

Gasification is the partial oxidation of biomass fuel, resulting in production of product gas (consisting of hydrogen, carbon monoxide, carbon dioxide, methane, water and other trace components). Product gas is easier and more versatile to use than the original biomass, e.g. it can be used to power gas engines and gas turbines, or as a chemical feedstock to produce liquid fuels via a Fischer-Tropsch process [27]. To accomplish gasification, it is always necessary to pass through a pyrolysis stage first [28]. In other words, pyrolysis is the first step in biomass gasification. However, a gasification process is normally carried out at higher temperatures than a pyrolysis process [28].

Due to incomplete oxidation, the chemistry of a gasification process is complex and involves a number of reactions. The main reactions during biomass gasification is summarized in Table II-2, classified into homogenous gas-phase-reactions and heterogeneous reactions [29].

Table II-2. Main reactions during biomass gasification.

Homogenous gas-phase-reactions	
$H_2 + ½ O_2 \rightarrow H_2O$	*Hydrogen combustion/oxidation*
$CO + ½ O_2 \rightarrow CO_2$	*Carbon monoxide combustion/oxidation*
$CH_4 + ½ O_2 \rightarrow CO + 2 H_2$	*Methane combustion/oxidation*
$CH_4 + CO_2 \rightarrow 2 CO + 2 H_2$	*Dry reforming reaction*
$CH_4 + H_2O \rightarrow CO + 3 H_2$	*Steam reforming methanisation*
$CO + H_2O \rightarrow CO_2 + H_2$	*Water-gas-shift reaction*
Heterogeneous reactions	
$C + O_2 \rightarrow CO_2$	*Carbon combustion/oxidation*
$C + ½ O_2 \rightarrow CO$	*Carbon partial combustion/oxidation*
$C + CO_2 \rightarrow 2 CO$	*Boudouard reaction*
$C + H_2O \rightarrow CO+H_2$	*Water gas reaction (steam reforming)*
$C + 2 H_2 \rightarrow CH_4$	*Methanisation reaction*

II.2.3 Combustion

Combustion may be defined as fast oxidation of biomass, producing heat at high temperatures. It is a proven technology for heat and power production [30], and is currently the most important energy application of solid biomass fuel. Biomass combustion is contributing to more than 90% of the global bioenergy deployment [8]. Biomass combustion systems are available in a very broad size range from very small stoves (for domestic heating) up to large-scale industrial plants. Co-combustion of biomass in coal-fired power plants is also interesting because of the high conversion efficiency of these plants for power or combined heat and power (CHP) production [31]. Biomass combustion includes a number of homogeneous and heterogeneous reactions, but overall they can be represented by the following global equation, in which minor elements with small and trace elements are neglected:

$$\mathrm{CH}_m\mathrm{O}_n + \lambda\psi(0.21\mathrm{O}_2 + 0.79\mathrm{N}_2) \rightarrow \mathrm{CO}_2 + a\mathrm{H}_2\mathrm{O} + b\mathrm{O}_2 + c\mathrm{N}_2 \tag{II-1}$$

where m and n are the H/C and O/C molar ratios in biomass, λ and ψ are the excess air ratio and the stoichiometric coefficient, respectively. The values a, b, and c can be calculated from elemental balances, as follows:

$$a = \frac{m}{2}, b = (\lambda - 1)\left(1 + \frac{m}{4} - \frac{n}{2}\right), c = 0.79\lambda\left[\frac{1 + \frac{m}{4} - \frac{n}{2}}{0.21}\right]$$

An important combustion parameter is the excess air ratio (λ) which describes the ratio between the available and the theoretically needed (stoichiometric) amount of combustion air [30]. Together with biomass composition, combustion temperature and residence time, the excess air ratio strongly affects the composition and quality of the combustion products such as $\mathrm{NO_x}$ emissions and other unburnt pollutants.

II.3 Biomass combustion technologies

A combustion system should supply fuel and combustion air with an optimal mixing and distribution in order to burn the fuel with maximum heat release and low pollutant emission. In principle, combustion technologies for biomass are mostly the same as for coal, which include fixed-bed, fluidized-bed and pulverized fuel combustion. They are demonstrated in Figure II-3 and briefly introduced in this section.

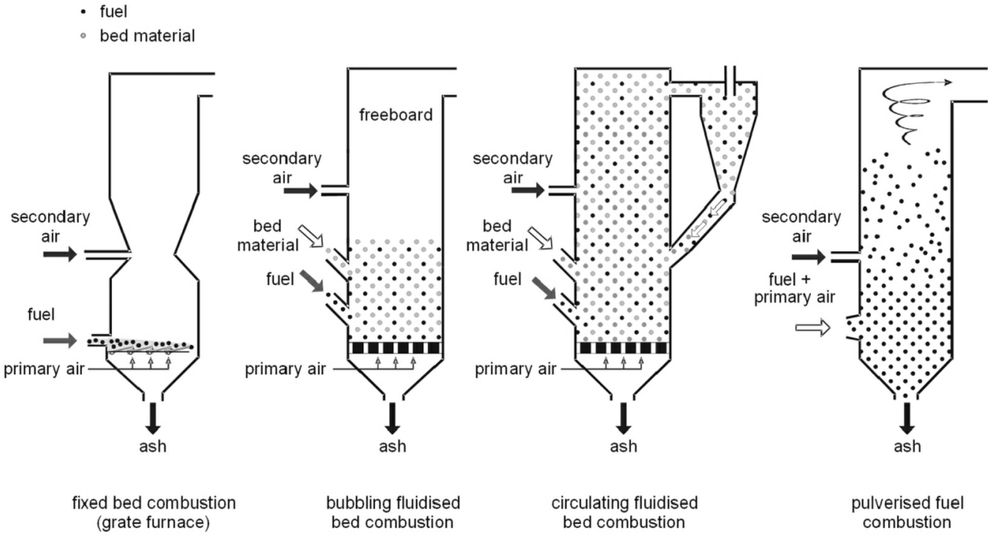

Figure II-3. Common systems for biomass combustion (adopted from [8]).

II.3.1 Fixed-bed combustion

Grate-firing, in which biomass is placed on a grate with air supplied through holes in the grate, is the main technology in this category. It includes fixed grate, moving grate, travelling grate, rotating grate and vibrating grate. The grate furnaces have some advantages such as low investment cost (for plants with capacity less than 20 MW_{th}) as well as low operating cost. They are also capable of working with heterogeneous fuels, large particles sizes and high moisture feedstock. In addition, grate-firing furnaces have good burn-out of carbon in fly ash particles and low dust load in the flue gas. Another advantage of grate-firing systems is that they are less sensitivity to slagging than fluidized-bed furnaces. However, the combustion condition in grate furnace is not as homogenous as in fluidized-bed furnace. In addition, it is difficult to mix woody and herbaceous fuels in grate-firing. Also, the energy efficiency of grate-firing systems is lower than for fluidized-beds due to a higher amount of excess air.

II.3.2 Fluidized-bed combustion

Fluidized-bed is a newer combustion method. In this technology, biomass is mixed with a medium (typically sand) and kept suspended in this mix by incoming high velocity air. The technology is classified into two subgroups: **bubbling fluidized-bed** (BFB) and **circulating fluidized-bed** (CFB). Fluidized bed combustion is currently considered the best technology to burn biomass [32].

II.3.3 Pulverized fuel combustion

The **pulverized fuel** (PF) technology is used for large-scale combustion systems which were previously largely coal fired. It requires that biomass is finely ground to reach a particle size less than 1 mm [32] prior to feeding to the combustion chamber. Also, the moisture content of the fuel should not exceed 20 wt%. The technology offers high combustion temperature, however, corrosion and slagging then become problems, especially for biomass fuel with high ash content. Apart from the above difficulties, PF combustion requires low excess air and thus increases the thermal efficiency. Good combustion control and versatile load can be easily achieved by this technology. Moreover, it is capable of reducing NO_x emission with an installation of cyclone or vortex burner, i.e. low-NO_x burners.

II.3.4 Co-combustion

Co-combustion or **co-firing** biomass with coal in existing coal fired power plants is an attractive retrofit application to reach near-term targets for significantly increasing the share of renewable energy sources and to reduce CO_2 emissions [33]. Co-combustion concepts can be distinguished as [8]:

- Direct co-combustion: direct feeding of biomass to the coal firing systems.
- Indirect co-combustion: gasification of biomass and then combustion of fuel gas with coal in the same plant.

- Parallel co-combustion: involves the combustion of biomass in a separate combustor and boiler producing steam, which is used within the coal-fired power plant.

Currently, about 48% of worldwide co-firing plants are equipped with PF boilers, the rest includes 24% with BFB boilers, 19% with CFB boilers, and 9% with grate-fired boilers [33]. These figures indicate among others the importance of improving the grindability of biomass fuels for co-combustion.

II.4 Challenges and pretreatment needs

Combustion and co-combustion are the main technologies as they account for more than 90% of the global bioenergy deployment [8]. However, utilization of biomass for energy applications is still problematic due to inherent properties of this feedstock. For example, drying and grinding prior to feeding into combustion systems are energy intensive steps. Moreover, storage and transportation of biomass material are also costly. The main challenges coupled with the drawbacks of biomass are listed in Table II-3.

In order to overcome these challenges, biomass normally requires a pretreatment step prior to the conversion process. **Torrefaction**, wet or dry, is a promising method to convert a diverse range of biomass to energy-dense fuels, readily suitable for subsequent thermochemical conversion processes. By means of torrefaction, the following main improvements in the fuel properties of torrefied biomass can be achieved: (1) increased heating value due to a reduction in the O/C ratio; (2) intrinsic transformation from hygroscopic into hydrophobic nature; (3) better grindability coupled with less energy requirement for size reduction of the fuel. In the next section, an overview of torrefaction technologies is presented.

Table II-3. Disadvantages of raw biomass materials utilized for thermochemical conversions.

Biomass drawbacks	Main challenges
High moisture content	*Reduce the heating value* *Require energy intensive drying step* *Reduce the efficiency of the conversion processes* *Increase storage and transportation costs* *Increase risks of biological degradation* *Increase corrosion because of condensation of water in flue gas*
Low bulk and energy density	*Increase storage and transportation costs* *Require high feeding capacity*
Poor grindability	*Increase grinding energy*
Hygroscopic nature	*Up-take moisture during storage* *Increase risks of biological degradation*
High oxygen content	*Reduce the number of C–H bonds* *Reduce the heating value and energy density* *Reduce the thermal stability*
High alkali metal content	*Cause ash-related problems*
Heterogeneity	*Wide variation in properties*

II.5 Biomass pretreatment via torrefaction

II.5.1 Dry torrefaction and its challenges

Dry or **conventional torrefaction** is defined as thermal treatment of biomass in an inert environment at atmospheric pressure and temperatures within the range of 200–300 °C [34-36]. Recently, the definition has been extended to include researches on dry torrefaction (DT) in the presence of oxygen and carbon dioxide [37-40], and under elevated pressures [41, 42].

During the last decade, research and development activities on DT for energy applications including combustion, gasification, and pyrolysis have been very active [11, 16, 34, 35, 43-51]. It has been reported that, during combustion, dry-torrefied biomass behaves more coal-like with more stable burning characteristics, compared with untreated biomass [11, 47]. The gasification efficiency and the syngas quality are improved by DT [46, 48, 49]. Moreover, for fast-pyrolysis, DT appears to decrease the yield of by-products and to improve the quality of bio-oil [50, 51].

The DT technology has been developed rapidly and is ready for market introduction and commercial operation [52]. However, it has been claimed that no clear winner in this area can be identified so far [52]. This situation is due to both technical and economical issues. DT requires an input feedstock with a moisture content not higher than 5–10 wt% [53], i.e. an energy intensive pre-drying step is needed to dry biomass prior to a DT process. Another problem associated with DT is that the relative ash content in dry-torrefied biomass is higher than native biomass, because of the volatiles mass loss during the torrefaction process. This can potentially make ash-related problems become even worse for dry-torrefied biomass compared with raw biomass. In addition, dry-torrefied biomass is very dry and brittle, which makes this kind of material more difficult to pelletize than untreated biomass [54-56]. It has been reported that no pellet could be made from spruce dry-torrefied at 300 °C [56]. Therefore, increased pelleting pressure and temperature or binder addition are required for pelletization of dry-torrefied biomass.

From an economic point of view, current DT technologies are using wood chips from stem wood, a feedstock of relatively high quality and thus cost. Utilization of inexpensive biomass resources such as agricultural residues, forest residues and other biomass waste sources may help reducing the total cost of biomass torrefaction at industrial scale. However, the DT process then will be more complicated due to high moisture content of these feedstocks. Moreover, DT also has other technical issues related to emissions from the process, product quality control and flexibility, heat integration and feedstock properties variations [52, 57].

To overcome the above mentioned challenges, wet torrefaction can be a promising alternative to DT. The WT process and its advantages over DT will be discussed in next section.

II.5.2 Wet torrefaction

Wet torrefaction (WT) may be defined as treatment of biomass in hydrothermal media or hot compressed water at temperatures within 180–260 °C [18, 19, 58-60]. Compared to DT, WT offers several advantages:

- WT employs water in sub-critical conditions as reaction media, and the energy intensive pre-drying for the feedstock is hence eliminated. Moreover, it is capable to utilize wet biomass resources such as agricultural residues, forest residues and other biomass wastes, which are available at a low cost. It should be reminded that these high moisture feedstocks are problematic for DT.
- In order to produce an equal solid yield, WT needs significantly lower temperature and shorter holding time than DT [18]. In addition, the fuel

properties of the solid produced by WT are better than DT, e.g. increased HHV, better grindability, and improved hydrophobicity.

- WT is capable of dissolving and thus washing out part of the inorganic components from solid biomass fuels, resulting in lower ash content in hydrochar than that in raw biomass. This suggests an efficient route to produce "cleaner" solid biomass fuels via WT, with regard to the inorganic impurities.
- The compressibility of hydrochar and the mechanical strength of pellets produced from hydrochar (from WT) are better than those produced from the untreated biomass and from dry-torrefied biomass [61-63]. Moreover, wet-torrefied biomass does not require water addition in order to improve the pelletability and binding capacity as is the case for DT [64, 65].
- After WT, the wet hydrochar can be effectively made dry by mechanical and/or natural dewatering, which is an attractive option capable of dramatically reducing the energy requirement for the post-drying step.

In addition to the solid product, many valuable organic chemicals including sugars, organic acids, furans, and furfurals [59, 66, 67] can be recovered from the aqueous phase products of WT in order to improve the economy of the WT process.

There are a number of concepts in the literature, which may be found similar to the WT concept. They include "hydrothermal carbonization" (HTC) [66-76], "hydrothermal conversion" [76-80] or "hydrothermal treatment" [81-86]. Among those, HTC has sometimes been used to refer to WT. However, it should be noted that there are significant differences between WT and HTC.

WT aims at decomposing primarily the hemicellulose component of biomass, even though small fractions of cellulose and lignin are also degraded, at temperatures within 180–260 °C. This temperature range is employed for WT because hemicellulose is degraded in sub-critical water conditions at temperatures below 250 °C [73]. The main product of WT is hydrochar, an upgraded solid biofuel with higher carbon content than that of the untreated biomass.

On the other hand, HTC requires further degradations of the two other biomass components (cellulose and lignin) to produce charcoal, which consists of mainly carbon and remaining ash. Due to this requirement, HTC is carried out at higher temperatures above 300 °C [87]. This is because the main hydrothermal decomposition of cellulose and lignin occurs at significantly higher temperatures, above 300 °C [73, 88-90]. However, HTC can also be carried out at temperatures below 300 °C, but with catalyst addition [91]. The temperature ranges of the two processes in a temperature-pressure phase diagram are demonstrated in Figure II-4.

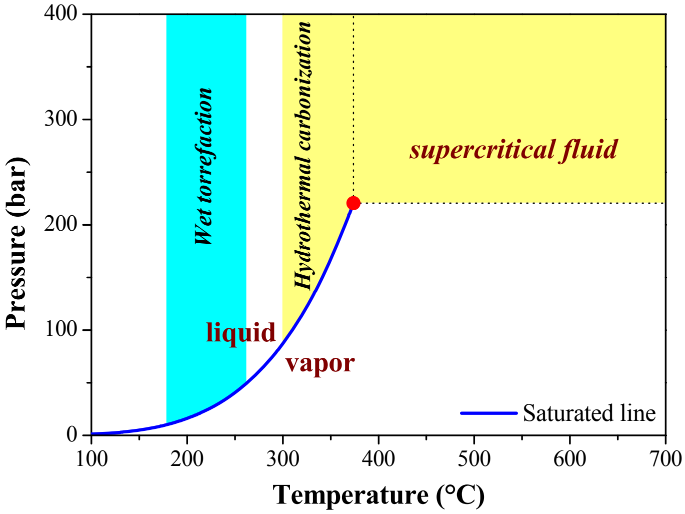

Figure II-4. Wet torrefaction and hydrothermal carbonization regions in a temperature-pressure phase diagram of water.

More importantly, while hydrochar produced via WT is used only for energy applications (combustion, gasification, and pyrolysis), hydrothermal charcoal produced via HTC can be used not only as fuel but also as soil enhancer, fertilizer, activated carbon, and even carbon material for synthesizing carbon nanotubes [87, 92, 93]. Due to these differences, it is obvious that the energy efficiency of the process and the fuel properties of solid products are more critical for WT than for HTC, whereas physical and chemical properties of hydrothermal charcoal may be of greater importance when other utilizations than as fuel are considered. The main differences between WT and HTC are summarized in Table II-4.

Table II-4. Main differences between WT and HTC.

	Wet torrefaction	**Hydrothermal carbonization**
Working temperature	180 – 260 °C	> 300 °C
Solid yield	> 60%	35 – 60%
Main product	Upgraded solid fuel	Charcoal, activated carbon
Applications	Heat and power generation	Heat and power, absorbent, soil enhancer, fertilizer, etc

II.5.3 Chemical and physical properties of water in subcritical condition

Hot compressed water (HCW) is defined as sub- and super-critical water above 200 °C and at sufficient high pressure [94]. At high temperature and pressure conditions, the properties of liquid water dramatically change [95-97], especially when approaching the critical point (T = 374 °C, p = 220.6 bar, ρ = 320 kg/m^3). Some physio-chemical properties of water at 30 MPa as a function of temperature are demonstrated in Figure II-5. In this section, an overview of the properties of sub-critical water, which is the media for most hydrothermal conversions of biomass, is presented.

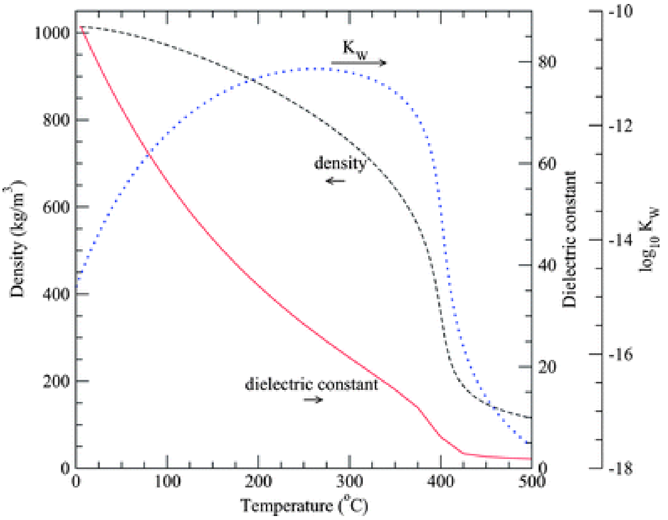

Figure II-5. Changes in physico-chemical properties of water at 30 MPa as a function of temperature (adopted from [97]).

II.5.3.1 Dielectric constant

The **dielectric constant** (ε) of a solvent is a measure of its polarity, i.e. higher ε means more polarity. Water is one of the most polar solvents, of which its dielectric constant is about 80 at 20 °C. However, as shown in Figure II-5, the ε value decreases to lower values when temperature increases. In the WT region, the dielectric constant of water is only 25–35, which is similar to common organic solvents at standard condition such as acetonitrile (ε=37.5), dimethylformamide (ε=36.7), or acetone (ε=20.7); thus, HCW behaves like an organic solvent which is suitable for many chemical reactions. In addition, as a protonic solvent, HCW can donate protons and becomes a natural acid catalyst.

II.5.3.2 Ion products

A unique property of HCW is that it may behave like a non-polar solvent, but the single molecules are still polar, hence it possesses very unusual properties for new reactions [98]. As can be seen in Figure II-4, the **ion products** of water (K_w)

increase from 10^{-14} at 25 °C to about 10^{-11} in the range between 200–275 °C. These ions may act as acid or base catalysts and thus HCW can play the role of a proton donator or acceptor. Therefore, no addition of catalyst is required in WT since it is carried out in HCW.

II.5.3.3 Transport property

Both **density** and **viscosity** of HCW are decreased to lower values, which increase its diffusion rate, compared with “normal” water [95]. A high diffusion rate helps avoid mass transfer limitations. The transport properties of HCW (high diffusion rate, low viscosity) can enhance the rate of chemical reactions, making HCW an excellent reaction media [98].

II.5.4 Degradation of biomass in subcritical water conditions

In hydrothermal media, hydrolysis is the key mechanism for the decomposition of the three main components of plant biomass. For WT, which normally employs pure water, hydrothermal hydrolysis (hydrothermolysis) is the main route. However, as HCW can donate protons and become an acid catalyst, acid hydrolysis may also take part in the decomposition of biomass constituents.

Similar to DT, WT aims at decomposing hemicellulose from biomass in order to destroy its fibrous structure. In fact, hemicellulose is poorly resistant to hydrolysis and is easily dissolved in water from approximately 180 °C. Many researchers [19, 99] have successfully extracted hemicellulose into an eluted solution under hydrothermal condition. However, hemicellulose is a heterogeneous branched polysaccharide. Therefore, the hydrolysis reactions of hemicellulose to form monosaccharides and other substances are complex, and what kinds of organic compounds that are present in the hydrolysis product are not clearly enumerated. According to Huber et al. [100], the main content of degraded hemicellulose products in hydrolysis is subject to xylose, a depolymerization product of its xylan backbone. The others are glucose, arabinose, fucose, galactose, glucuronic acid and galacturonic acid [98]. A simple pathway for hydrothermolysis of hemicellulose can be shown as follows [100]:

$$\text{Hemicellulose} \rightarrow \text{Xylose} \rightarrow \text{Degradation products} \tag{II-2}$$

In hydrothermal condition, cellulose is more stable than hemicellulose and start decomposing at temperatures higher than 200 °C. The main degraded product from cellulose hydrolysis is glucose, which results from the breakage of glycosidic bonds in the cellulose macromolecule. Most cellulose hydrolysis mechanisms are based on that developed by Saeman [101]:

$$\text{Cellulose} \rightarrow \text{Glucose} \rightarrow \text{Degradation products} \tag{II-3}$$

As can be seen from Figure II-6, showing the hydrothermal degradation of cotton cellulose at different temperatures and times, cellulose degrades rapidly at temperatures higher than 250 °C, which is undesired for WT purpose. Therefore, the maximum WT temperature in this study was chosen as 225 °C. In addition, some studies have found that the crystallinity of cellulose increased after hydrothermal treatment [102-104], which may be subject to the repolymerization of degraded products.

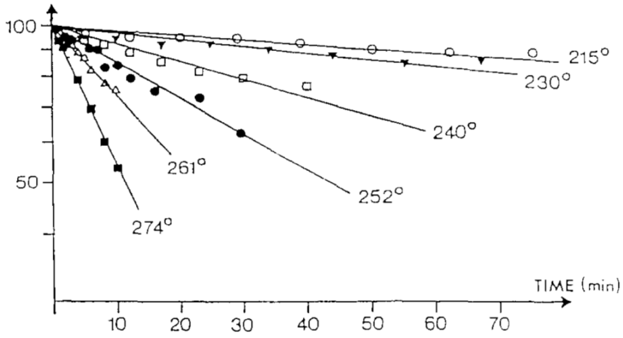

Figure II-6. Hydrothermal degradation of cotton cellulose as a function of reaction time and temperature (adopted from [105]).

The main part of lignin is thermally stable and requires relatively high temperature as well as enough time for complete degradation. Dinjus et al. [106] reported that the temperature range of 180 to 250 °C is too low for a strong chemical modification of lignin, and only a small fraction of lignin is degraded at such temperatures. Li et al. [107] also agreed that only a limited amount of lignin is removed as a result of simultaneous depolymerization and repolymerization reaction during the treatment at 185–220 °C. However, the repolymerized lignin can precititate and bind the cellulose irreversibly.

Chapter III

METHODOLOGY

III.1 Hydrochar production

III.1.1 Materials

Stem woods from Norway spruce (softwood) and birch (hardwood) were used as feedstock in the three first papers in this thesis. The wood samples were obtained from a local supplier in Trondheim, Norway in form of 1 cm and 3 cm cubes. The wood cubes were used for WT as received, with only an additional drying step (at 103 ± 2 °C for 48 h).

In the other papers, Norway spruce and birch branches were selected to represent forest residues. Fresh branches of 2–2.5 cm in diameter were collected from a local forest in Trondheim, Norway. The bark was then removed from the core wood of the branches in order to avoid possible interferences caused by impurities, contaminants and composition differences. The bark-free branches were then cut into 3–4 mm thick slices and washed with water. The cleaned slices were then stored in a climate cabinet (series VC^3 0100 of Vötsch Industrietechnik) to maintain the moisture content of the branches. The samples prepared this way are referred to as “wet” sample or feedstock hereafter in this paper. Parts of the samples were dried at 103 ± 2 °C in an oven for 48 h to obtain "dry" or "oven-dried" feedstock.

III.1.2 Experimental setup

WT experiments were carried out in a 250 ml Parr reactor model 4651 (Figure III-1), which is made of stainless steel (T316SS) and equipped with a bench-top ceramic heater (4923EE), a temperature controller (4838EE), a pressure gauge, and two valves as shown in Figure III-2. A thermocouple for monitoring the reaction temperature (temperature of water in the reactor) is connected to the controller by which the electrical duty of the heater is controlled. The thermocouple is introduced into the reactor via a thermo-well, which is cast in the reactor head. In addition, a self-made detachable perforated glass plate is mounted to the thermo-well in order to keep the wood cubes and dried branches entirely submerged in the water as shown in the Figure III-2. However, the glass plate is not needed in WT of wet branches. The reactor is connected to a gas (nitrogen or carbon dioxide) cylinder via Valve 1.

Distilled water was used as the reaction media. The ratio of dry feedstock over water was 1:5 by weight. In addition, for studying the effect of pressure, a ratio of 1:10 was employed with the feedstock prepared in powder form of 0.5–1 mm to minimize heat and mass transfer limitations during the torrefaction process. All the experiments were duplicated, from which data were collected and processed to generate average values for relevant assessments.

Figure III-1. The Parr 4651 reactor (adopted from parrinst.com).

III.1.3 Wet torrefaction procedure

Before every torrefaction run, the furnace (the heater) without the reactor was heated for 30 min to a preset temperature. At the same time, the reactor was loaded, closed, sealed, and purged with compressed nitrogen gas for 10 min. Then the reactor was pressurized and placed in the preheated furnace which was set to the maximum power, giving a heating rate of approximately 12 °C/min. The holding time was counted from the time at which the reactor temperature reached the preset temperature to the end point when the reactor was taken out from the furnace and submerged in an ice bath for cooling. When the reactor cooled to room temperature, the pressure was gradually released and the reactor was opened for products collection.

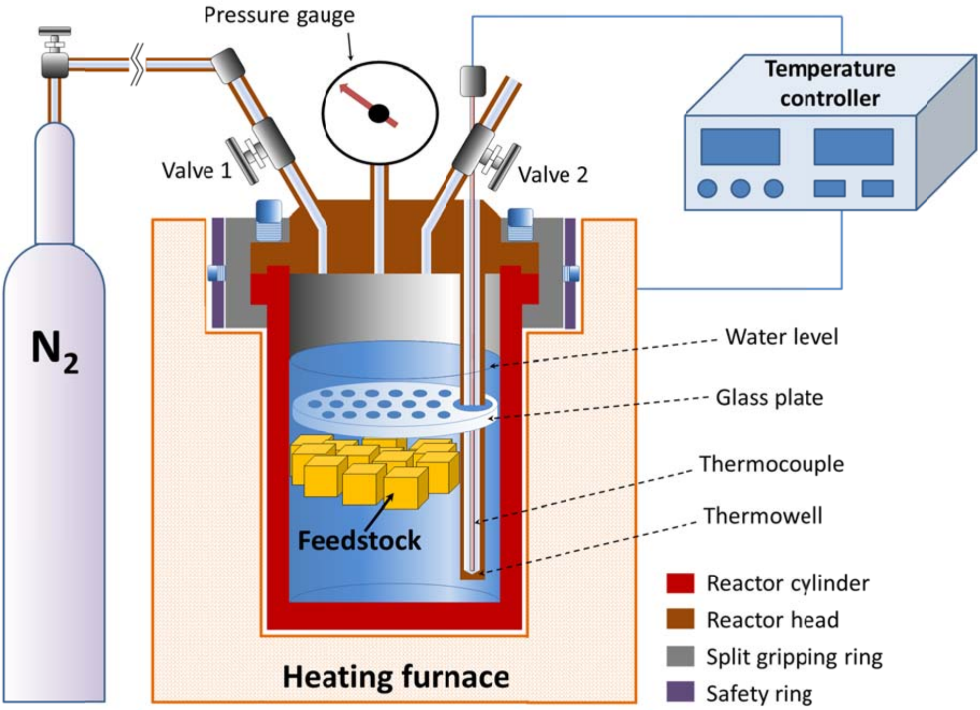

Figure III-2. Schematic diagram of the WT reactor and the experimental setup.

III.1.4 Products separation

Due to practical difficulty in handling the gases, only products in the solid and liquid phases were collected in this study. They were separated from each other by filtration using a filter paper with a pore size of 5–12 μm. After separation, the collected solid (hydrochar) was dried at 103 ± 2 °C for 48 h and then balanced. Readings from the balance were tabulated as the mass of solid product from the WT. The dried solid was then stored in a desiccator filled with silica gel for further studies.

III.2 Hydrochar characterization

III.2.1 Proximate and ultimate analyses

Proximate analyses of all the feedstock were performed according to the ASTM standards: E781, E872 and D1102 for moisture content, volatile matter and ash content, respectively. Ultimate analyses of the fuels on dry basis were determined by an "EA 1108 CHNS-O" elemental analyzer (Carlo Erba Instruments).

III.2.2 Higher heating value calculation

The higher heating value of raw biomass and hydrochar were calculated according to a correlation proposed by Channiwala and Parikh [108], shown in Eq. (III-1)

$$HHV\ (MJ/kg) = 0.3491\mathbf{C} + 1.1783\mathbf{H} + 0.1005\mathbf{S} - 0.1034\mathbf{O} - 0.0151\mathbf{N} \tag{III-1}$$

where C, H, O, N, and S represent the mass fractions (wt%) of carbon, hydrogen, oxygen, nitrogen, and sulfur in the biomass fuel, respectively. The elemental composition was obtained from an ultimate analysis.

III.2.3 Specific grinding energy

For this assessment, an IKA MF 10 cutting mill (IKA®-Werke GmbH & Co. KG) equipped with a 1 mm bottom sieve was used. An analog current input module NI 9203 (from National Instruments Corporation) was employed to record the electrical current during grinding. A LabView program was used for the data acquisition and the calculation of the energy consumption which was logged to a file every 2 seconds. The power of the mill under no-load conditions was measured and subtracted from the power of grinding the biomass samples. The grinding energy was determined by integrating the power curve during the grinding period.

Finally, the data was normalized to the initial sample weight, expressed in kWh/ton.

III.2.4 Moisture up-take test

The ground biomass sample obtained from the SGE assessment was used in this test. It is screened through a sieve (Fritsch Analysette 3 Pro) to obtain the sample particles smaller than 250 µm. The powder is then dried at 103 ± 2 °C for 24 h to remove any water up-taken during grinding. Next, an amount of approximately 2 grams of dried powder is spread on a glass Petri dish, which is then placed in a climate chamber (series VC^3 0100 of Vötsch Industrietechnik) operated under the controlled conditions of 20 °C and 90% relative humidity. The mass changes by time due the moisture up-take of the tested material are recorded every 24 h for the total test period of one week. The moisture content of the tested material is then calculated according to Eq. (III-2):

$$MC_i(\%) = \frac{m_i - m_0}{m_0} \times 100\%, \qquad i = 1, \dots, 7 \tag{III-2}$$

where MC_i is the moisture content of the tested material on the i^{th} day; m_0 and m_i is the mass of the sample before the test and measured on the i^{th} day, respectively.

III.2.5 Morphology and structure study

The morphology and structure of raw and wet-torrefied biomass were studied by means of a table top SEM Hitachi TM 3000. The tested sample was attached on a holder and loaded into a vacuum chamber for the morphology observation, in which an accelerating voltage of 15 kV was applied.

III.2.6 Pelletability

III.2.6.1 Pelletization

The pelletization was carried out using a single pellet press [54], presented in Figure III-3, which allows precise control and adjustment of compressing pressure and pelleting temperature. The unit consists of a steel cylinder (8 mm inner diameter) and a tungsten carbide pressing rod. The press is heated by a jacket heater (450 W) of which the temperature was controlled by a PID. The compressing force is applied to the rod using an Instron 100 kN texture analyzer.

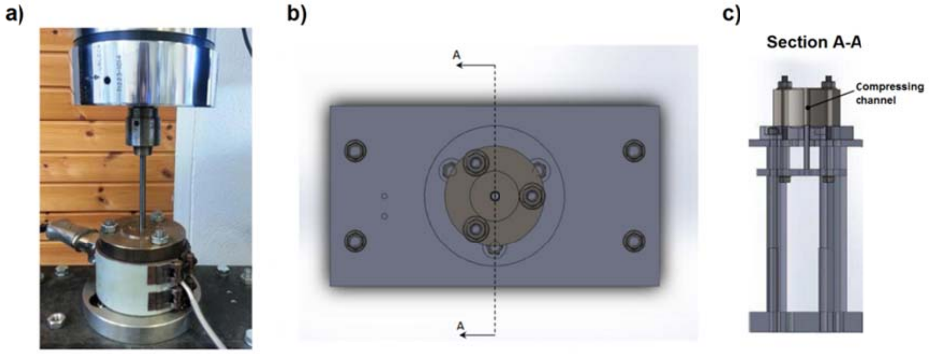

Figure III-3. Single pellet press unit: a) picture of the equipment. Drawing of the single pellet unit: (b) top view, (c) section view A-A.

The steel cylinder was first heated to a preset temperature. After a steady temperature was reached, the channel was filled with biomass material and the pressing rod was placed into the die. In order to obtain pellets with nearly equal length at different pressures, the amount of material was varied. The length of the pellets was set to be no longer than 16 mm to avoid differences in the density between the bottom and top part of the pellet (density gradient). After tempering for 3 minutes, the biomass material was compressed at a rate of 2 mm/min until the preset pressure was reached. Afterwards, the pressure was released, the bottom rod removed and the pellet was pressed out from the channel. The discharging speed of the rod was set to 15 mm/min. The total retention time of the material in the channel was 8–10 min. The obtained pellets were stored in sealed plastic bags at room temperature and humidity (≈ 25 °C; ≈ 30%) until further testing.

III.2.6.2 Pellet density

The pellet density was calculated by dividing the weight by the volume of the pellets. The length and diameter of the pellets were measured by means of a digital caliper.

III.2.6.3 Compressing test

The compressing tests were carried out at 48 h after the pellets were produced. A 60 mm diameter probe connected to a Lloyd LR 5K texture analyzer (Lloyd Instruments, England) was employed for this test. The compression speed was set to 1 mm/min, and the maximum normal force at breakage was recorded automatically. The pellet strength was expressed as the maximum force per length of the pellet (N/mm).

III.2.7 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a technique in which the mass of a substance is monitored as a function of temperature or time when the sample specimen is subjected to a controlled temperature program and in a controlled atmosphere [109]. TGA is commonly used to determine the mass loss characteristics of biomass for studying its thermal behavior in many processes (pyrolysis, gasification, combustion) and in a wide range of temperature, heating rates, and even at pressurized conditions. The most important application of TGA is to study the degradation mechanisms and reaction kinetics of biomass materials in these thermochemical conversion processes. In addition, TGA is also useful for estimation of the proximate and chemical (through kinetic modelling) compositions in biomass fuel.

The output data from TGA are normally used to construct a thermogravimetric (TG) curve, from which the mass losses versus temperature or time can be observed. In order to know the conversion rate of biomass during the thermal process, TG data are differentiated to obtain the differential thermogravimetric (DTG) data.

III.3 Kinetic study for thermal conversions of solid biomass fuels

It is important to understand the thermal behavior and kinetics of biomass during thermal conversion processes for technical design, modification or optimization of thermal conversion units (pyrolyzers, gasifiers, boilers and combustors). Because of this, the pyrolysis and combustion kinetic studies for solid biomass fuels have been extensively studied for many decades [25, 110-113]. A difficulty in kinetic analysis for combustion at full industrial scales is that it is not easy to separate the effects of chemistry and transport phenomena. However, by using a sufficiently small sample mass in fine powder form and employing a low heating rate, a regime controlled by chemical kinetics is established and thus heat and mass transport limitations can be neglected [25]. In order to meet these requirements, thermogravimetric analysis (TGA) is normally employed and it has been recognized as a proven technique for studying the thermochemical conversions of biomass in the kinetic regime [25, 110-117]. In the next sections, different reaction mechanisms for kinetic study on pyrolysis and combustion by means of TGA technique will be presented.

III.3.1 Kinetic models

III.3.1.1 Pyrolysis

Besides being a method for production of biochar and bio-oil, pyrolysis or devolatilization is also known as the first step in a gasification or combustion process. Understanding pyrolysis kinetics is therefore important. The process consists of a large number of reactions and produces a huge number of chemical compounds. However, for engineering applications, the pyrolysis products are often simplified into only char and volatiles [25]. The volatiles include permanent gases and condensable vapors, which results in a black viscous liquid (bio-oil/tar) after cooling. A single reaction or one-step model is based on the simple idea of the formation of char and volatiles from initial solid biomass fuel. In a more detailed kinetic model, the decomposition of biomass fuel includes both primary and secondary reactions. The latter model is known as two-step or consecutive-reaction model.

As mentioned above in section II.1.1, biomass fuel is composed of hemicellulose, cellulose and lignin. The thermal behaviors of these components are different [22]. During pyrolysis, hemicellulose degrades first in the temperature range of 200–300 °C and its degradation is associated with a so-called shoulder found on the left side of the pyrolysis peak in a DTG curve. The decomposition of cellulose occurs at 325–375 °C and couples with the main pyrolysis peak while lignin degradation occurs in a very broad temperature range from 250–500 °C [22, 118]. A model with three parallel reactions is thus proposed to look at the pyrolysis behavior of each biomass component independently. Nevertheless, it is not easy to separate the reaction of each component because the degradation of one may overshadow the others [118]. Therefore, the term "pseudo-component" is normally used to refer to the lumped biomass components and to describe possible overlapped reactions. Detailed reaction mechanisms for common models are presented hereafter.

III.3.1.1.1 Single reaction model

Single reaction model, also known as one-step model, is the simplest model in pyrolysis modelling. In this model, solid fuel (S) is decomposed with a reaction rate k to produce char (C) and volatiles (V):

$$S \xrightarrow{k} C + V \tag{III-3}$$

The advantage of this model is of course its simplicity. However, because of using only one reaction to describe biomass pyrolysis, the fit quality of the model is poor. Especially, for solid fuel having high hemicellulose content (e.g. hardwood), the fit quality can be dramatically reduced due to the appearance of the mentioned shoulder in the DTG curve. In order to improve the fit quality of the single reaction model, either a two-step or a three-pseudo-component model can be used instead.

III.3.1.1.2 Two-step model

A two-step model or consecutive-reaction model assumes that solid fuel S is first converted to an intermediate solid S^* and volatiles V_1 in a primary reaction. The intermediate solid reacts afterwards to form the final char C and the additional volatiles V_2 in secondary step. The rate constants of the primary and secondary reactions are k_1 and k_2, respectively.

$$S \xrightarrow{k_1} S^* + V_1 \tag{III-4}$$

$$S^* \xrightarrow{k_2} C + V_2 \tag{III-5}$$

This model was first applied for studying the pyrolysis of cellulose [119] and then extended to biomass materials [112, 120]. Recently, the model has also been employed for kinetic modelling of dry torrefaction [121-124].

III.3.1.1.3 Three-pseudo-component model

Solid biomass fuel consists of three main components with different thermal behaviors, as mentioned above. Therefore, it is difficult to use one reaction to represent all the components during the pyrolysis process. A three-pseudo-component model can overcome this limitation. The model has three parallel reactions, as shown below:

$$S_1 \xrightarrow{k_1} C_1 + V_1 \tag{III-6}$$

$$S_2 \xrightarrow{k_2} C_2 + V_2 \tag{III-7}$$

$$S_3 \xrightarrow{k_3} C_3 + V_3 \tag{III-8}$$

where S_i (i = 1, 2, 3) is a single pseudo-component, C_i and V_i is the char and volatiles produced from the respective pseudo-component during pyrolysis, and k_i is the reaction rate of each pseudo-component.

This three-pseudo-component model can represent the parallel reactions of the three main components of biomass, thus the fit quality increases significantly [125]. In addition, this model can describe well the possible overlapped reactions of the lumped components in biomass [114, 126, 127]. Moreover, some researchers have modified this model by including additional steps in order to further improve the fit quality. Then, the modified model may contain up to five or six parallel reactions [128, 129]. However, the model with three pseudo-components is the most commonly used.

III.3.1.2 Combustion

Combustion of solid biomass fuel generally consists of two main steps: devolatilization (or pyrolysis) and char combustion (or char burn-off). The reaction mechanisms for combustion are based on those for pyrolysis because the thermal decompositions of biomass in oxidative and inert environments are qualitatively similar [126, 130, 131]. In the first step, all pyrolysis kinetic models introduced in the previous section can be adopted. Then, it normally needs to include an additional reaction for char (C) combustion, releasing combustion product (V_4):

$$C \xrightarrow{k_4} V_4 \tag{III-9}$$

III.3.2 Mathematical modelling

Besides choosing a reaction mechanism or a physical model, the mathematical processing of the experimental data to formulate the selected reaction mechanisms and to estimate the kinetic parameters is also an important part in the kinetic study.

In most kinetic formulations of biomass decomposition, the conversion rate $(\frac{d\alpha}{dt})$ of a reaction virtually obeys the fundamental Arrhenius expression:

$$\frac{d\alpha}{dt} = k(T).f(\alpha) = A\,exp\left(\frac{-E_a}{RT}\right).f(\alpha) \tag{III-10}$$

where α is the degree of conversion, t is the conversion time, A is the pre-exponential factor, E_a is the activation energy of the reaction, R is the universal gas constant, T is the absolute temperature. The conversion degree (α) is defined as the mass fraction of decomposed solid or released volatiles:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} = \frac{v}{v_f} \tag{III-11}$$

where m_0 and m_f are the initial and final masses of solid, m is the mass of solid at any time; v_f is the total mass of released volatiles and v is the mass of released volatiles at any time. The function $f(\alpha)$ in Eq. (III-10) depends on the reaction mechanism.

Many mathematical treatments for Eq. (III-10) can be applied including differentiation, integration, and linear transformation which are presented in this section. Moreover, it is worth noting that a complex mathematical model may offer excellent fit between calculated and experimental data, but also requires more powerful computer recourses. In actual engineering contexts and for kinetic study, a simpler model with a reasonably good fit is more favorable than a complex one which gives only a slightly better fit [132, 133].

III.3.2.1 Model-free method

Model-free method is employed to determine approximately the activation energy and pre-exponential factor from TG data at any conversion rate without knowledge about the reaction mechanism, via a linear transformation of Eq. (III-10). Several approximate methods with different mathematical approaches can be found in the literature [111] including Ozawa, Flynn–Wall–Ozawa, Kissinger, Kissinger–Akahira–Sunose, Coats–Redfern, Vyazovkin, etc. Among those, the Flynn–Wall–Ozawa (FWO) method is commonly used. A demonstration of this method is shown below.

For non-isothermal experiments with a linear heating rate $\beta = \frac{dT}{dt}$ Eq. (III-10) can be re-written to:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) exp\left(\frac{-E_a}{RT}\right).f(\alpha) \tag{III-12}$$

Integrating both sides of the Eq. (III-12) leads to the following equation:

$$g(\alpha) = \left(\frac{A}{\beta}\right) \int_{T_0}^{T} exp\left(\frac{-E_a}{RT}\right) dT = \left(\frac{AE_a}{\beta R}\right) p(u) \tag{III-13}$$

where $p(u) = \int_{\infty}^{u} -\left(\frac{e^{-u}}{u^2}\right) du$ and $u = \frac{E_a}{RT}$

The FWO method assumes that A, $f(\alpha)$ and E_a are independent of T; and A, E_a are independent of α. With these assumptions, Eq. (III-13) can be integrated to give a logarithmic form:

$$g(\alpha) = log\left(\frac{AE_a}{R}\right) - log\beta + log\left[p\left(\frac{E_a}{RT}\right)\right] \tag{III-14}$$

The temperature integral $p(u)$ is simplified using Doyle's approximation [134]. Then, Eq. (III-14) is re-written as:

$$log\beta = log\left(\frac{AE_a}{Rg(\alpha)}\right) - 2.3125 - 0.4567\left(\frac{E_a}{RT}\right) \tag{III-15}$$

At a constant conversion rate (α), the plot of $log\beta$ versus T^{-1} should be a straight line, whose slope can be used for calculation of the activation energy (E_a). Furthermore, the pre-exponential factor (A) can be determined via the ordinate.

The advantages of the model-free methods include: (1) kinetic data can be estimated without any selection of a reaction mechanism; (2) very simple mathematical treatments are applied to process the experimental data. However, the applicability of these models is limited to only a single process [135]. More seriously, some problems with data manipulation may occur during the use of logarithmic transformation [135]. Lastly, the model itself cannot reproduce a simulated curve, and if coupled with a single reaction mechanism, the obtained fit quality is poor.

III.3.2.2 Global kinetic model

A **global kinetic model** (GKM) can easily overcome the limitation of the model-free method by producing a calculated curve that can be used to compare with the experimental curve to evaluate the fit quality. In this model, Eq. (III-10) is re-written as Eq. (III-16), in which n represents the reaction order.

$$\frac{d\alpha}{dt} = A\, exp\left(\frac{-E_a}{RT}\right).(1-\alpha)^n \tag{III-16}$$

It generally assumes that the reactions in the pyrolysis stage are first order, although n^{th} reaction order can also be used [129, 136]. On the other hand, a power law (n^{th} order) expression is applied for the char combustion, for which the rate law is generally related to the partial pressure of oxygen through an empirical exponent and the char porosity. Due to a relatively small amount of sample tested in an air flow in a TGA, it is reasonable to assume that the oxygen mass fraction remains constant during the reaction process.

Generally, the GKM consists of three 1st order reactions when it is applied for pyrolysis modelling. On the order hand, for combustion kinetic study, GKM requires three 1st order reactions for the devolatilization of the three biomass components and one *n*th order reaction for the char combustion. In addition, many variations of GKM can be found in the literature. For a simpler calculation, the number of reactions can be reduced. In order to improve the fit quality, either the number of pseudo-components can be increased or pyrolysis reactions are forced to be *n*th order.

The disadvantages of this model include [135]: (1) more kinetic constants (compared to model-free method) are generated and must be optimized to obtain the best fit; and (2) more than one differential equation must be integrated at the same time. Nevertheless, with the fast development of processor technology nowadays, a standard commercial computer can solve those algorithms smoothly.

III.3.2.3 Distributed activation energy model

The above models assume that the activation energy is constant during the reaction to simplify the simulation process. However, a pseudo-component may involve a large number of different reacting species and the reactivity differences are described by different activation energy values [137]. These differences can be taken into account by employing the **distributed activation energy model** (DAEM) for modelling the thermal decomposition of each pseudo-component. The DAEM was first proposed by Pitt [138] to study the kinetics of volatiles released during coal devolatilization. In the DAEM, a complex reaction can be described by a series of first-order reaction. The parallel first order reactions have different activation energy values but the same pre-exponential factor. The *n*th order DAEM was later developed by Braun et al. [139]. The DAEM was first applied for biomass lignin by Avni et al. [140]. Recently, this model was employed for kinetic study of various biomass materials [116, 137, 141, 142]. A general equation for the DAEM is shown below:

$$1-\frac{v}{v_f}=\int_0^\infty exp\left(-A\int_0^t e^{\frac{-E_a}{RT}}dt\right)f(E)dE \qquad \text{(III-17)}$$

where v and v_f are the volatile released at any time and in total, $f(E)$ is the distribution function of the activation energy. Several types of mathematical distribution functions can be used for $f(E)$, which include Gaussian, Weibull, and Gamma distribution [143]. Among these, Gaussian distribution is favorable for modelling the pyrolysis and combustion of various biomass materials [116, 137, 142]. Eq. (III-18) shows a common Gaussian function with a mean activation value (E_0) and a standard deviation (σ):

$$f(E)=\frac{1}{\sigma\sqrt{2\pi}}exp\left(-\frac{(E_a-E_0)^2}{2\sigma^2}\right) \qquad \text{(III-18)}$$

The DEAM offers an excellent fit between calculated and experimental data. However, it requires testing the fuels with TGA at different heating programs, which include linear, stepwise, modulated and constant reaction rate profiles. In addition, a difficulty in applying the DAEM to study the thermal degradation of biomass is that the model has a double-layer integral and a variable (E) that goes from zero to infinite, and cannot be calculated directly. Therefore, the data processing requires a strong programming capacity and powerful computer recourses. It is reported that data processing for DAEM may take up to 10 h on a desktop computer equipped with a 3.4 GHz Intel Core i7 processor under Windows environment [137]. Such long processing time may limit the use of DAEM in practical situations.

III.3.3 Thermogravimetric data collection

The solid biomass fuels were first ground using an IKA MF 10 cutting mill. Then the particles passing through a 125 μm sieve (Fritsch Analysette 3 Pro) were collected for the kinetic study to ensure the experiments to be in the chemical reaction kinetic regime [144, 145]. A Mettler Toledo TGA/SDTA851e was employed for the thermogravimetric study. For each TGA run, a sample amount of about 0.5 mg (for combustion study in synthetic air consisting of 21 vol% oxygen and 79 vol% nitrogen) or 2 mg (for pyrolysis study in nitrogen) was spread in a 150 µl alumina pan located inside the TGA. It is worth noting that the buoyancy effect plays a significant role for such a small sample weight. Therefore, it is mandatory to run a blank TG curve first. The weight change of the blank experiment was subtracted from the experimental curves automatically. The experiment started from room temperature, the fuel sample was heated to 105 °C and held at this temperature for 1 h for drying. Thereafter, the sample was heated to 700 °C at a constant heating rate of 10 °C/min. A gas flow rate of 80 ml/min was applied for all experiments. Moreover, three repetitions were run for each fuel sample, and the average kinetic values are reported.

III.3.4 Data processing

III.3.4.1 Model selection

As mentioned above, biomass is a complex material and the biomass conversion processes (pyrolysis, combustion) consist of a huge number of reactions and products. Kinetic modelling of those processes requires several assumptions and simplifications at different levels. Some reviews on biomass pyrolysis and combustion kinetics have indicated that, while some researchers tried extreme simplifications, others used elaborate mechanisms to explain very detailed [25, 110, 111]. However, in kinetic modelling and simulation, it is essential to select a kinetic model which reasonably represents the physical phenomenon under the investigated condition without too many mathematical complexities if possible [133]. It is of little use to develop a model which very closely mirrors reality but is so complicated that we cannot use it in practical applications. This argument is supported by a recent study [125], which has evaluated various pyrolysis kinetic models for stump biomass fuel including the model-free method, one-step model, GKM and DAEM. It has been concluded that, among three-pseudo-component models, DAEM offers the best fit quality but GKM is the optimal choice when considering both fit quality and complexity. Based on the results and recommendations from previous works, GKM with three and four pseudo-components were selected for pyrolysis and combustion modelling, respectively, in the kinetic study. It is because, among others, GKM offers reasonable fit quality, and requires less computer resources than DAEM.

III.3.4.2 Kinetic evaluation

Data collected from the TG experiments show the relationship between mass loss and temperature. They were first differentiated to obtain the DTG data, and presented in the form of conversion rate ($\frac{d\alpha}{dt}$) versus temperature T. A mathematical model corresponding to the selected physical model was then employed for simulation and comparison with the experimental DTG data. The optimization of the predicted DTG curves was based on the non-linear least squares method (NLSM), which minimize the sum of the square differences between the experimental and calculated data. A protocol by Kemmer and Keller [146] and MATLAB codes were used for the curve fitting process.

The most important equation in NLSM is the objective function (OF), which shows the difference between the actual value and the value predicted by the model.

$$OF = \sum_{j=1}^{N} \left[\left(\frac{d\alpha_j}{dt} \right)_{exp} - \left(\frac{d\alpha_j}{dt} \right)_{cal} \right]^2 \tag{III-19}$$

where $\left(\frac{d\alpha_j}{dt}\right)_{exp}$ and $\left(\frac{d\alpha_j}{dt}\right)_{cal}$ represent the experimental and calculated conversion rates, respectively; and N is the number of experimental points.

The function needs to be minimized in order to obtain the best fit. To validate the optimization or the curve fitting process, the fit quality between actual and modelled data is calculated according to Eq. (III-20) [130, 131]:

$$Fit\ (\%) = \left(1 - \frac{\sqrt{\frac{OF}{N}}}{\left[\left(\frac{d\alpha_j}{dt}\right)_{exp}\right]_{max}}\right).100\% \qquad \text{(III-20)}$$

The actual simulation was run until the maximum fit value was found, at which the convergence criteria of the optimization process are achieved. The extracted kinetic parameters are: the activation energies (E_i), the pre-exponential factors (A_i), the mass fractions (c_i), and the reaction orders (n_i) for each pseudo-component. In a combustion study, there are 12 kinetic parameters for the 1st order model and 16 parameters for the *n*th order model. In a pyrolysis study, there are only 9 kinetic parameters for the 1st order model and 12 parameters for the *n*th order model.

Chapter IV

CONCLUDING SUMMARY

IV.1 Concluding summary

IV.1.1 Paper I - Wet torrefaction of stem woods

In this work, WT of Norway spruce and birch wood was studied and compared with DT. Effects of process parameters (temperature 175–225 °C, holding time: 10–90 min; pressure: 15–250 bar; and feedstock particle size: 1–3 cm) on the yield and fuel properties of solid products were investigated.

Effect trends similar to that of DT have been observed. The yield of solid product is reduced with decreasing feedstock particle size. Both reaction temperature and holding time have significant effects on solid product yield, energy yield, and fuel properties of wet torrefied biomass. When torrefaction temperature or holding time is increased, the product and energy yields of the torrefied solid fuels decrease but the improvements in fuel properties of the solid products increase, which include increased fixed carbon contents, greater heating values, better hydrophobicity and improved grindability. In addition, the consistent lower ash contents of the fuels after WT suggest that WT can be employed to reduce the ash content of biomass fuels.

On the other hand, it appears that birch wood is more reactive and produces less solid product than spruce wood, in the same WT conditions. Heating values of birch wood increase faster than spruce wood when the severity of WT is increased. The investigation of pressure effects suggests that WT should be carried out at pressures higher than the saturated vapor pressure of water at a given temperature. It is because the rate of WT is enhanced by pressure. In addition, this pressure control can avoid the energy penalty due to water vaporization. However, pressures that are too high are not recommended.

A comparison between WT and DT supported by regression analyses and numerical predictions has shown that WT can produce solid fuels with a greater HHV, higher energy yield, and better hydrophobicity at much lower temperature and holding reaction time. The morphology study of the fuels produced by both torrefaction methods were investigated and the wet-torrefied fuel exhibits less pronounced changes in their structure compared with the dry-torrefied fuel.

IV.1.2 Paper II - Combustion reactivity of hydrochar

The objective of this work was to evaluate the combustion reactivity of hydrochar produced from wood via WT, by looking at the effects of WT on the combustion kinetics of woods. The woods, Norway spruce and birch, and hydrochar products from Paper I were studied by means of a TGA operated in the non-isothermal mode. Four-pseudo-component models with first or n^{th} reaction order were adopted for the kinetic analysis. The models include three pseudo-components for the three main biomass components (hemicellulose, cellulose and lignin) and one pseudo-component for char produced during the devolatilization stage. The following conclusions were drawn from this study:

- WT pressure has insignificant effects on the combustion reactivity of the woods.

- WT temperature and holding time have similar effects on the combustion reactivity of the woods. Increasing either temperature or holding time makes the woods more reactive in the devolatilization stage, but less reactive in the char combustion stage. However, too severe WT conditions (from 225 °C and 30 min) make the trends reversed due to the decomposition of cellulose in the devolatilization stage and the competition between catalyzing and inhibiting effects of char ash on the char combustion stage.

In addition, the kinetic analysis using the four-pseudo-component model with $n \neq 1$ shows that the activation energy of hemicellulose and char is reduced, but that of cellulose is increased by WT. The activation energy of hemicellulose was reduced from 103.8 to 44.8 kJ/mol for the spruce wood, and from 144.7 to 41.3 kJ/mol for the birch wood. That of char was reduced from 183.1 to 109.4 kJ/mol for the spruce and from 222.0 to 132.3 kJ/mol for the birch. The activation energy of the cellulose was increased from 221.5 to 239.0 kJ/mol for the spruce, and from 204.7 to 236.7 kJ/mol for the birch. The mass fraction of hemicellulose was reduced by WT (from 0.15 to 0.05 for the spruce and from 0.23 to 0.06 for the birch), while that for char was increased gradually (from 0.20 to 0.40 for spruce and from 0.14 to 0.34 for birch).

IV.1.3 Paper III - Pyrolysis reactivity of hydrochar

Similar to the work presented in Paper II, this work was carried out in order to evaluate the pyrolysis reactivity of hydrochar produced from wood via WT, by looking at the effects of WT on the pyrolysis kinetics of woods. The woods, Norway spruce and birch, and hydrochar products from Paper I were studied by means of a TGA operated in the non-isothermal mode. The three-pseudo-component model with n^{th} order was adopted for the kinetic analysis. In addition, a kinetic evaluation for different model variants by assuming common parameters was also performed to identify possibilities for describing the thermal decomposition of different biomass materials by a common model.

The study shows that wet torrefaction resulted in higher pyrolysis peaks for the woods, but less mass of volatiles was released during pyrolysis. The effects of wet torrefaction on pyrolysis of the lignocellulosic components are different. The activation energy of hemicellulose was significantly reduced, from 95.67 kJ/mol to 26.63 kJ/mol and 106.80 kJ/mol to 34.18 kJ/mol for the spruce and birch, respectively, after torrefaction in the conditions of 225 °C and 30 min. However, that for cellulose was slightly increased from 188.27 kJ/mol to 193.17 kJ/mol and 189.47 kJ/mol to 194.54 kJ/mol for the spruce and birch, respectively. The average activation energy of lignin was also affected by wet torrefaction, being increased from 40.22 kJ/mol to 48.09 kJ/mol for the spruce and from 38.95 to 40.69 kJ/mol for the birch.

In addition, a kinetic evaluation with assumption of common parameters was performed. The results confirm that some kinetic parameters can be assumed to be common for pyrolysis kinetic modelling of different biomasses without substantial reductions in the fit quality. Wet torrefaction has positive effects on the possibilities for biomass pyrolysis kinetic modeling with assumption of common parameters.

IV.1.4 Paper IV - Wet torrefaction of forest residues

In this work, WT of Norwegian forest residues, Norway spruce and birch branches, were experimentally studied and compared with the results on WT of stem woods from the Paper I. The effects of torrefaction temperature (175, 200, 225 °C) and holding time (10, 30, 60 min) on the yield and fuel properties of the hydrochar products were investigated. Increasing either torrefaction temperature or holding time decreases the solid yield but enhances the fuel properties of the hydrochar. Increases in heating value up to 13.5% and reductions of specific grinding energy up to 16.0 times for the branches by WT are observed. The ash contents in the hydrochars are lower than those in the untreated forest residues. Birch branches are more reactive than spruce branches in identical WT conditions.

The comparison on WT of the branch and the stem woods show that the effect trends of WT on the yield and fuel properties of the hydrochars from branches and stems were similar. However, branch woods are more reactive than stem woods in identical WT conditions. The trend of reduction in SGE of branches is similar to stem woods for spruce, but that for birch is somehow inconsistent. Improvements in hydrophobicity of the branches are more pronounced than that of the stems. This may be attributed to the higher hemicellulose and extractives contents of the branches compared to stem woods.

IV.1.5 Paper V - Effects of carbon dioxide on wet torrefaction

This study aimed to identify opportunities and gain knowledge for WT process integration, considering that hot flue gas from thermal power plants can be utilized for WT continuous processes at industrial scales to reduce the cost. The problem however is that, apart from N_2, flue gas contains other gases, of which CO_2 is the main species and may have important effects on the WT process and the fuel properties of the solid product. For this purpose, WT of forest residues in different conditions (temperature: 175, 200, 225 °C; holding time: 10, 30, 60 min) and two atmospheres (N_2 and CO_2) were experimentally investigated.

The results show that WT in CO_2 produced 4.6–6.0% less solid product with decreased heating value but improved hydrophobicity and better grindability than that in N_2. An increase of up to 1.4% in EMC and a reduction of 6.5 kWh/t in SGE were observed for the solid product obtained from WT in CO_2, compared with that in N_2, in an identical condition of 200 °C and for 30 min. The proximate analyses show higher fixed carbon and lower volatile matter contents for the hydrochars obtained from WT in CO_2. Additionally, the ash content of these products is significantly reduced, compared with WT in N_2. It suggests that WT in CO_2 is capable of removing even more ash elements in the solid biomass fuel, compared with WT in N_2.

IV.1.6 Paper VI - Pelletability and pellet properties of hydrochar

Finally, pelletability and pellet properties of the hydrochar from forest residues were studied and presented in this paper. The pelletization was performed using a single pellet press for both raw and wet-torrefied forest residues. The pellet strength was then investigated via diametric compression tests, employing a 60 mm diameter probe connected to a Lloyd LR 5K texture analyzer.

The results show that the pellets made from wet-torrefied forest residues are more compressible and mechanically stronger than the pellets made from raw forest residues. The effect of pelleting temperature on pellet density is unpronounced but the effect on pellet strength is significant due to different behaviors of lignin below and above its glass transition temperature. In identical condition, birch pellets are denser than spruce pellets and the effect of torrefaction temperature is more pronounced for birch than spruce. Increases in density for the hydrochar pellets compared with the pellets made from raw materials is up to 159 kg/m^3 for spruce and 213 kg/m^3 for birch. Improvements in the strength of torrefied pellet compared with raw pellet are up to 3.4 and 2.7 times for spruce and birch, respectively. Increasing compacting pressure increases the mass density and strength of the pellets. Moreover, compression strength and density of the pellets are correlated following a power law trend. Below the density of 1000 kg/m^3, large increases in density results in only small increases in the strength. However, this relationship was reversed when the density was higher than 1000 kg/m^3.

IV.2 Recommendation for further works

- WT of agricultural wastes and aquatic energy crops such as algal biomass.
- Detailed studies on aqueous and gaseous products from WT.
- Detailed studies on removal of ash elements of biomass during WT.
- Gasification reactivity and kinetics of hydrochar obtained from WT.
- Experimental studies on thermochemical conversions of hydrochar and its pellets in drop-tube furnaces.
- Continuous processes for WT, process optimization and integration.
- A comparative study on the techno-economics of WT and DT processes.

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Paper I

Comparative assessment of wet torrefaction

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Comparative Assessment of Wet Torrefaction

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ABSTRACT: Wet torrefaction of typical Norwegian biomass fuels was studied within the temperature window of 175−225 °C, using a benchtop autoclave reactor of 250 mL in volume from Parr Instrument. Two types of local biomass fuels were employed as feedstock, Norway spruce (softwood) and birch (hardwood). Effects of process parameters including pressure, reaction temperature, holding time, and feedstock particle size on the yield and properties of the solid products were investigated. It appears that birch wood is more reactive and produces less solid products than spruce wood in the same wet torrefaction conditions. Increasing pressure above the saturated vapor pressure of water enhances the torrefaction rate. Both reaction temperature and holding time have significant effects on solid product yield and fuel properties of wet torrefied biomass. The yield of solid products is slightly reduced with decreasing feedstock particle size. The ash content of biomass fuel is significantly reduced by wet torrefaction. In addition, a comparison between wet and dry torrefaction supported by regression analyses and numerical predictions shows that wet torrefaction can produce solid fuels with greater heating values at much lower temperatures and shorter holding times.

1. INTRODUCTION

Biomass is a renewable and carbon neutral energy resource which has a high potential for replacing fossil fuels. However, the use of biomass for energy applications is not straightforward. Typical disadvantages of using biomass as fuel, compared to coal, include the lower bulk density, higher moisture content, inferior heating value, and poorer grindability. Although biomass resources are distributed over the world more evenly than the world proven coal reserves, an additional substantial disadvantage of biomass is its relatively less concentrated occurrence compared to coal which normally occurs highly concentrated in coal mines. These drawbacks increase the cost for handling, transport, and storage of biomass fuels, limiting the use of biomass for bioenergy applications. In addition, ash forming elements especially alkali metals may cause technical and performance problems for the downstream equipment in thermal energy conversion processes such as gasification and combustion.[1−3]

One way to overcome the aforementioned disadvantages of using biomass as fuel is to preprocess the fuel via torrefaction, which may be defined as mild pyrolysis of biomass. This is due to the fact that the main product of the torrefaction process is a hydrophobic solid fuel,[4−6] which may be referred to as "biochar",[7,8] with much better grindability[9,10] and superior heating value.[11−13] The handling, transport, storage, and use of the biochar as fuel become easier and less expensive compared to the native biomass fuel. In addition to the solid product and depending on the treatment conditions, torrefaction produces byproducts in liquid and gas phases. However, their fractions are normally considered to be small, being less than 30% by weight on dry basis and containing less than 10% of the energy of the raw biomass to make the process energetically viable.[14−16]

There are two torrefaction techniques, dry and wet torrefaction. Dry torrefaction (DT) is thermal treatment of biomass in an inert environment at atmospheric pressure and temperatures within the range of 200−300 °C.[17,18] Wet torrefaction (WT) may be defined as treatment of biomass in a hydrothermal media (HM), or hot compressed water (HCW), at temperatures within 180−260 °C.[19−21]

During the past decade, research and development activities on DT for energy applications including combustion, gasification, and pyrolysis have been very active.[16,22−33] It has been reported that, during combustion, torrefied biomass behaves more coal-like with more stable burning characteristics, compared to its untreated biomass.[28,29] The efficiency of gasification and the quality of syngas are improved by torrefaction.[16,30,31] Moreover, for fast-pyrolysis, torrefaction appears to decrease the yield of byproducts and to improve the quality of bio-oil.[32,33] The technology of DT has been rapidly developed to the stage of market introduction and commercial operation. Several torrefaction installations have recently been built in Europe and North America, with a total capacity of several hundred thousand tons per year.[34] However, it has been claimed that no clear winner in this area can be identified so far. This is partly due to the fact that optimal process conditions have not been well established for the various concepts and feedstocks. The majority of research and development in this area have been carried out for clean wood feedstocks, and it is

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Table 1. Proximate and Ultimate Analyses for the Feedstock (Dry Basis)

	proximate analysis			ultimate analysis					
type of biomass	ash[a]	VM[a]	fixed C[a]	C[a]	H[a]	O[a]	N[a]	S[a]	HHV[b]
Norway spruce	0.23	86.50	13.27	50.31	6.24	43.38	0.07	<0.02	19.94
Norway birch	0.28	89.46	10.26	48.94	6.35	44.60	0.11	<0.02	20.42

[a] wt %. [b] MJ/kg, ash free.

therefore likely that the first commercial torrefaction plant will be designed for relatively high quality biomass sources. Torrefaction of agricultural residues and biomass wastes, especially wet biomass, will be more complicated due to the technical challenges related to the air emissions from the process, product quality and flexibility, product quality control, heat integration, and feedstock properties variations.[34,35]

WT of biomass has also been studied for the energy applications (combustion, gasification, and pyrolysis) with a focus on using biomass wastes as feedstock, which include sewage sludge[36] and wet agricultural wastes such as cow and swine manure.[37,38] Due to the fact that WT processes employ water in subcritical conditions as reaction media, the energy intensive predrying for the feedstock is eliminated. After WT, similar to DT, a hydrophobic solid fuel is also obtained and can be effectively made dry by mechanical and/or natural dewatering, an attractive option capable of dramatically reducing the energy requirement for the postdrying step.[39] Other potential advantages of WT include the ease of pelletization, where wet torrefied biomass does not require water addition in order to improve the pelletability and binding capacity as in the case for DT.[40,41] The yield and the fuel quality of solid products obtained from WT are reported to be even better than that from DT.[19] At 200 °C, for example, WT of loblolly pine can give a mass yield as high as 88.7%, and 95% for the energy yield, compared to 83.8% and 89.7% respectively for DT at 250 °C with the same feedstock type and holding time.[19] Furthermore, apart from the solid fuel product, some water, CO_2, small amounts of CO, H_2, some hydrocarbons, and dissolved organic and inorganic compounds are released from biomass during WT.[39] The fact that WT is capable of dissolving and thus washing out the inorganic components from solid biomass fuels is an additional advantage of WT over DT since it produces "cleaner" solid fuels, with respect to inorganic content, which are more suitable for combustion and gasification processes. On the other hand, many valuable organic compounds, including acetic acid, formic acid, lactic acid, glycolic acid, levulinic acid, phenol, furfural, HMF, and sugars are found in the aqueous phase products of WT, making up approximately 10% by mass of the feedstock.[19,20] The potential use of these water-soluble organic fractions for production of valuable products may contribute to further improving the economy of the WT process.

Despite the various advantages of WT over DT, only a few studies on WT have been reported.[19,20] This may be due to the inherent disadvantages of WT, as a method for biofuel processing in hydrothermal media,[42−44] which include the engineering challenges of reactor material corrosion, precipitation and deposition of inorganic salts released during WT process of biomass, and handling of aqueous residues produced from WT. As WT is operated at elevated pressures, continuous production could be an additional challenge, e.g., a high pressure feeding system is required. Corrosion resistant material capable of standing at elevated pressures and temperatures must be used for building the WT reactor which may increase the investment cost. However, several studies for a process similar to WT can be found in the literature under the terminology of "hydrothermal carbonization" (HTC).[45−47] These studies can be beneficial and complementary to further research and development in WT of biomass for energy applications. Nevertheless, it should be mentioned that, although the terminologies of WT and HTC have been sometimes used interchangeably, there is a significant difference between them. While WT processes aim at producing upgraded solid fuels for energy applications only, HTC processes are employed mainly for producing charcoal, with a high carbon content, which can be used not only as fuel but also as activated carbon, soil enhancer, fertilizer, etc. Clearly, energy efficiency is more critical for the WT process than for the HTC, and thus the former tends to be performed at relatively lower temperatures than the latter.

In this present work, WT of Norwegian biomass fuels was experimentally studied. Effects of process parameters such as pressure, temperature, holding time, and particle size of the feedstock on the products yield and fuel properties of the solid product were investigated. Two types of woody biomass, Norway spruce (softwood) and birch (hardwood), were selected as feedstock. In addition, numerical analyses using a regression approach were employed to support a comparison between wet and dry torrefaction.

2. MATERIALS AND METHODS

2.1. Materials. Stem wood from Norway spruce (softwood) and birch (hardwood) were selected as feedstock for the present study since they are the main wood species in Norwegian forests. The selection aims among others to utilize the results from a previous study of DT,[26] recently published by our research group, for a comparison between wet and dry torrefaction. The wood samples were obtained from a local supplier in Trondheim, Norway. Proximate analyses of the feedstock were performed according to ASTM standards: ASTM E871, ASTM E872, and ASTM D1102 for moisture content, volatile matter, and ash content, respectively. Ultimate analyses of the fuels on dry basis were determined by an "EA 1108 CHNS-O" elemental analyzer (Carlo Erba Instruments). In addition, the higher heating value (HHV) was calculated according to a unified correlation proposed by Channiwala et al.[11] Results from the ultimate, proximate analyses and the HHVs of the feedstocks are given in Table 1.

2.2. Experimental Setup and Procedure. In this study, WT experiments were carried out in a 250 mL Parr reactor model 4651, which is made of stainless steel (T316SS) and equipped with a benchtop ceramic heater (4923EE), a temperature controller (4838EE), a pressure gauge, and two valves. A thermocouple for monitoring the reaction temperature (temperature of water in the reactor) is connected to the controller by which the electrical duty of the heater is controlled. The thermocouple is introduced into the reactor via a thermo-well, which is cast in the reactor head. In addition, a self-made detachable perforated glass plate is mounted to the thermo-well in order to keep the feedstock entirely submerged in the water. The reactor is connected to a nitrogen (99.99% purity) cylinder via a valve.

Distilled water was used as the reaction media. The ratio of dry feedstock over water was 1:5 by weight. However, for studying the effect of pressure, a ratio of 1:10 was employed with the feedstock prepared in powder form of 0.5−1 mm to minimize the effects of heat and mass transfer limitations during torrefaction process. For studying the effects of feedstock particle size on the process and products, the feedstock was cut into cubes with 1 and 3 cm sides (hereafter called 1 and 3 cm cube, respectively). All of the experiments were duplicated, from which data were collected and processed to generate average values for relevant assessments.

Before every torrefaction run, the furnace (the heater) without the reactor was heated for 30 min to a preset temperature. At the same time, the reactor was loaded, closed, sealed, and purged with compressed nitrogen gas for 10 min. Then the reactor was pressurized and placed in the preheated furnace which was set to the maximum power, giving a heating rate of approximately 12 °C/min. The holding time was counted from the time at which the reactor temperature reached the preset temperature to the end point when the reactor was replaced from the furnace and submerged in a water bath filled with tap water for cooling. When the reactor cooled to room temperature, the pressure was gradually released and the reactor was opened for products collection.

In this study, only products in the solid and liquid phases were collected. They were separated from each other by filtration using a filter paper with a pore size of 5−12 μm. After separation the collected solids were dried at 105 °C for 48 h and then balanced. Readings from the balance were tabulated as the mass of solid product from the WT. The dried solids were then stored in a desiccator filled with silica gel for further studies.

2.3. Assessment Methods. *2.3.1. Method for Assessment of Hydrophobicity.* To our present knowledge, there exists no standard method for assessment the hydrophobicity of torrefied biomass fuels. Researchers have had to develop or adopt methods on their own for such investigations. Pimchuai et al.[4] and Tapasvi et al.[26] immersed the fuel samples in water for 2 h, while Bergman et al.[5] soaked torrefied pellets in water for up to 15 h and then compared the differences in water uptake level. Yan et al.[19] measured the equilibrium moisture content (EMC) of the fuels in various conditions differing in relative humidity. Li et al.[6] and Lam et al.[48] measured the moisture absorption rates of the fuels using a controlled humidity chamber.

It is important to highlight that solid biomass fuels, especially biochar obtained from woody biomass torrefaction, are porous materials. The porosity of tested materials may significantly interfere with the hydrophobicity test results, considering the fact the water may be up-taken by the pores as well. Therefore, size reduction for the materials to be tested is necessary in order to minimize the interference. For this reason the method of exposing tested materials in the powder form to water vapor in a climatic chamber, similar to the method employed by Li et al.,[6] has been adopted for this present study. For each test, an amount of approximately 2 g of the material to be tested is first ground manually in an agate mortar and screened through a sieve (Fritsch Analysette 3 Pro) to obtain the sample powder with particles smaller than 250 μm. The powder is then dried at 105 °C for 24 h. Next, the dried powder is spread on a glass Petri dish, which is then placed in a climatic chamber (series VC^3 0100 of Vötsch Industrietechnik) operated under the controlled conditions of 20 °C and 90% relative humidity. The mass changes by time due the moisture up-take of the tested material are recorded every 24 h for the total test period of 1 week. The moisture content of the tested material is then calculated according to eq 1

$$\mathrm{MC}_i(\%) = \frac{m_i - m_0}{m_0} \times 100\%, \quad i = 1, 2, ..., 7 \tag{1}$$

where MC$_i$ is the moisture content of the tested material on the ith day; m_0 and m_i are the mass of the sample before the test and measured on the ith day, respectively.

2.3.2. Quantitative Assessment of Grinding Energy Saving Due to Grindability Improvement by Torrefaction. It is widely recognized that torrefaction improves the grindability of biomass fuels, which consequently helps reduce energy requirement for the fuel communition. However, a practical question of how much grinding energy that can be saved has not been sufficiently addressed. There are two methods reported in the literature, which can be considered to adopt and answer this question for WT. In one method, the power consumption of the mill during operation is recorded and regarded as the energy required for grinding of the biomass fuel. The grinding energy of native and torrefied biomass fuels are normalized to their total ground mass, and then compared.[9,10] This method gives a comparative measurement of the energy requirement, with no control over the particle size distribution of the samples. Therefore, the particle size distribution should be analyzed in a separate step. The second method estimates the grindability by measuring the portion of materials passing through a 75 μm sieve and comparing it with that of standard coals.[29,49] This method can show how fine the fuel particles are, but it does not explicitly show the grinding energy. More recently, a multistage assessment similar to the second method has been reported by Tran et al.[50] In this study, the quantity of comparison is the total grinding time summed up from the grinding times recorded from multiple stages of grindings and sieving of the same mass for different materials until the whole mass goes through a 1.4 mm sieve.

It appears that the aforementioned methods have their pros and cons. However, there is no better method for this purpose so far. For this present study, the first method has been adopted for a quantitative estimation of the specific grinding energy for raw and wet torrefied biomass. An IKA MF 10 cutting mill (from IKA-Werke GmbH & Co. KG) equipped with a 1 mm bottom sieve was used. An analog current input module NI 9203 (from National Instruments Corporation) was employed to record the electrical current during grinding. Samples of 1 cm cubes were used for the assessment. A LabView program was used for the data acquisition and the calculation of the energy consumption which was logged to a file every 2 s. The power of the mill under no-load conditions was measured and subtracted from the power of grinding the biomass samples. The grinding energy was determined by integrating the power curve during the grinding period. Finally, the data was normalized to the initial sample weight.

2.3.3. Numerical Approach for Comparison between Wet and Dry Torrefaction. Due to the differences in working pressure, it is not straightforward to directly compare wet and dry torrefaction of biomass. Multiple regression analysis method was therefore employed to numerically assess and establish relevant mathematical models based on the data collected from the WT experiments. The models were then used to predict the operation points for WT comparable with DT, on the basis of a common solid product yield, for a comparison of the heating value, grindability, and hydrophobicity. The solid product yield (Y_{solid}) is defined and determined according to eq 2

$$Y_{\mathrm{solid}}(\%) = \frac{m_{\text{torrefied solid product}}}{m_{\text{initial dry biomass}}} \times 100\% \tag{2}$$

where the term of $m_{\text{torrefied solid product}}$ means the mass of solid product and the mass of initial dry biomass is for the term of $m_{\text{initial dry biomass}}$.

Multiple regression analysis is a useful tool for simulating experimental data. It was successfully applied and reported for both DT[24] and hydrothermal treatment[51] of biomass. The general form of the multiple regression model adopted for the present work is given in eq 3

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + ... + \beta_p X_p + \varepsilon \tag{3}$$

where Y is the dependent variable; X_1, X_2, ..., X_p are the process or independent variables; β_0, β_1, β_2, ..., β_p are constants to be determined from experimental data; and ε is the noise or error observed in the variable Y.

3. RESULTS AND DISCUSSION

3.1. Effects of Process Parameters on Solid Product Yield. *3.1.1. Effects of Pressure.* For this investigation only the spruce sample was used as feedstock, with a biomass/water ratio of 1:10 by weight. In order to minimize possible effects of heat and mass transfer limitations in this investigation, feedstock in powder form with particle size of 0.5−1 mm was used. The experiments were performed in the common conditions of 200 °C as torrefaction temperature and 10 min as holding time. Four different pressures were investigated, including 15.54 (the saturated vapor pressure of water at 200 °C), 70, 160, and 250 bar. Results from this investigation are shown in Figure 1.

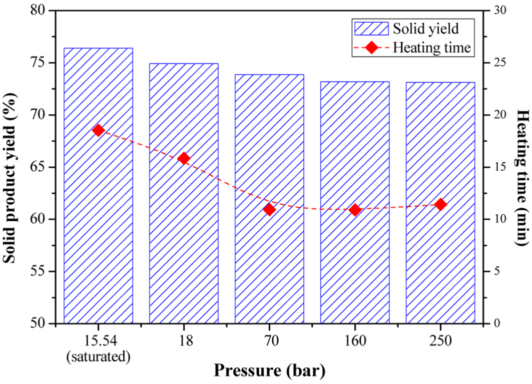

Figure 1. Effects of pressure on solid product yield for WT of spruce at 200 °C for 10 min.

As can be seen from Figure 1, pressure has a weak effect on the solid yield of WT. When pressure increases from 15.54 to 250 bar the yield decreases from 76.4% to 73.1%. This indicates that the reaction rate increases with increasing pressure. In the first instance, this effect can be due to the increase in thermal conductivity of water with increasing pressure.[52] Another possible reason for this reduction in solid yield may be related to the acidity change of subcritical water with increasing pressure due to the acid hydrolysis of hemicellulose and cellulose.[21,53] In addition, this can also be attributed to the fact that in subcritical conditions water exists in both liquid and gas phases. However, more water would remain in the liquid phase at pressures higher than the saturated vapor pressure, considering Le Chatelier's principle. Since the feedstock is solid biomass immerged in the liquid, water in the gas phase is not in direct contact with the feedstock and thus more liquid water would improve the reaction rate as well. This is also in agreement with observations reported in the literature showing that the reaction rate increases with decreasing ratios of feedstock over water.[54−56] Furthermore, the thermal conductivity of water in the liquid phase is obviously higher than in the gas phase, which in turn would result in better heat transfer in the reactor and thus higher reaction rates. The improved heat transfer in the system can also be observed from the heating time defined as time needed for heating the reactants (water and biomass) from 25 to 200 °C, which is also presented in Figure 1. It appears that the heating time decreases dramatically from 18.5 to 10.9 min when pressure increases from the saturated vapor pressure of water at 200 °C (15.54 bar) to 18 and then 70 bar. However, no significant change in heating time is observed when pressure is increased further. At 250 bar the heating time even turns up to 11.4 min, being slightly longer than that at 70 and 160 bar. From these observations, it is reasonable to believe that in the conditions of 200 °C and 70 bar most of the water in the reactor is in the liquid phase. From this point, further increases in pressure is not useful with respect to preventing water from vaporization, which aims to improve the heat transfer in the system and the reaction rate, as well as to reduce the energy loss in the form of latent vaporization heat. The slightly longer heating time (reduced heat transfer) at 250 bar compared to that at 70−160 bar might be due to experimental and measurement uncertainty.

More interestingly, it is also observed from Figure 1 that the reduction in solid yield or the increase in reaction rate in other words becomes less pronounced at pressures higher than 160 bar. This indicates that the observed reaction rate enhancements in subcritical water conditions upon increasing pressure have probably been caused mainly by the increase of the water portion present in the liquid phase, rather than by the improved thermal conductivity of the system. Nevertheless, the improved thermal conductivity does help shorten the heating time and thus reduce the energy requirement of the process.

By considering the energy requirement for vaporization of water at a temperature within the WT temperature window (180−260 °C approximately), in combination with the observations from this investigation, it is suggested that WT of biomass for energy application should be carried out at pressures higher than the saturated vapor pressures. In such conditions, the potential energy penalty by phase transformation of water in the form of latent heat can be minimized and the reaction rate can be enhanced. However, it is not advisable to perform WT at pressures much higher than the saturated vapor pressures of water, since further increases in reaction rate are less significant. In addition, the higher the pressure, the more energy and more investment for the reactor are required. For these reasons, the pressure of 70 bar has been selected for other investigations in this present work.

3.1.2. Effects of Torrefaction Temperature and Holding Time. For the experiments reported in this section feedstock of 1 cm^3 cubes as particle size were used. The effects of torrefaction temperature on solid yield was investigated for the constant holding time of 30 min, whereas a reaction temperature of 200 °C was kept unchanged for the investigation of holding time. Figure 2 presents the effects of torrefaction temperature (Figure 2A) and holding time (Figure 2B) on the yield of solid products from WT of the spruce and birch wood samples.

As can be seen from Figure 2, similar trends are observed for the effects of torrefaction temperature and holding time on the solid product yield. When reaction temperature or holding time increases, the yield decreases. However, the effect of temperature is more pronounced than that of holding time within the tested conditions. When temperature is increased from 175 to 225 °C the solid product yield decreases from 88.3 to 69.7% and from 79.5 to 58.0% for spruce and birch, respectively. Similarly, when holding time is increased from 10 to 60 min the solid product yield decreases from 82.5 to 73.3% for spruce and from 66.4 to 63.1% for birch.

The difference in effect of temperature and holding time on the solid product yield can be explained by the theory of chemical reaction kinetics. In general, for a thermal decomposition reaction of reactant C, the rate law can be written as $-dC/dt = k[C]$, where $[C]$ is concentration of the reactant and k is the reaction rate constant. The rate constant k virtually obeys Arrhenius' law $k = Ae^{-E/(RT)}$, where A is a pre-exponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature. This Arrhenius' equation indicates that the rate constant, and thus the reaction rate, is exponentially proportional to the reaction temperature. On the other hand, the reaction rate is just directly proportional

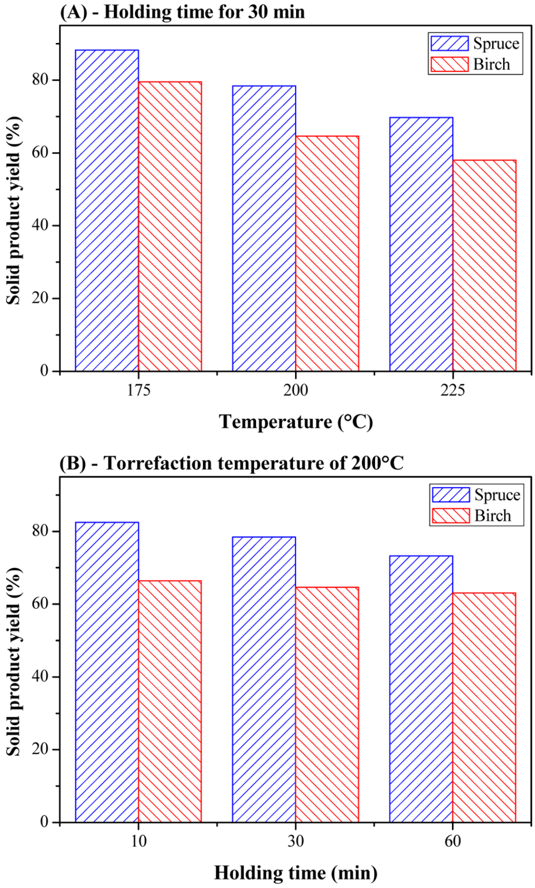

Figure 2. Effects of temperature (A) and holding time (B) on the solid product yield.

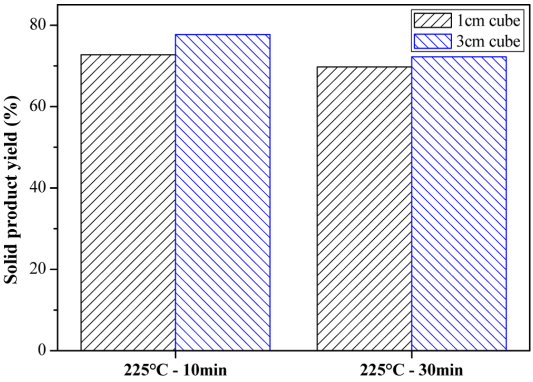

Figure 3. Effects of feedstock particle size on the solid product yield for spruce.

to the reaction (holding) time. That is the reason why temperature has more significant effects on solid yield than holding time.

Figure 2 also indicates that birch wood is more reactive than spruce wood, which can be attributed to the fact that birch is a hardwood generally containing more hemicellulose than softwood.[57] It is known that, during hydrothermal treatment, hemicellulose starts to degrade first among the three main components of lignocellulosic materials.[21,58] Moreover, hemicelluloses of hardwood contains even more xylan than that of softwood,[15] which is the most reactive hemicellulosic compound within the torrefaction temperature window.

3.1.3. Effects of Feedstock Particle Size. The effect of feedstock particle size on the yield of solid products from WT for the spruce sample was studied in the conditions of 225 °C as torrefaction temperature, and 10 or 30 min as holding time, using feedstock of 1 and 3 cm cubes. Results from these experiments are presented in Figure 3, showing that the yield of solid products slightly decreases with decreasing feedstock particle size. In addition, the solid yield reduction caused by decreasing feedstock particle size becomes less pronounced when the holding time is increased from 10 to 30 min. This indicates that the effects of feedstock particle size can basically be attributed to the heat and mass transfer limitations within the feed particles. This effect may disappear if WT is carried out in the conditions of relatively lower temperatures and longer holding times. However, the effects may be critical for WT at relatively higher temperatures and shorter holding times.

3.2. Effect of Process Parameters on Fuel Properties of Torrefied Biomass.

3.2.1. Proximate Analyses for Torrefied Biomass Fuels. Results from proximate analyses of biochar obtained from WT of the spruce and birch wood samples at different temperatures and holding times are presented in Table 2, in which the data for the raw fuels is also included for comparison. Compared with the raw materials, the fixed carbon content increased from 13.3% to 27.1% for the torrefied spruce and from 10.3% to 27.5% for the torrefied birch. It can also be observed that both increased reaction temperatures and holding times enhance the fixed carbon content of biochar obtained from WT. These

Table 2. Proximate Analysis of Torrefied Spruce and Birch Wood

torrefaction condition	spruce wood			birch wood		
	ash[a]	VM[a]	fixed C[a]	ash[a]	VM[a]	fixed C[a]
raw	0.23	86.50	13.27	0.28	89.46	10.26
1 cm, 175 °C, 30 min	0.11	85.72	14.17	0.09	88.57	11.34
1 cm, 175 °C, 60 min	0.09	85.42	14.49	0.08	87.75	12.17
1 cm, 175 °C, 90 min	0.10	84.82	15.08	0.07	87.22	12.71
1 cm, 200 °C, 10 min	0.14	84.64	15.22	0.08	87.97	11.94
1 cm, 200 °C, 30 min	0.12	83.92	15.95	0.09	85.15	14.76
1 cm, 200 °C, 60 min	0.09	81.87	18.03	0.10	82.64	17.27
1 cm, 225 °C, 10 min	0.14	78.58	21.28	0.09	80.32	19.59
1 cm, 225 °C, 30 min	0.14	74.74	25.12	0.13	73.78	26.09
3 cm, 225 °C, 10 min	0.20	77.56	22.25	0.13	77.71	22.16
3 cm, 225 °C, 30 min	0.20	72.66	27.14	0.15	72.34	27.50

[a] wt %, dry basis.

Table 3. Ultimate Analysis of Selected Torrefied Spruce and Birch Wood

	spruce wood				birch wood			
torrefaction condition	C[a]	H[a]	O[a]	N[a]	C[a]	H[a]	O[a]	N[a]
raw	50.31	6.24	0.07	43.38	48.94	6.35	0.11	44.60
175 °C, 30 min	51.34	6.18	0.07	42.42	49.42	6.38	0.12	44.07
200 °C, 10 min	51.21	6.39	0.06	42.35	49.61	6.16	0.13	44.10
200 °C, 30 min	52.55	6.15	0.06	41.23	51.25	6.18	0.11	42.46
200 °C, 60 min	53.69	5.89	0.06	40.36	51.34	5.94	0.13	42.59
225 °C, 30 min	56.99	5.87	0.07	37.07	56.92	5.86	0.09	37.13

[a] wt %, dry basis.

observations are in the trends similar to DT and in agreement with the literature.[19]

It is interesting to see from Table 2 that the ash contents of biochar obtained from WT are lower than that of the corresponding raw materials. This is definitely not the case for DT, where the ash content of torrefied biomass always increases with increasing mass loss[4,27,28] (known as concentration effect[9]). The observed lower ash content of wet torrefied biomass relative to its raw material can be regarded as a result of the so-called leaching effect in wet chemistry. However, no consistent trend was observed for the changes in the ash content of the solid fuels obtained from WT, with respect to changes in either torrefaction temperature or holding time. This is probably due to the competition between the two effects: concentration effect and leaching effect, which are present at the same time during WT of biomass. If the concentration effect is dominant, the ash content of biochar products may increase, and vice versa. In addition, heat and mass transfer limitations can also have interference on the ash content of the wet torrefied biomass. For example, the ash content of biochar obtained from the 3 cm cubes torrefied at 225 °C is significantly higher than that from the 1 cm cubes torrefied in identical conditions. Nevertheless, the fact that the ash content of wet torrefied biomass is always lower than that of the raw material suggests a possibility to produce cleaner solid fuels from biomass via WT, with regard to inorganic impurities.

3.2.2. Ultimate Analyses for Torrefied Biomass Fuels. Table 3 presents results from ultimate analyses of selected torrefied fuels. Ultimate analysis data of the raw fuels is imported from Table 1 into this table for comparison. Similar to DT, general trends of effects of torrefaction temperature and holding time on the carbon content, O/C and H/C ratios can be observed for WT. Here WT also increases the carbon content, decreases hydrogen and oxygen contents when torrefaction temperature or holding time increases. The changes in carbon, hydrogen and oxygen contents after WT consequently result in reduction of both H/C and O/C ratios in torrefied biomass compared with their origins. On the other hand, the changes in nitrogen content are virtually insignificant and the sulfur content is lower than the detection limit.

In order to have a more comprehensive overview of the effects of WT condition on H/C and O/C ratios, the data from Table 3 are further processed and presented in forms of a Van Krevelen diagram as shown in Figure 4. In this figure, the filled markers denote the raw materials while the empty ones refer to the torrefied fuels. An arrow is also included in each subfigure to show the decreasing trend of these ratios with increases in torrefaction temperature and/or holding time, which is similar to DT and has been well documented in the literature.[22−27] In Figure 4A, the holding time of 30 min was kept constant for investigating the effects of torrefaction temperature on reduction of H/C and O/C ratios. For both types of feedstock, the decreasing trend is virtually linear. Moreover, the ratios for the spruce and birch fuels torrefied at 225 °C for 30 min are almost identical, despite that fact that the ratios for raw spruce and birch are different. However, the effect of residence time at 200 °C presented in Figure 4B do not show a clear trend as the effect of reaction temperature, although the ratios exhibit a decreasing trend and the ratio points move toward the corner on the left and at the bottom of the graph when the residence time increases.

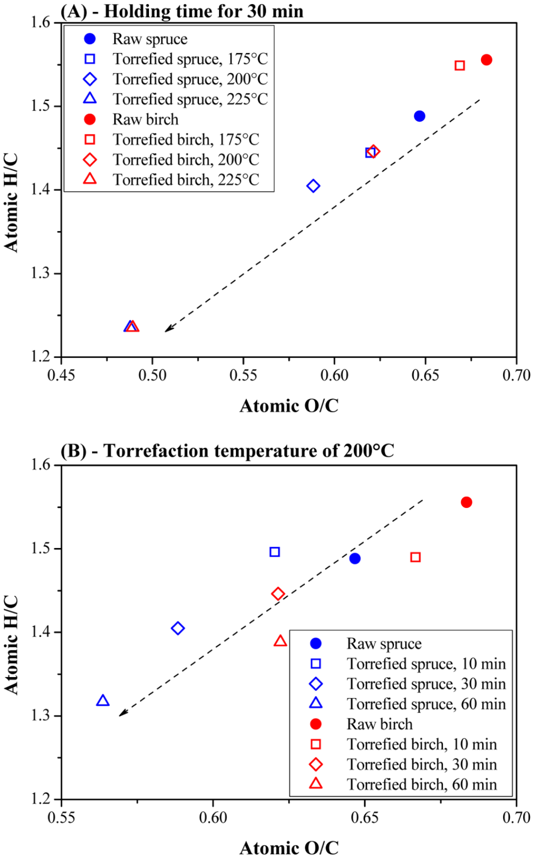

Figure 4. Van Krevelen diagram for the raw and torrefied biomass fuels.

3.2.3. Effects of Process Parameters on the Heating Value. HHVs of wet torrefied biomass were calculated on the basis of the ultimate analysis data presented in Table 3. Figure 5 shows the calculation results for selected experiments at different temperatures with a constant holding time of 30 min (Figure 5A) or various holding times at a constant temperature of 200 °C (Figure 5B). It is observed that the heating values increase when either torrefaction temperature or holding time increases. However, the effect of temperature is more pronounced than the effect of holding time. Moreover, the effect of torrefaction temperature for birch wood is also more pronounced than for spruce. The increases in HHV vary from 1.9 to 12.5% for the torrefied spruce and 1.3−15.0% for the torrefied birch in the temperature range of 175 to 225 °C. Consequently, the HHV of birch wood torrefied at 225 °C is close to spruce wood treated in the same condition, although the HHV of raw birch wood is lower than that of raw spruce wood.

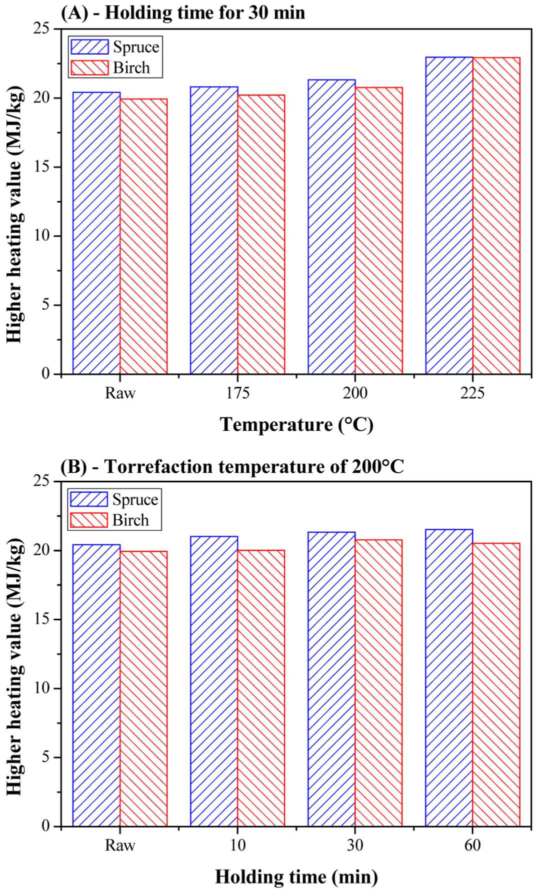

Figure 5. Effect of (A) temperature and (B) holding time on the heating value of torrefied biomass.

3.2.4. Effects of Process Parameters on the Energy Yield. An important aspect of torrefaction is the overall energy balance. For this reason and for an eventual comparison with DT, the energy yield of the ash-free solid product obtained from WT, $Y_{\text{energy}}(\%)$, defined in the same way as for DT was determined according to eqs 4 and 5:

$$Y_{\text{energy}}(\%) = Y_{\text{solid}} D_{\text{energy}} \tag{4}$$

$$D_{\text{energy}} = \frac{\text{HHV}_{\text{torrefied solid product}}}{\text{HHV}_{\text{initial dry biomass}}} \tag{5}$$

where the term of $\text{HHV}_{\text{torrefied solid product}}$ denotes the HHV of the solid product, the HHV of initial dry biomass is the term of $\text{HHV}_{\text{initial dry biamass}}$, and Y_{solid} has been defined earlier in section 2.3.3.

Figure 6 demonstrates the effects of torrefaction temperature and holding time on the energy yield of the solids obtained from WT of the spruce and birch woods. Data presented in Figure 6A was collected from the experiments with a constant holding time of 30 min and varied temperatures, whereas that in Figure 6B was from the experiments in the conditions of 200 °C and varied holding times. It can be seen from the figures that the energy yield decreases with either increasing torrefaction temperature or increasing holding time. This trend is valid for both types of the feedstock. However, the

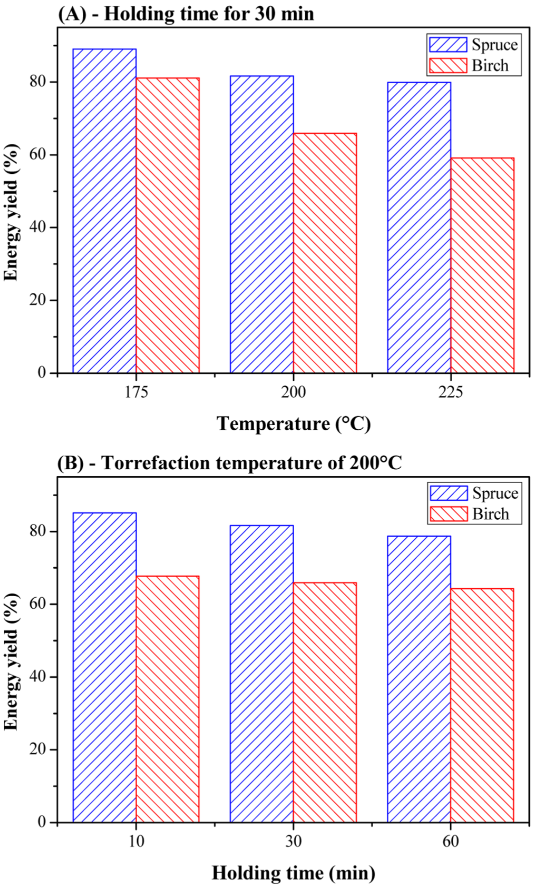

Figure 6. Effects of temperature (A) and holding time (B) on the energy yield.

effect of holding time on the energy yield is not as pronounced as the effect of temperature. The energy yield decreases observed when temperature is increased from 175 to 225 °C are significant, being from 89.1 to 80.0% and from 81.1 to 59.1% for spruce and birch, respectively. When holding time is increased from 10 to 60 min the energy yield decreases from 85.1 to 78.7% for spruce, and from 67.7 to 64.3% for birch. In addition, it can be observed from Figure 6A that when temperature is increased from 175 to 225 °C the differences in energy yield between spruce and birch are enlarging from 8.0% to 20.8%. This is similar to the observation of the temperature-sensitive differences in solid product yield discussed in section 3.1.2.

3.2.5. Effects of Process Parameters on the Hydrophobicity. Figure 7 represents results from the tests of moisture uptake for raw and wet torrefied spruce samples. The effects of torrefaction temperature and holding time are demonstrated in Figure 7, panels A (samples torrefied for 30 min) and B (samples torrefied at 200 °C), respectively. The figure clearly shows that all of the tested samples approach their equilibrium or saturation levels of moisture content on the second day, and the saturation level decreases with either increasing torrefaction temperature or holding time. The reduction in moisture uptake or the increase in hydrophobicity of torrefied biomass is the result from the breakdown and removal of hydroxyl groups in the wood cell wall components during the pretreatment.[59] The devastation strongly depends on the severity of the torrefaction condition, therefore, the hydrophobicity of the torrefied fuel increases or the moisture uptake decreases with increasing of treatment temperature and holding time. The results are in good agreement with other studies.[4,5,19] However, the effect of feedstock particles size on the hydrophobicity of torrefied fuels is not pronounced. Similar trends were also observed in the case of birch wood.

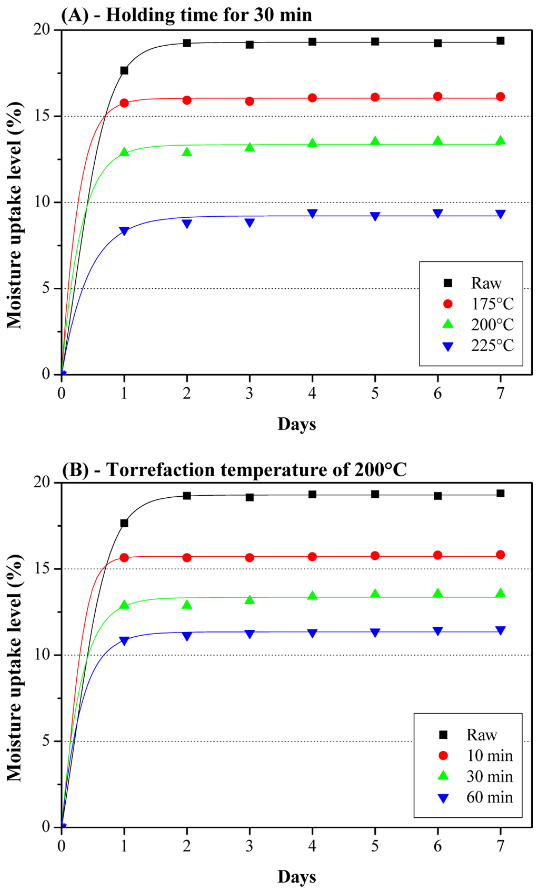

Figure 7. Effect of (A) torrefaction temperature and (B) holding time on the moisture uptake behavior of spruce biomass torrefied in HCW.

3.2.6. Effects of Process Parameters on the Grindability. As presented earlier in section 2.3.2, a quantitative assessment of grinding energy savings due to improvement in grindability of biomass fuel via torrefaction was performed for this present study through a measurement campaign of the specific grinding energy (SGE) required for fuel communition. Results from this campaign are presented in Figure 8, which show the influences of reaction temperature (Figure 8A) and holding time (Figure 8B) on the SGE of wet torrefied spruce and birch in different conditions.

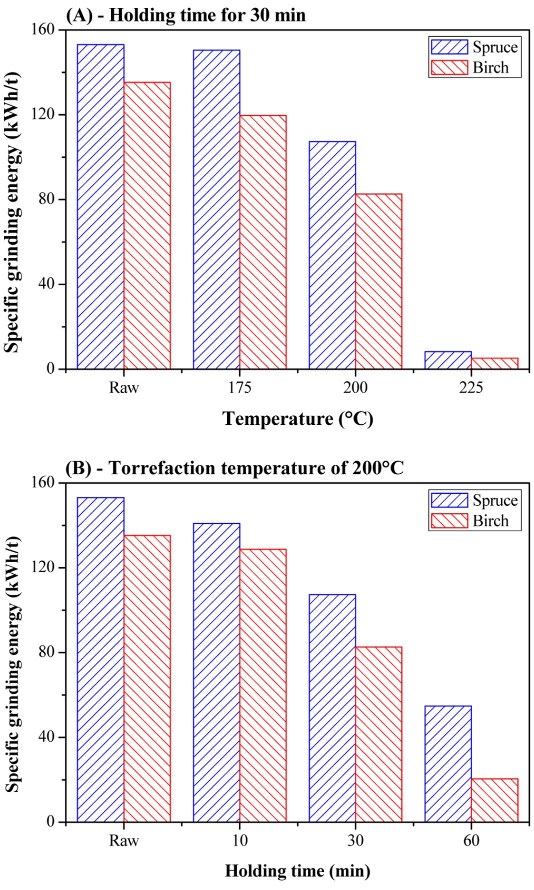

Figure 8. Effect of (A) reaction temperature and (B) holding time on specific grinding energy of wet torrefied biomass.

By examining qualitatively the data in Figure 8, panels A and B, one can observe that the grindability of both spruce and birch is improved when either torrefaction temperature or holding time increases. Also, torrefaction temperature has stronger effects on the grindability than holding time. In addition, temperature appears to have stronger effects on the grindability of birch than spruce.

The most significant reduction in SGE is observed for the samples torrefied at 225 °C for 30 min, being the most severe torrefaction among the tested conditions. The reduction is by a factor of 18.3 for spruce and 25.6 for birch, compared with the raw materials. However, the biomass torrefied at 175 and 200 °C shows only a small decrease in specific grinding energy consumption.

4. COMPARISON WITH DRY TORREFACTION

As discussed in section 2.3.3, a regression model has been adopted to support a comparison between wet and dry torrefaction. By implementing a regression analysis in MS Excel, using the general model (eq 3) and the experimental data obtained from the WT experiments of the present work, three second-order polynomial models were generated for two dependent variables (temperature and holding time): the solid yield Y_{solid} (eq 6), the higher heating value HHV (eq 7), and the specific grinding energy SGE (eq 8).

$$\begin{aligned} Y_{\text{solid}}(\%) = {} & 205.83 - 0.70T - 0.99t + 0.01T^2 \\ & + 3.36 \times 10^{-3}Tt + 2.44 \times 10^{-3}t^2 \end{aligned} \tag{6}$$

$$\begin{aligned} \text{HHV(MJ/kg)} = {} & 38.54 - 0.24T - 0.04t + 0.73 \times 10^{-3}T^2 \\ & - 6.24 \times 10^{-5}Tt - 1.69 \times 10^{-4}t^2 \end{aligned} \tag{7}$$

$$\begin{aligned} \text{SGE}(kWh/t) = {} & -1038.19 + 14.55T + 2.43t - 0.04T^2 \\ & - 0.02Tt + 0.01t^2 \end{aligned} \tag{8}$$

where, T and t represent torrefaction temperature and holding time, respectively. The quality of the regression analysis (with a confidence interval of 95%) and the standard deviations (ε) of these models are summarized in Table 4.

Table 4. Quality of the Regression Analysis (Confidence Interval = 0.95)

summary statistics	model of eq 6 Y_{solid}	model of eq 7 HHV	model of eq 8 SGE
R^2	0.994	0.998	0.962
R^2 adjusted	0.986	0.996	0.866
standard deviation	1.541	0.208	22.249

For the comparison, selected data from a previous study[26] on DT of Norway spruce wood (from the same source as for this present study) was utilized, being a solid yield of 74% and an increase in HHV of 7.8% (compared with the untreated sample). These data were obtained from the DT conditions of 275 °C and for 60 min. The use of the HHV data in increasing percent for the comparison aims to eliminate possible interferences which may be caused by the slight differences in fuel characterization of the two studies, though the samples were from the same source. Using the solid yield model (eq 6) to search for torrefaction temperatures, at which WT of the spruce sample can produce the same solid yield of 74% with a holding time of 5, 10, 20, and 30 min give the results of 222, 220, 216, and 210 °C, respectively. From these two sets of torrefaction temperature and corresponding holding time, the HHV of the solid products can be predicted using the HHV model (eq 7). Results from these predictions are summarized in Table 5, which indicate that in all cases the HHV of solid fuels obtained from WT is always higher than that from DT. The differences are significant, varying from 9 to 21% of the increase in HHV compared with the case of DT (7.8%). Having greater increases in HHV for the same product yield, the predicted cases of WT obviously have higher energy yields than the DT. In addition, the torrefaction temperature is much lower, and the holding time is much shorter for WT than DT.

Table 5. Predicted Results for WT of Norway Spruce with a Solid Yield of 74%

temp[a]	holding time[b]	increase in HHV[c]	energy yield[c]
222	5	9.4	80.96
220	10	9.3	80.88
216	20	8.9	80.59
210	30	8.5	80.29

[a] Units in °C. [b] Units in min. [c] Units in %.

Two extra WT experiments, 222 °C for 5 min and 210 °C for 30 min, were carried out to validate the predictions and thus the comparison. Results from these experiments are presented in Table 6, which includes the data of the DT experiment used for the comparison. From Table 6 it can be seen that the actual solid yields, increases in HHV, and energy yields are in good agreement with the predictions.

To compare the effects of two different torrefaction methods on the structure of the fuels, the morphology of raw spruce, both wet and dry torrefied spruce samples having the same solid yield, was examined by means of a Hitachi TM-1000 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX). The EDX was employed for the elemental analysis of the surface layer with 1 μm depth. The SEM images (not shown) indicate that the openings and long fractures occur on the surface of the torrefied particles, which is not the case for the raw material. These changes in structure are believably caused by the release of gaseous products during the torrefaction. However, the changes for the dry torrefied sample appear more pronounced than for the wet torrefied sample. This observation is reasonable, considering that, for the same solid yield, the DT was carried out at a higher temperature (275 °C) than the WT experiments (at 225 °C). In addition, results from the EDX analysis presented in Figure 9 confirm that the content of potassium and calcium in wet torrefied fuel are significantly lower than that in raw and dry torrefied fuels. It should be noted that the normalized data are showing relative amounts of the elements in the quite low content of inorganic constituents in the wood. Changes in content of other elements are not pronounced. These results confirm the possibility to reduce the ash content of fuel by WT. However, further studies focusing on this direction are needed.

In addition, the SGE for the spruce samples torrefied by either method, WT or DT, is compared to each other on the basis of the same solid product yield. For this comparison, the SGE of the dry torrefied fuel is extracted from the previous work,[26] and those for the wet torrefied fuels are calculated using eq 8. The obtained SGE data are summarized in Table 6. Interestingly, despite having the same solid yield and greater heating values, wet torrefied fuels exhibit slightly higher SGE

Table 6. Validation Results

torrefaction condition	solid yield[a] predicted	solid yield[a] actual	increase in HHV[a] predicted	increase in HHV[a] actual	energy yield[a] predicted	energy yield[a] actual	SGE[b]
DT, 275 °C, 60 min		74.0		7.82		79.79	52.0
WT, 222 °C, 5 min	74	73.8	9.44	9.31	80.96	80.67	57.2
WT, 210 °C, 30 min	74	74.1	8.46	8.30	80.29	80.25	64.1

[a] Units in %. [b] Units in kWh/t.

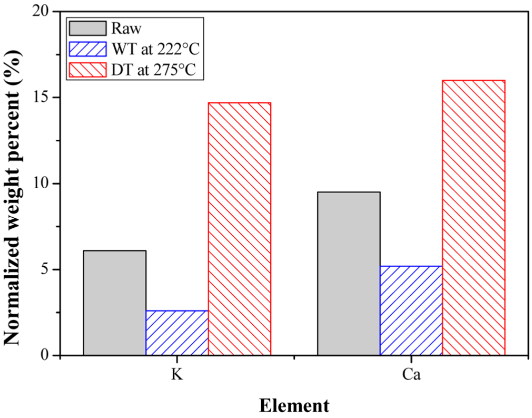

Figure 9. X-ray elemental analysis for main elements in spruce torrefied by DT and WT.

values compared with the dry torrefied fuel. Table 6 indicates that temperature is a major parameter in reduction of SGE for torrefied fuel, i.e., higher torrefaction temperature reduces grinding energy. However, it should be kept in mind that the DT conditions (275 °C and 30 min) may require more energy than the WT conditions (210 °C and 30 min or 222 °C and 5 min).

Furthermore, the moisture uptake of the wet torrefied biomass was also tested using the same method adopted in this present study for a comparison with WT. Data collected from the test are presented in Figure 10, which clearly show that the wet torrefied fuels uptake less water than the dry torrefied fuel, despite the fact that the dry torrefied sample was treated at a much higher temperature and for a longer residence time.

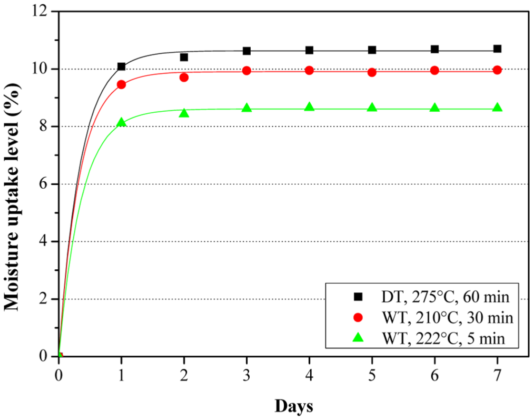

Figure 10. Moisture uptake behavior of spruce biomass torrefied by different methods.

5. CONCLUSIONS

Wet torrefaction of Norway spruce and birch wood has been studied and compared with dry torrefaction. Effects of process parameters on the yield and fuel properties of solid products have been investigated. Effect trends similar to that of DT have been observed. The yield of solid product is reduced with decreasing feedstock particle size. Both reaction temperature and holding time have significant effects on solid product yield, energy yield, and fuel properties of wet torrefied biomass. When torrefaction temperature or holding time is increased, the product and energy yields of the torrefied solid fuels decrease but the improvements in fuel properties of the solid products increase, which include increased fixed carbon contents, greater heating values, better hydrophobicity and improved grindability. In addition, the consistent lower ash contents of the fuels after WT suggest that WT can be employed to reduce ash content of biomass fuels.

On the other hand, it appears that birch wood is more reactive and produces less solid products than spruce wood, in the same WT conditions. Heating values of birch wood increase faster than spruce wood when the severity of WT is increased. The investigation of pressure effects suggests that WT should be carried out at pressures higher than the saturated vapor pressure of water at a given temperature. It is because the rate of WT is enhanced by pressure. In addition, this pressure control can help avoid the energy penalty due to water vaporization. However, pressures that are too high are not recommended.

The comparison between WT and DT supported by regression analyses and numerical predictions has shown that WT can produce solid fuels with a greater HHV, higher energy yield, and better hydrophobicity at much lower temperature and holding reaction time. The morphology analyses of the fuels produced by both torrefaction methods were investigated and the wet torrefied fuel exhibits less pronounced changes in their structure compared with the dry torrefied fuel.

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Notes

The authors declare no competing financial interest.

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Paper II

Effects of wet torrefaction on reactivity and kinetics of wood in air combustion

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Effects of wet torrefaction on reactivity and kinetics of wood under air combustion conditions

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HIGHLIGHTS

- Torrefaction temperature and holding time significantly influence the combustion reactivity and kinetics of woody biomass.
- The effect of torrefaction pressure is insignificant.
- Mass fraction and activation energy of hemicellulose are reduced by wet torrefaction.
- Activation energy of cellulose is increased by wet torrefaction.

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ABSTRACT

This work continues our assessment of wet torrefaction for energy applications, looking at effects of the process parameters (temperature, holding time and pressure) on the reactivity and intrinsic kinetics of wood under air combustion conditions. Woody materials, Norway spruce and birch, were wet torrefied in various conditions (temperature: 175, 200, 225 °C; holding time: 10, 30, 60 min; and pressure: 15.54, 70, 160 bar). The reactivity of the treated and untreated woods was thermogravimetrically examined under a synthetic air environment (21% O_2 and 79% N_2 in volume). A four-pseudo-component model with different reaction orders was adopted for kinetic modelling and extracting the kinetic parameters. The results showed that when increasing either torrefaction temperature or holding time, the torrefied woods behaved more char-like than the raw fuels. However, pressure did not show significant effect on the reactivity. Relatively longer char combustion stages and higher conversion rates (up to $0.5 \times 10^{-3}\ \mathrm{s}^{-1}$) were observed for the woods after torrefaction. The activation energy was decreased for hemicellulose and char, but increased for cellulose after torrefaction, whereas the trend for lignin is not clear. In addition, the hemicellulose mass fraction decreased after torrefaction (from 0.15 to 0.05 for spruce and from 0.23 to 0.06 for birch). The amount of char in the torrefied woods increased gradually with increasing torrefaction temperature or holding time (from 0.24 to 0.40 for spruce, and from 0.18 to 0.34 for birch).

1. Introduction

Wet torrefaction (WT), which may be defined as treatment of biomass in hydrothermal media (HM) or hot compressed water (HCW) at temperatures within 180–260 °C [1–5], is a promising method for production of high quality solid fuels from low cost wet biomass resources such as forest residues, agricultural waste, aquatic energy crops, and sewage sludge. The concept of WT is very similar to "hydrothermal carbonization" (HTC) [6–15] and sometimes is discussed under the general term "hydrothermal conversion" [15–19] or "hydrothermal treatment" [20–25]. Although the terminologies of WT and HTC have sometimes been used interchangeably, there is a significant difference between them. While WT aims at producing upgraded solid fuels for energy applications only, HTC is employed mainly for producing charcoal, with much higher carbon content, which can be used not only as fuel but also as activated carbon, soil enhancer, fertilizer, etc. Clearly, energy efficiency of the process, fuel properties and combustion properties of the product are more critical for WT than for HTC, and thus the former tends to be performed at lower temperatures (180–260 °C) than the latter (from 300 °C).

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Like dry torrefaction (DT), which may be defined as thermal treatment of biomass in an inert environment at atmospheric pressure and temperatures within the range of 200–300 °C [26–28], WT results in the following main improvements in the fuel properties of biomass: (1) increased heating value due to a reduction in the O/C ratio; (2) intrinsic transformation from hygroscopic into hydrophobic nature of biomass; (3) better grindability coupling with less energy requirement for size reduction of the fuel. After WT, the wet hydrophobic solid product can be effectively made dry by mechanical and/or natural dewatering, which is an attractive option capable of dramatically reducing the energy requirement for the post-drying step. In addition to the solid fuel product, many valuable organic compounds including acetic acid, formic acid, lactic acid, glycolic acid, levulinic acid, phenol, furfural, HMF, and sugars are found in the aqueous phase products of WT, making up approximately 10 wt% of the feedstock [4,6]. The potential use of these water-soluble organic fractions for production of valuable products may contribute to further improving the economy of the WT process.

Recently, an assessment of WT for energy applications (combustion, gasification, and pyrolysis) in comparison with DT has been reported by our research group [1]. The assessment includes a literature review of past studies relevant to WT, which will not be repeated in this present work. A core theme of the assessment was to investigate the effects of process parameters including pressure, reaction temperature, holding time, and feedstock particle size on the yield and fuel properties of the solid product. For reaction temperature and holding time, positive trends of their effects on the yield and fuel properties of the solid products were observed, which are similar to those for DT. However, pressure and feedstock particle size only have minor effects. More interestingly, the ash content of biomass fuel is significantly reduced by WT. This suggests that WT can be employed to produce "cleaner" biomass solid fuels as well, with respect to inorganic elements. In addition, a comparison between WT and DT supported by regression analyses and numerical prediction showed that WT can produce solid fuel with greater heating value, higher energy yield, and better hydrophobicity at much lower temperatures and holding times than DT [1].

Despite various advantages of WT over DT, only a few studies on WT have been reported [1–5] compared to a sharply increasing number of studies on DT during the last few years [26–34]. In addition, most WT studies focused on the effects of process parameters on the yield and fuel properties of the solid product. To our knowledge, no study of using solid fuel obtained from WT for energy applications has been reported so far. Combustion is currently the most important energy application of biomass solid fuel, considering its contribution to more than 90% of the global bioenergy deployment [35–39]. It is therefore important and necessary to investigate into the effects of WT on combustion reactivity and kinetics of biomass solid fuels.

Several studies on combustion of dry torrefied biomass have been reported [30,40–43], which would be beneficial for studying combustion behavior of wet torrefied biomass fuel. Pimchuai et al. [40] and Bridgeman et al. [30], for example, studied the combustion of biochars obtained from DT of different biomass materials. They found that the combustion of dry torrefied husks and herbaceous biomass released more heat than that of the raw materials due to the higher fixed carbon content of the biochars. However, no kinetic data was reported from these studies. Arias et al. [41] applied a simple first-order kinetic model to estimate the activation energy and pre-exponential factor of raw and dry-torrefied eucalyptus samples in a two-stage combustion process (devolatilization followed by combustion). The results showed that both kinetics parameters (the activation energy and pre-exponential factor) increased in stage 1 and decreased in stage 2 after DT. Nevertheless, the model was based on an empirical method which was not validated because the model itself could not either reproduce simulated curves or give any information about the fit quality between the predicted and experimental data. Recently, studies on the combustion kinetics of dry torrefied woody biomass materials using multi pseudo-component models have been reported by Broström et al. [42] and Tapasvi et al. [43]. The former employed a global kinetic model and the latter employed a distributed activation energy model (DAEM). The results from the two approaches showed that DT had little effect on the kinetic parameters of the torrefied biomass regardless of the treatment conditions. Broström et al. [42] reported that the activation energy values of hemicellulose, cellulose and lignin were constant at 100.6, 213.1, and 121.3 kJ/mol, respectively for both raw and dry-torrefied spruce. Tapasvi et al. [43] found that the activation energy values for cellulose, non-cellulosic part and char remained at 135, 160 and 153 kJ/mol, respectively for different types of feedstock and DT conditions.

This present study is a follow-up of our first assessment of WT for energy applications [1], which has been published as mentioned earlier. The objective of the present work was to assess the effects of WT conditions (temperature, holding time and pressure) on the combustion reactivity and kinetics of biomass solid fuels. Thermogravimetric analysis (TGA) was employed for this work as it is a proven method for studying devolatilization and combustion of biomass in the kinetic regime [44,45].

2. Materials and methods

2.1. Materials

As mentioned in the introduction, the present work is a follow-up of our first report on comparative assessment of WT for energy applications. The biomass materials used for this work were obtained from the previous work, in which the full details about materials and experimental methods were presented and can be found elsewhere [1]. For a convenience, a brief extraction is imported in this present work.

Stem wood from Norway spruce (softwood) and birch (hardwood) were selected as feedstock for the study since they are the main wood species in Norwegian forests. The samples were cut into 1 cm cubes for WT in hot compressed water, using a 250 ml Parr reactor series 4650 (Parr Instrument, USA) at different temperatures (175, 200, 225 °C), pressures (15.54, 70, 160 bar) and holding times (10, 30, 60 min). The corresponding vapour pressures of water at 175, 200, and 225 °C are 8.93, 15.54, and 25.50 bar, respectively. However, in order to keep more water in the liquid phase, the pressure of 70 bar was used for all of the WT experiments, except for the investigation of the pressure effect at 200 °C [1]. For this investigation, the pressures of 15.54, 70 and 160 bar were employed. Distilled water was used as the reaction media. The ratio of dry feedstock over water was 1:5 by weight.

After WT, the wet solid products were dried at 105 °C for 48 h and then stored in a desiccator for further analyses. The proximate and ultimate analyses of the samples used for this work are presented in Table 1. The proximate analyses were performed according to ASTM standards: ASTM E871, ASTM E872 and ASTM D1102 for moisture content, volatile matter and ash content, respectively. The ultimate analyses were determined (on a dry basis) by means of an "EA 1108 CHNS-O" elemental analyzer (Carlo Erba Instruments). The higher heating values (HHVs) were calculated on dry and ash free basis, according to Channiwala and Parikh [46].

2.2. Thermogravimetric analysis method and procedure

A thermogravimetric analyzer (Mettler Toledo TGA/SDTA851e) was employed for this study. The biomass solid fuels were first

Table 1
Proximate and ultimate analyses of raw and wet torrefied fuels (dry and ash free).

Sample	Solid yield[a]	Proximate analysis			Ultimate analysis					HHV[b]
		Ash[a]	VM[a]	FC[a]	C[a]	H[a]	N[a]	O[a]	S[a]	
Spruce										
Raw	–	0.23	86.50	13.27	50.31	6.24	0.07	43.38	<0.02	20.42
175 °C, 30 min	88.27	0.11	85.72	14.17	51.34	6.18	0.07	42.42	<0.02	20.81
200 °C, 10 min	82.48	0.14	84.64	15.22	51.21	6.39	0.06	42.35	<0.02	21.02
200 °C, 30 min	78.45	0.12	83.92	15.95	52.55	6.15	0.06	41.23	<0.02	21.33
200 °C, 60 min	73.28	0.09	81.87	18.03	53.69	5.89	0.06	40.36	<0.02	21.51
225 °C, 30 min	69.74	0.14	74.74	25.12	56.99	5.87	0.07	37.07	<0.02	22.97
Birch										
Raw	–	0.28	89.46	10.26	48.94	6.35	0.11	44.60	<0.02	19.94
175 °C, 30 min	79.53	0.09	88.57	11.34	49.42	6.38	0.12	44.07	<0.02	20.21
200 °C, 10 min	66.42	0.08	87.97	11.94	49.61	6.16	0.13	44.10	<0.02	20.01
200 °C, 30 min	64.64	0.09	85.15	14.76	51.25	6.18	0.11	42.46	<0.02	20.78
200 °C, 60 min	63.06	0.10	82.64	17.27	51.34	5.94	0.13	42.59	<0.02	20.51
225 °C, 30 min	58.01	0.13	73.78	26.09	56.92	5.86	0.09	37.13	<0.02	22.93

VM: volatile matter, FC: fixed carbon, HHV: higher heating value.
[a] wt%.
[b] MJ/kg.

ground using an IKA MF 10 cutting mill. Then the particles passing through a 125 µm sieve (Fritsch Analysette 3 Pro) were collected for the kinetic study to ensure the experiments to be in the chemical reaction kinetic regime [47,48]. For each TGA run, an amount of about 0.5 mg sample was spread in a 150 µl alumina pan located inside the TGA reactor. It is worth noting that the buoyancy effect plays a significant role for such a small sample weight. Therefore, it is mandatory to run a blank TG (mass loss versus temperature) curve first. The weight change of the blank experiment was subtracted from the experimental curves automatically. The experiment started from room temperature, the fuel sample was heated to 105 °C and held at this temperature for 1 h for drying. Thereafter, the sample was heated to 700 °C at a constant heating rate of 10 °C/min. A synthetic air flow rate of 80 ml/min was applied for all experiments. Moreover, three repetitions were run for each fuel sample, and the average kinetic values are reported.

2.3. Kinetic model selection

Branca and Di Blasi [49] proposed and examined two different models to describe the combustion of biomass fuel. They are series- and parallel-reaction models, of which each model consists of four reactions (3 reactions for the devolatilization of the three main components of lignocellulosic biomass, and 1 reaction for the char burn-off). It was concluded that both models gave similar results for the estimated kinetic parameters. However, the parallel-reaction mechanism, or the pseudo-component model, is favorable and widely used [42,50,51] because it can describe the possible overlapped reactions of the lumped components in biomass. According to this model, the biomass sample is regarded as a sum of four pseudo-components, and the activation energies were assumed to be constant during the reactions to simplify the simulation process.

For the present study, the parallel-reaction model proposed by Branca and Di Blasi [49] was adopted. The four parallel reactions applied for the model are as follows:

$$A_v \xrightarrow{+O_2} V_1 \tag{1}$$

$$B_v \xrightarrow{+O_2} V_2 \tag{2}$$

$$C_v \xrightarrow{+O_2} V_3 \tag{3}$$

$$D_v \xrightarrow{+O_2} V_4 \tag{4}$$

where A_v, B_v, C_v and D_v are the pseudo-components; and V_i ($i = 1, 2, 3, 4$) is the lumped volatiles and/or gases released from the thermal degradation of the respective pseudo-component. The three first reactions (Eqs. (1)–(3)) are associated with the devolatilization of the three main components of biomass including hemicellulose, cellulose and lignin, respectively. The rates of these reactions can be presented by the general power law (nth-order) expression, although $n = 1$ is usually used [42,49,51,52]. The last reaction (Eq. (4)) represents the char combustion, for which the rate law is generally related to the partial pressure of oxygen through an empirical exponent and the char porosity. Due to a relatively small amount of the sample tested in an air flow, it is reasonable to assume that the oxygen mass fraction remains constant during the reaction process. Consequently, the general power law (nth-order) expression can also be applied to represent the char combustion. Overall, the conversion rate of these four reactions can be described by the following Arrhenius expression:

$$\frac{d\alpha_i}{dt} = A_i \exp\left(-\frac{E_i}{RT}\right)(1-\alpha_i)^{n_i}, \quad i = 1, \ldots, 4 \tag{5}$$

where A is the pre-exponential factor, E is the activation energy of the reaction, R is the universal gas constant, T is the absolute temperature, n is the reaction order, and i is for the ith pseudo-component. The conversion degree (α) is defined as the mass fraction of decomposed solid or released volatiles:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} = \frac{v}{v_f} \tag{6}$$

where m_0 and m_f are the initial and final masses of solid, m is the mass of solid at any time; v_f is the total mass of released volatiles and v is the mass of released volatiles at any time.

The overall conversion rate is the sum of the partial conversions, where c_i indicates the mass fraction of each pseudo-component in the following equation:

$$\frac{d\alpha}{dt} = \sum_{i=1}^{4} c_i \frac{d\alpha_i}{dt} \tag{7}$$

2.4. Numerical method

Data collected from the TGA experiments was differentiated to obtain the DTG data, and presented in the form of conversion (mass loss) rate ($\frac{d\alpha}{dt}$) versus temperature T. A mathematical model corresponding to the selected model was then employed for simulation and comparison with the experimental DTG data. The optimization of the predicted DTG curves was based on the non-linear least squares method, which minimized the sum of the square differences between the experimental and calculated data. The objective function is given in Eq. (8):

$$S = \sum_{j=1}^{N}\left[\left(\frac{d\alpha_j}{dt}\right)_{\text{exp}} - \left(\frac{d\alpha_j}{dt}\right)_{\text{cal}}\right]^2 \tag{8}$$

where $\left(\frac{d\alpha_j}{dt}\right)_{\text{exp}}$ and $\left(\frac{d\alpha_j}{dt}\right)_{\text{cal}}$ represent the experimental and calculated conversion rates, respectively; and N is the number of experimental points.

In order to validate the optimization or the curve fitting process in other words, the fit quality between actual and modelled data is calculated according to Eq. (9) [49,53]:

$$\text{Fit } (\%) = \left(1 - \frac{\sqrt{\frac{S}{N}}}{\left[\left(\frac{d\alpha_j}{dt}\right)_{\text{exp}}\right]_{\max}}\right)\cdot 100\% \tag{9}$$

The actual simulation was run until the maximum fit value was found, at which the convergence criteria of the optimization process are achieved. The extracted kinetic parameters are: the activation energies (E_1–E_4), the pre-exponential factors (A_1–A_4), the mass fractions (c_1–c_4), and the reaction orders (n_1–n_4) for each pseudo-component. Totally, there are 12 kinetic parameters for the 1st order model and 16 parameters for the nth order model.

3. Results and discussions

3.1. Thermogravimetric analysis of spruce and birch wood in air

Fig. 1 shows the TG and DTG curves, representing the thermal behavior of the raw spruce and birch woods in the temperature range of 100–600 °C. The standard deviation of the conversion rate data for the tested samples was 1.38×10^{-5} s^{-1}. For both types of feedstock, the decomposition starts at around 180 °C with a low conversion rate. Then the decomposition rate increases rapidly from around 250 °C to the devolatilization peaks ($\approx 2.3 \times 10^{-3}$ s^{-1}) at 321–324 °C, from which the rate decreases quickly, down to 0.30×10^{-3} s^{-1} for the spruce wood and 0.25×10^{-3} s^{-1} for the birch wood at around 350 °C. This marks the end of the devolatilization and the beginning of the char combustion, which has much lower rates than the devolatilization. In addition, a clear shoulder in the devolatilization stage is observed for the raw birch wood, but not for the raw spruce. This is because the hemicelluloses content of birch (hardwood) is normally higher than that of spruce (softwood) [54]. Also, hemicellulose of hardwood usually contains more xylan than softwood, which is the most reactive compound in the temperature range of the devolatilization (200–350 °C) [54].

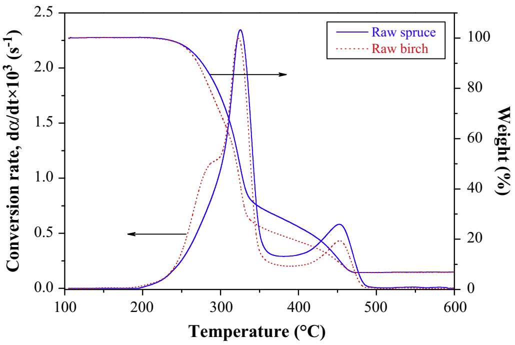

Fig. 1. TGA and DTG curves in air for raw spruce and birch woods.

In the char combustion stage, the birch wood char exhibits lower reactivity than that of spruce wood char. The char combustion rate peak is only 0.38×10^{-3} s^{-1} for the birch, but 0.53×10^{-3} s^{-1} for the spruce.

3.2. Effects of torrefaction conditions on reactivity of wood in air combustion

3.2.1. The effect of torrefaction temperature

The woods torrefied at three different temperatures (175, 200, and 225 °C), in the common conditions of 30 min as holding time and 70 bar as pressure were used for this test. The test results are presented in Fig. 2, which includes the data collected for the raw woods for comparison. Fig. 2A is for the spruce wood and Fig. 2B for the birch wood. As can be seen, the torrefied woods start decomposing at temperatures around 150 °C, somehow lower than those for the raw woods (around 180 °C). However, the conversion rates in this early stage are very low, approximately being less than 0.2×10^{-3} s^{-1} in all cases. A slightly higher reactivity of the torrefied woods than their origins in the early decomposition stage may be due to the higher reactivity of a small amount of remaining organic compounds, with low molecular weights, produced from the degradation of hemicellulose during the WT processes [55,56]. Most of these organic compounds were washed out and collected in the water-soluble product portion, but some of them

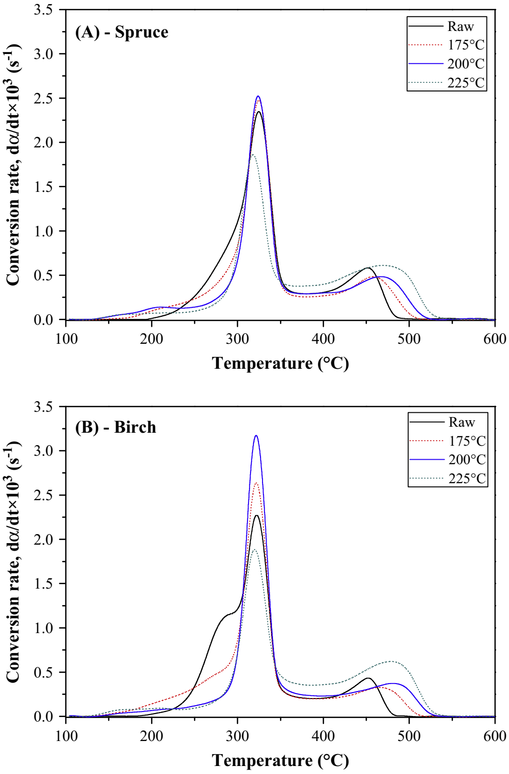

Fig. 2. DTG analyses in air for spruce (A) and birch (B) woods torrefied at 70 bar for 30 min.

may have been trapped in the pores and/or adsorbed on the surface of the torrefied biomass. At temperatures from 250 °C up to 310 °C, the torrefied woods become less reactive than their origins. This is probably due to the degradation of hemicellulose in the raw woods as discussed earlier in Section 3.1, considering that torrefied woods contain less or no hemicellulose compared to their origins. At temperatures above 310 °C, the devolatilization peaks, mainly contributed by cellulose decomposition [57,58], are established. The peaks for the woods torrefied at 175 °C and 200 °C are higher than those for the raw woods, but occur at the same location (around 321–324 °C). In addition, the peaks for the woods torrefied at 200 °C are higher than those for the woods torrefied at 175 °C. However, the peaks for the woods torrefied at 225 °C are the lowest and the peak locations slightly shifted to the left, at around 317 °C.

At temperatures above 350 °C, where the char formed from the devolatilization stage starts combusting, the situation is reversed. The char combustion stage of the torrefied woods starts at temperatures somehow lower than the raw woods, with the combustion peaks clearly shifting to the right. The woods torrefied at 225 °C (the highest one among the temperatures employed for the WT) exhibit the highest reactivity with the highest combustion rate peaks ($0.50 \times 10^{-3}\ s^{-1}$) and the longest DTG tails (last until 550 °C) compared with the others. This is probably due to the highest fixed carbon content of the woods torrefied at 225 °C (Table 1). However, the combustion peaks of the woods torrefied at 175 °C and 200 °C are lower than that of the raw woods. Nevertheless, the combustion stages of the woods torrefied at 175 °C and 200 °C last longer than those of the raw woods. This inconsistent trend, together with the inconsistence observed for the devolatilization peaks, makes it hard to identify a general trend for the effect of WT temperature on the reactivity of wood in air combustion, and therefore no firm conclusion on this can be drawn at this stage. Nevertheless, it is suspected that severer WT conditions would cause higher devolatilization peaks. However, when the WT severity factor is too high, such as at WT temperatures of 225 °C, cellulose starts to decompose (about 10% at 225 °C for 30 min [2,56]). Consequently, the devolatilization peak heights of the DTG curves for the woods torrefied in these conditions are lower than the others, even those of their origins.

3.2.2. The effect of torrefaction time

Fig. 3 presents the effect of holding time (10, 30, and 60 min) during WT on the combustion behavior for the woods torrefied at 200 °C and 70 bar as the common conditions. Fig. 3A is for the spruce wood and Fig. 3B for the birch wood. The figures indicate that increases in WT holding time make the woods less reactive at TGA temperatures below 300 °C and more reactive during the char combustion stage. Again, similar explanations based on the role of the hemicellulose and fixed carbon content of the tested samples can be applied for these observed trends. In addition, inconsistencies in the devolatilization peak heights, which are similar to those for the effect of torrefaction temperature, were also observed.

3.2.3. The effect of torrefaction pressure

Fig. 4 presents DTG curves for the combustion of the spruce wood torrefied at various pressures: 15.54 (the vapour pressure of water at 200 °C), 70 and 160 bar, in the common conditions of 200 °C and 10 min. Changes in the conversion rate were observed to be within $7.11–14.35 \times 10^{-5}\ s^{-1}$.These indicate that the effect of WT pressure on the reactivity of the woods was insignificant. Increasing pressure made the wood slightly less reactive during the devolatilization, but somewhat more reactive in the char combustion stage, considering the peaks height. However, the peaks locations were almost at the same temperatures.

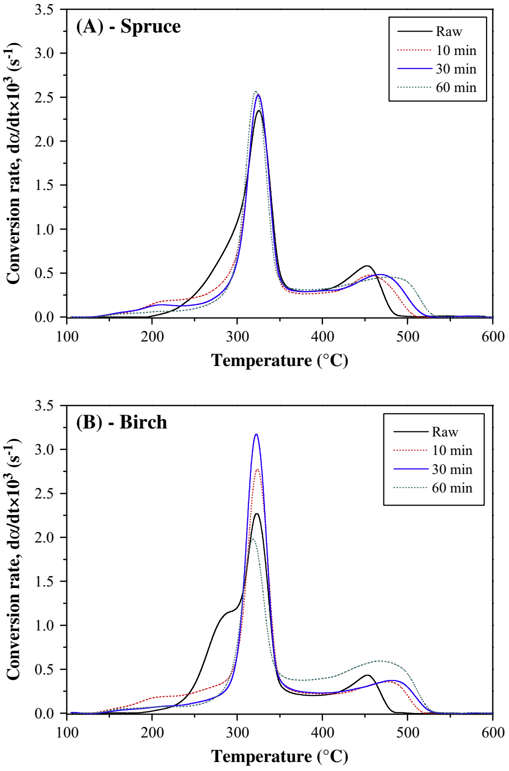

Fig. 3. DTG analyses in air for spruce (A) and birch (B) torrefied at 200 °C and 70 bar.

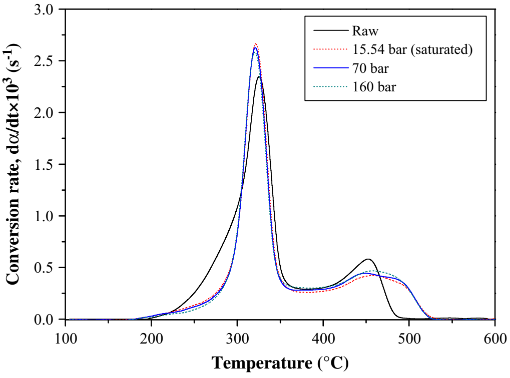

Fig. 4. DTG curves in air for spruce torrefied in the condition of 200 °C, 10 min at different pressures.

3.3. Kinetic analysis

A kinetic analysis employing the four-pseudo-component model with different reaction orders ($n = 1$ and $n \neq 1$) was performed for a quantitative evaluation of the effects of WT on the combustion reactivity of wood. Because the effect of pressure during WT on the reactivity of wood in air combustion is not significant, only the wood samples torrefied at a constant pressure of

Table 2
Combustion kinetic data for spruce fuels.

Torrefaction condition		First order reactions				nth order reactions				
		E (kJ/mol)	A (s^{-1})	c	Fit (%)	E (kJ/mol)	A (s^{-1})	c	n	Fit (%)
Raw	H	103.80	3.70E+07	0.14	99.27	103.76	3.89E+07	0.15	1.01	99.28
	C	221.58	2.43E+17	0.42		221.53	2.46E+17	0.44	1.06	
	L	66.17	1.33E+03	0.23		68.40	1.80E+03	0.21	1.01	
	Char	178.49	5.90E+10	0.21		183.09	1.27E+11	0.20	1.01	
175 °C, 30 min	H	66.23	1.47E+03	0.12	98.90	66.97	1.47E+03	0.12	1.01	98.90
	C	241.17	1.31E+19	0.40		241.13	1.32E+19	0.41	1.03	
	L	40.60	1.39E+01	0.23		40.27	1.40E+01	0.23	1.01	
	Char	132.50	1.58E+07	0.24		132.58	1.58E+07	0.24	1.01	
200 °C, 10 min	H	47.11	2.32E+02	0.12	98.92	47.41	2.35E+02	0.13	1.01	98.96
	C	239.33	9.59E+18	0.44		239.46	1.00E+19	0.45	1.06	
	L	66.55	1.48E+03	0.21		67.12	1.47E+03	0.18	1.01	
	Char	135.34	2.49E+07	0.24		135.50	2.53E+07	0.24	1.01	
200 °C, 30 min	H	43.98	1.54E+02	0.09	98.69	46.75	2.27E+02	0.11	1.01	98.93
	C	243.41	2.21E+19	0.43		259.18	5.93E+20	0.47	1.20	
	L	71.70	3.35E+03	0.21		82.85	2.20E+04	0.17	1.04	
	Char	131.32	9.46E+06	0.26		142.27	5.78E+07	0.25	1.04	
200 °C, 60 min	H	43.32	1.63E+02	0.04	98.49	43.93	1.63E+02	0.05	1.01	98.61
	C	247.46	6.34E+19	0.43		247.27	6.34E+19	0.46	1.12	
	L	71.32	3.05E+03	0.22		72.45	3.05E+03	0.19	1.01	
	Char	111.63	2.77E+05	0.31		111.77	2.77E+05	0.30	1.01	
225 °C, 30 min	H	44.03	2.90E+02	0.04	98.32	44.82	2.89E+02	0.05	1.01	98.41
	C	238.92	1.44E+19	0.30		238.97	1.54E+19	0.33	1.18	
	L	67.72	1.60E+03	0.25		68.78	1.62E+03	0.21	1.01	
	Char	109.03	1.94E+05	0.41		109.38	2.01E+05	0.40	1.01	

H: hemicellulose, C: cellulose, L: lignin.

70 bar (at different temperatures and with different holding times) were selected for the kinetic analysis. The selection of this pressure was based on the recommendation discussed in our previous study [1]. In total, 12 experimental data sets were analyzed kinetically, of which 6 were for the spruce wood and 6 for the birch wood. The kinetic data extracted from this analysis are presented in Tables 2 and 3 for the spruce and birch, respectively. The quality of the fit between the experimental and predicted data is also included in the tables. In addition, for a graphical demonstration of the fit quality, curves fittings for the raw woods and the woods torrefied at 200 °C for 30 min (at 70 bar) are presented in Figs. 5 and 6, respectively. In these figures, the actual conversion rates from the experiments are presented by the black dotted curves. The red solid curves denote the predicted rates. The other four curves are presenting the conversion rates of the three main components of wood (hemicellulose, cellulose, and lignin) and the char formed from the devolatilization step. The figures show good fits between the experimental and modelled results. The fit quality numerically presented in Tables 2 and 3 is within 98–99% in all cases.

Tables 2 and 3 show that the modelling with different reaction orders generated quite similar kinetic data. The data of the activation energy and pre-exponential factor are comparable with those reported in the literature [45,49,53,59,60]. In addition, most of the calculated n values are close to 1. However, the nth order model still exhibits somehow better fit and gives more information about the reaction order. Therefore, the kinetic data obtained from the nth order model are chosen for further assessments hereafter.

It can be seen that, while there is no clear trend for the effect of WT on the pre-exponential factor, the activation energy of hemicellulose is reduced dramatically by WT, e.g. decreases from 103.76 to 44.82 kJ/mol and from 144.68 to 41.29 kJ/mol for the spruce and birch, respectively, by WT at 225 °C (and 70 bar) for 30 min. This effect can also be observed from the hemicellulose curves in Figs. 5 and 6, which show clearly that WT caused a shift of the hemicellulose curves to a lower temperature range. This is in agreement with the literature [61] and can be explained by that during WT the hemicellulose component of the wood was decomposed and cracked into smaller molecules such as polysaccharides [55,56], which remained in the solid products.

However, the effect trend of WT on the activation energy of lignin is not clear. Similar observations were described by Biswas et al. [61], which reported that the thermal reactivity of woody lignin may either increase or decrease due to hydrothermal pretreatment, depending on the severity of the pretreatment conditions which may result in condensation and re-polymerization reactions.

In contrast to hemicellulose, the activation energy of cellulose is increased by WT. This is presumably due to the increased crystallinity of cellulose caused by hydrothermal treatment [62–64]. It is because that during thermal degradation, crystalline cellulose was reported to have much higher activation energy than non-crystalline cellulose due to the increased cross linking [65].

Similar to hemicellulose, the activation energy of char combustion is decreased by WT (from 183.09 kJ/mol for the raw spruce to 109.38 kJ/mol for spruce torrefied at 225 °C and 30 min; from 222.00 kJ/mol for raw birch to 132.26 kJ/mol for birch torrefied at 225 °C for 30 min). This is presumably due to the changes in ash content of the woods after WT since it was reported in the literatures [66–69] that the ash content and ash composition of char from biomass would both enhance or inhibit the char reactivity. It is because both mass transfer limitations and catalytic effects of the ash.

The mass fraction of hemicellulose is reduced by WT. In addition, the mass fraction is decreased gradually with increasing WT severity, from 0.15 for the raw spruce to 0.05 for the spruce torrefied at 225 °C and 30 min; and from 0.23 for the raw birch to 0.06 for the birch torrefied at 225 °C and 30 min. From the conditions of 200 °C and 30 min to more severe conditions (higher temperatures or longer holding times), the hemicellulose mass fraction of the torrefied fuel is small, less than 10% of the total mass. With the reduction of hemicellulose fraction, the mass fraction of the other component fractions in the torrefied biomass fuels (cellulose, lignin, and char) are relatively increased compared with the raw materials, as presented in Tables 2 and 3.

Table 3
Combustion kinetic data for birch fuels.

Torrefaction condition		First order reactions				nth order reactions				
		E (kJ/mol)	A (s^{-1})	c	Fit (%)	E (kJ/mol)	A (s^{-1})	c	n	Fit (%)
Raw	H	138.17	1.14E+11	0.22	98.79	144.68	4.69E+11	0.23	1.01	98.98
	C	194.25	1.13E+15	0.50		204.71	9.71E+15	0.48	1.01	
	L	83.96	2.71E+04	0.14		83.51	2.77E+04	0.16	1.06	
	Char	221.99	8.74E+13	0.14		222.00	8.87E+13	0.14	1.04	
175 °C, 30 min	H	58.34	2.66E+03	0.17	98.59	64.69	1.12E+04	0.18	1.01	98.76
	C	246.38	4.84E+19	0.44		263.00	1.54E+21	0.46	1.16	
	L	65.14	1.20E+03	0.20		65.80	1.20E+03	0.18	1.08	
	Char	127.47	5.48E+06	0.19		127.71	5.51E+06	0.18	1.01	
200 °C, 10 min	H	49.02	4.61E+02	0.13	98.49	48.99	4.60E+02	0.13	1.01	98.55
	C	254.86	2.43E+20	0.46		254.85	2.43E+20	0.46	1.04	
	L	61.56	4.42E+02	0.23		68.70	2.13E+03	0.23	1.28	
	Char	152.51	2.77E+08	0.18		150.04	1.81E+08	0.18	1.01	
200 °C, 30 min	H	50.30	8.01E+02	0.06	98.31	52.71	1.25E+03	0.07	1.01	99.11
	C	267.74	3.85E+21	0.52		263.29	1.62E+21	0.56	1.14	
	L	80.54	2.24E+04	0.19		82.31	2.08E+04	0.15	1.03	
	Char	118.13	8.26E+05	0.23		123.53	1.93E+06	0.22	1.01	
200 °C, 60 min	H	50.31	1.21E+03	0.05	98.24	50.78	1.19E+03	0.05	1.02	98.42
	C	235.27	6.95E+18	0.33		237.06	1.04E+19	0.35	1.14	
	L	79.94	2.03E+04	0.22		81.18	2.30E+04	0.20	1.10	
	Char	104.16	9.15E+04	0.41		104.91	1.02E+05	0.40	1.01	
225 °C, 30 min	H	40.88	1.33E+02	0.06	98.22	41.29	1.26E+02	0.06	1.01	98.48
	C	231.51	2.66E+18	0.32		236.66	8.13E+18	0.34	1.18	
	L	67.79	1.39E+03	0.27		71.58	2.56E+03	0.25	1.08	
	Char	129.38	4.98E+06	0.36		132.26	7.80E+06	0.34	1.01	

H: hemicellulose, C: cellulose, L: lignin.

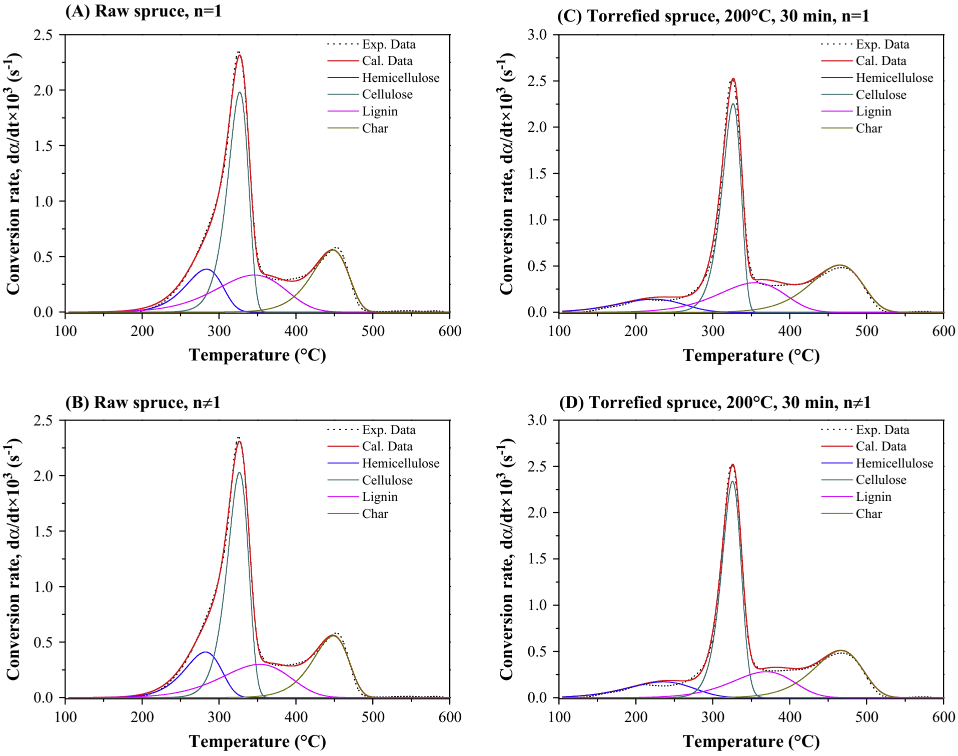

Fig. 5. Curve fitting for raw and torrefied spruce fuels.

The mass fraction of cellulose in the torrefied fuels from both feedstocks increased to a maximum value, 0.47 and 0.56 for spruce and birch torrefied at 200 °C and 30 min, and then decreased with either increasing temperature or holding time. The contribution of cellulose fractions is in good agreement with the heights of the devolatilization peaks shown in Figs. 2 and 3.

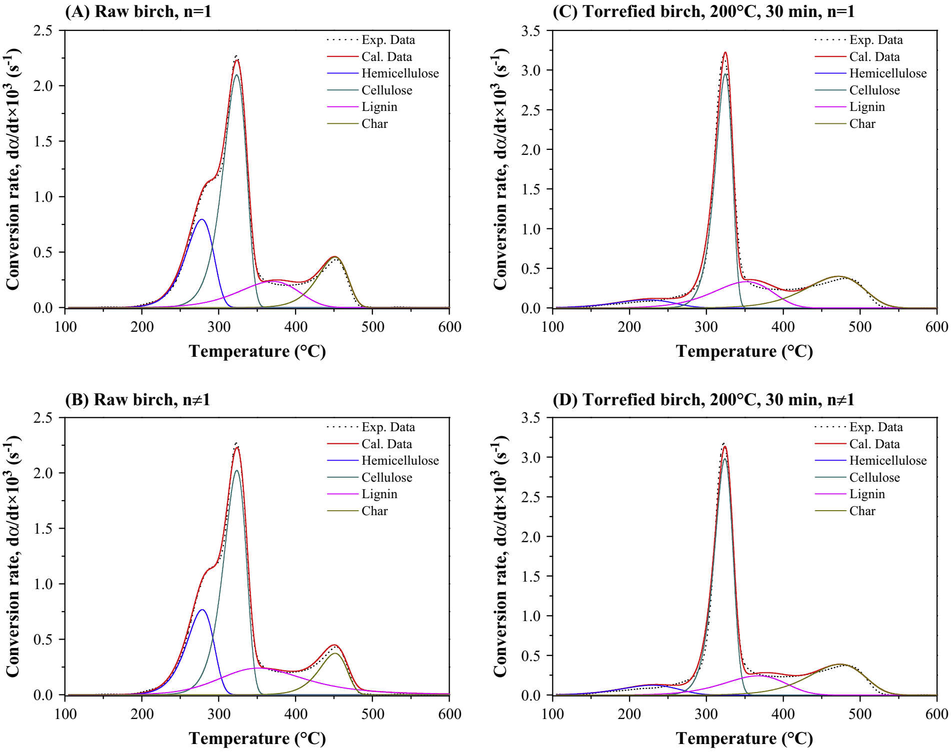

Fig. 6. Curve fitting for raw and torrefied birch fuels.

The higher cellulose fraction is, the higher devolatilization peak is observed. This helps confirm the suspicion and explain the inconsistent trend in the effects of WT temperature or holding time on the devolatilization peaks height as observed and discussed earlier in this paper.

The mass fraction of lignin varies in a narrow range (0.17–0.23 for torrefied spruce and 0.15–0.25 for torrefied birch) because the hydrothermal media within the WT conditions has little effects on the overall degradation of lignin [22]. On the other hand, the mass fraction of char is increased gradually (from 0.20 and 0.14 for raw spruce and birch to 0.40 and 0.34 for spruce and birch torrefied at 225 °C and 30 min, respectively) with torrefaction temperature and holding time.

4. Conclusions

The effects of WT on the reactivity and kinetics of woods under air combustion conditions were investigated using thermogravimetric method and kinetic modelling. Two types of woody biomass, Norway spruce and birch woods were used as feedstock. The following conclusions can be drawn from this study:

- WT pressure had insignificant effects on the combustion reactivity of the woods.
- WT temperature and holding time had similar effects on the combustion reactivity of the woods. Increasing either temperature or holding time make the woods more reactive in the devolatilization stage, but less reactive in the char combustion stage. However, too severe WT conditions (from 225 °C and 30 min) made the trends reversed due to the decomposition of cellulose in the devolatilization stage and the competition between catalyzing and inhibiting effects of char ash on the char combustion stage.

In addition, the kinetic analysis using the four-pseudo-component model with $n \neq 1$ showed that the activation energy of hemicellulose and char was reduced, but that of cellulose was increased by WT. The activation energy of hemicellulose was reduced from 103.8 to 44.8 kJ/mol for the spruce wood, and from 144.7 to 41.3 kJ/mol for the birch wood. That of char was from 183.1 to 109.4 kJ/mol for the spruce and from 222.0 to 132.3 kJ/mol for the birch. The activation energy of the cellulose was increased from 221.5 to 239.0 kJ/mol for the spruce, and from 204.7 to 236.7 kJ/mol for the birch. The mass fraction of hemicellulose was reduced by WT (from 0.15 to 0.05 for the spruce and from 0.23 to 0.06 for the birch), but that for char was increased gradually (0.20–0.40 for spruce and 0.14–0.34 for birch).

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Paper III

Effects of wet torrefaction on pyrolysis of woody biomass fuels

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Abstract: The pyrolysis of Norway spruce and birch woods under nitrogen atmosphere was studied by means of a thermogravimetric analyzer operated in the non-isothermal mode, followed by a kinetic analysis employing a three-pseudo-component model with nth-order reactions. Raw woods and the woods treated via wet torrefaction in the conditions of various temperatures (175, 200, 225 °C) and holding times (10, 30, 60 min) were included in this work. The study showed that wet torrefaction resulted in higher pyrolysis peaks for the woods, but less mass of volatiles was released during pyrolysis. The effects of wet torrefaction on pyrolysis of the lignocellulosic components are different. The activation energy of hemicellulose was significantly reduced by wet torrefaction. However, those for cellulose and lignin were slightly increased by wet torrefaction. In addition, a kinetic evaluation with assumption of common parameters was performed. The results confirmed that some kinetic parameters can be assumed to be common for pyrolysis kinetic modelling of different biomasses without substantial reductions in the fit quality. Wet torrefaction has positive effects on the possibilities for biomass pyrolysis kinetic modeling with assumption of common parameters.

Highlights

- Torrefaction temperature and holding time significantly influence the pyrolysis reactivity and kinetics of woody biomass.
- Mass fraction and activation energy of hemicellulose are significantly reduced by wet torrefaction.
- Activation energies for cellulose and lignin are slightly increased by wet torrefaction.
- Some kinetic parameters could be assumed common without substantial reductions in the fit quality.

Effects of Wet Torrefaction on Pyrolysis of Woody Biomass Fuels

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Abstract

The pyrolysis of Norway spruce and birch woods under nitrogen atmosphere was studied by means of a thermogravimetric analyzer operated in the non-isothermal mode, followed by a kinetic analysis employing a three-pseudo-component model with n^{th}-order reactions. Raw woods and the woods treated via wet torrefaction in the conditions of various temperatures (175, 200, 225 °C) and holding times (10, 30, 60 min) were included in this work. The study showed that wet torrefaction resulted in higher pyrolysis peaks for the woods, but less mass of volatiles was released during pyrolysis. The effects of wet torrefaction on pyrolysis of the lignocellulosic components are different. The activation energy of hemicellulose was significantly reduced by wet torrefaction. However, those for cellulose and lignin were slightly increased by wet torrefaction.

In addition, a kinetic evaluation with assumption of common parameters was performed. The results confirmed that some kinetic parameters can be assumed to be common for pyrolysis kinetic modelling of different biomasses without substantial reductions in the fit quality. Wet torrefaction has positive effects on the possibilities for biomass pyrolysis kinetic modeling with assumption of common parameters.

Keywords: Wet torrefaction, Biomass fuel, Hydrochar, Pyrolysis kinetics, Kinetic modelling

1 Introduction

Wet torrefaction (WT) is a promising method for biomass pretreatment and production of advanced solid biofuels. It may be defined as processing of lignocellulosic materials in hydrothermal media (HM) or hot compressed water (HCW) at temperatures between 180-260 °C [1-6]. The main product of the WT is "*hydrochar*" (hydrothermal biochar), a hydrophobic solid fuel with much better grindability, lower moisture content and higher calorific value compared with the untreated biomass [1-6]. In addition to hydrochar, WT also produces various water-soluble byproducts including acetic acid, formic acid, lactic acid, glycolic acid, levulinic acid, phenol, furfural, hydroxymethylfurfural (HMF), and sugars, which account altogether for approximately 10 wt% of the dry feedstock [4-6]. Separation and utilization of these organic fractions may contribute to an economic improvement of the WT process at industrial scales.

Recently, a study on WT of biomass for energy applications has been reported by our research group [1]. The study also included a comparison with dry torrefaction (DT), which may be defined as mild pyrolysis of biomass within the temperature range of 200-300 °C [7-9]. The results showed that WT can produce solid fuels with greater heating values, higher energy yields, and better hydrophobicity at significantly lower temperatures and shorter holding times than DT. In addition, WT is capable of removing parts of the ash components and hence produces cleaner solid fuels, with respect to inorganic elements.

At present, combustion is the most important energy application of solid biomass fuel, considering its contribution to more than 90% of the global bioenergy deployment [10-14]. Pyrolysis (devolatilization) is the first step, after drying, in the combustion process of solid biomass fuel. In addition, pyrolysis can be used as a standalone process for further treatments of biomass fuels [15]. Therefore, it is important to understand the thermal behavior and kinetics of biomass pyrolysis for the design, modification or optimization of the thermal conversion units. For these reasons, past research in the field was very active. For example, Broström et al. [16] employed a multi pseudo-component kinetic model to study effect of DT on the pyrolysis of Norway spruce. The model described closely the actual pyrolysis, assuming first order reactions. Later, Tapasvi et al. [17] established an even more detailed and more complex model, mainly based on the distributed activation energy model (DAEM), to describe better the pyrolysis and combustion kinetics of biomass. On the other hand, Manyà et al. [18] and Conesa and Domene [19] found that the pseudo-component kinetic model with n^{th} order described the biomass pyrolysis kinetics better than the model with first order reactions. More recently, a comparative kinetic evaluation on pyrolysis of dry-torrefied stump biomass has been reported [20]. The results showed the differences in fit quality of the three-pseudo-component model with first order, the three-pseudo-component model with n^{th} order, and DAEM were insignificant. In addition, the three-pseudo-component model with n^{th} order was recommended for a pyrolysis kinetic study of solid biomass fuel.

Despite the advantages of WT over DT and the importance of understanding the thermal behavior and kinetics of biomass pyrolyis, only few studies on WT [1-6] can be found in the literature, of which the focus was on the effects of process parameters on the yield and fuel properties of the solid product. To our knowledge, there is no open literature available for pyrolysis of hydrochar, except for the one reported by Yan et al. [21]. In that study, the pyrolysis of solid obtained from HTC of loblolly pine was thermogravimetrically analyzed and compared with that of the untreated pine. Two simple kinetic models, Kissinger's and Ozawa’s methods, were employed for a kinetic study of the pyrolysis. However, the kinetic information obtained by these methods is limited and does not closely represent the reality, considering the complexity in the chemical composition of lignocellulosic biomass materials. It is therefore crucial for WT technology to carry out more relevant studies on thermal behavior and kinetics of hydrochar pyrolysis.

In addition, Trninić et al. [22] indicated that, in kinetic modelling for thermal decomposition of biomass, it is possible to have common kinetic parameters for various types of lignocellulosic biomass fuels, considering the similarities and differences between the fuels. Also, Tapasvi et al. [17] suggested that if some of the kinetic parameters are assumed to be common, the following benefits can be achieved: (1) the common parameters indicate the similarities in the kinetic behavior of different samples; (2) a given parameter value is based on more experimental data, it is therefore less dependent on the experiment uncertainties. For this purpose, a first approximation of similarities for lignocellulosic biomass materials can be made based on the fact that their main organic components are hemicellulose, cellulose, and lignin [17, 22]. If the approximation is good enough, then only the contribution factors for the pseudo-components need to be varied from biomass to biomass.

In this present work, the pyrolysis kinetics of hydrochars produced from woods via WT in different conditions was studied by means of thermogravimetric analysis (TGA) and compared with the untreated materials. The three-pseudo-component model with n^{th} order was adopted for the kinetic analysis, including a kinetic evaluation for different model variants by assuming common parameters.

2 Materials and methods

2.1 *Materials*

The raw and torrefied woods used in this work were obtained from our previous work [1]. A brief description of the materials preparation is given here. Norway spruce and birch wood cubes with sides of 1 cm were used as feedstock. The dry feedstock and distilled water (with a ratio of 1:5 by weight) were placed in a 250 ml Parr reactor series 4650 (Parr Instrument, USA) for WT at a constant pressure of 70 bar but different temperatures (175, 200, 225 °C) and holding times (10, 30, 60 min). After WT, the wet solid products were dried in an oven at 105 °C for 48 h and then stored in a desiccator for further analyses. The proximate and ultimate analyses of the raw and wet torrefied samples used for the TGA in this work are listed in Table 1. The higher heating values (HHVs) were calculated on dry and ash free basis, according to Channiwala and Parikh [23].

2.2 *Thermogravimetric experiments*

TGA is a proven method for studying the pyrolysis of biomass [24-27]. In the present work, a Mettler Toledo TGA/SDTA851e was employed and operated in a non-isothermal mode. The fuel samples were first ground by an IKA MF 10 cutting mill, and particles less than 125 μm (sieved by a Fritsch Analysette 3 Pro vibrator) were collected for the pyrolysis/devolatilization study to ensure that the experiments were in the kinetic control regime [28-30]. A sample of 2 mg was put in a 150 µl alumina pan for the TGA in a Mettler Toledo TGA/SDTA851e reactor. It should be noted that the buoyancy effect plays a significant role for such a small sample weight. Therefore, running a blank curve is mandatory, and the weight change of the blank experiment was subtracted from the experimental curves automatically. The experiment started from room temperature, the fuel sample was heated to 105 °C and held at this temperature for 1 h for drying. Thereafter, the sample was heated up to 700 °C at a constant heating rate of 10 °C per minute. A nitrogen flow rate of 100 ml/min was applied for all experiments.

2.3 Kinetic modeling

In this study, a global kinetic model with three parallel reactions adopted from Branca et al. [28] was employed for modelling pyrolysis kinetics. One advantage of this model is that it does not require testing the fuel at different heating rates. It is because the heating rate within the range from 3 to 108 °C/min does not affect the activation energy, pre-exponential factor and reaction order. Moreover, the model can well describe the separate decompositions of the three main components of lignocellulosic biomass including hemicellulose, cellulose, and lignin [16-19, 28, 31, 32]. The three independent parallel reactions used in this work are shown below:

$$A_v \longrightarrow V_1 \qquad (1)$$

$$B_v \longrightarrow V_2 \qquad (2)$$

$$C_v \longrightarrow V_3 \qquad (3)$$

where A_v, B_v, and C_v are the pseudo-components; and V_i (i = 1, 2, 3) is the total volatiles released from the pyrolysis of the respective pseudo-component.

The conversion rates of all reactions follow the Arrhenius expression:

$$\frac{d\alpha_i}{dt} = A_i \exp\left(-\frac{E_i}{RT}\right)(1-\alpha_i)^{n_i}, \;\; i = 1, 2, 3 \qquad (4)$$

where A is the pre-exponential factor, E is the activation energy of the reaction, R is the universal gas constant, T is the absolute temperature, n is the reaction order, and i is for the i^{th} pseudo-component. The conversion degree (α) is defined as the mass fraction of decomposed solid or released volatiles:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} = \frac{v}{v_f} \qquad (5)$$

where m_0 and m_f are the initial and final masses of solid, m is the mass of solid at any time; v_f is the total mass of released volatiles and v is the mass of released volatiles at a given time.

The overall conversion rate is the sum of the partial conversion rates, where c_i indicates the contribution factor or the volatile fraction produced from each component in the following equation:

$$\frac{d\alpha}{dt} = \sum_{i=1}^{3} c_i \frac{d\alpha_i}{dt} \qquad (6)$$

Curves fitting were based on the non-linear least squares method, in which the objective function to be minimized is:

$$S = \sum_{j=1}^{N} \left[\left(\frac{d\alpha_j}{dt} \right)_{exp} - \left(\frac{d\alpha_j}{dt} \right)_{cal} \right]^2 \qquad (7)$$

where $\left(\frac{d\alpha_j}{dt}\right)_{exp}$ and $\left(\frac{d\alpha_j}{dt}\right)_{cal}$ represent the experimental and calculated conversion rates, respectively, and N is the number of experimental points. The fit between measured and simulated values is defined as:

$$Fit\ (\%) = \left(1 - \frac{\sqrt{\frac{S}{N}}}{\left[\left(\frac{d\alpha_j}{dt} \right)_{exp} \right]_{max}} \right) .100\% \qquad (8)$$

The curve fitting process was run until a best fit between the simulated data and the experimental results was obtained. Then, kinetic parameters can be extracted, including: the activation energies (E_1, E_2, E_3), the pre-exponential factors (A_1, A_2, A_3), the contribution factors

(c_1, c_3, c_3), and the reaction orders (n_1, n_2, n_3). Conventionally, the names of pseudo-component 1, 2, and 3 are assigned to hemicellulose, cellulose and lignin, respectively.

3 Results and discussion

3.1 Thermal decomposition behavior of spruce and birch woods

Figure 1 shows the TG and DTG curves, respectively representing the mass loss and the conversion rate of the raw spruce and birch woods in the temperature range of 100-600 °C. The TG curves indicate that both woods started decomposing at around 200 °C and most of the mass losses were taking place within 200-380 °C. The mass losses were more significant for birch wood than for spruce. This difference can be attributed to the difference in the volatile matter content of birch and spruce, as presented in Table 1.

The DTG curves give additional information about the pyrolysis of the woods. Indeed, they show that the decomposition of both feedstocks actually started at around 180 °C and became significant from 200 °C. At temperatures higher than 400 °C the decompositions were less significant. More importantly, the DTG curves reveal locations of the decomposition rate peaks, which were at about 362 °C for spruce and 364 °C for birch. It appears that the peak locations of the woods were very close to each other, but the peak heights were different. The height for the birch (1.75×10^{-3} s^{-1}) was higher than that for the spruce (1.55×10^{-3} s^{-1}). In addition, a clear shoulder was observed for the DTG curve of the raw birch, but not for the raw spruce. This difference is due to the fact that birch (hardwood) has higher hemicelluloses contents than spruce (softwood) [33].

3.2 Effects of wet torrefaction on pyrolysis of spruce and birch woods

3.2.1 The effect of torrefaction temperature

Figure 2 presents the DTG curves for spruce and birch wood torrefied at different temperatures (175, 200, and 225 °C) under the common conditions of 30 min and 70 bar. The curves for the untreated woods are also included in the figures for comparison. The figures show that the torrefied woods started decomposing at temperatures, around 150 °C, i.e. lower than those for the raw woods (around 180 °C), and with slightly higher conversion rates. The higher reactivity of the torrefied woods, compared to the raw woods, in the early stage of the decomposition may be due to the presence of a small amount of remaining organic compounds, with low molecular weights and thus high reactivity, produced from the degradation of hemicellulose during the WT process [34, 35].

At temperatures from 250 °C up to 350 °C, the torrefied woods were less reactive than the raw woods. This is due to the fact that within this temperature window the degradation of hemicellulose is the most dominant compared to other components, and the torrefied woods have less or no hemicellulose compared with the original feedstock [2]. On the other hand, the DTG peak locations were slightly affected by WT. For the birch, the DTG peak locations were slightly shifted towards higher temperatures, indicating an increase in the activation energy. However, an unclear trend was observed for the spruce. Similar observations can be noted for the DTG peak heights. Indeed, when increasing the torrefaction temperature from 175 °C to 200 °C, the peak height increased (from 1.90×10^{-3} s^{-1} to 2.04×10^{-3} s^{-1} for spruce and from 2.20×10^{-3} s^{-1} to 2.43×10^{-3} s^{-1} for birch). However, further increasing the torrefaction temperature to 225 °C decreased the peak height. The peak height for spruce torrefied at 225 °C was even lower than that for the raw spruce. This observation will be discussed further in combination with a kinetic analysis.

3.2.2 The effect of torrefaction time

The effects of torrefaction time on pyrolysis of the woods are presented in Figure 3, which includes DTG data for the woods torrefied for 10, 30 and 60 min under the common conditions of 200 °C and 70 bar, and the raw woods. It can be seen from the figures that the effect of holding time was more pronounced for the birch wood (Figure 3B) than for the spruce wood (Figure 3A). The trends in shifting the DTG peak location and height by torrefaction time were similar to those by torrefaction temperature. When torrefaction time was increased from 10 to 30 min, the peak height of torrefied spruce and birch increased. Further increased torrefaction time to 60 min resulted in almost no further change for the birch, but caused a decrease for the spruce, with respect to the peak height. However, the peak height for the spruce torrefied for 60 min was still higher than that of the raw spruce (not the case for the effect of torrefaction temperature, Figure 2B). This observation will also be discussed later in combination with a kinetic analysis.

3.3 Kinetic evaluation by assuming three-pseudo-component model with n^{th}-order

A kinetic analysis employing the three-pseudo-component model with n^{th}-order was performed for a quantitative evaluation of the effects of WT on the pyrolysis reactivity of wood. In total, 12 experimental data sets were analyzed kinetically, of which 6 were for the spruce wood and 6 for the birch wood. The kinetic data extracted from this analysis are presented in Table 2 and Table 3 for the spruce and birch, respectively. The quality of the fit between the experimental and predicted data is also included in the tables. In addition, for a graphical demonstration of the fit quality, curves fittings for the raw woods and the woods torrefied at 200 °C for 30 min (at 70 bar) are presented in Figure 4 and Figure 5, respectively. In these figures, the actual conversion rates from the experiments are represented by the black dotted curves. The red solid curves denote the predicted rates. The other three curves are presenting the conversion rates of the three main components of wood (hemicellulose, cellulose, and lignin). The figures show good fits between the experimental and modelled results. The fit quality numerically presented in Table 2 and Table 3 is within 98-99% in all cases. In addition, most of the calculated *n* values are close to 1.

It can be seen that both the activation energy and pre-exponential factor of hemicellulose are reduced dramatically by WT. The activation energy of hemicellulose decreases respectively from 95.67 to 26.63 kJ/mol and from 106.80 to 34.18 kJ/mol for the spruce and birch; and pre-exponential factor decreases respectively from 1.63×10^{6} s^{-1} to 1.60 s^{-1} and from 3.34×10^{7} s^{-1} to 1.98×10^{1} s^{-1} for the spruce and birch, by WT at 225 °C (and 70 bar) for 30 min. This effect can also be observed from the hemicellulose curves in Figure 4 and Figure 5, which show clearly that WT caused a shift of the hemicellulose curves to a lower temperature range. This is in agreement with the literature [36] and can be explained by the decomposition and cracking of hemicellulose into smaller molecules [34, 35], which remained in the solid products.

In contrast to hemicellulose, the activation energy and pre-exponential of cellulose is increased by WT. It can be seen from the tables that the average activation energy values of cellulose for the torrefied spruce and birch are respectively 194.54 ± 0.76 kJ/mol and 193.17 ± 0.75 kJ/mol. In addition, the pre-exponential factors of cellulose vary in a very narrow range of $6.87\text{-}6.92\times10^{13}$ s^{-1} for both torrefied spruce and birch, compared to the values of 188.27 kJ/mol and 2.56×10^{13} s^{-1} for raw spruce and 189.47 kJ/mol and 3.17×10^{13} s^{-1} for raw birch. This is presumably due to the increased crystallinity of cellulose caused by hydrothermal treatment [37-39]. It is reported that crystalline cellulose has higher activation energy during thermal degradation than non-crystalline cellulose due to increased cross-linking [40].

The effects of WT temperature and holding time on the activation energy and pre-exponential of lignin are not clear, although these values are increased by WT. In detail, the activation energy is increased respectively from 40.22 kJ/mol and 38.95 kJ/mol for the raw spruce and birch to an average value of 48.09 ± 0.58 kJ/mol and 40.69 ± 0.71 kJ/mol for the torrefied spruce and birch, respectively. In addition, the pre-exponential factor of lignin is increased from 2.05 s^{-1} for raw spruce to 1.06-1.11×10^1 s^{-1} for torrefied spruce, and from 1.26 s^{-1} for raw birch to 4.23-4.28 s^{-1} for torrefied birch. Similar observations were described by Biwas et al. [36], who reported that the thermal reactivity of woody lignin may either increase or decrease due to hydrothermal pretreatment, depending on the severity of the pretreatment conditions which may result in condensation and re-polymerization reactions.

The contribution factor of hemicellulose is reduced by WT. In addition, the reduction is decreased gradually with increasing WT severity, from 0.29 for the raw spruce to 0.05 for the spruce torrefied at 225 °C and 30 min; and from 0.36 for the raw birch to 0.03 for the birch torrefied at 225 °C and 30 min. From the conditions of 200 °C and 30 min to more severe conditions (higher temperatures or longer holding times), the hemicellulose mass fraction of the torrefied fuel is small, less than 15% of the total mass. With the reduction of hemicellulose fraction, the mass fraction of the other component fractions in the torrefied biomass fuels (cellulose, lignin, and char) are increased proportionately compared with the raw materials, as presented in Table 2 and Table 3.

The contribution factor of cellulose in the torrefied fuels from both feedstocks increased to a maximum value, 0.53 for spruce torrefied at 200 °C, 60 min and 0.62 for birch torrefied at 200 °C, 30 min, and then decreased with either increasing temperature or holding time. The contribution of cellulose fractions is in good agreement with the heights of the pyrolysis peaks shown in Figure 2 and Figure 3. The higher the cellulose fraction is, the higher pyrolysis peak is observed. This explain the inconsistent trend in the effects of WT temperature or holding time on the pyrolysis peaks height as observed and discussed earlier in this paper.

The contribution factor of spruce lignin is almost unchanged (0.16 to 0.15) when torrefaction temperature is increased from 175 to 200 °C, but then it is increased from 0.15 to 0.27 when the torrefaction temperature is increased from 200 to 225 °C. In addition, the factor is increased from 0.12 to 0.18 when holding time is prolonged from 10 to 60 min. On the other hand, when torrefaction temperature is increased (from 175 to 225 °C), contribution factor of birch lignin is increased (from 0.11 to 0.32). However, the effect of holding time on the contribution factor of birch lignin is not clear, e.g. it decreases from 0.29 to 0.19 when holding time is increased from 10 to 30 min but then it increased to 0.35 when holding time was further increased to 60 min. The variation in the observed contribution factors may be due to various reasons, which include the condensation or re-polymerization between decomposition products of hemicellulose and lignin [36], the increasing fraction of acid soluble lignin [41], or the softening, melting and carbonization of lignin [42].

Moreover, it should be noted that the sum of the contribution factors is not equal to 1 because these factors indicate the mass fraction of the volatiles released from the dry biomass components (hemicellulose, cellulose and lignin), i.e. the solid residue is accounting for the difference [26, 43]. It can be seen that the sum of c values of woods are gradually reduced with increasing the WT severity. The decreasing trend of the sum of c values is similar to that of the volatile matter in the proximate analyses. Moreover, the sum of c values are only 1.2-3.6% lower than the volatiles fraction presented in Table 1, showing good agreement in volatile content between the proximate analysis and the values calculated from the modeling results.

3.4 *Evaluation with assumption of common parameters*

As discussed earlier in the introduction, an evaluation with assumption of common kinetic parameters was attempted and reported in this section to identify possibilities for describing the thermal decomposition of different biomass materials by a common model. For this purpose, data collected from the TG experiments for the raw woods were evaluated first. A similar evaluation was then performed for the woods torrefied under the same conditions (200 °C, 30 min and 70 bar). The evaluation identifications and results are presented in Table 4 and Table 5 for the original and torrefied woods, respectively. In these tables, the kinetic analysis presented in the preceding section (3.3) was employed to serve as the base case (Evaluation 1, Model Variant *III*), for which none of the kinetic parameters was assumed common.

Let us now examine the component curves of the base case, presented in Figure 4A and Figure 5A for the native woods. It is observed that the pink curves of the third pseudo-component (lignin) are wide and flat compared to those of cellulose and hemicellulose, the second and first pseudo-components. A major part of the pink curves overlaps with the temperature domains of the curves for the second and first pseudo-components. A change of the pink curves in these domains can be compensated by relatively small changes by pseudo-components 1 and 2 without significant worsening of the overall fit quality. Accordingly, the kinetic parameters for lignin (activation energy E_3 and pre-exponential factor A_3) of both native woods can be forced to be identical in value [17] and were assumed common in Evaluation 2 (Table 4).

It can also be observed from Table 2 and Table 3 that the kinetic parameters of cellulose (E_2 and A_2) for both native woods are similar. Consequently, these parameters could also be forced to have common values [17] in Evaluation 3 (Table 4). Finally, all of the kinetic parameters for the three pseudo-components, including the activation energy values (E_1, E_2 and E_3) and pre-exponential factors (A_1, A_2 and A_3), were assumed common [17] in Evaluation 4 (Table 4).

For the torrefied woods (Table 5) evaluations similar to those for the native woods (Table 4) were postulated and performed to serve the comparison purpose of this work. In addition, as can see in Figure 4B and Figure 5B, the component (blue) curves for hemicellulose appear flat. Therefore, Evaluation 5 with assumption of E_1 and A_1 as common parameters was performed for the torrefied woods and included in Table 5.

In addition to Model Variant *III*, the evaluations were also tested for two other model variants (Variant *II* and Variant *I*) formulated by partially giving the value of one to the reaction order of i^{th} pseudo-component (n_i). It is because of the fact that while some believe the decomposition during pyrolysis of biomass can be described by first reaction order ($n_i = 1$) [17,27-29], others reported that reaction orders higher than one gave better description for the pseudo-components of biomass [17-19]. Partially fixing the value of n_i to one would bring about model variants, which may produce better fits and thus more closely describe the biomass pyrolysis. Indeed, it is observed from Table 2 and Table 3 that, in most of the cases, n_2 is close to one, but n_3 is far from 1. In addition, n_1 varies within the range of 1.01 - 1.49. On the basis of these observations and information from the literature [17, 22], three model variants were selected for the evaluations and presented in Table 4 and Table 5. Variant *III* is actually from the base case, n^{th}-order, for which none of the component reaction orders was fixed to one ($n_i \neq 1$; and $i = 1, 2, 3$). Variant *II* is different from Variant *III* by fixing n_2 to one ($n_1 \neq 1$, $n_2 = 1$, $n_3 \neq 1$). Finally, Variant *I* has two common reaction orders of unity ($n_1 = 1$, $n_2 = 1$, $n_3 \neq 1$).

Results from all of the evaluations with assumptions of common parameters for different model variants are tabulated in Table 4 and Table 5 for the raw and torrefied woods, respectively. The higher value the fit quality is, the better the model variant represents the biomass decomposition. In addition, the curve fitting of Evaluations 1, 3 and 4 (Variant *III*) for the untreated and torrefied woods is presented respectively in Figure 6 and Figure 7 for a graphical demonstration of the fit quality.

As can be seen from the tables, the trends of changes in fit quality for both of the untreated and torrefied woods are similar, inversely proportional to the number common parameters assumed. These trends are mathematically obvious and in agreement with the literature [17, 22]. Indeed, the fit quality reduces consistently when moving from Evaluation 1 downward to Evaluation 4, for each of the model variants. Similarly, the reduction trend in fit quality is observed for each of the evaluations, when moving from Variant *III* toward Variant *I*.

For the untreated woods (Table 4) the fit qualities of the base case (Evaluation 1, Variant *III*) are 99.25% and 99.21% for spruce and birch, respectively. Further examination of the data in two columns of Variant *III*, one for spruce and one for birch, from the top to the bottom give the information that the fit qualities in Evaluation 2 slightly reduce to 99.24% and 99.14% for spruce and birch, respectively. These insignificant reductions in fit quality confirm that the assumptions of Evaluation 2 are reasonable. Similar observations and confirmations are also noted for both woods in Evaluation 3. However, the fit quality in Evaluation 4 reduces significantly to 94.60% and 96.85% for spruce and birch, respectively. This suggests that the assumptions of Evaluation 4 for the untreated woods are not reasonable.

In addition, analyses similar to those applied for different evaluations in one column as above can also be applied for assessment of different model variants in each of the evaluation rows, by examining the data from the right to the left or from Variant *III* to Variant *I*. As the results of the overall assessment, by column and by row throughout the table, all the cases with insignificant reductions in fit quality are summarized by highlighting with red and blue colors for the native spruce and birch, respectively, in Table 4. Furthermore, all of the analyses presented above for the untreated woods can also be applied for the torrefied woods, Table 5, from which the results are also highlighted in the same way by the same colors for comparison.

Table 4 and Table 5 show that, although the effects of WT on the fit quality in the first three evaluations are varied being somewhat positive or negative, the variations are insignificant. However, the effects become clear and significant for Evaluation 4, in which all of the kinetic parameters are forced to be common. These improvements in fit quality of Evaluation 4 are presumably due to the normalization of the fuels with particular respect to component 1, considering the very high fit quality obtained from Evaluation 5 (Table 5) in which E_1 and A_1 are forced common.

Overall, the data in Table 4 and Table 5 indicate that WT has positive effects on the possibilities for biomass pyrolysis kinetic modeling with assumption of common parameters. These can be attributed to the effect of WT on normalizing the composition of different biomasses, which is similar to carbonization.

4 Conclusions

The effects of WT on the thermal decomposition behavior and pyrolysis kinetics of spruce and birch woods were investigated by means of a thermogravimetric analyzer, followed by a kinetic analysis employing the three-pseudo-component model with n^{th}-order reactions. The torrefaction conditions were varied within three different temperatures (175, 200, 225 °C) and holding times (10, 30, 60 min). It appears that, in most of the cases, WT enhanced the pyrolysis peak height, but decreased the total volatiles released from the thermal decomposition. Too severe WT conditions (e.g. 225 °C and 30 min) resulted in decreased pyrolysis rate due to the accelerated decomposition of cellulose. The kinetic parameters of hemicellulose were gradually reduced by WT. The kinetic parameters of cellulose were all increased due to its crystallization in hydrothermal media. In addition, WT increases the activation energy and pre-exponential factor of lignin, although the effect trends of WT temperature and holding time are not clear.

In addition, a kinetic evaluation with assumption of common parameters was performed. The results confirmed that some kinetic parameters can be assumed to be common for pyrolysis kinetic modelling of different raw biomasses without substantial reductions in the fit quality. WT has positive effects on the possibilities for biomass pyrolysis kinetic modeling with assumption of common parameters.

5 Acknowledgement

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Table 1. Heating values, proximate and ultimate analyses of raw and torrefied woods

Sample		**Solid yield**^{a}	***Proximate analysis***			***Ultimate analysis***					**HHV**^{b}
			Ash^a	**VM**^{a}	**FC**^{a}	**C**^{a}	**H**^{a}	**N**^{a}	**O**^{a}	**S**^{a}	
Spruce	Raw	–	0.23	86.50	13.27	50.31	6.24	0.07	43.38	< 0.02	20.42
	175°C, 30min	88.27	0.11	85.72	14.17	51.34	6.18	0.07	42.42	< 0.02	20.81
	200°C, 10min	82.48	0.14	84.64	15.22	51.21	6.39	0.06	42.35	< 0.02	21.02
	200°C, 30min	78.45	0.12	83.92	15.95	52.55	6.15	0.06	41.23	< 0.02	21.33
	200°C, 60min	73.28	0.09	81.87	18.03	53.69	5.89	0.06	40.36	< 0.02	21.51
	225°C, 30min	69.74	0.14	74.74	25.12	56.99	5.87	0.07	37.07	< 0.02	22.97
Birch	Raw	–	0.28	89.46	10.26	48.94	6.35	0.11	44.60	< 0.02	19.94
	175°C, 30min	79.53	0.09	88.57	11.34	49.42	6.38	0.12	44.07	< 0.02	20.21
	200°C, 10min	66.42	0.08	87.97	11.94	49.61	6.16	0.13	44.10	< 0.02	20.01
	200°C, 30min	64.64	0.09	85.15	14.76	51.25	6.18	0.11	42.46	< 0.02	20.78
	200°C, 60min	63.06	0.10	82.64	17.27	51.34	5.94	0.13	42.59	< 0.02	20.51
	225°C, 30min	58.01	0.13	73.78	26.09	56.92	5.86	0.09	37.13	< 0.02	22.93

^{a} wt%, ^{b} MJ/kg

VM: volatile matter, **FC**: fixed carbon, **HHV**: higher heating value

Table 2. Pyrolysis kinetic data for spruce woods

Torrefaction condition		**Kinetics parameters**				**Fit** (%)
		E (kJ/mol)	***A*** (s^{-1})	***c***	***n***	
Raw spruce	H	95.67	1.63E+06	0.29	1.01	99.25
	C	188.27	2.56E+13	0.38	1.01	
	L	40.22	2.05E+00	0.19	3.70	
	Sum			**0.86**		
175°C, 30min	H	64.39	1.99E+03	0.21	1.03	98.98
	C	194.86	6.91E+13	0.47	1.03	
	L	47.85	1.06E+01	0.16	3.00	
	Sum			**0.85**		
200°C, 10min	H	37.09	4.95E+00	0.23	1.10	98.82
	C	194.85	6.90E+13	0.48	1.01	
	L	48.20	1.08E+01	0.12	1.96	
	Sum			**0.83**		
200°C, 30min	H	32.99	2.55E+00	0.15	1.21	99.23
	C	195.03	6.85E+13	0.51	1.01	
	L	48.53	1.11E+01	0.15	1.84	
	Sum			**0.81**		
200°C, 60min	H	30.24	1.05E+00	0.09	1.06	99.19
	C	194.76	6.92E+13	0.53	1.04	
	L	48.64	1.07E+01	0.18	1.64	
	Sum			**0.80**		
225°C, 30min	H	26.63	1.60E+00	0.05	1.01	99.12
	C	193.19	6.90E+13	0.40	1.05	
	L	47.22	1.06E+01	0.27	1.62	
	Sum			**0.72**		
H: hemicellulose, **C**: cellulose, **L**: lignin						

Table 3. Pyrolysis kinetic data for birch woods

Torrefaction condition		**Kinetics parameters**				**Fit** (%)
		E (kJ/mol)	***A*** (s^{-1})	***c***	***n***	
Raw birch	H	106.80	3.34E+07	0.36	1.55	99.21
	C	189.47	3.17E+13	0.44	1.01	
	L	38.95	1.26E+00	0.07	1.33	
	Sum			**0.87**		
175°C, 30min	H	56.06	6.06E+02	0.18	1.15	99.15
	C	194.00	6.87E+13	0.55	1.01	
	L	41.18	4.25E+00	0.11	1.18	
	Sum			**0.85**		
200°C, 10min	H	54.74	3.05E+03	0.06	1.49	98.52
	C	193.79	6.87E+13	0.50	1.01	
	L	39.79	4.31E+00	0.28	1.45	
	Sum			**0.84**		
200°C, 30min	H	38.61	2.67E+01	0.03	1.01	99.08
	C	192.67	6.92E+13	0.62	1.05	
	L	40.08	4.23E+00	0.19	2.10	
	Sum			**0.84**		
200°C, 60min	H	35.62	1.80E+01	0.03	1.11	98.34
	C	193.17	6.91E+13	0.42	1.03	
	L	41.40	4.27E+00	0.35	1.91	
	Sum			**0.80**		
225°C, 30min	H	34.18	1.98E+01	0.03	1.07	98.89
	C	192.22	6.92E+13	0.37	1.01	
	L	41.01	4.26E+00	0.32	1.84	
	Sum			**0.71**		

H: hemicellulose, **C**: cellulose, **L**: lignin

Table 4. Fit quality with assumption of common parameters for the native woods

Evaluation	**Common parameters**	**Fit quality, %**					
		Raw spruce			Raw birch		
		Variant *I*	**Variant *II***	**Variant *III***	**Variant *I***	**Variant *II***	**Variant *III***
		$n_1=1$ $n_2=1$ $n_3\neq1$	$n_1\neq1$ $n_2=1$ $n_3\neq1$	$n_1\neq1$ $n_2\neq1$ $n_3\neq1$	$n_1=1$ $n_2=1$ $n_3\neq1$	$n_1\neq1$ $n_2=1$ $n_3\neq1$	$n_1\neq1$ $n_2\neq1$ $n_3\neq1$
1	None	**99.24**	**99.24**	**99.25**	**98.97**	**99.20**	**99.21**
2	E_3 and A_3	**99.21**	**99.21**	**99.24**	**98.97**	**99.14**	**99.14**
3	E_2, E_3 and A_2, A_3	**98.44**	**98.89**	**98.89**	**98.50**	**98.89**	**98.90**
4	E_1, E_2, E_3 and A_1, A_2, A_3	93.17	94.61	94.60	95.61	96.85	96.85

Table 5. Fit quality with assumption of common parameters for the woods torrefied at 200 °C for 30 min.

Evaluation	**Common parameters**	**Fit quality, %**					
		Torrefied spruce			Torrefied birch		
		Variant *I*	**Variant *II***	**Variant *III***	**Variant *I***	**Variant *II***	**Variant *III***
		$n_1=1$ $n_2=1$ $n_3\neq1$	$n_1\neq1$ $n_2=1$ $n_3\neq1$	$n_1\neq1$ $n_2\neq1$ $n_3\neq1$	$n_1=1$ $n_2=1$ $n_3\neq1$	$n_1\neq1$ $n_2=1$ $n_3\neq1$	$n_1\neq1$ $n_2\neq1$ $n_3\neq1$
1	None	**99.22**	**99.22**	**99.23**	**99.30**	**99.30**	**99.32**
2	E_3 and A_3	**98.79**	**98.86**	**99.07**	**99.20**	**99.20**	**99.28**
3	E_2, E_3 and A_2, A_3	**97.08**	**97.08**	**97.71**	**98.06**	**98.95**	**98.96**
4	E_1, E_2, E_3 and A_1, A_2, A_3	96.51	96.51	**97.71**	96.98	96.99	**97.04**
5	E_1 and A_1	**99.07**	**99.21**	**99.21**	**99.29**	**99.29**	**99.31**

Figure 1. Thermogravimetric analysis for pyrolysis of the untreated spruce and birch woods

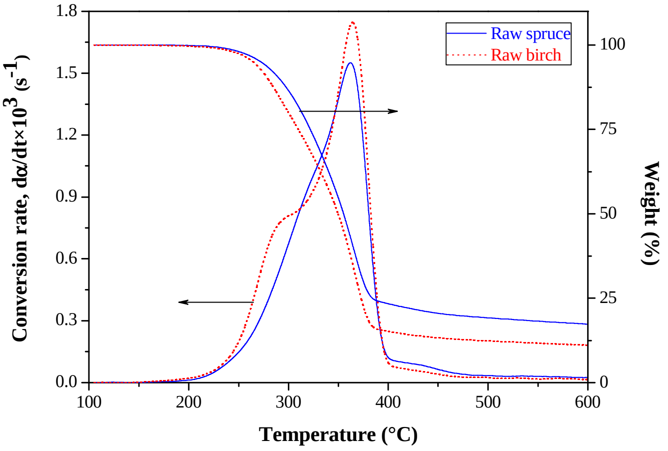


Figure 2. DTG data for (A) the native spruce and (B) the birch wood torrefied at different temperatures (175, 200, or 225 °C), and common conditions: time = 30 min, pressure = 70 bar

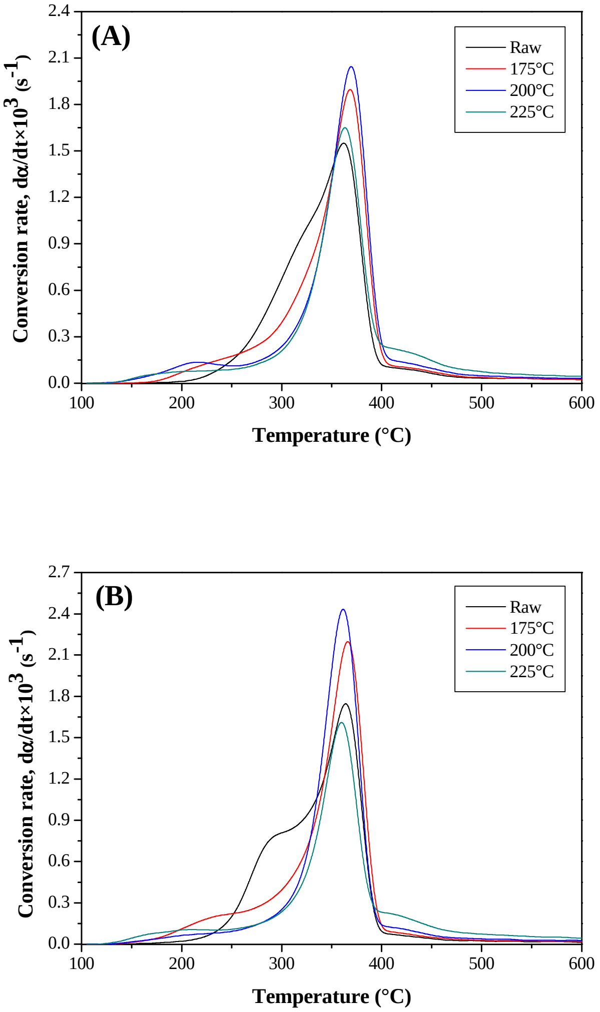


Figure 3. DTG data for (A) the native spruce and (B) the birch torrefied for different time (10, 30, or 60 min), in common conditions: temperature = 200 °C, pressure = 70 bar

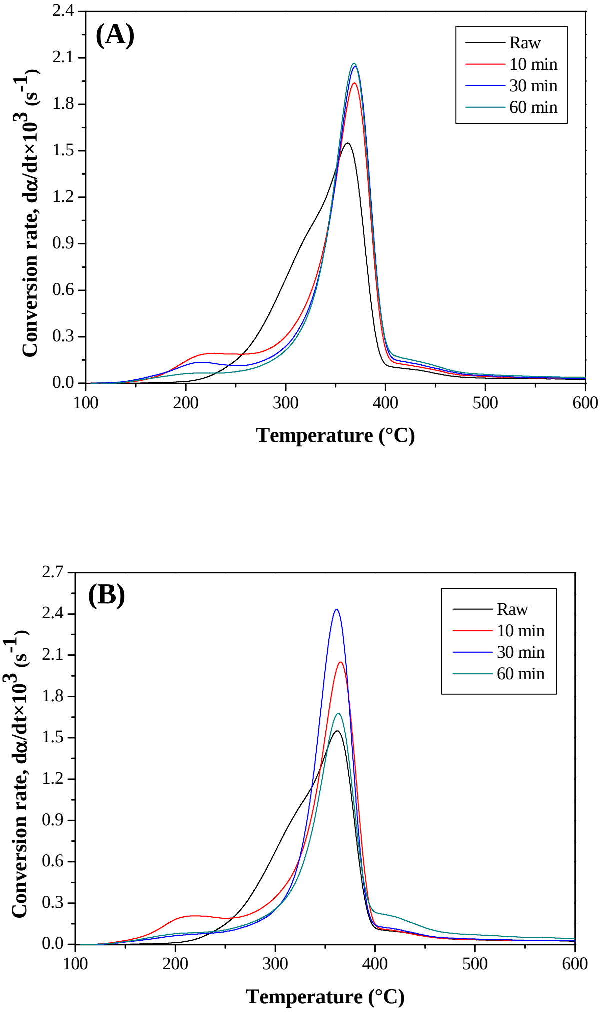


Figure 4. Curve fitting for (A) the untreated spruce and (B) the spruce torrefied at 200 °C and 30 min

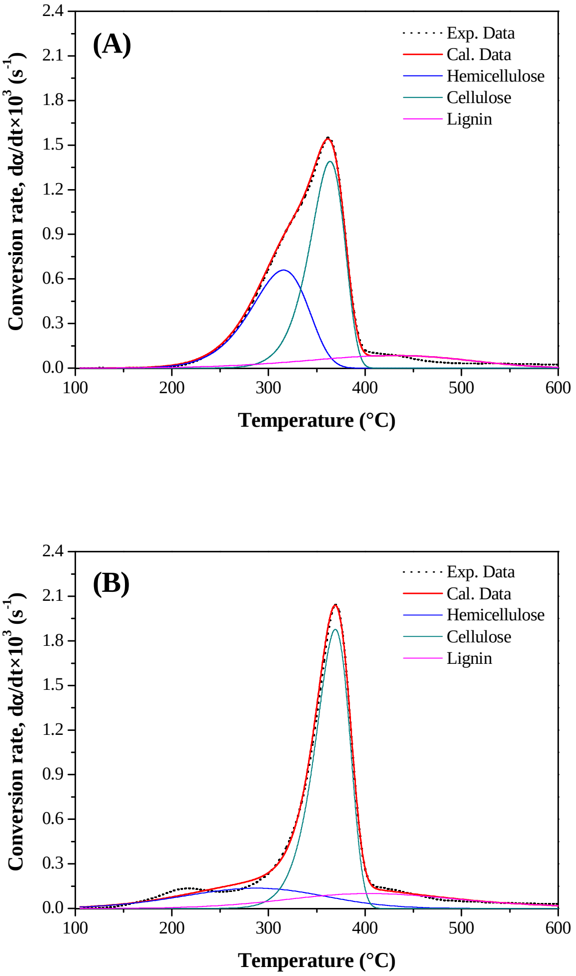


Figure 5. Curve fitting for (A) the untreated birch and (B) the birch torrefied at 200 °C and 30 min

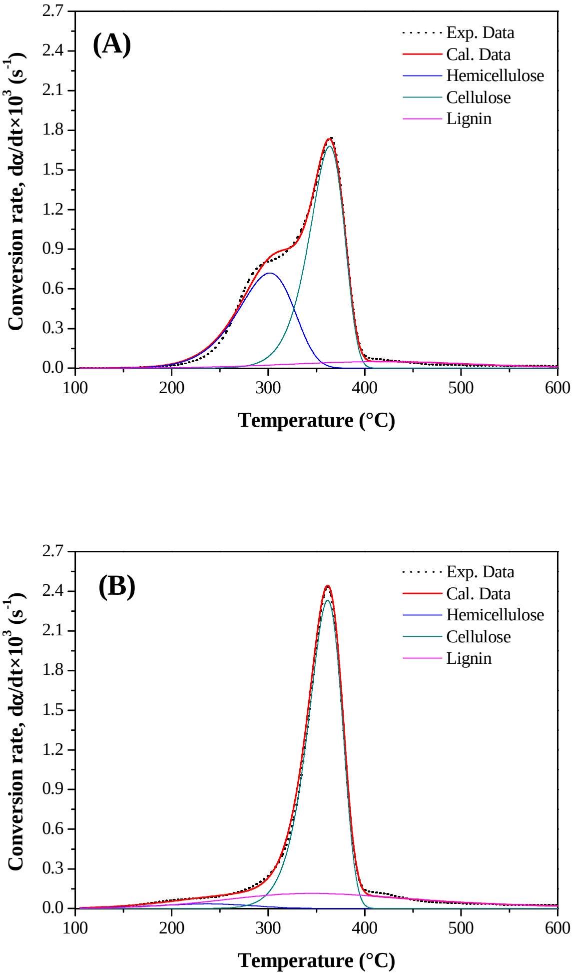


Figure 6. Curve fitting for the untreated woods by Evaluation 1, 3, and 4 of Variant *III*

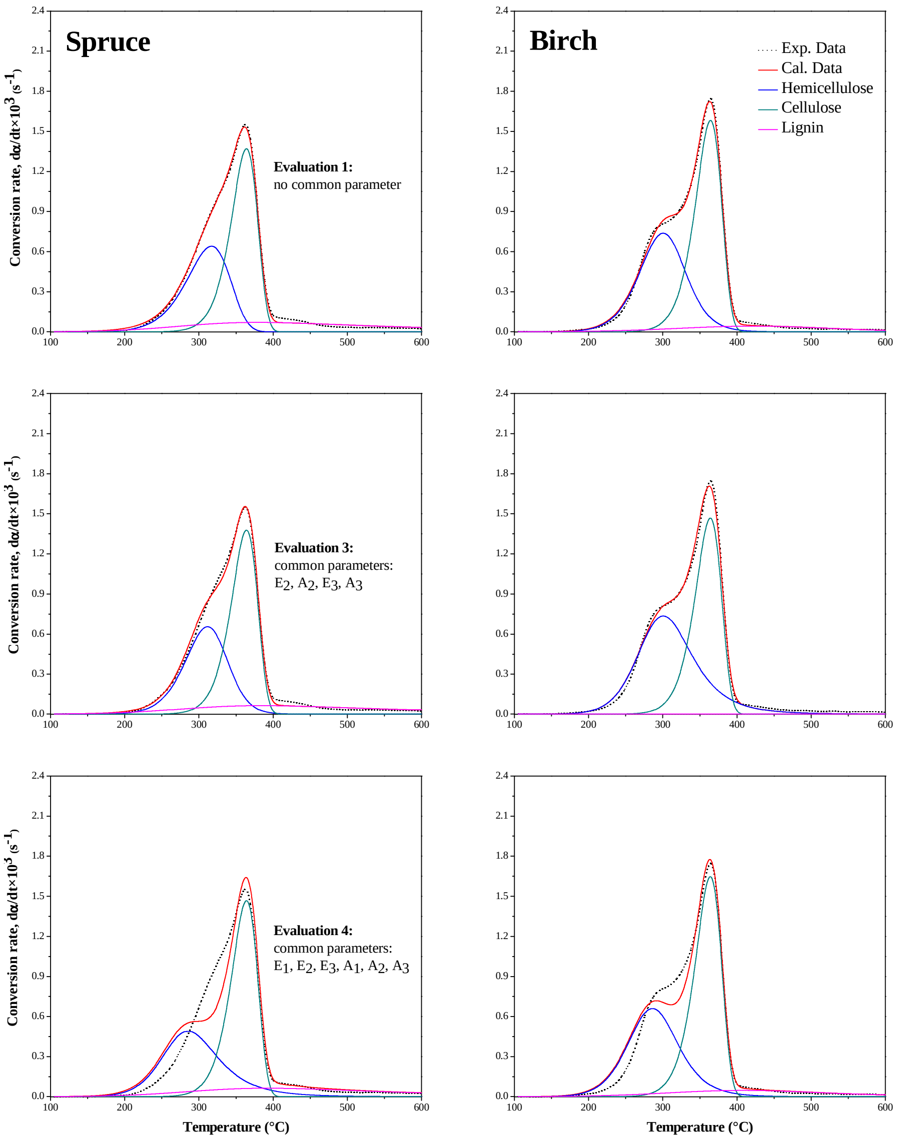
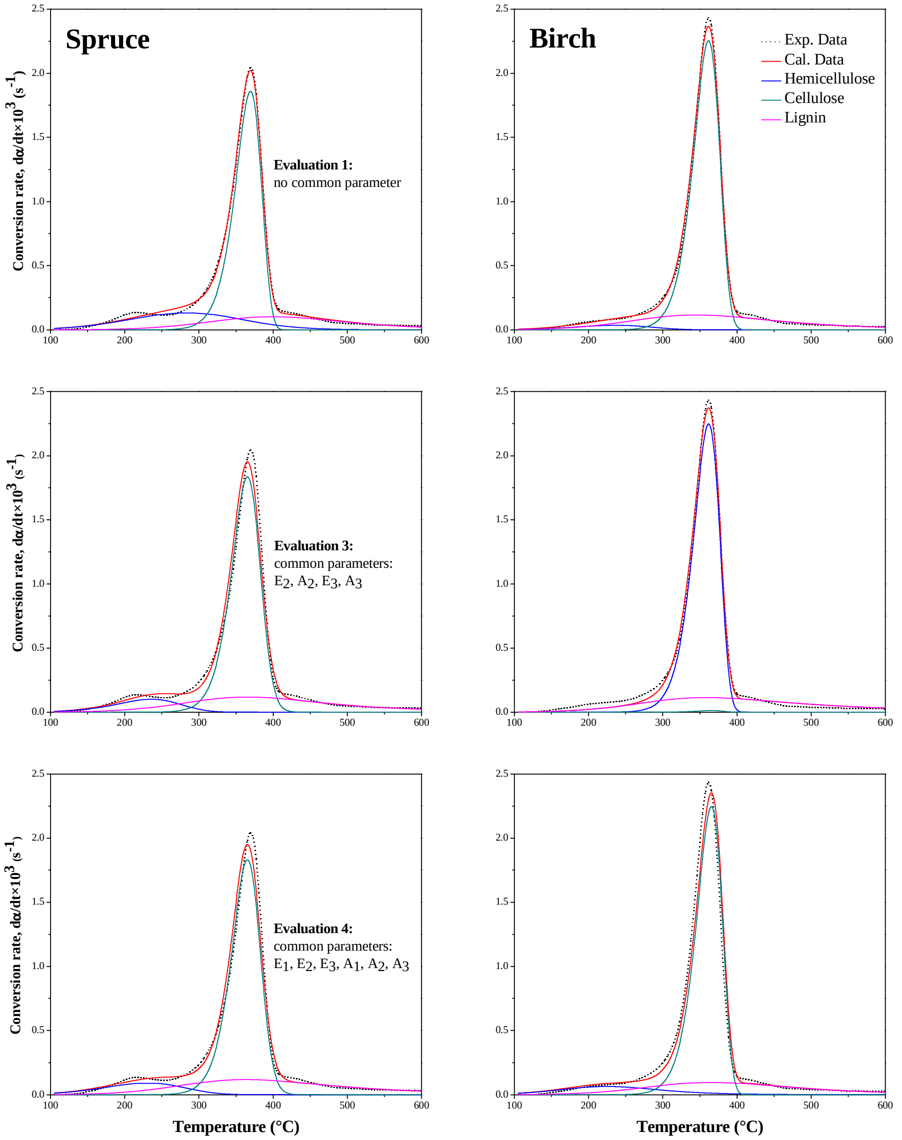


Figure 7. Curve fitting for the woods torrefied at 200 °C and 30 min by Evaluation 1, 3, and 4 of Variant *III*



Paper IV

Torrefaction of forest residues in subcritical water

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Abstract: In this study, effects of temperature (175, 200, 225 °C) and holding time (10, 30, 60 min) on wet torrefaction of branch woods was simultaneously studied and compared with the results from a previous study on wet torrefaction of stem woods. Similar effect trends were observed between the studies. Birch branch wood is more reactive than spruce branch wood. Both torrefaction temperature and holding time have significant effects on the solid yield and the fuel properties of hydrochars. Branch woods are slightly more reactive than stem woods under identical torrefaction conditions. The effects of torrefaction temperature on the grindability and hydrophobicity of hydrochar from branch woods are more significant than those from stem woods. In all cases, the differences in solid and energy yield between branch and stem woods are within 2.1-6.3% w/w and 1.0-3.0% for spruce and birch, respectively. The differences in grindability and hydrophobicity between branch and stem woods are respectively up to 8.1% and 15.7% for spruce, whereas 10.3% and 10.9% for birch.

Highlights (for review)

- Wet torrefaction of branch woods was simultaneously studied and compared with that of stem woods.
- Birch branch wood is more reactive than spruce branch wood
- Branch woods are slightly more reactive than stem woods under identical torrefaction conditions
- The differences in solid and energy yield between branch and stem woods are within 2.1-6.3% (w/w) and 1.0-3.0% (w/w) for spruce and birch, respectively.

Torrefaction of forest residues in subcritical water

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Abstract

In this study, effects of temperature (175, 200, 225 °C) and holding time (10, 30, 60 min) on wet torrefaction of branch woods was simultaneously studied and compared with the results from a previous study on wet torrefaction of stem woods. Similar effect trends were observed between the studies. Birch branch wood is more reactive than spruce branch wood. Both torrefaction temperature and holding time have significant effects on the solid yield and the fuel properties of hydrochars. Branch woods are slightly more reactive than stem woods under identical torrefaction conditions. The effects of torrefaction temperature on the grindability and hydrophobicity of hydrochar from branch woods are more significant than those from stem woods. In all cases, the differences in solid and energy yield between branch and stem woods are within 2.1-6.3% (w/w) and 1.0-3.0% (w/w) for spruce and birch, respectively. The differences in grindability and hydrophobicity between branch and stem woods are respectively up to 8.1% and 15.7% for spruce, whereas 10.3% and 10.9% for birch.

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1 Introduction

The use of solid biomass fuels for heat and power generation has received increasing interest [1-3]. This is because biomass is a renewable and carbon neutral resource, which is considered as an alternative energy source for a sustainable development [4]. However, the use of native biomass for heat and power generation is not straightforward [5, 6]. Compared to coal, biomass fuel has some drawbacks, which include lower bulk density, higher moisture content, inferior heating value, and poorer grindability. Due to these disadvantages, the expenses for handling, transport, and storage of biomass fuels are increased. In order to overcome these drawbacks of biomass as fuel, torrefaction is considered as a promising upgrading method [7-10].

Indeed, torrefaction is capable of converting a wide range of biomass types to energy-dense solid fuels with much better grindability and increased heating value, compared to the native materials. The technology can be classified into two categories: dry and wet torrefaction. Dry torrefaction (DT) may be defined as thermal treatment of biomass in the absence of oxygen at temperatures within the range of 200-300 °C and at atmospheric pressure [4, 11, 12]. Recently, research on DT has been extended to work in the presence of oxygen and carbon dioxide [13-16], and under elevated pressures [17, 18]. Wet torrefaction (WT) may be defined as processing of biomass in hydrothermal media, subcritical or hot compressed water at temperatures within 180-260 °C [19-23]. The concept of WT is very similar to “hydrothermal carbonization” (HTC) [24-33] and sometimes can be found in the literature under different terms such as “hydrothermal conversion” [33-37] or “hydrothermal treatment” [38-43]. Although the terminologies have sometimes been used interchangeably, it is worth noting that the fuel properties and applications of the solid products from WT and HTC are significantly different from each other. WT aims at upgrading solid biomass fuels and produce hydrochar for energy applications (combustion, gasification, and pyrolysis) only. HTC is employed mainly for producing charcoal with much lower volatile matter but higher carbon content than hydrochar. The charcoal can be used not only as fuel but also as activated carbon, soil enhancer, fertilizer, and even more [44-46]. In addition, WT is usually performed at relatively low temperatures (180-260 °C), resulting in relatively high yields of hydrochar (more than 60%), whereas HTC are commonly conducted at temperatures higher than 300 °C, from which the solid yield may be as low as 35% [36].

Research and development activities on DT biomass for energy applications including combustion, gasification, and pyrolysis have been very active during the last decade [4, 7-9, 11, 12, 47-59]. The DT technology has been developed rapidly and is ready for market introduction and commercial operation [49]. However, it has been claimed that no clear winner in this area can be identified so far [49]. This situation might partially be due to the fact that current technologies of DT use wood chips from stem wood, a feedstock of relatively high quality and thus cost. Utilization of inexpensive biomass resources such as agricultural residues, forest residues and other biomass waste sources may help reducing the total cost of biomass torrefaction at industrial scale. A problem associated with DT is that this method normally requires the input feedstock to have a moisture content not higher than the critical value of 5-10% by weight [60], which is much lower than that of the low cost biomass resources aforementioned. In order to meet this requirement, pre-drying of the inexpensive feedstocks is needed and thus raising up the cost again. To overcome this challenge, WT may be an alternative for DT, because it involves water as reaction medium and thus the energy intensive step of pre-drying the feedstock is eliminated.

Recent studies on WT demonstrated several advantages of WT over DT in upgrading solid biomass fuels [20, 23], which include the possibility to produce solid fuels with better fuel properties at lower temperatures and holding times, compared to DT. In addition, parts of the ash-forming inorganic components are dissolved in the water during WT and thus the hydrochar products have lower ash contents compared with the origin materials [23, 61]. Moreover, the compressibility of hydrochar and the mechanical strength of pellets produced from hydrochar (from WT) are reported to be better than those produced from the native material and the biochar (from DT) [61-63].

Despite the advantage of WT over DT with respect to the capacity of upgrading wet biomass with no need of pre-drying the feedstock, most of the past studies on WT [20, 23, 62, 63] or HTC [24-33] used dry woods as feedstock. Only a few works [64-66] tested WT for wet sewage sludge. However, no study on WT of fresh forest residues has been reported in the open literature so far. Forest residues refer to branches and tops of trees, usually discarded during wood harvesting in the Nordic forests [67]. In general, chemical compositions of forest residues are significantly different from stem woods. Branches for example contain much more hemicelluloses and extractives than stem woods [68, 69]. The behaviour of branches during torrefaction can therefore be expected to be different from stem woods. Therefore, the study reported in this present paper was carried out, of which the primary objective is to evaluate the process of WT for fresh branches. For this purpose, effects of torrefaction temperature and holding time on the yield and fuel properties of hydrochar produced from branch woods were experimentally investigated and assessed. In addition, results from this study were compared with those from our previous study [23] on WT of stem woods of the same plant species.

2 Materials and methods

2.1 Materials

Norway spruce and birch branches were selected to represent forest residues. Fresh branches of 2-2.5 cm in diameter were collected from a local forest in Trondheim, Norway. The bark was then removed from the core wood of the branches in order to avoid possible interferences caused by impurities and contaminants. The bark-removed branches were then cut into 3-4 mm thick slices. The cleaned slices were then stored in a climate cabinet (series VC^3 0100 of Vötsch Industrietechnik) to maintain the moisture content of the branches as collected.

Proximate analyses of the feedstocks were performed according to ASTM standards: E871, E872 and D1102 for moisture content, volatile matter and ash content, respectively. Ultimate analyses of the fuels were determined on dry basis by an "EA 1108 CHNS-O" elemental analyzer (Carlo Erba Instruments). Results from the proximate and ultimate analyses are presented in Table 1, which includes the higher heating values (HHV) calculated according to the method proposed by Channiwala and Parikh [70].

2.2 Experimental setup and torrefaction conditions

Figure 1 demonstrates the experimental setup used in the present study, of which the main components include a 250 ml Parr reactor model 4651, a bench-top ceramic heater (4923EE) connected to a temperature controller (4838EE). The reactor is made of stainless steel (T316SS) and equipped with a pressure gauge, a thermo-well, and two valves. A thermocouple, introduced into the reactor via the thermo-well, for monitoring the WT temperature (temperature of water in the reactor), is connected to the controller by which the electrical duty of the heater is controlled.

The WT procedure reported in our previous study [23] was adopted for the present work and the torrefaction conditions are summarized in Table 2. Distilled water was used as the reaction media. The ratio of dry feedstock over water was 1:5 by weight. Before every torrefaction run, the furnace (the heater) without the reactor was heated for 30 min to a preset temperature. At the same time, the reactor was loaded, closed, sealed, and purged with compressed nitrogen gas (99.99% purity) for 10 minutes. Then the reactor was pressurized and placed in the preheated furnace operating at the maximum power, giving a heating rate of approximately 12 °C per minute. The holding time was counted from the time at which the reactor temperature reached the preset temperature to the end point when the reactor was removed from the furnace and submerged in an ice bath for cooling. When the reactor cooled to room temperature, the pressure was gradually released and the reactor was opened for collection of the products in solid and liquid phases. The solid products (hydrochars) were separated from the liquid by filtration using a filter paper with a pore size of 5-12 μm. After separation, the collected hydrochars were washed with acetone prior to being dried at 103 ± 2 °C for 24 h and then balanced. Readings from the balance were recorded as the mass of dry solid product from the WT (m_{tor}). The dried hydrochars were then stored in a desiccator filled with silica gel for further analyses.

2.3 Assessment methods

2.3.1 Assessment of grindability

The specific grinding energy (SGE) of the branches before and after torrefaction was determined using an IKA MF 10 cutting mill (from IKA®-Werke GmbH & Co. KG) equipped with a 1 mm bottom sieve. The grinder was connected to a current input module NI 9203 (from National Instruments Corporation) to record the electrical current during grinding. A LabView program was used for the data acquisition. The energy consumption was calculated and logged to a file every 2 seconds. The grinding energy was determined by integrating the power curve during the grinding period. The power of the mill under no-load condition was measured and subtracted from the power of grinding the tested samples. Finally, the data was normalized to the initial sample weight to obtain the specific grinding energy. More details about this assessment method can be found in our earlier study [23].

2.3.2 Assessment of hydrophobicity

The hydrophobicity assessment method discussed and reported in our previous study [23] were adopted for the present work. The tested branches were ground and sieved through a Fritsch Analysette 3 Pro vibrator to select the particles smaller than 250 µm for a moisture up-take test. The remaining fine powder was dried at 103 ± 2 °C for 24 h to remove any moisture up-taken during the grinding and sieving periods. Approximately 2 grams of the tested sample was spread on a glass Petri dish. Then the dish loaded with the powder sample was placed in a climate cabinet (series VC^3 0100 of Vötsch Industrietechnik) operated under controlled conditions of 20 °C and 90% relative humidity. The mass changes due to the moisture up-take of the tested material were recorded every 24 h for the total test period of one week. The moisture content of the tested sample was calculated according to Eq. (1):

$$MC_i(\%) = \frac{m_i - m_0}{m_0} \times 100\%, \qquad i = 1, 2, \dots, 7 \tag{1}$$

where MC_i is the moisture content of the tested sample on the i^{th} day; m_0 and m_i is the mass of the initial dry sample and mass recorded on the i^{th} day, respectively

3 Results and discussions

3.1 Effects of temperature and time on wet torrefaction of branch woods

In this section, results from studying the effects of the most important process parameters, torrefaction temperature and holding time, on the yield and fuel properties of hydrochar obtained from WT of the fresh branches are reported. For studying the effect of temperature (175, 200, 225 °C), the holding time was kept constant at 30 min, whereas the temperature was maintained at 200 °C for studying the effect of holding time (10, 30, 60 min). All of the experiments in this investigation were conducted at a constant pressure of 70 bar, adopted from our previous study [23]. The experiments were duplicated or triplicated, from which data were collected and processed to generate average values for relevant assessments.

3.1.1 Effects on solid yield

As discussed earlier in the introduction part, solid yield is a critical indicator for a biomass torrefaction processes. Therefore, it is important to investigate the effects of torrefaction temperature and holding time on the yield of solid obtained from WT of the wet spruce and birch branches. Figure 2 presents results from this investigation, for which the solid yield (Y_{solid}) is defined and determined according to Eq. (2):

$$Y_{solid}(\%) = \frac{m_{tor}}{m_{raw}} \times 100\% \qquad (2)$$

where m_{tor} and m_{raw} denote the mass of hydrochar and its native biomass, respectively, on a dry basis.

As can be seen from Figure 2 the solid yield decreases with either increasing temperature or holding time. When the temperature is increased from 175 to 225 °C the solid yield decreases from 82.0 to 67.6% and from 78.5 to 56.9% for the spruce and birch branches, respectively. Also, when the holding time is varied from 10 to 60 min the solid yield decreases from 77.6 to 69.5% and from 64.2 to 60.2% for the spruce and birch branches, respectively. However, the effect of holding time is less pronounced than that of temperature, which is similar to earlier observations in comparable studies [23, 24]. In addition, these effects are more significant for the birch than for the spruce, which is due to the fact that birch is a hardwood and contains more hemicellulose, a poor thermal resistant component, than spruce [71].

3.1.2 Effects on energy yield and chemical composition of hydrochar

Another important indicator of a biomass torrefaction process is energy yield, Y_E, which indicates how much energy that remains in the solid after the processing. Y_E is defined according to Eq. (3) and (4)

$$Y_E(\%) = Y_{solid} \times D_E \qquad (3)$$

$$D_E = \frac{HHV_{tor}}{HHV_{raw}} \qquad (4)$$

where HHV_{tor} and HHV_{raw} respectively denote the HHV of hydrochar and the native branches, on a dry basis; Y_{solid} is the yield of hydrochar defined in Eq. (2).

Table 2 presents the calculated values of energy yield for WT of the branches in different conditions. The table includes data from proximate and ultimate analyses and the higher heating values (HHV) for the untreated branches and hydrochars obtained from the WT process. It can also be observed that the energy yield constantly decreases with either increasing torrefaction temperature or holding time. This trend is valid for both softwood and hardwood, being decreased from 86.1 to 76.7% and from 80.4 to 64.3% for the torrefied spruce and birch, respectively. However, the energy yield for spruce is always higher than that of birch in identical WT conditions. This difference is presumably caused by the higher reactivity of birch than spruce, as discussed earlier in section 3.1.1.

In addition, Table 2 also show that the HHV increases with either increasing torrefaction temperature or holding time. The increases in HHV vary from 5.0-13.5% for the torrefied spruce and 2.4-13.0% for the torrefied birch, when temperature is increased from 175 to 225 °C. On the other hand, when holding time was prolonged from 10 to 60 min, increases in HHV are 6.2-10.7% and 4.2-9.5% for the torrefied spruce and birch, respectively. It can be seen that the effect of temperature is more pronounced than the effect of holding time. As a consequence of increasing heating value, the mass energy densification of all torrefied branches increases. More importantly, increases in the severity level of WT conditions result in decreases in hydrogen and oxygen contents, but increases in carbon content of the hydrochar products. Consequently, both H/C and O/C ratios of the hydrochar are reduced compared with their origins, as can be seen in the Van Krevelen diagram presented in Figure 3. A decreasing trend of these ratios with increasing levels of WT severity is also observed for both fuel types.

3.1.3 Effects on grindability

The improvement in grindability of the branches by WT was qualitatively assessed, employing the method of the specific grinding energy (SGE) described earlier. The lower SGE a material exhibits, the better grindability it has. Figure 4 presents the effects of torrefaction temperature (Figure 4A) and holding time (Figure 4B) on the SGE of the torrefied spruce and birch branches in different conditions. The SGE of the torrefied branches is higher than that of the native material, and decreases with increasing torrefaction temperature or holding time. This clearly indicates that the grindability of the branches is improved by WT and the improvement increases with increasing temperature or reaction time. Among the tested conditions, the highest reduction in SGE is 13.3 times for the spruce and 16.0 times for the birch. In addition, the grindability of birch is improved more significantly than for spruce in identical conditions. Moreover, the figures show a huge decrease in SGE of torrefied branches when the temperature increases from 200 to 225 °C, which may be due to a change in the microstructure of the fuel. This will be discussed in more detail in the next section, which presents a morphology study.

3.1.4 Effects on hydrophobicity

Results from the moisture up-take tests for the raw and torrefied spruce branches are shown in Figure 5, of which Figure 5A and Figure 5B present the effects of torrefaction temperature and holding time, respectively. Similar to the SGE for grindability, the lower moisture up-take level a material exhibits, the better hydrophobicity it has. It can be seen from the figures that all of the tested samples reached the equilibrium moisture content (EMC) on the second day. More importantly, the hydrophobicity of the forest residue is improved by WT. The EMC decreases with either increasing torrefaction temperature or holding time. Very similar trends were observed for the birch branches, which are therefore not shown.

3.1.5 Morphology and structure study

A morphology and structure study for the native spruce branches and branches torrefied at different temperatures (for a constant holding time of 30 min) was carried out by means of a table top scanning electron microscope (SEM) Hitachi TM 3000, with an accelerating voltage of 15 kV. SEM images at a magnification of ×500 are presented in Figure 10A (for the cross section) and Figure 10B (for the longitudinal section). The images show that WT alters the structure of the branch wood with the occurrence of cracks and openings. The degree of structure alteration by WT is not significant at 175 °C, but increases thereafter significantly with increasing temperatures. This suggests a correlation with the significant reduction in SGE of the samples torrefied at 200 to 225 °C, as presented earlier in section 3.1.3.

3.2 Comparison with wet torrefaction of stem woods

In this section, the processes of WT for branch woods and stem woods are compared. The compared indicators include solid yield, energy yield, grindability and hydrophobicity. The comparison focuses only on the effect of torrefaction temperature (175, 200, 225 °C), i.e. holding time was kept constant at 30 min. Relevant data from our previous study on WT of Norway spruce and birch stem woods [23] are used to serve this comparison.

3.2.1 Comparison on solid yield

The yields of hydrochars obtained from WT of the stem woods and branches are presented in Figure 7. Decreasing trends of the hydrochar yield with increasing WT temperature are observed for all types of feedstocks. More importantly, the yields for branch woods are always lower than those for the stem woods of the same plant species, torrefied in identical conditions. The differences are significant for both soft and hard woods, being 6.3% at 175 °C for spruce and 3.0% at 200 °C for spruce and birch, respectively. These differences can be attributed to the higher hemicelluloses and extractives contents of branch woods compared to stem woods as presented in the introduction. However, while the solid yield difference between spruce branch and stem woods decrease with increasing temperature, no clear trend can be observed in the case of birch.

3.2.2 Comparison on energy yield

The energy yields for WT of the four feedstocks at different temperatures are presented in Figure 8. Similar to solid yield, decreasing trends of energy yield with increasing WT temperature are observed for all of the feedstocks. In addition, the energy yields for branch woods are always lower than those of the stem woods, torrefied in identical conditions. This similarity can only be attributed to the decreasing trend of solid yield with increasing temperature, considering the relationship between solid yield and energy yield in Eq. (3). It is because of the fact that HHV, embedded in the D_E term of Eq. (3), of hydrochar increases with increasing torrefaction temperature (discussed in Section 3.1.2). This indicates that the solid yield decreases faster than the HHV increase with increasing torrefaction temperature. In addition, no clear trend of differences in energy yield between branch and stem woods can be observed.

3.2.3 Comparison on grindability

Figure 9 presents the results from SGE measurements for the stems and branches, untreated and torrefied at different temperatures. The data of the first point (Raw) were calculated on the basis of triplicate measurements, but those of the others were based on single measurements only due to the small reactor volume and thus limited amounts of hydrochar produced in the WT experiments. The triplicate measurements were performed for the untreated woods confirm that while the grindability of untreated spruce branch is better than untreated spruce stem wood, the situation for untreated birch is opposite. In order to understand this observation, different strength measurements are needed which is beyond the scope of the present work. More importantly, differences in grindability between branch and stem woods for spruce are always more significant and consistent than for birch. At 200 °C, the grindability of both spruce and birch branches are better than their stem woods. The difference at this point is 8.1% for torrefied spruce and 10.9% for torrefied birch. Thereafter, virtually no significant difference in SGE between branch and stem woods can be observed at point 225 °C. Overall, reductions in SGE with increasing torrefaction temperature are observed for all tested woods. In addition, the SGE dramatically decreases when temperature is increased from 200 to 225 °C. The highest reduction occurs at the treatment condition of 225 °C (for 30 min).

3.2.4 Comparison on hydrophobicity

The EMC data for the stems and branches, untreated and torrefied in various conditions are presented in Figure 10. It appears that untreated branches consistently exhibit higher EMC values than the corresponding stem woods. This is presumably due to the higher hemicelluloses and extractives contents of branches compared to stem woods. It is because hemicelluloses possess more hydroxyl groups than celluloses and lignin [71]. In addition, extractives may be hydrophilic in nature.

At 175 °C, WT makes branches more hydrophobic than the corresponding stem woods. This confirms the hydrophilic nature of the extractives. It is because plant biomass extractives have smaller molecular and thus less thermally stable than hemicelluloses. In other words, the extractives should have been decomposed first and responsible for the significant reductions in EMC at point 175 °C. In addition, the differences in EMC between branch and stem woods become most significant at 200 °C, being 15.7% and 10.3% for spruce and birch, respectively. Finally, similar to the grindability comparison, virtually no significant difference in EMC between branch and stem woods can be observed at point 225 °C.

4 Conclusions

WT enhances significantly the fuel properties of Norway spruce and birch branches. The yield of hydrochars produced from branch woods via WT processes decreases with increasing torrefaction temperature and/or holding time. However, the improvements in fuel properties of hydrochar increase with increasing torrefaction temperature and/or holding time. Increases in HHV up to 13.5% and reductions of specific grinding energy up to 16.0 times for the wet branches could be achieved via WT. In addition, birch branches are more reactive than spruce branches in identical WT conditions.

The comparison on WT of the branches and the stem woods show that the effect trends of WT on the yield and fuel properties of the hydrochars from branches and stems were similar. However, branch woods are more reactive than stem woods in identical WT conditions. The trend of reduction in SGE of branches is similar to stem woods for spruce, but that for birch is somehow inconsistent. Improvements in hydrophobicity of the branches are more pronounced than that of the stems. This may be attributed to the higher hemicellulose and extractives contents of the branches compared to stem woods.

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Table 1. Fuel characteristics of the feedstocks.

Type of feedstock	**Moisture content**[a]	**Proximate analysis**[b]			**Ultimate analysis**[b]					**HHV**[c]
		Ash	**VM**	**FC**	**C**	**H**	**O**	**N**	**S**	
Spruce	49.96±2.34	0.68±0.05	85.18±0.26	14.14±0.15	51.31±0.14	6.22±0.09	42.35±0.06	0.122±0.01	<0.02	20.84±0.07
Birch	56.31±1.93	0.64±0.04	89.74±0.32	9.63±0.09	48.55±0.17	6.19±0.06	45.09±0.14	0.165±0.03	<0.02	19.63±0.06

[a] wt %; [b] wt %, dry basis; [c] MJ/kg, dry and ash free basis

VM: volatile matter, **FC**: fixed carbon

Table 2. Torrefaction conditions and fuel characteristics of hydrochars obtained from wet torrefaction of forest residues (dry basis).

Torrefaction conditions (at 70 bar)		**Proximate analysis** (wt%)			**Ultimate analysis**[a] (wt%)					**HHV**[a] (MJ/kg)	D_E	Y_E (%)
		Ash	**VM**	**FC**	**C**	**H**	**N**	**O**	**S**[*]			
Spruce	Raw	0.68	85.18	14.14	51.31	6.22	0.122	42.35	< 0.02	20.86	–	–
	175°C-30min	0.54	82.40	17.06	54.08	6.06	0.140	39.72	< 0.02	21.91	1.05	86.09
	200°C-10min	0.58	81.61	17.81	54.73	6.02	0.147	39.10	< 0.02	22.16	1.06	82.48
	200°C-30min	0.52	80.76	18.72	56.86	5.88	0.160	37.09	< 0.02	22.95	1.10	80.98
	200°C-60min	0.46	76.04	23.50	57.51	5.77	0.148	36.58	< 0.02	23.09	1.11	76.98
	225°C-30min	0.50	74.82	24.68	59.41	5.55	0.167	34.87	< 0.02	23.67	1.13	76.75
Birch	Raw	0.64	89.74	9.63	48.55	6.19	0.165	45.09	< 0.02	19.56	–	–
	175°C-30min	0.56	88.19	11.25	49.84	6.10	0.184	43.88	< 0.02	20.03	1.02	80.44
	200°C-10min	0.61	86.66	12.73	50.87	6.01	0.228	42.90	< 0.02	20.39	1.04	66.94
	200°C-30min	0.55	83.40	16.04	52.48	5.98	0.232	41.31	< 0.02	21.08	1.08	66.98
	200°C-60min	0.61	81.63	17.76	53.63	5.84	0.206	40.32	< 0.02	21.42	1.09	65.97
	225°C-30min	0.65	79.67	19.68	55.23	5.80	0.231	38.74	< 0.02	22.10	1.13	64.28

VM = volatile matter: **FC** = fixed carbon; [a]: ash free; [*]: lower than the detection limit.

Figure 1. Schematic diagram of the experimental setup and the reactor.

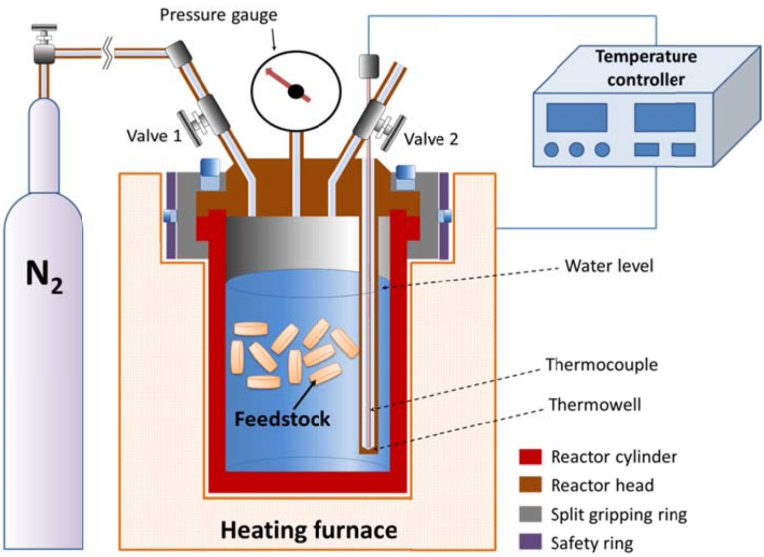


Figure 2. Effects of (A) torrefaction temperature and (B) holding time on the hydrochar yield of spruce and birch branches.

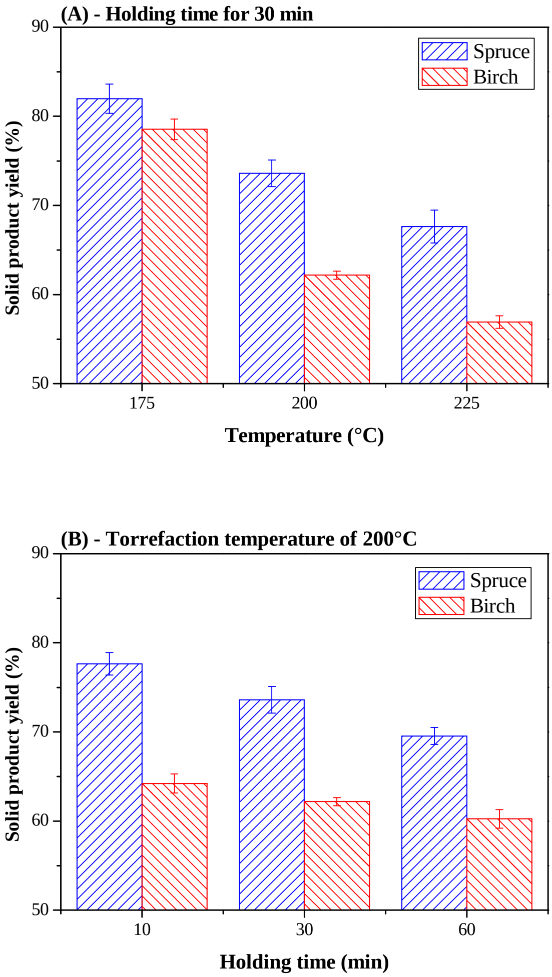


Figure 3. Van Krevelen diagram for the raw and torrefied branches in different conditions.

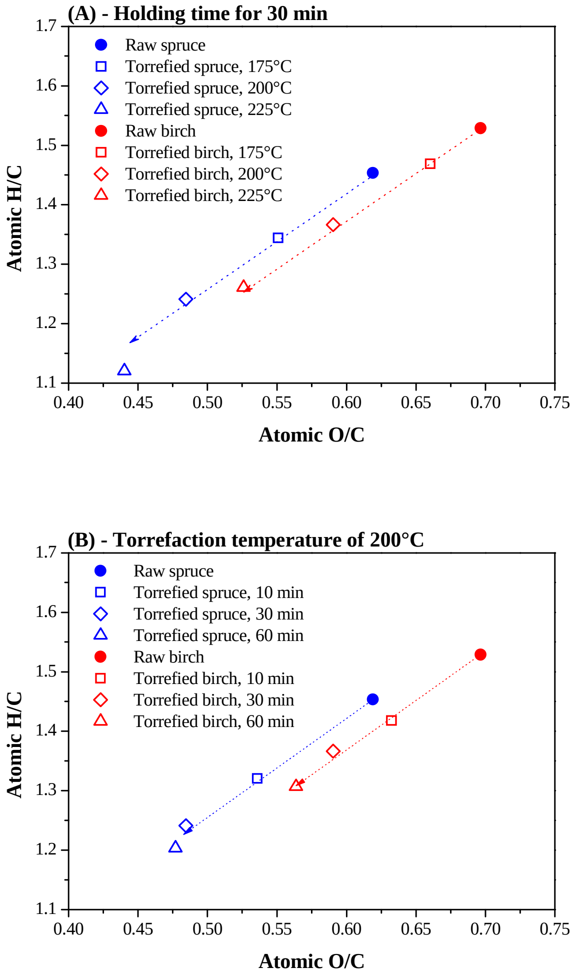


Figure 4. Effects of (A) torrefaction temperature and (B) holding time on specific grinding energy of raw and torrefied branches.

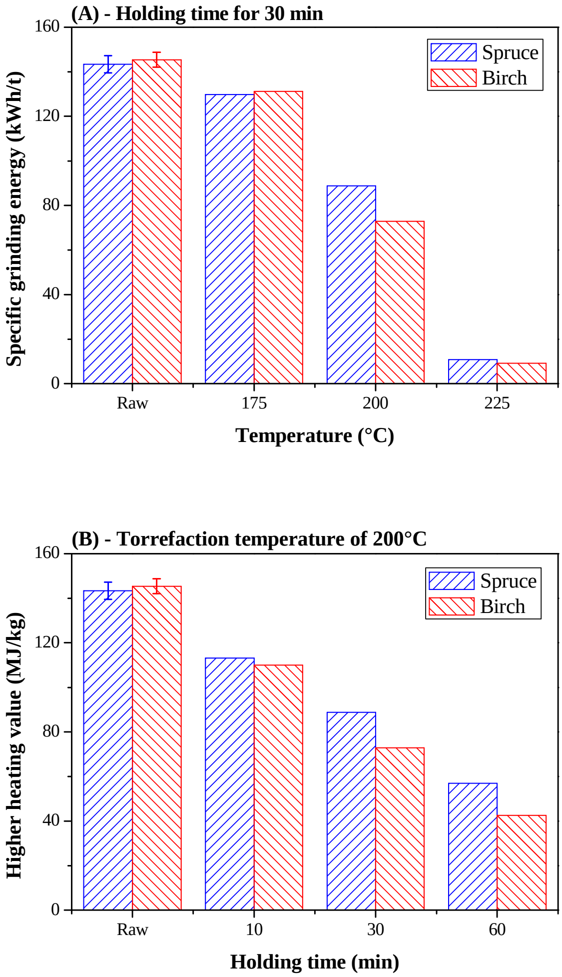
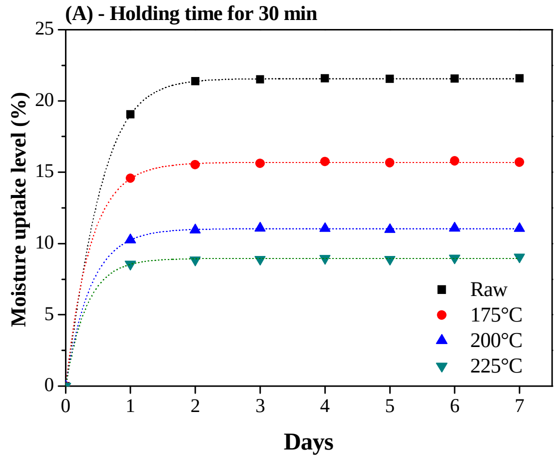


Figure 5. Moisture uptake behavior of raw spruce branches and spruce branches torrefied at different (A) torrefaction temperatures and (B) holding times.



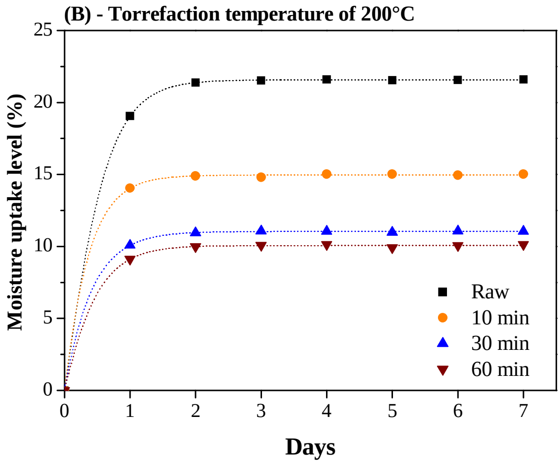
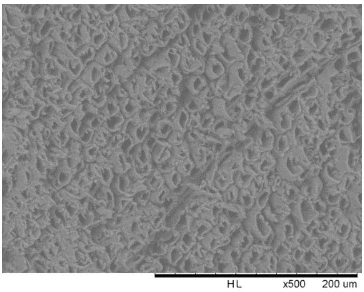
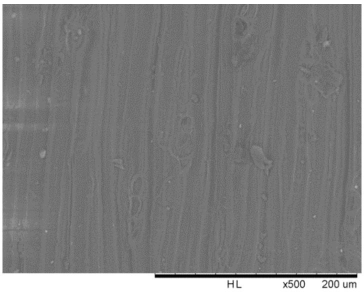
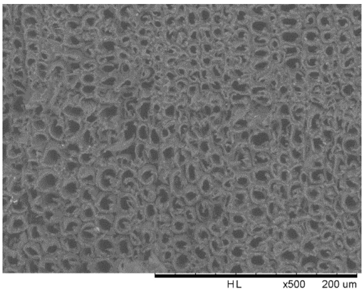
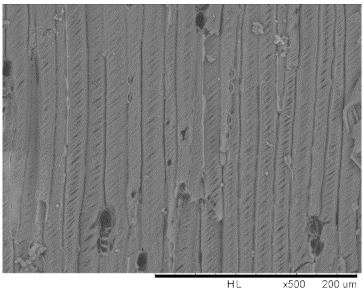
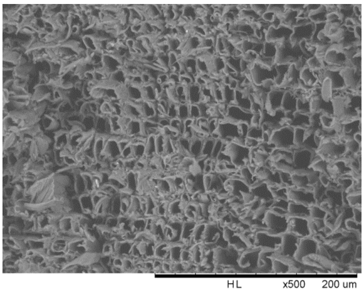
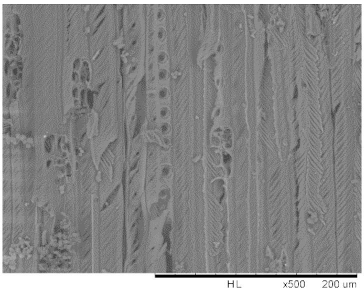


Figure 6. SEM images of the raw spruce branches and branches torrefied at different temperatures.

Torrefaction temperature	Cross section	Longitudinal section
Raw sample		
175 °C		
200 °C		

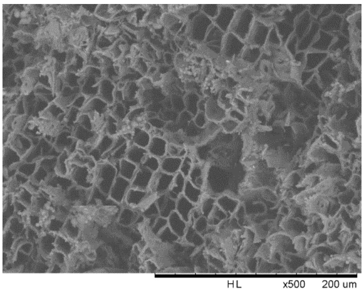
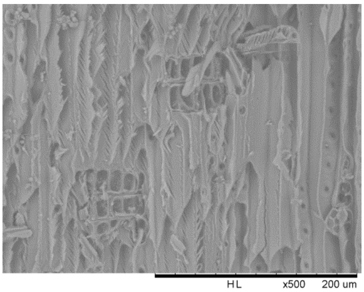
225 °C		

Figure 7. Hydrochar yield for branch and stem woods torrefied in subcritical water for 30 min.

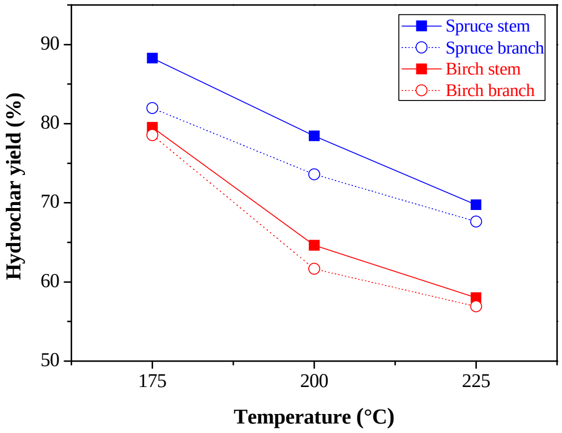


Figure 8. Energy yield for branch and stem woods torrefied in subcritical water for 30 min.

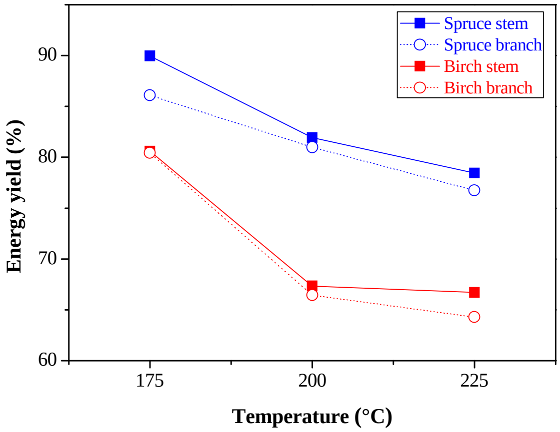


Figure 9. Specific grinding energy (SGE) for branch and stem woods torrefied in subcritical water for 30 min.

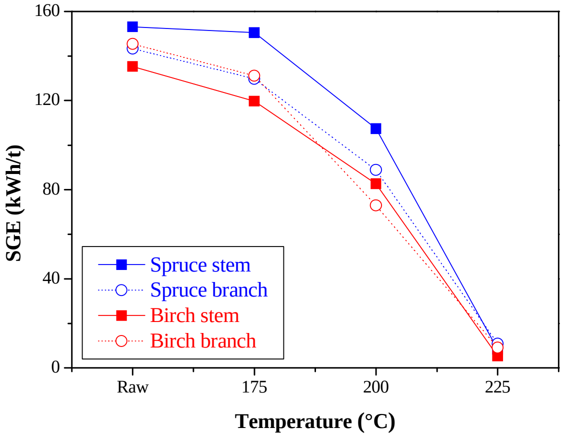
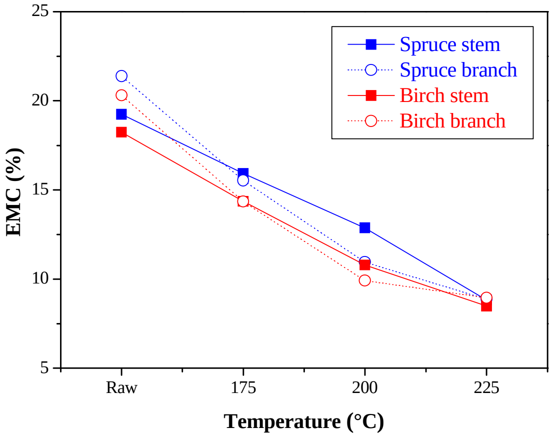


Figure 10. Equilibrium moisture content (EMC) for branch and stem woods torrefied in subcritical water for 30 min.



Paper V

Effects of CO_2 on wet torrefaction of biomass

Quang-Vu Bach, Khanh-Quang Tran, Roger A. Khalil, and Øyvind Skreiberg.

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Effects of CO_2 on wet torrefaction of biomass

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Abstract

Effects of CO_2 on the yield and fuel properties of the solid product obtained from wet torrefaction of biomass were experimentally investigated. Norwegian forest residues were used as feedstock. CO_2 and N_2 were employed as purge gas, separately. The results show that, compared with wet torrefaction in N_2, the process in CO_2 is taking place faster, producing 4.6-6.0% less solid product with lower heating value in identical condition. A reduction of 6.5kWh/t in SGE and an increase of up to 1.4% in EMC were observed for the solid product obtained from WT in CO_2 compared with that in N_2. In addition, CO_2 enhances the capacity of wet torrefaction to remove ash elements from solid biomass fuels.

Selection and/or peer-review under responsibility of ICAE

Keywords: Wet torrefaction; Biomass fuels; Forest residues; Flue gas utilization.

1. Introduction

Wet torrefaction (WT) of biomass is a method of hydrothermal processing for upgrading and production of solid fuels with improved fuel properties such as increased heating value and better grindability [1, 2]. The process may be defined as mild pyrolysis of biomass in hot compressed water, in the temperature range of 180-260°C [1, 2], and therefore is very much suitable for wet feedstocks, which include forest residues, wet agricultural wastes, sewage sludge, and aquatic energy crops. In addition to the main solid product, WT also produces liquid by-products including water soluble and insoluble organic compounds, which can be further treated for the production of biogas, liquid fuels and/or valuable chemicals [3, 4].

Recent study in a batch reactor show that WT exhibits several advantages compared with dry torrefaction (DT), which include the capacity of washing out ash elements from biomass fuels [2]. However, like DT, WT requires an inert atmosphere, for which a large amount of nitrogen for purging and pressurizing is normally used. The nitrogen requirement will be much larger for industrial applications and up-scaling of the technology, for which continuous processes may also be employed. In

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such a context, the concept of process integration including heat integration should be considered [5, 6]. For this purpose, utilization of hot flue gas from thermal power plants would be a potential option. The problem however is that, apart from N_2, flue gas contains other gases, of which CO_2 is the main species and may have important effects on the WT process and the fuel properties of the solid product. For this reason, some studies on influences of CO_2 addition have been reported [7, 8] for DT of biomass, but not for WT. In the present work, WT of Norwegian forest residues (FR) was experimentally studied under different conditions with N_2 or CO_2 addition. The effect of CO_2 addition on the solid product yield and its fuel properties was investigated.

2. Materials and methods

The feedstock used for this study is Norway spruce branches of 2-2.5 cm in diameter. The branches were collected from a local forest in Trondheim, Norway. The bark was completely removed from the collected branches to avoid possible interferences caused by impurities/contaminants and composition differences between the core and the bark. The moisture content (determined by the standard method ASTM D4442-07) of the feedstock was 49.96 ± 2.34%. Prior to the WT experiments, the bark-free branches were cut into slices having a thickness of 3-4 mm to improve the heat and mass transfers during torrefaction. The common WT conditions, procedure and assessment method reported in our previous study [2] were adopted for this present work. It was at 70 bar and three temperatures (175, 200, 225°C), and for three holding times (10, 30, 60 min), with addition of N_2 or CO_2.

3. Results

3.1. Effects on the solid yield

Fig. 1. Solid yield for WT of FR at different temperatures (A) and holding times (B)

Fig. 1 A and B show the yield of solid products obtained from the WT in N_2 or CO_2 atmosphere with varying temperature or holding time, respectively. The figures indicate no difference in the trend of the effects of these two process parameters on the solid yield for the two different cases with regards to the gas atmosphere. The solid yield for both cases decreases with either increasing torrefaction temperature or holding time. However, at the same hydrothermal conditions less solid is produced in the case of CO_2 addition than that of N_2 addition. This indicates that CO_2 has a positive effect on the reaction rate of biomass WT, compared to N_2. In addition, this effect seems more significant at higher temperatures and longer holding times. The yield difference is within 4.6-6.0% and 3.8-5.7% for temperatures of 175-225°C and holding times of 10-60 min, respectively.

3.2. Effects on fuel properties of the solid product

Fig. 2 A and B present the heating value of solid products obtained from the WT in N_2 or CO_2 atmosphere with varying temperature or holding time, respectively. In all cases, the heating value of the solid product obtained from the WT with CO_2 addition is slightly lower than that of N_2 addition.

Moreover, the difference in HHV of solid from the WT in CO_2 and N_2 becomes less significantly when either increasing WT temperature or holding time.

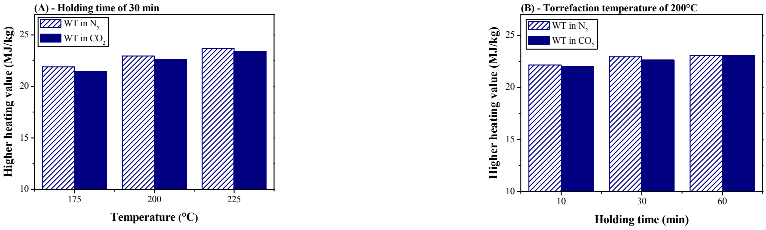

Fig. 2. Heating values of solids from WT of FR at different temperatures (A) and holding times (B)

Proximate analysis data for the solid obtained from the WT in different gas atmospheres are presented in Table 1, and indicates that increased reaction temperature or holding time results in increased fixed-carbon (FC) content but decreased volatile matter (VM) content of the solid product. More interestingly, the ash content of the FR torrefied in CO_2 is significantly lower than that in N_2.

Table 1. Proximate analysis of raw and torrefied FR

Torrefaction condition	**WT in N_2**			**WT in CO_2**		
	Ash (%)	VM (%)	FC (%)	Ash (%)	VM (%)	FC (%)
175°C–30min	0.54	82.40	17.06	0.35	82.29	17.36
200°C–10min	0.58	81.61	17.81	0.34	81.18	18.49
200°C–30min	0.52	80.76	18.72	0.21	78.79	21.00
200°C–60min	0.46	76.04	23.50	0.26	75.84	23.90
225°C–30min	0.50	74.82	24.68	0.21	72.83	26.96

Data for dry raw feedstock: **Ash: 0.68%**, **VM: 85.18%**, **FC: 14.14%**

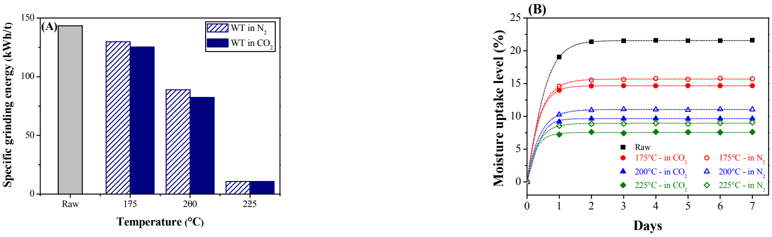

Fig. 3. Effect of WT temperature on the specific grinding energy (A) and the moisture uptake level (B)

The specific grinding energy (SGE) and the moisture uptake level of raw and torrefied FR are presented in Fig. 3A and 3B, respectively. The reductions in SGE and moisture uptake level show similar trends for the materials torrefied in CO_2 or N_2. However, the samples torrefied in CO_2 exhibit lower SGE values than those in N_2. The most significant reduction in SGE is 6.5kWh/t recorded for the samples torrefied in the conditions of 200°C and 30 min. Further increases in temperature led to no more reduction in SGE. Nevertheless, the equilibrium moisture content (EMC) of the samples torrefied in CO_2 is significantly lower than that in N_2. The difference in EMC becomes more significant, being up to 1.4% when the temperature is increased from 175 to 225°C. The effects of holding time on the grindability and hydrophobicity show similar trends but less pronounced compared with the effects of temperature.

4. Discussion

The use of CO_2 for WT of biomass instead of N_2 results in lower yield and slightly decreased heating value of the solid product in identical WT conditions. This can be translated to positive effects of CO_2 addition on the reaction rate of WT. Similar effects of CO_2 addition have been found for DT [7], in which increased weight loss and improved grindability when adding CO_2 was reported. For WT in the present work, the effects of CO_2 may be explained by the fact that dissolved CO_2 in water has an acidic catalyst effect and enhances the reaction rate of biomass treatment in hydrothermal conditions [9, 10]. This catalytic enhancement effect is also valid for the solubility of inorganic ions present in biomass during hydrothermal pre-treatment. It suggests that WT in CO_2 is capable of removing even more ash elements in the solid biomass fuel, compared with WT in N_2. If utilizing hot flue gases, the positive CO_2 effect on the WT process will depend on its CO_2 content.

5. Conclusion

Wet torrefaction of Norwegian forest residues in different conditions and atmospheres were experimentally investigated. WT in CO_2 produced 4.6-6.0% less solid product with decreased heating value but improved hydrophobicity and better hydrophobicity than in N_2. An increase of up to 1.4% in EMC and a reduction of 6.5kWh/t in SGE were observed for the solid product obtained from WT in CO_2 compared with that in N_2. The proximate analyses show higher fixed carbon and lower volatile matter contents for the solid products obtained from WT in CO_2. Additionally, the ash content of these products is significantly reduced, compared with that in N_2.

6. Acknowledgement

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Paper VI

Influences of wet torrefaction on pelletability and pellet properties of Norwegian forest residues

Quang-Vu Bach, Nevena Mišljenović, Khanh-Quang Tran, Carlos Salas-Bringas, and Øyvind Skreiberg.

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Influences of wet torrefaction on pelletability and pellet properties of Norwegian forest residues

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ABSTRACT

The compressibility of Norway spruce and birch tree branches torrefied in subcritical water conditions and the mechanical strength of the obtained pellets were experimentally studied in comparison with the raw materials. The pelletization was performed on a single pellet press. The pellet strength was investigated via diametric compression tests, employing a 60 mm diameter probe connected to a Lloyd LR 5K texture analyzer. The results showed that wet torrefaction improved the compressibility and strength of the tested material. In addition, compressing pressure affected both the pellet density and strength, while pelletizing temperature influenced the pellet strength only.

Keywords: Biomass pelletization; Pellet physical properties; Wet torrefaction; Forest residues.

INTRODUCTION

Wet torrefaction (WT), which may be defined as pretreatment of biomass in hot compressed water at temperatures within 180-260 °C [1, 2], is a promising method for production of high quality solid fuels (hydrochars) from low cost wet biomass resources such as forest residues, agricultural waste, aquatic energy crops, and sewage sludge. The concept of WT is very similar to "hydrothermal carbonization" (HTC)[3] and sometimes is discussed under the general term "hydrothermal conversion"[4] or "hydrothermal treatment" [5]. The main improvements in fuel properties of hydrochars produced from WT of biomass include the change from hydrophilic to hydrophobic nature, increased heating values, and improved grindability. However, the bulk and volumetric energy densities of biomass are reduced by WT[6-8]. In addition, hydrochar becomes more flaky and dusty, compared to the raw biomass[6-8]. These drawbacks may cause problems for the storage, logistics, and further utilizations (combustion, gasification, and pyrolysis) of hydrochars[6-8]. Therefore, an additional step of pelletization is usually required to overcome the drawbacks.

Pelletization is a mechanical process that convert bulky solid biomass fuels into pellets with uniform shapes and reduced dust formation. More importantly, the bulk and volumetric energy densities of solid biomass fuels are both significantly improved via pelletization[8-10]. The pellet form of biomass fuels is suitable for many industrial and residential applications[11, 12].

In the open literature, there are few reports dealing with pelletization of biomass pretreated in subcritical water conditions[6-8]. It was reported that pellets produced from hydrochars were denser, more durable and mechanically stronger than pellets produced from the corresponding raw biomass [6-8]. Nevertheless, pelletizing hydrochars is more challenging than the raw biomass because the friability and hydrophobicity of hydrochars reduce significantly the bonding capacity between hydrochar particles [6-8]. However, many factors such as pelletizing temperature, compacting pressure, type of feedstock, processor type may affect the compressibility and the physical properties of pellets[8, 13]. The effects of these factors have not been fully understood and therefore more research in this area is needed.

This present study aimed to investigate the effects of WT on the pelletability and physical properties of Norwegian forest residues (FRs). Norway spruce and birch tree branches were used as feedstocks and torrefied in subcritical water conditions at different temperatures.

Table 1. WT conditions and fuel properties of the raw forest residues and their hydrochars

Sample		**Solid yield[a]**	**MC[b]**	**Ash[a]**	**VM[a]**	**FC[a]**	**HHV[c]**
Spruce	Raw	–	10.30	0.23	86.50	13.27	20.42
	Torrefied for 30 min in water at 70 bar and different temperatures						
	175°C	88.27	6.67	0.11	85.72	14.17	20.81
	200°C	78.45	4.90	0.12	83.92	15.95	21.33
	225°C	69.74	4.26	0.14	74.74	25.12	22.97
Birch	Raw	–	9.74	0.28	89.46	10.26	19.94
	Torrefied for 30 min in water at 70 bar and different temperatures						
	175°C	79.53	6.10	0.09	88.57	11.34	20.21
	200°C	64.64	5.05	0.09	85.15	14.76	20.78
	225°C	58.01	4.69	0.13	73.78	26.09	22.93

[a] wt%, dry basis; [b] Moisture content, wt%, wet basis; [b] MJ/kg, dry and ash free basis.

MATERIALS AND METHODS

Materials

Fresh branches with diameter of 2-2.5 cm of Norway spruce and birch trees were collected from a local forest in Trondheim, Norway, to simulate Norwegian FRs. The WT procedure and fuel characterization methods employed for this present work are adopted from our earlier study[1]. The feedstocks were torrefied in a Parr 4650 autoclave reactor at three different temperatures (175, 200, 225°C), for a constant holding time of 30 min and at a constant pressures of 70 bar. The WT conditions and some fuel properties of the tested materials are presented in Table 1.

Pelletization

The pelletization was carried out using a single pellet press [10] presented in Fig 1, which allows precise control and adjustment of compressing pressure and pelletizing temperature. The unit consists of a steel cylinder (8 mm inner diameter) and a tungsten carbide pressing rod. The press is heated by a jacket heater (450W) of which the temperature was controlled by a PID. The compressing force is applied to the rod using an Instron 100 kN texture analyzer. Two pelletizing temperatures (120, 180°C) and five compacting pressures (20, 40, 80, 160, 240 MPa) were tested. More details of the press and pelleting procedure can be found in our previous study[10].

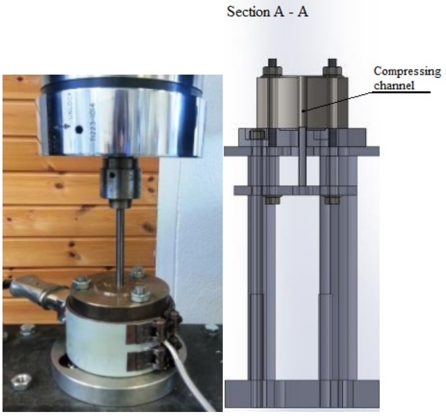

Fig 1. Single pellet press unit: picture of the equipment (left) and section view A-A (right).

Characterization of pellets

The density of pellets was calculated by dividing the weight by the volume of the pellets. The length and diameter of the pellets were measured by means of a digital caliper (from Biltema Sweden).

The compressing tests were carried out at 48 h after the pellets were produced. A 60 mm diameter probe connected to a Lloyd LR 5K texture analyzer (Lloyd Instruments, England) was employed for this test. The compression speed was set to 1 mm/min, and the maximum normal force at breakage was recorded automatically. The pellet strength was expressed as the maximum force per length of the pellet (N/mm).

RESULTS

Effects of wet torrefaction on the grindability and particle size distribution

A pulverization step was required prior to pelletization. A quantitative evaluation of the specific grinding energy (SGE) was carried out for all samples being used for pelleting. Results from the evaluation are presented in Fig. 2, which indicates that WT improved the grindability of the biomass. When torrefaction temperature increases, the SGE decreases. The reduction in SGE was up to 13.3 times for spruce and 27.5 times for birch torrefied at 225°C for 30 min, compared to the raw materials.

The particle size distribution (PSD) of the ground sample was determined by a Mastersizer 3000 laser diffraction particle size analyser, and the results for this test are presented in Fig. 3. The distribution curves show that WT resulted in lower fractions of the coarser particles and larger fractions of finer particles. This effect of WT for birch was more pronounced than that for spruce. Moreover, the curve for spruce torrefied at 225°C exhibits two peaks, while only one peak is observed for the other samples.

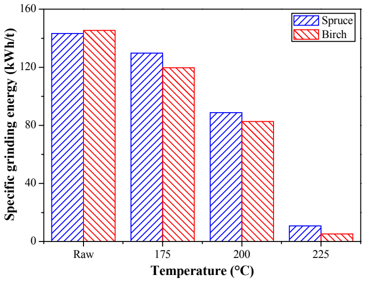

Fig 2. Specific grinding energy of raw and wet-torrefied forest residues.

Effects of wet torrefaction on the compressibility

The compressibility of a biomass fuel can be evaluated via examining the density of the pellet produced from the fuel powder at various pelletizing pressures.

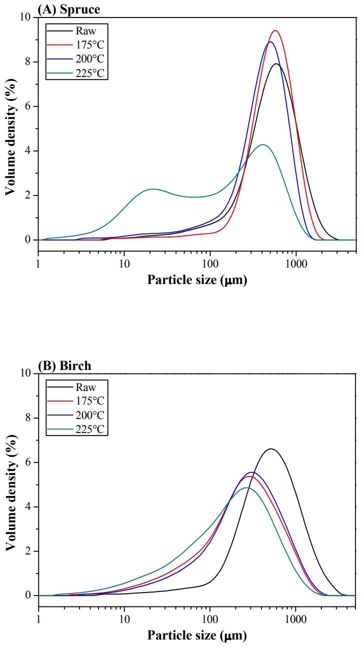

Fig 3. Particle size distribution of ground (A) spruce and (B) birch.

The results from such an evaluation for the raw FRs and hydrochars produced in different WT conditions are shown in Fig. 4, in which the density values at zero pelletizing pressure indicate the bulk density of the ground materials. As expected, the pellet density in all cases increased with increasing pelletizing pressure. The effect of pelletizing temperature was not pronounced, but the effect of biomass type was clear. In the identical condition, birch pellets were denser than spruce pellets and the effect of torrefaction temperature was more pronounced for birch than spruce. More importantly, WT improved the density of pellets. In other words, WT increases the compressibility of the tested materials. In the case of spruce, pellets made from the material torrefied at 175 and 200°C had higher density than it raw material. However, the hydrochar produced at 225°C was the least compressible at low compacting pressures. From the pressure of 80 MPa, the compressibility of this hydrochar sharply increased and became higher than that of the raw spruce. This increasing trend continued and got close to the compressibility of the spruce hydrochars, produced at the other temperatures, at the highest compressing pressure (240 MPa). Similar trends were observed for birch but the improvements in the compressibility by WT were more pronounced than those for spruce. However, unlike spruce, the birch torrefied at 225°C was better compressible than the raw birch at any pelletizing pressure. The highest density of 159 kg/m^3 was obtained from the spruce torrefied at 175°C and pelletized at 20 MPa, 180°C, whereas it was 213 kg/m^3 for the birch torrefied at 175°C, pelletized at 40 MPa, 180°C.

Mechanical strength of pellets

Results from the mechanical strength tests of the pellets produced from raw FRs and their hydrochars are presented in Fig 5. The figure shows that the pellet strength was significantly improved by WT. Moreover, both torrefaction temperature and pelletizing temperature affected the mechanical strength of the pellets. A general trend observed from the figure is that the pellet strength increases with the pelletizing temperature. The smallest increases in the strength of the hydrochar pellets compared to the pellets of the raw materials were 1.3 and 0.7 times for spruce and birch, respectively. On the other hand, the largest increases were 3.4 and 2.7 times for spruce and birch, respectively. In addition, when WT temperature was increased from 175 to 200°C, the spruce pellet strength increased but that for birch decreased. At low compacting pressures, the strength of the pellet made from the FRs torrefied at 225°C was not as good as that of the pellets made from the FRs torrefied at 175 and 200°C, but better than that of the pellets of the raw materials. Thereafter, the strength of pellets made from the materials torrefied at 225°C increased rapidly and became the strongest at the highest compressing pressure (240 MPa).

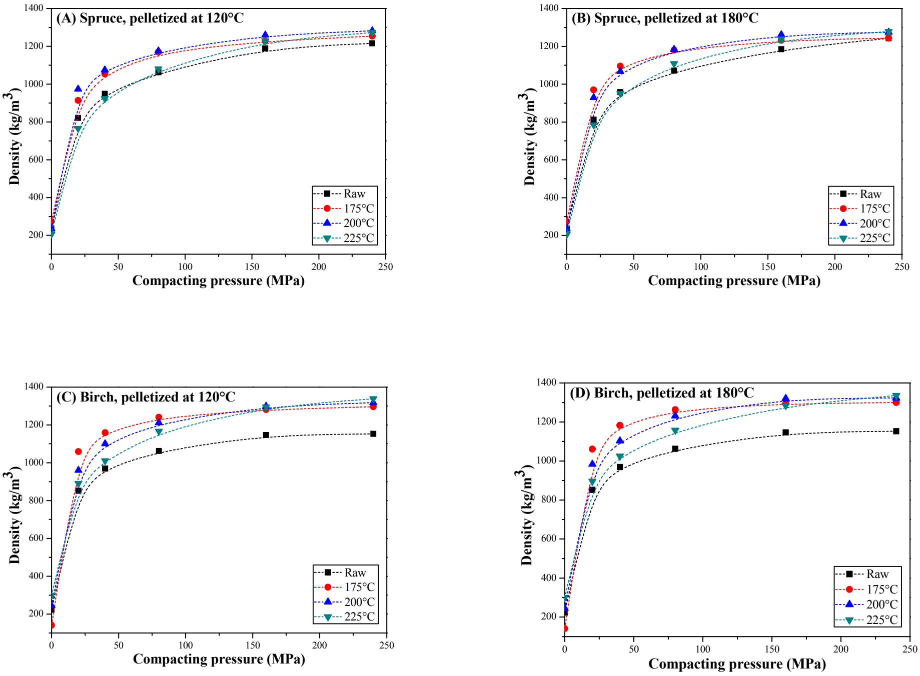

Fig 4. Density of pellets made at different pelletizing pressures and temperatures.

Since the density and mechanical strength of the pellets were both increased with pelletizing pressure, the correlation between these two properties was evaluated. Results from this evaluation are presented in Fig 6, in which fitting curves also are included. The figure shows an exponential relationship between the two properties. The pellets with higher density also had higher mechanical strength. At the same density value, hydrochar pellets were mechanically stronger than the raw material pellets. The effect of WT temperature was more pronounced for spruce than birch. Below the density of 1000 kg/m^3, large increases in density results in only small increases in the strength. However, this relationship was reversed when the density was higher than 1000 kg/m^3.

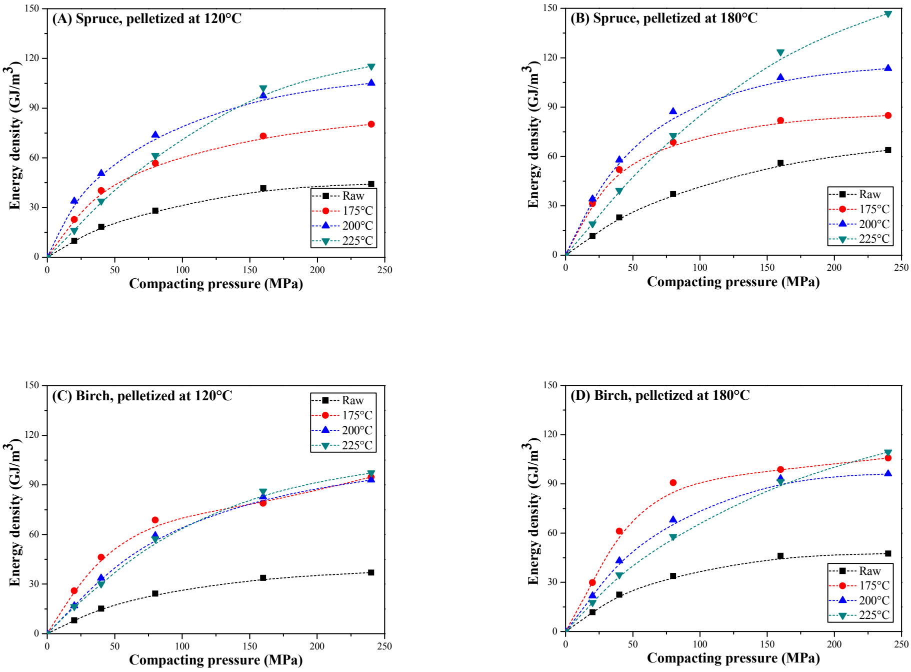

Fig 5. Mechanical strength of pellets made from different compacting pressures and temperatures.

DISCUSSION

WT not only enhanced the fuel properties but also reduced the SGE of the FRs. Compared to the raw FRs, wet-torrefied FRs had larger fractions of fine particles, and the particle size distribution peaks shifted to a smaller particle size range. Except for the spruce torrefied at 225°C, most of the pellets produced from the wet-torrefied FRs had higher density than the raw material pellets. These indicate the WT improved the compressibility of the FRs. However, in order to obtain hydrochar pellets with higher density than pellets of the raw materials, torrefaction temperatures higher than 225°C and pelletizing pressures above 80 MPa should be applied for spruce. Moreover, all of the pellets produced from wet-torrefied FRs exhibited higher mechanical strength than the pellets produced from the raw FRs, at the same pelletizing pressure. These results are in good agreement with the other studies[6-8].

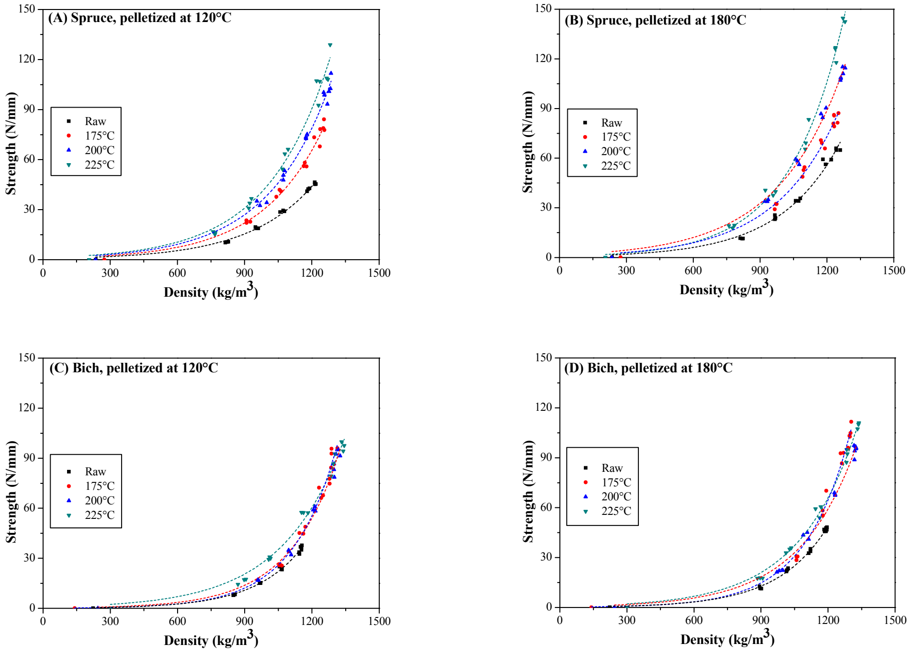

Fig 6. Relationship between density and strength of pellets produced at different compacting temperatures.

Increasing the pelletizing temperature from 120 to 180°C had a little effect on the pellet density but improves the pellet strength. This is addressed to the behaviours of lignin below and above its glass transition temperature (T_g), which is around 135-165°C[8]. At a temperature higher than the T_g, lignin softens and enhances the inter-particles binding, which improves the mechanical strength of pellets[13]. Therefore, the pellets made at 180°C were stronger than pellets produced at 120°C, at the same compacting pressure.

Pelletization at higher compacting pressure produced pellets with higher density and strength. It is also shown that a small increase in density resulted in a large increase in strength if the density of pellet was higher than 1000 kg/m^3, which can be achieved by applying a compacting pressure above 80 MPa. Although more energy is required, it is recommended a pressure higher than 80 MPa for the production of pellets due to the benefit form the exponential relationship between the pellet strength and density.

CONCLUSION

WT improved the fuel properties and reduced specific grinding energy of the FRs. The average particle size of ground hydrochar was smaller than that for raw FR and gradually decreased with increasing WT temperature. The pellets of wet-torrefied FR were better compressible and stronger than the pellets of raw FR. Increases in density for the hydrochar pellets compared to the pellets of raw materials was up to 159 kg/m^3 for spruce and 213 kg/m^3 for birch. Improvements in the strength of torrefied pellet compared to raw pellet were up to 3.4 and 2.7 times for spruce and birch, respectively. The effect of pelleting temperature on pellet density was unpronounced but the effect on pellet strength was significant due to different behaviours of lignin below and above its glass transition temperature. Increasing compacting pressure increased the mass density and strength of the pellets.

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