Commoditization of wet and high ash biomass: wet torrefaction—a review

K.J. Moscicki[a], L. Niedzwiecki[a,*], P. Owczarek[b], M. Wnukowski[a]

[a]*Wroclaw University of Science andTechnology, Faculty of Mechanical and Power Engineering , Wyb.Wyspianskiego 27, 50-370 Wroclaw, Poland;*
[b]*University of Twente, Drienelolaan 5, 7522 NB, Enschede, Netherlands*

Abstract

Biomass is a non-intermittent energy source, which can play an important role in grid-based energy systems, since they need some non-intermittent sources in order to balance the variability of intermittent sources as wind and solar energy. Currently, this role is played mostly by fossil fuels, mainly because of the bulk size of a single source. Higher variability and lower energy concentration, among with some properties of biomass, are obstacles that prevent it from fully becoming a commodity. There are processes, such as dry torrefaction and hydrothermal carbonization (HTC) that could potentially help in terms of making biomass a tradable commodity, as is the case with fossil fuels. HTC, also known as wet torrefaction, might help solve problems that dry torrefaction is incapable of solving. These obstacles are, namely: high ash content, slagging and fouling properties of biomass (along with corrosion). Also the high moisture content of some types of biomass poses a problem, since they usually require substantial amounts of heat for drying. This paper reviews current knowledge about a process that could possibly transform problematic types of biomass into tradable commodities and compares it with other processes offering similar outcomes.

Keywords: commoditization of biomass; torrefaction; hydrothermal carbonization; wet torrefaction; valorization of biomass

1. Introduction

Biomass is an energy source that is considered neutral in terms of CO_2 emissions [1]. That statement is based on a simplification. Carbon dioxide is always released as a product of combustion when carbon is burned. However, biomass absorbs carbon bounding CO_2 particles during photosynthesis [2]. Carbon along with oxygen and hydrogen is one of the three main elements present in biomass, namely in the three main carbohydrate compounds (cellulose, hemicelluloses and lignin) that form the orthotropic, composite organic structure of plants [3]. It is possible to obtain biomass on a long term, sustainable basis and this practice is well known [4].

The authors consider the commoditization of biomass as a set of technical means that make it possible for solid biomass fuel to become a tradable commodity, the goals being:

• making biomass more uniform by changing its properties, relevant from the point of view of its final use (the last energy conversion stage before delivering useful energy to the final user)

• optimizing properties relevant from the fuel logistics point of view (transportation and handling).

It is difficult to define the extent to which uniformity is achieved and properties are optimal, therefore the authors present a comparative review. Comparison is made with other existing technologies that seek to transform biomass into a commodity. This paper shows trends that could be relevant in terms of the design of commercial scale units (parameters for optimal operation), which could determine the suitability of the technology for particular types of feedstock.

In light of the breadth of this topic, the paper limits itself to solid fuels only. Some papers suggest potential for hydrochars to become soil amendments in agriculture [5], or a synthesized material for other various applications [6–12]. This could also allow hydrochar to become tradable, but that falls ouside the remit of this review. The example of energy transformation in countries like Germany [13] suggests that solid, tradable biofuels, with potential to replace coal, could play an important role in the introduction of additional intermittent sources (like solar and wind) into the grid. Currently, that role is played, to some extent, by hard coal [13]. Dry torrefaction was covered in a previous review by the authors [14] and this paper should be viewed a continuation.

While dry torrefaction may solve many problems related to the use of biomass as a solid biofuel [14–19] some still

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*Corresponding author
Email address: `lukasz.niedzwiecki@10g.pl` (L. Niedzwiecki)

remain unresolved. The mineral content in combination with high amounts of chlorine may give rise to serious operational problems in combustion and co-combustion facilities [20–25]. Slagging and fouling could become serious problems, impacting availability [22]. These could be minimized by adjustments in boiler design. Some sources state that lowering the temperature in the convectional pass could be helpful [26]. If a flue gas containing alkali chlorides has a low enough temperature, then any deposits are solid, not molten. Thus, when brought into contact with the tube surfaces their corrosion potential is reduced. At issue are temperatures in the region of 650°C. This is a common design in waste incinerators [26]. Other sources advise temperatures below 600°C [22]. Turning to other measures, soot blowers may be installed and occasionally blow out deposits [22]. Problematic biomass can be co-burned with fuels containing sulfur. This produces an S/Cl molar ratio close to 2 [26]. Unfortunately, this limits fuel flexibility and in principle seems to run contrary to the goal of commoditization in general. As a consequence, such installations are usually customized to use a particular source of biomass. Hence there is a need to carry out an assessment of what biomass is available and how suitable it is for any particular end use [1, 27]. This necessarily leaves the fuel and the supplier of useful energy to the final user inherently tied, and that makes biomass more "local". Another approach to solving the problem is to alter the properties of the fuel, by using additives like AlSi (kaolin, dolomite), dicalcium phosphate and ammonium sulfate [26]. This can be done during pelletization of torrefied biomass, but it involves additional cost (purchase of the additive) and introduces the problem of optimizing the pelletization process with respect to such additives. Moreover, the magnitude of the problem is hard to assess, because it is not easy to find published materials on pelletization with additives of these types. Another problem that traditional torrefaction is unable to solve relates to some low grade, moist types of biomass, which typically require pre-drying (e.g., algae extraction waste [28]). This may significantly reduce the overall efficiency of the process, when all unit operations are taken into account. Due to these factors, hydrothermal processes are being investigated. The principles of those processes are not a novelty. The first fully described experiments were performed as early as 1913 by Bergius, who tried to imitate the natural coalification of organic material [29]. He used the name hydrothermal carbonization (abbreviation HTC is frequently used). Some works are even older—the earliest patent submitted by Vignoles was submitted in 1850 for "wet carbonization of peat" [30]. The process is also called wet torrefaction, because in principle it resembles torrefaction (called "dry torrefaction" to have some distinction between the two) [31].

In general, it has similar goals, i.e., making a solid fuel more closely resemble coal. In wet torrefaction the carbonization process is also done at elevated temperature [32]. The difference is the surrounding environment. The process is performed in subcritical water rather than inert gases [32]. As a consequence (water is kept in subcritical conditions)
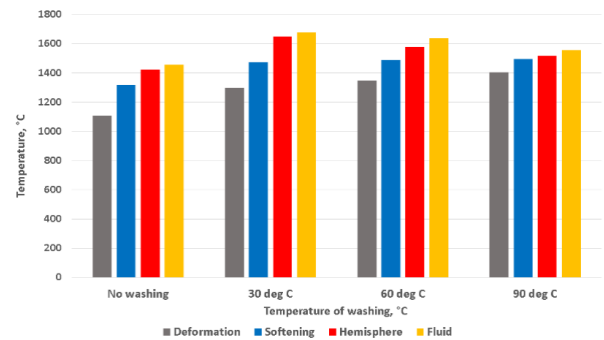

Figure 1: Ash softening temperatures for different water temperatures during water washing of wheat straw (3 hours) [38]

pressure is also elevated to keep the water liquid in this temperature range (to keep water pressure over its saturation pressure at the desired temperature). To date the process has been performed mainly at laboratory scale in batch reactors, with autogenous pressure [7, 29, 30, 32–35]. In general, it is assumed that fossil fuels were "produced" by nature in a similar process [30]. The only difference is that in the natural environment the process was performed under lithostatic pressure [30]. There are some existing reviews on the topic [5, 8, 36], but none of them covers the commoditization aspect. Some studies investigated other applications such as pretreatment of bagasse for the production of ethanol and use for pulp and paper products [37].

Introducing subcritical water achieve (in comparison to the dry torrefaction process) further improvement of the fuel, i.e., washing out mineral content of feedstock (discussed further in Section 6). That mechanism is well-known and works in ambient conditions too. It is used to decrease mineral and chlorine content in straw. In agricultural practice it is performed by simply leaving the straw out on the field [39]. Leaching occurs with rainfall water. Alternatively, leaching might be intensified by washing, performed with twater [40]. This might bring satisfactory results (Fig. 1), although significant residence time is involved (3 h [38] to 20 h [40]). At present now wood pellets are the most widely utilized commodity, derived from biomass, with over 13 million tons consumed around the world [41]. Techno-economic simulations [42] suggest the production cost of 13.48 €/GJ for standalone HTC pellets and 9.73 €/GJ for wood pellets. To justify this difference some additional gains should be obtained.

2. HTC-process conditions

Wet torrefaction takes place at elevated temperatures (typically 200 to 260°C) and at elevated pressure. Raw material is put into a pressure tight, heat conducting container. Then water is poured into the reactor and the raw biomass is submerged in the water. Afterwards, the reactor is sealed to keep it completely pressure tight. In a batch reactor the pressure is obtained by achieving a desired temperature [32]. When the temperature rises, part of the water evaporates and at a certain temperature some gaseous products (mainly
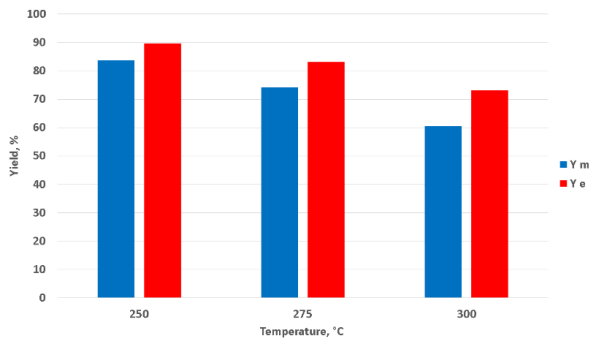
Figure 2: Typical mass and energy yield of dry torrefaction process for different process temperatures (Loblolly Pine; residence time 5 min) [32]
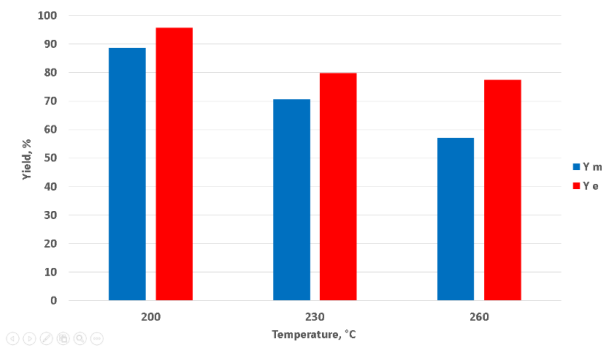

Figure 3: Typical mass and energy yield of wet torrefaction process for different process temperatures (Loblolly Pine; residence time 5 min; water to biomass ratio 5:1) [32]

CO_2) emerge. Vapor pressure keeps the remaining water as a liquid. It seems justified to use a simplification and state that the pressure of vapors is to some extent the saturation pressure of water at the desired temperature. The main product is of course Wet Torrefied Biomass, and as in Dry Torrefaction [16], there are some condensable products that become liquid after the batch is cooled. Part of the vapors remain gaseous at the ambient temperature [30]. This is differs from dry torrefaction, where energy lost during the process is bound in the torgas, which is a mixture of non-condensable gases and tarry volatile compounds condensable in ambient conditions [14]. Among non-condensable gases, combustible CO is dominant and there is a small amount of CO_2 present [14]. There are two very commonly used quantitative indicators to quantify process output with respect to process conditions, namely mass yield (Ym) and energy yield (Ye) [34]. The former is simply the ratio of (i) dry mass of solids that remain after the process to (ii) dry solids of input feedstock. The latter is simply mass yield multiplied by the ratio of the higher heating value (HHV) of the product divided by the higher heating value of the feedstock. Energy yield will always be higher than mass yield for any process condition that produces fuel with HHV greater than HHV of feedstock. From a practical point of view this is essential to achieve energy densification.

Both mass yield and energy yield are lower for wet torrefaction of biomass in a similar temperature range (Fig. 2

and Fig. 3). Mass yield for HTC may reach approximately 2/3 of the dry torrefaction value (Fig. 2 and Fig. 3). There is a smaller difference in energy yield. Energy yield for wet torrefaction may reach approximately 3/4 of the dry torrefaction value (Fig. 2 and Fig. 3). In practice it means that slightly less energy is lost in the process, because a lower temperature is needed to achieve the same effect.

Unfortunately, since CO_2 is dominant in the gaseous products, it is harder to recover part of the energy bound in the feedstock prior to hydrothermal carbonization. It is much easier in dry torrefaction, where gases could be simply combusted. However, it is not that straightforward in practice, since most torrefaction technologies now use flue gases from combustion to heat the feedstock directly in the reactor [14]. This results in a relatively low calorific value of torgas due to dilution of combustible gases with nitrogen (coming from the combustion air). This also makes recirculation of this high volume of low calorific torgas problematic. Combustion of torgas is relatively easier in airless torrefaction systems that use fluids to deliver process heat externally [15, 43]. In the case of hydrothermal carbonization, recovery of energy bound in the liquid is possible only by producing biogas with anaerobic digestion. One study [44] reported a biogas production rate of up to 0.25 L/(L*d) in both a continuously stirred-tank reactor (CSTR) and an anaerobic filter (AF), with a constant organic load (COD) rate of 1 g COD/(L*d). This degraded up to 80% of phenolic compounds in post process water. Biogas yield of 0.5 L/g TOC (Total Organic Carbon) is reported for post process water after HTC of sewage sludge[5]. Digestion was performed using a mesophilic (35°C) batch digester. Another study [45] performed with the use of a 40 L up-flow anaerobic solid-state (UASS) reactor reports methane yield of 0.165 L/g of organic dry mass (ODM) input. The process took place in thermophilic conditions (55°C) and posted a fixed organic load rate of 2.5 g/(L*d) on a dry basis. A study focused on hydrothermal carbonization of agricultural residues reported a minimum biogas yield 9.6 L/kg Fresh Mass and a maximum of 21.1 L/kg Fresh Mass [46].

3. Properties of wet torrefied material

There are some differences between the products of dry torrefaction and hydrothermal carbonization. The higher difference between mass and energy yield also indicates that there is greater HHV growth (Fig. 4).

Wet torrefaction achieves a higher carbon concentration compared to dry torrefaction (Fig. 5, Fig. 6) [32, 47]. Some see it as potentially interesting in the context of possible carbon sequestration in the soil [5, 48]. In addition, a lower temperature is required for wet torrefaction in order to obtain similar results to dry torrefaction.

Both ultimate analysis (Fig. 5 and Fig. 6) and proximate analysis (Fig. 7 and Fig. 8) show that wet torrefaction is superior in terms of making biomass resemble coal.

Oxygen concentration is lower for HTC than for dry torrefaction product, which makes it a potentially more suitable
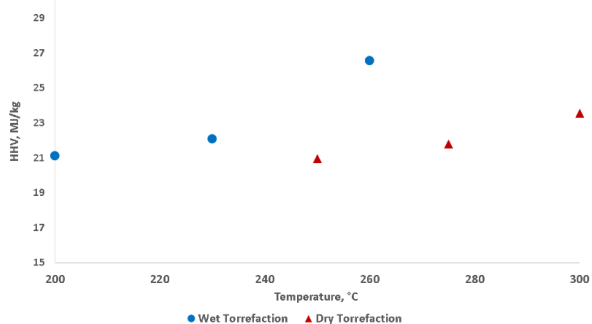
Figure 4: Higher Heating Value of torrefied solid fuels (dry and wet torrefaction) with respect to different process temperatures (Loblolly Pine; residence time 5 min; water to biomass ratio 5:1 in the case of HTC) [32]

Figure 5: Ultimate analysis of wet torrefied wood with respect to different process temperatures (Loblolly Pine; residence time 5 min; water to biomass ratio 5:1 in the case of HTC) [32]
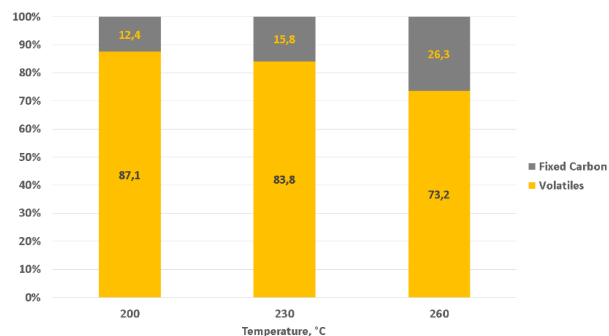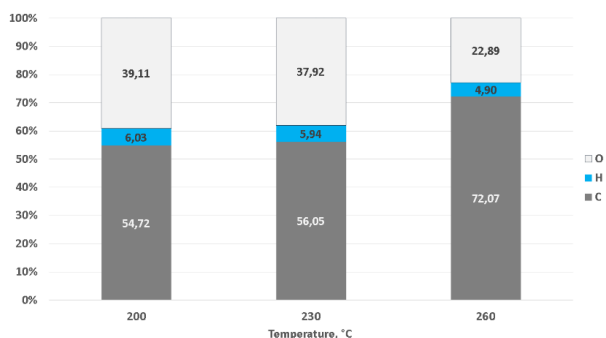

Figure 7: Fixed carbon and volatiles of wet torrefied wood with respect to different process temperatures (Loblolly Pine; residence time 5 min; water to biomass ratio 5:1 in the case of HTC) [32]
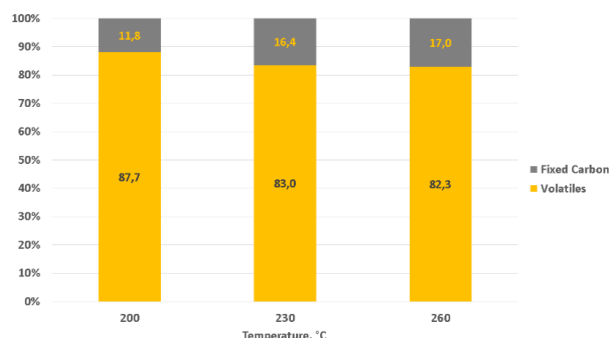

Figure 8: Volatiles and fixed carbon of dry torrefied wood with respect to different process temperatures (Loblolly Pine; residence time 5 min) [32]

pretreatment prior to fast pyrolysis [49].

Wet torrefaction decreases a volatile content more than dry torrefaction and increases the amount of fixed carbon to a greater extent for the same process temperature (Fig. 7 and Fig. 8).

Fiber analysis brings some interesting results (Figures 9, 10 and 11). Both dry and wet torrefaction decrease the amount of cellulose in biomass and the degree of conversion is comparable.

However, wet torrefaction is able to convert hemicelluloses almost completely, which occurs in dry torrefaction only

at higher torrefaction temperatures (for the same residence time).

The most significant difference among the two compared processes is the concentration of lignin and aqueous solubles in the product. Aqueous solubles consist mostly of polysaccharides, saccharides, proteins and starch [50]. Of the three main constituents of wood (hemicellulose, cellulose and lignin) lignin was not measured directly in some of the studies [50], due to method used (Van Soest method [50]). Therefore, it is possible that there were some other substances, repolymerized during the process, that "posed" as
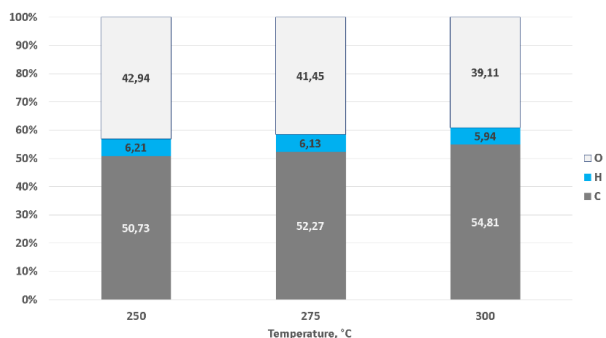

Figure 6: Ultimate analysis of dry torrefied wood with respect to different process temperatures (Loblolly Pine; residence time 5 min) [32]
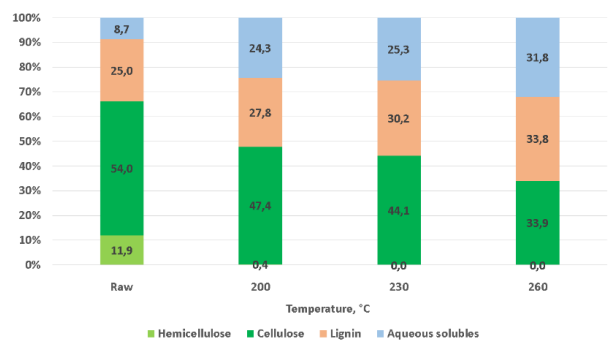

Figure 9: Fiber analysis of wet torrefied biomass with respect to different process temperature (Loblolly Pine; residence time 5 min; water to biomass ratio 5:1 in case of HTC) [32]
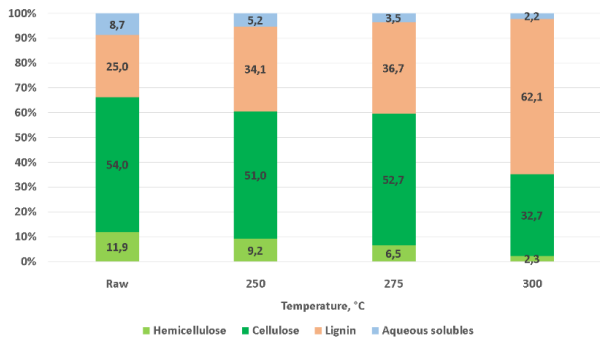
Figure 10: Fiber analysis of dry torrefied biomass with respect to different process temperature (Loblolly Pine; residence time 5 min) [32]
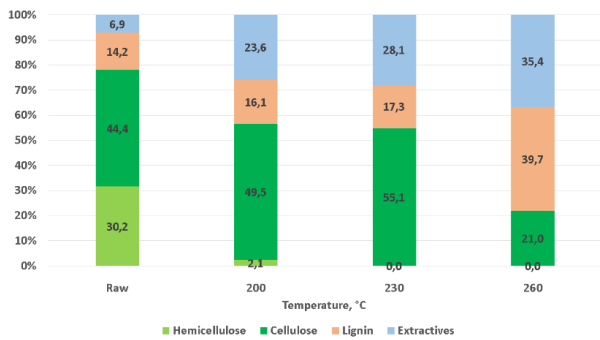

Figure 11: Fiber analysis of wet torrefied Miscanthus with respect to different process temperature [50]

lignin, since they could not be solved by any of the detergents and were left as a solid residue [50]. This is extremely important, since for the purpose of commoditization the ability to densify biomass after pretreatment is of crucial importance.

This might mean different behavior during pelletization or briquetting, since lignin is a basic binder in wood pellets. However, it is not possible to predict this behavior, since the similarity of those components to lignin as well as their origin might make them an equally good binder or better. In terms of wet torrefied biomass aqueous solubles consist of substances that are commonly used as binders (starch) or might prove their value as one. That indicates one of the
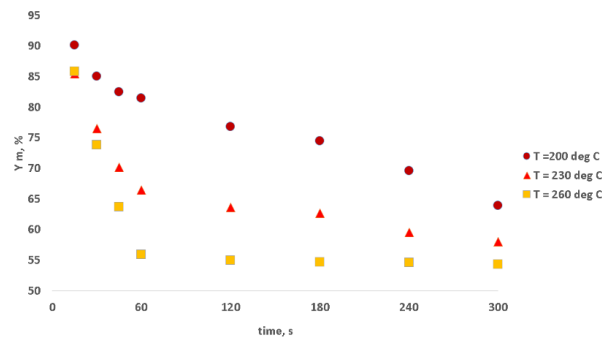

Figure 12: Mass yield of HTC Loblolly Pine depending on different residence time and process temperature [35]
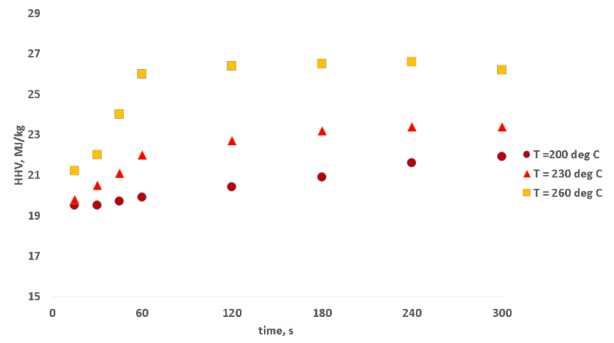

Figure 13: HHV of wet torrefied Loblolly Pine depending on different residence time and process temperature [35]

most important directions for future research. It was shown that particle size does not seem to play a significant role in terms of mass yield, but experiments were performed only within a limited range of particle sizes [35]. In the range of average particle diameter of between 0.88 and 2.1 mm, the mass yield was at a level of about 70% in all the cases (with residence time of 1 minute and 230°C). Results for very small particles might be different, but from the supply chain point of view they would have limited practical applicability. It would be impractical to grind biomass into very small particles prior to torrefaction and the range presented in the literature is similar to a typical particle size in pelletization. In general, wet torrefaction is a time dependent process (Fig. 12 and 13) and searching for the most optimum time should not be overlooked—as in the case of dry torrefaction.

Knowledge of the kinetics involved seems to be an obvious target. However, both dry and wet torrefaction are heterogeneous processes that consist of a multitude of concurrent and complicated reactions. A similar situation arose with pyrolysis, where a multitude of existing models did not bring much insight in terms of practical process applications. This has been commented on [51].

It is possible that simple correlations between process conditions and parameters of the feedstock and products might bring more practical, short and medium term benefits from the process design angle. Having one uniform, complete theoretical description is obviously beneficial. However, the need to make biomass a commodity determines different desired outcomes of the process. These should be related to problems (final use—Section 1 and [14]) that pretreatment can solve. These problems varyfrom feedstock to feedstock.

4. Chemistry of the process

Subcritical water is used during hydrothermal carbonization. At temperatures of 200 to 280°C the ionic constant of water is increased by nearly two orders of magnitude and the liquid water behaves as a non-polar solvent [50]. Reaction pathways for Wet Torrefaction are quite complicated. Hydrolysis is the reaction that occurs initially [30]. The literature mentions that the rate of hydrolysis is diffusion controlled and therefore is limited by transport phenomena within the fibrous

structure of biomass [35]. High temperature overall should enhance hydrolysis reactions, since it lowers the viscosity of the water. The increase in Thiele modulus along with temperatures indicates that the overall reaction rate is dominated by mass transfer [35]. HTC process overall makes the fibrous structure collapse, which can be seen when observing wet torrefied material [52]. That may lead to further reactions and therefore affects the whole process to a greater extent than the chemical kinetics of all other reactions. The principal sum reactions that mostly affect the elemental composition of wet torrefied biomass are dehydration and decarboxylation [33]. Dehydration is generally explained as the elimination of hydroxyl groups (OH) [30]. During dehydration colloidal structures are destroyed. That decreases the amount of hydrophilic groups and promotes gas formation, thereby facilitating physical dewatering [30]. Elimination of OH groups should lower the O/C ratio, which also affects the water content (a linear relation was determined for lignite [52]). Decarboxylation is the degradation of carboxyl (COOH) and carbonyl (C=O) groups, which happens rapidly over approx. $150°C$. That produces an increase in CO_2 and CO yield (to a lesser extent) [30]. In consequence, it slightly decreases the O/C ratio of the solid product. Since decarboxylation is one of the main reactions, measuring the CO_2 might be an effective way to control the HTC process [30]. Some of the fragments formed from degradation of biomacromolecules are highly reactive. Those compounds polymerize quite easily [30]. It is mainly a condensation polymerization, in particular aldol condensation. Condensation most likely proceeds mainly with H_2O formation. Free-radical mechanisms may appear in hydrothermal conditions, but are more likely to be dominant in supercritical conditions and at a low density [30]. At subcritical conditions free radicals are effectively saturated by the water and hydrogen present, donated from aromatization [30]. Polymerization forms a solid precipitation, which is highly unwanted in other hydrothermal processes (liquefaction and gasification) [30]. However, in terms of HTC it might be beneficial, if those polymers are able to act as a binder during the pelletization process. Even though cellulose and hemicellulose consist of carbohydrates, they are able to form aromatic structures in both hydrothermal and non-hydrous conditions [30]. Alkaline conditions appear to enhance the formation of aromatic structures [30]. Cross-linking condensation of aromatic rings also substitutes for major constituents of coal. This might explain the good agreement between natural coalification and hydrothermal carbonization in terms of product properties [30]. The presence of some stable compounds with a crystalline structure and oligomer fragments that do not hydrolyze might provide proof of some transformation reactions. Such reactions happen during natural coalification, preserving some physical structures for millions of years. However, it is believed to be of minor importance in terms of HTC [30]. Activation energies for HTC degradation of cellulose and hemicellulose have been reported to be 73 and 30 kJ/mol respectively [36], but since the process is supposedly controlled by mass transfer, not by kinetics, fur-

ther determination of the kinetics seems to lose relevance from the practical point of view. Heat of reaction is an uncertainty, just as it is in terms of dry torrefaction. The literature mentions the heat of reaction for wood at $240°C$ to be -0.76 MJ/kg daf (exothermic) [33]. On the other hand, some sources claim that heat of reaction is positive and as high as 0.53 MJ/kg (endothermic) [34]. Both results are accompanied by very high standard deviations ranging from ca. 30% to approx. 150% of the result [33, 34]. That range of possible values reduces the practical possibility for a straightforward application of data in design practice, since the influence on actual reactor efficiency should be insignificant. In that case, heat loses due to temperature difference should be more meaningful. In general, for biomass and other solid fuels from a biological origin (i.e. peat) coalification seems to follow similar pathways [29].

5. Process water, product dewatering and water recirculation

Generally, three reaction pathways together lead to the formation of different precipitates during wet torrefaction:

1. Water at $200°C$ breaks the b-(1-4) glycosidic bonds of hemicellulose [50]. That makes hemicellulose degrade into oligosaccharides and then subsequently into monomeric xylose, which dehydrates and forms furfural, which subsequently polymerizes [52].

2. Lignin forms several phenols which polymerize rapidly [52].

3. Cellulose hydrolysis initially forms oligosaccharides and subsequently monomeric glucose. This isomerizes and forms fructose which then dehydrates and forms furfurals, mostly 5-HMF (hydroxyl methyl furfural). The latter is assumed to either polymerize to char or rehydrate to levulinic and formic acid [52]. Some part, however, can still be found in HTC products, with the concentration increasing with temperature.

Since the HHV of 5-HMF (22.1 MJ/kg) is higher than the HHV of hemicellulose (17.6 MJ/kg) and other extractives, some literature sources describe it as one of the main reasons why the HHV of HTC biomass is higher than for dry torrefied biomass (for two processes performed in the same conditions) [50]. It is believed that 5-HMF may be absorbed by the porous structure of wet torrefied biomass.

Among the organic acids present in the precipitates acetic acid is the one with the highest concentration (Fig. 14) [34, 53]. It has been reported that an acidic condition might overall positively improve the reaction rate for wet torrefaction and act as an autocatalyst [30, 33]. However, catalysis from organic acids is insignificant unless pH drops below 3 [33]. In practical terms it does not happen even after multiple water recirculation cycles (Fig. 15). The ability to wash out inorganic content (discussed extensively in Section 6) seems to be influenced by the pH of the process water [54]. Since heating the water up to the temperature of the process consumes by far the biggest amounts of energy, recirculation
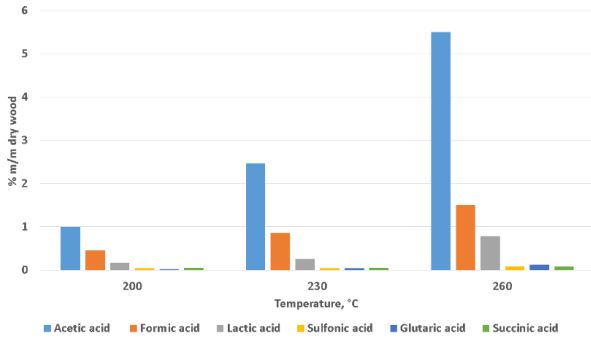
Figure 14: Ion Chromatography analysis of organic acids in post process water (Loblolly Pine; residence time 5 min; water to biomass ratio 5:1 in the case of HTC) [34]

Figure 15: Total organic carbon and pH—post process (HTC) water after a number of recirculations [52]

of process water is one of the pre-requisites for making the process energy efficient. In general, wet torrefaction lowers the equilibrium moisture (EMC) content of produced fuels [52, 55]. However, process water recirculation does not seem to have a significant influence on the EMC of the product [55].

Dewatering properties are important in terms of both the amount of water recirculated and the next unit operation (i.e. pelletization). An overly high moisture content of the wet torrefaction product might imply a need for additional drying before pelletization, which triggers both investment cost and

Figure 16: Elemental analysis with respect to process water recirculation (Poplar; 5 mm chips; T HTC = 200°C; residence time 1.5 h; water to biomass ratio 5:1 in the case of HTC) [52]
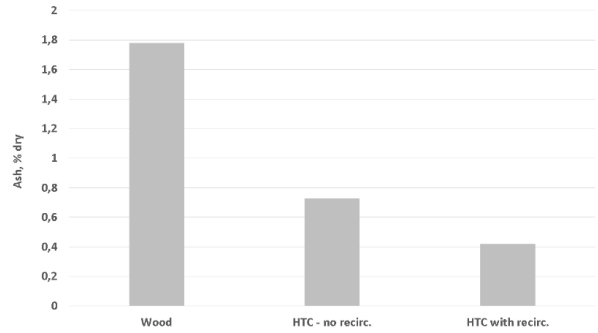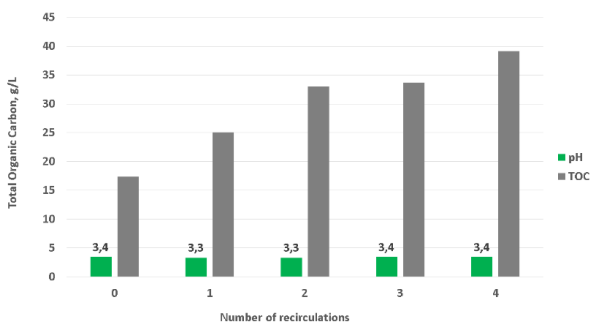

Figure 17: Ash content of wet torrefied biomass with respect to process water recirculation (Poplar; 5 mm chips; T HTC = 200°C; residence time 1.5 h; water to biomass ratio 5:1 in the case of HTC) [52]

energy losses. In general, part of the water is chemically bound in biomass by OH groups. A decrease in functional groups leads to better dewaterability [52]. The literature also reports that additional amounts of organic acids lead to an additional reduction of functional groups [52]. That along with mechanical changes in the torrefied material (collapsed wood structure after wet torrefaction) facilitates mechanical dewatering. Dewatering by piston press is reported to be 35.6% with and 45.2% without recirculation [52].

Recirculation affects many important parameters of the process and significantly impacts wet torrefaction products, namely ([52, 55]):

- process water properties and composition of Total Organic Hydrocarbon concentration
  - it changes until it reaches an asymptotic value of concentration of organic acids
- gaseous products
- elemental composition of HTC product (CHNS) (Fig. 16)
- ash content (Fig. 17)
- Higher Heating Value
- mass and energy yield
- carbonization
- mechanical dewatering possibilities

Importantly, some sources suggest the possible toxicity of both hydrochar and post process water [5]. It is mentioned in the context of "problematic" feedstocks like sewage sludge [56]. One study shows that the amount of dioxins and furans (PCDD/F) increased, nearly doubling TEQ (toxic equivalent) [56]. This does not seem to be a trend for all wet torrefied biomass. The ability to produce biogas from post process water, already mentioned in Section 2, seems to suggest that this water is not extremely harmful for living organisms. Reported soil effects of hydrochar use as a soil amendment in agriculture do not give any definite answer

either. Some results show increased yield of plants up to 240% and some show yield as low as 2% [5]. Despite that, many believe that HTC is promising in terms of processing sewage sludge and municipal solid waste [57–59], which are problematic anyway when use as a fuel is involved. Also the combustion of treated fuel, after dewatering, could possibly be much easier (due to lower moisture content) and compensate all the efforts. Surely more investigation is needed in order to assess the possible effects of utilizing post process water, both with and without anaerobic digestion as a post process treatment. This is essential in order to design environmentally sound processes, because there will always be some liquids that need to be disposed of, even if process water recirculation is incorporated.

6. Inorganics

Plants need inorganics to live and grow [4]. They acquire inorganics from the soil they are grown upon. If fertilizers are in use, mineral content might become higher. Mineral content in biomass might cause serious maintenance problems for energy conversion appliances, namely slagging and fouling as indicated in Section 1. Cl, due to its involvement in slagging and fouling related problems [23], should be discussed along with inorganics. Though the problem might be mitigated by proper handling ("natural" washing by leaving straw on site) [39] it involves both costs and uncertainty. The cost is caused by prolonged, on site storage (money received later is worth less). The uncertainty involves the weather, because rainfall is required to achieve the desired result [39]. Industrial washing involves significant residence time (residence time of 3 hours is recommended [39]), much higher than for typical wet torrefaction (5 to 10 min), although much longer residence times were also investigated (96 h—[68]; Table 1). This high residence time raises a question of economic feasibility connected with productivity of the unit.

There are some existing measures to assess the solid fuel potential of fouling and slagging.

Among them are [50, 69, 70]:

- Slagging index,
- Fouling index,
- Alkali index,
- Slag viscosity index,
- Cl content.

The two most common are the fouling index (IF) and the slagging index (IS) [50, 70, 72]. Both depend on B/A value. B indicates basic oxides (Fe_2O_3, CaO, MgO, Na_2O, K_2O—are being attacked by acids) and A stands for acidic oxides (SiO_2, Al_2O_3—are being attacked by basics) [50, 70]. These values may be used to assess how helpful the wet torrefaction process might be in mitigating these problems. Finding these values as a function of temperature and residence time may give an indication of process conditions in order to
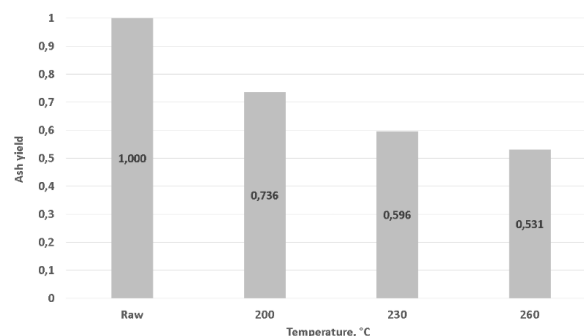

Figure 18: Ash yield with respect to different process temperatures (wet torrefied Miscanthus, 5 min of residence time) [50]

achieve the desired fuel quality. It does not seem possible to apply a simple rule of thumb to describe washing mineral content out of pretreated biomas. Results presented in the literature vary depending on the type of biomass and process conditions, as depicted by Table 1. In some cases pretreatment might also lead to increased risk of slagging and fouling, as shown by the published results [50, 72]. However, a general trend could be observed for each case independently (Fig. 18). There is a separate indicator, mentioned in the literature [50, 66], which could be potentially used to optimize the process with respect to the amount of ash removed. It is called ash yield. It is defined as an analogy to mass yield and energy yield. It is a quantitative descriptor that can be used to assess the amount of ash in fuel after wet torrefaction, if the ash content of feedstock and mass yield are known. Since mass yield itself is dependent on the process conditions, ash yield is a function of process conditions as well (Fig. 18) [50]. Ash yield depends on the mass yield itself [66]. As is shown by the literature data (Table 1, 2 and 3), in some of the cases low mass yield could cause the fuel to have increased ash content.

This is probably caused by proportionally higher loss of the organic matter. Usually it is caused by an overly long residence time. In any case ash yield is almost always smaller than 1.00, which indicates that inorganics are always removed to some extent. The only exemption is mixed MSW (Table 3) (Municipal Solid Waste), due to the high content of insoluble inorganic materials (9.6% of glass and 10.9% of metal [58]). In that particular case ash yield slightly higher than one is most likely the effect of cumulative error (no new inorganics could have been produced). That means that at least part of the inorganics is being removed from the solid phase (Hydrochar).

An important question that needs to be answered is the ability of HTC process to upgrade biomass in a way that would be less problematic for energy conversion appliances. Trends shown in the literature [50, 72] seem to confirm that Wet Torrefaction could produce less problematic fuel (Fig. 19 and 20), even though the ash content could be higher at the same time. Some explanations of this phenomena have been proposed [50]. Most Ca, S, P, Mg, and K in lignocellulosic biomass exist in either hemicellulose or extrac-

Table 1: Ash content before and after Hydrothermal Carbonization of various types of biomass—part 1

Feedstock	Type	Ash content		Parameters			Ym	Ya**	Ref.
	as in [60]	Raw	HTC	Temp.	t res.	W:B	-	-	Ref.
		%	%	ºC	min	-			
Corn cobs	Herbaceous	5.80	2.38	175			0.78	0.32	[61]
			3.59	185	5	9	0.65	0.40	
			4.42	195			0.53	0.40	
Miscantus	Herbaceous	0.80	0.54	190			0.83	0.56	[62]
			0.68	225	5	6	0.67	0.57	
			0.97	260			0.48	0.58	
Spruce	Woody	0.23	0.08	210	30	5	0.74	0.26	[63]
			0.10	222	5		0.74	0.32	
Grape pomace	Fruit	5.4	1.4	175	30	4	0.62 *	0.16	[64]
			1.1	200			0.60 *	0.12	
			1.9	200	10		0.59 *	0.21	
			1.7	225	30		0.58 *	0.18	
			2.1	225	60		0.57 *	0.22	
			3.4	250	30		0.53 *	0.33	
			2.7	275			0.47 *	0.24	
Bagasse	Herbaceous	3.55	1.70	180	5	10	n.s.	-	[65]
			2.13		10				
			2.55		15				
Miscanthus	Herbaceous	2.11	1.39	180		12	0.94	0.61	[66]
			1.34	200			0.82	0.52	
			1.00		10		0.70	0.33	
			2.54	220		3	0.80	0.97	
			1.58			6	0.79	0.59	
			1.25			16	0.68	0.40	
Grape merc	Fruit	6.00	3.38	180	60	5	0.76 *	0.43	[67]
			4.62		180		0.72 *	0.55	
			4.62		480		0.75 *	0.58	
			3.83	220	60		0.70 *	0.45	
			3.53		180		0.67 *	0.39	
			3.98		480		0.60 *	0.40	
			4.09	250	60		0.63 *	0.43	
			5.26		180		0.58 *	0.51	
			4.20		480		0.57 *	0.40	

W:B—water to biomass ratio (mass/mass)
Ym—mass yield
Ya—ash yield
*value read from a graph
**calculated, based on ash content and mass yield data
n.s.—not specified

Table 2: Ash content before and after Hydrothermal Carbonization of various types of biomass—part 2

Feedstock	Type as in [60]	Ash content Raw %	Ash content HTC %	Temp. ºC	t res. min	W:B -	Ym -	Ya** -	Ref.
Pine	Woody	0.74	0.24	180			0.73 *	0.24	[71]
			0.28	200			0.68 *	0.26	
			0.45	220	180	6	0.63 *	0.38	
			0.71	240			0.59 *	0.57	
			0.59	250			0.56 *	0.45	
			0.22	180			0.67 *	0.20	
			0.88	200			0.60 *	0.71	
			0.58	220	360	6	0.57 *	0.45	
			0.64	240			0.53 *	0.46	
			0.77	250			0.52 *	0.54	
			0.27	180			0.68 *	0.25	
			0.32	200			0.64 *	0.28	
			0.5	220	180	8	0.59 *	0.40	
			0.47	240			0.56 *	0.36	
			1.07	250			0.54 *	0.78	
Olive mill		5.51	2.26	225	120		0.60	0.24	[72]
			2.19		240		0.57	0.23	
			2.07		480		0.53	0.20	
			2.17		1440		0.47	0.19	
	Fruit		3.35	200			0.63	0.38	
			1.95	250		n.s.	0.45	0.16	
Cnd. Artich.		6.46	7.06	200			0.55	0.60	
			6.96	225	120		0.50	0.53	
			7.35	250			0.33	0.37	
Orange wst.		3.34	4.01	200			0.67	0.80	
			4.45	225			0.62	0.83	
			4.05	250			0.51	0.62	
Orange pmc.	Fruit	5.5	4.1 up to 4.9	175 up to 260	30 up to 120	8	0.53 up to 0.37*	-	[73]
Wheat straw	Herbaceous	8.8	7.0 up to 10.4	200	360	20	0.50 up to 0.54	-	[54]
			10.4 up to 12.7	260			0.31up to 0.34		

Cnd. Artich.—canned Artichoke
pmc.—pomace
wst.—waste
nt.—nuttalli
W:B—water to biomass ratio (mass/mass)
Ym—mass yield
Ya—ash yield
*value read from a graph
**calculated, based on ash content and mass yield data
n.s.—not specified

Table 3: Ash content before and after Hydrothermal Carbonization of various types of biomass—part 3

Feedstock	Type as in [60]	Ash content		Parameters			Ym	Ya**	Ref.
		Raw	HTC	Temp.	t res.	W:B	-	-	
		%	%	ºC	min	-			
Elodea nutalli	Aquatic	29.2	39.4	200	840	2	0.56	0.56	[74]
			41.9	240			0.51	0.51	
Eucalyptus	Woody	6.2	5.4	250	120	n.s.	0.4	0.35	[75]
Sewage sludge	Sewage sludge	27.54	22.89	140	240		0.75	0.62	[76]
			33.03	160	60		0.81	0.97	
			31.81		120		0.71	0.82	
			34.4		240		0.67	0.84	
			33.46	180	30		0.71	0.86	
			34.05		60		0.67	0.83	
			37.65		120	n.s.	0.64	0.87	
			39.17		240		0.62	0.88	
			35.87	200	15		0.69	0.90	
			36.29		30		0.67	0.88	
			35.93		60		0.64	0.83	
			38.07		120		0.61	0.84	
			38.94		240		0.60	0.85	
Paper Waste	Municipal Waste	10.9	24.2	250	1200	n.s.	0.29	0.64	[58]
Food Waste		7.5	11.2				0.44	0.66	
Mixed MSW		28.4	46.0				0.63	1.02	
A.D. solid res.		35.9	55.8				0.47	0.73	

A.D. solid res.—Anaerobic Digestion solid residues
W:B—water to biomass ratio (mass/mass)
Ym—mass yield
Ya—ash yield
*value read from a graph
**calculated, based on ash content and mass yield data
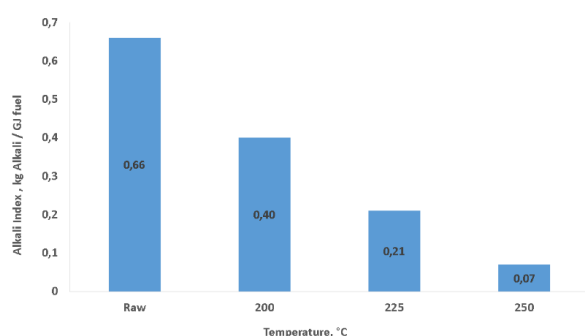n.s.—not specified

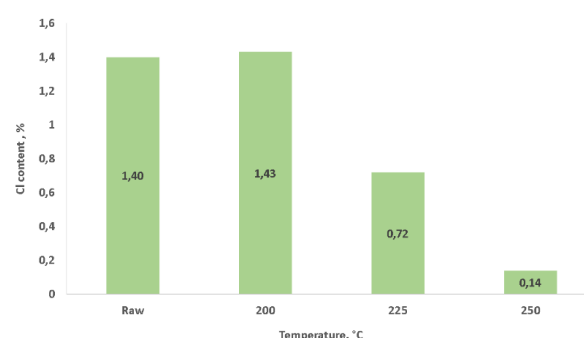Figure 19: Alkali index of Olive Mill Waste after HTC treatment [72]

Figure 20: Cl content of HTC treated Olive Mill Waste with respect to the different temperatures of the process [72]

tives [50]. However, not all of them seem to correlate in terms of their concentration in ash, either with hemicellulose or with extractives concentration in the wet torrefaction product. The main reason for that is the fact that the concentration of hemicellulose decreases with time, which is not the case for extractives. The porous structure of wet torrefied biomass [6, 54, 62, 75] and rising concentration of extractives might explain the fact that in some cases the concentration of some elements (Al, S, Si, and Fe) rises [50].

That seems to be the answer to why some of the indexes (named at the beginning of this paragraph) happen to be similar or higher [50] when wet torrefied material is being compared to raw biomass (for some parameters of HTC process). Nonetheless, ash yield decreases with temperature. Cl content decreases with temperature as well (Fig. 20). It

is clear that for higher HTC temperatures the wet torrefaction process has a positive influence on pretreated feedstock with respect to fouling and slagging behavior. The reason for that may be both the amount of minerals washed out and the change in S/Cl ratio.

Some authors suggest tht solids may lose part of their original inorganic content during dry torrefaction. A research team at Tampere University of Technology has shown that it was possible to decrease the Cl content for different samples of biomass through dry torrefaction [77]. A team from the University of Guelp (Canada) demonstrated the possibility of decreasing the content of Ca, Mg, P, K, Na, S and Fe [62] although the results were better for wet torrefaction treatment.
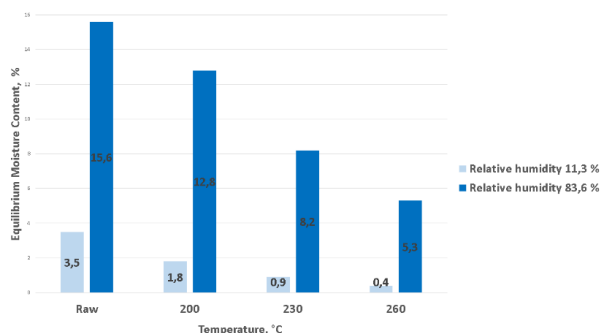
Figure 21: Equilibrium moisture content of wet torrefied biomass with respect to different process temperature (Loblolly Pine; residence time 5 min; water to biomass ratio 5:1 in the case of HTC) [32]

7. Handling and logistics

Handling and logistics aspects of the fuel are crucial in terms of making it a commodity, because the final customer will only buy fuel he can happily handle and use. The number of unit operations and the difficulty of performing them always adds to the cost of the fuel supply chain [1]. Handling aspects combined with energy densification are suspected to have an influence on the economics of the supply chain of dry torrefaction systems [78–80]. Moisture content is an important aspect of solid fuels. It is a subject of quality control in raw biomass pellets and for EN+ pellets the limit is set at 10% (wet basis) [81].

The hygroscopic nature of the raw biomass is an important factor. Tests performed on wood pellets show that moisture content could rise above the 10% threshold for Relative Humidity (RH) of the air to higher than 70% [82]. Values of RH higher than 80% are not uncommon in Europe. For example, monthly average values in Germany are typically higher than 80% in between October and February [83]. For the UK the long term annual average (between 1961 and 1990) of RH is higher than 79% for the vast majority of the country [84]. The results of some research also reveal other merits of the process in terms of commoditization of biomass. These results show that biomass pretreated with hydrothermal carbonization is not as hydrophilic as raw biomass (Fig. 21). That demonstrates long term stability in terms of moisture content and the possibility to maintain it below 10% (for some process conditions).

8. Issues relevant for industrial scale unit

Similar results were reported by another study [85]. This one showed that even for biomass carbonized at 200°C it is possible to obtain equilibrium moisture content of below 10% for RH below 75%. At 84% RH Equilibrium Moisture Content (EMC) for Wet Torrefied biomass (260°C) was reported to be 5.3%. For the same RH Dry Torrefied biomass (300°C) achieved EMC of 8.7%. The result for raw biomass (Loblolly pine) for the same RH was reported as high as

15.6%. Another study investigated the properties of wet torrefied Humulus lupulus (common hop plant), Lumeria alba (an evergreen shrub) and Calophyllum inophyllum L. (an evergreen tree) [86]. Wet torrefaction was carried out between 180°C and 260°C. The study showed it was possible to achieve EMC lower than 10% at 75% RH for all investigated types of biomass. For Humulus lupulus and Lumeria alba wet torrefaction at 180°C sufficed. For Calophyllum inophyllum L. wet torrefaction in 240°C resulted in material with EMC lower than 10%. EMC for all of the tested raw biomass samples was higher than 15% and with Calophyllum inophyllum L reached nearly 20%. Another study [62] compared HTC (190°C, 225°C and 260°C) and Dry Torrefaction (260°C) of Miscanthus and revealed that EMC was lower than 10% for all of the investigated cases. This general trend, which shows an increase in hydrophobic properties, has also been confirmed for peat [29]. This is an important aspect for the commoditization of biomass due to issues related to long term storage that could potentially be avoided or at least mitigated. Taking into account the fact mentioned in Section 3 that the content of lignin increases relative to other constituents, could be promising in terms of further densification of wet torrefied biomass. Various trials on dry and wet torrefied biomass have been performed to date. A study performed on Miscanthus [62] reports that the durability of raw Miscanthus pellets was 92.2%. The durability of HTC treated Miscanthus at 190°C and 225°C was found to be higher. It was determined that HTC treated Miscanthus and Dry Torrefied Miscanthus, both at 260°C, resulted in lower durability than for raw pellets. Pelletizing was performed using a single pellet press, with pressure of 8.6 MPa and temperature of 100 C. Durability was assessed by the drop test (4 times from a 1.85 m height). Another study [87], on properties of HTC treated Loblolly pine, reported slightly higher densities of the HTC pellets (up to 1316.8 kg/m^3) compared to raw pellets (1217.7 kg/m^3). Densification was performed using a laboratory pellet press with pressure of 160 MPa. A study performed on pinewood sawdust, rice husk, coconut fiber and coconut shell and on the hydrochars produced from these materials (250°C, 20 minutes) [88] revealed that particle density was higher for each of the hydrochars compared to the raw pelletized materials. Pelletizing was performed using a lab scale pelletizer with pressure of 280 MPa. Another study [89] compared pellets made from hydrochar, dry torrefied material (with different torrefaction temperatures) and their blends as well as pellets from raw material (Loblolly pine). Pelletizing was performed using a lab scale pelletizer with a temperature of the dye of 140°C and pressure of 250 MPa. Durability was assessed using a rotating drum tumbler (smaller version of the MICUM tester). It was found that the highest durability, very close to 100%, was achieved for hydrochar pellets. The durability of raw pine pellets was slightly lower (still above 95%). The durability of dry torrefied pellets ranged from 78% for dry torrefied material in 250°C and 9% for 350°C dry torrefied pellets respectively. Blending hydrochar with dry torrefied biomass increased durability in each of the cases. SEM images included in the study

showed many cracks and an apparent lack of binder for 100% dry torrefied pellets [89]. SEM images of 50/50 blend of dry torrefied and HTC treated biomass pellets shown solid bridge type bonding [89]. Astudy that investigated densification of Raw, Torrefied and HTC treated "Tahoe Mix" (woody biomass from thinning operations in Tahoe National Forest, California) reported somewhat different results [90]. Pellets made from Tahoe Mix hydrochar (carbonization at 255°C) obtained durability of 99.22%. Dry torrefied pellets obtained durability of 96.13%. Pellets made from Raw Tahoe Mix obtained 98.69% durability. Dry torrefied material was delivered by a commercial supplier that did not state the torrefaction conditions. However, the authors stated that: "exact torrefaction conditions used by Integro and Astec were not specified, but are known to be commercially relevant" [90]. Pellets were produced using a lab scale press with hydraulic pressure of 20 MPa, which according to the authors corresponded to approximately 295 MPa on the surface of the particle [90]. The temperature of the pelletizing was 140°C. Durability was assessed using the tumbling test with the tumbling barrel rotating for a total of 3000 revolutions at a speed of 38 RPM (revolutions per minute). A total amount of 40 pellets was loaded per trial. Although the presented results could give some indication in terms of trends and some rough predictions, it is hard to perform a direct comparison with wood pellets presently sold on the market. EN+ requires durability of greater than 97.5% (as received basis) [81]. The presented data suggests that this level of durability can be achieved. However, wide differences in terms of pelletization conditions and methods of durability testing militate against straightforward comparisons. The EN standard for durability testing [91] specifies a test portion of 500 g and a tumbling speed of 50 RPM for a total of 500 rotations. The dimensions and configuration of the tumbling box are specified. The safety issues should be factored in when assessing any fuel which is to become a tradable commodity. Studies for off-gassing of wood pellets started after a fatal accident in Sweden in 2006, while the vessel was discharging a bulk load of pellets from British Columbia (Canada) [92, 93]. This is not an issue exclusively for large scale bulk transport. In 2010 in Germany an engineer died after opening the door of a pellet bunker, with a storage capacity of approximately 155 tons of pellets [94]. A second worker was affected as well, but was able to call for help. Workers needed to enter the storage room, because of the problems with the pellet filling level gauge [94]. Another case happened in Switzerland in 2011, when a 28 year old woman, 4 months pregnant, was found in an 82 m^3 pellet storage room [94]. She entered the room because there was a problem with a pellet conveyor [94]. In all of the cases fatalities could have been prevented by proper ventilation of the area [95]. However, this is only remotely connected with the moisture uptake issue discussed earlier in this paragraph. If ambient air and natural ventilation is used, there is a risk of additional moisture absorption. On the other hand, having a controlled atmosphere (pre-drying of the air) inside the storage rooms inevitably introduces additional costs. So far off-gassing experiments were performed

for a dried torrefied material [93]. A plateau of CO concentration, for tests performed at 20°C, was slightly lower for torrefied material in comparison to European Wood Pellets (259 ppm and 335 ppm respectively) and much lower than for British Columbia (BC) Wood Pellets (5510 ppm). Off gassing at 40°C resulted in a plateau CO concentration of 4833 ppm for torrefied biomass, 13973 ppm for European Wood Pellets and 14334 ppm for BC Wood Pellets. The plateau was reached by torrefied material after 27 days and by European and BC wood pellets after 42 and 56 days respectively. None of the above concentrations can be considered safe. For example, in the United Kingdom the short time exposure limit (15 minutes) is 200 ppm [96]. No off-gassing data has been published to date for wet torrefied biomass. That knowledge gap must be filled before wet torrefied biomass could possibly become a commodity. Another safety concern is the explosion characteristics of wet torrefied biomass. A number of studies have been published on the explosion potential of torrefied biomass [97, 98]. For example, the reported Minimum Explosion Concentration (MEC) range for dry torrefied biomass ranges from 50 g/m^3 [98] to 63 g/m^3 [97]. These values are roughly comparable to typical values for woody biomass [98, 99] and lower than typical values for coals [99]. This is another knowledge gap that must be filled before HTC treated biomass could become a tradable commodity.

9. Issues relevant for industrial scale units

In general, while testing performed on industrial scale units could be considered as proof of concept, lab scale tests always precede them, pointing out all the possible gains and issues. There are records of successful trials performed with torrefied biomass on industrial scale units. A trial was performed on a 49 MW coal fired unit near Sneads, Florida [100]. All different variants, ranging from 100% coal operation, through co-combustion (with different ratios of torrefied material to coal) up to 100% of torrefied biomass, were subject to trials [100]. The trials showed a slight decrease in the efficiency of the boiler (approximately 14% total loss of efficiency for 0% torrefied biomass up to approximately 16% loss of efficiency for 100% torrefied biomass) [100]. Registered SO_2 emissions were 4 lb/MMBtu for 0% torrefied biomass and 0 lb/MMBtu for 100% torrefied biomass [100]. NOx emissions were 0.5 and 0.3 lb/MMBtu for 0% and 100% of torrefied biomass respectively (adjusted to 4% O_2) [100]. Maximum sustained load was limited by the mills and for 100% of torrefied biomass 21 MW was achieved. Maximum renewable energy output (26 MW) was achieved for co-burning of 74% of torrefied biomass. Other sources reported successful co-combustion of up to 25% of torrefied biomass with coal in the Netherlands (Amer power plant in Geertruidenberg) [101]. A total of 2300 tons was burned during the tests [102]. Another source reported co-gasification of 1200 tons of torrefied biomass (70% co-gasification on an energy basis) in Willem Alexander Centrale (Buggenum, the Netherlands) [103]. There are some strong indications that the grindability of wet torrefied biomass will be greater

than for raw biomass [62, 66]. For the same temperature of the process better results (higher amounts of fine material) are reported for HTC treated biomass (HTC and dry torrefaction at 260°C) [62]. However, straightforward comparison is difficult, because none of the papers use the Hardgrove Index—widely established by the industry in the form of a standard [104] which seems more appropriate if burning in pulverized coal boilers is to be assessed. Large scale trials do not seem feasible at present, because only scarce information on existing pilot HTC units is currently available [105, 106].

10. Conclusions

Wet torrefaction seems to have great potential in terms of commoditization of low grade biomass. However, this process will inevitably compete with dry torrefaction and with pelletization (without additional thermal pretreatment).
The following points should be emphasized:

- HTC is comparable to dry torrefaction in terms of mass and energy yield, leading to a similar densification of energy. It can be done at comparably lower process temperatures, therefore reducing the demand for process heat.

- Dry torrefaction can utilize energy from the process by-product (torgas) simply by combustion. Wet torrefaction systems would have to use different auxiliaries, like anaerobic digestion to utilize its own by-products.

- HTC does not require any pre-drying, therefore seems to be the favorable option for feedstocks with initially high moisture content. Mechanical dewatering could reduce the amount of heat required to dry the product prior to densification (although it would likely require an additional unit operation—drying, prior to pelletization).

- HTC can reduce the ash content and improve the parameters of the fuel in terms of slagging and fouling, but careful choice of process parameters is advised.

- Results from pelletizing trials of HTC treated biomass are promising. More trials on larger volumes, followed by the test procedures already established by the pellet industry, are needed before definite conclusions can be drawn.

- Scarce information currently exists on handling and safety aspects of solid fuels produced via wet torrefaction (explosivity, off-gassing, etc.). More research is definitely needed in that area.

- The low equilibrium moisture content of typical hydrochars suggests that storage requirements would be less demanding than untreated wood pellets.

- HTC seems to increase the grindability of wet torrefied biomass. It is similar for dry torrefied materials.

- There is only scarce information on HTC pilot units. They will be needed for the purpose of producing the volumes of fuel required to be able to assess handling and safety aspects. Also any eventual combustion trials on industrial scale boilers would require pilot HTC units capable of producing sufficient amounts of the wet torrefied material for these tests.

Wet torrefaction is able to upgrade biomass derived solid fuels by changing the parameters of the fuel to be more favorable. Therefore it seems reasonable to conclude that HTC is one of the processes that could help biomass become a tradable commodity in the long term. Additional research and a greater number of pilot units are pre-requisites for achieving "proof of concept".

References

[1] R. E. Sims, The brilliance of bioenergy: in business and in practice, Earthscan, 2002.

[2] D. L. Klass, Biomass for renewable energy, fuels, and chemicals, Academic press, 1998.

[3] J. Dinwoodie, Timber, its nature and behaviour, Taylor & Francis, 2000.

[4] R. Björheden, P. Hakkila, A. Lowe, C. Smith, Bioenergy from Sustainable Forestry: Guiding Principles and Practice, Dordrecht, Kluwer Academic Pub, 2002.

[5] M. T. Reza, J. Andert, B. Wirth, D. Busch, J. Pielert, J. G. Lynam, J. Mumme, Hydrothermal carbonization of biomass for energy and crop production, Applied Bioenergy 1 (1) (2014) 11–29.

[6] F. Vilela, K. Zhang, M. Antonietti, Conjugated porous polymers for energy applications, Energy & Environmental Science 5 (7) (2012) 7819–7832.

[7] A. Kruse, A. Funke, M.-M. Titirici, Hydrothermal conversion of biomass to fuels and energetic materials, Current opinion in chemical biology 17 (3) (2013) 515–521.

[8] M. Titirici, M. Sevilla, Hydrothermal carbonization: a greener route towards the synthesis of advanced carbon materials, Boletin del Grupo Español del Carbon 1 (25) (2012) 7–17.

[9] M.-M. Titirici, M. Antonietti, Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization, Chemical Society Reviews 39 (1) (2010) 103–116.

[10] M. Antonietti, M.-M. Titirici, Coal from carbohydrates: The "chimie douce" of carbon, Comptes Rendus Chimie 13 (1) (2010) 167–173.

[11] M.-M. Titirici, M. Antonietti, N. Baccile, Hydrothermal carbon from biomass: a comparison of the local structure from poly-to monosaccharides and pentoses/hexoses, Green Chemistry 10 (11) (2008) 1204–1212.

[12] L. Zhao, N. Baccile, S. Gross, Y. Zhang, W. Wei, Y. Sun, M. Antonietti, M.-M. Titirici, Sustainable nitrogen-doped carbonaceous materials from biomass derivatives, Carbon 48 (13) (2010) 3778–3787.

[13] B. Burger, Electricity production from solar and wind in germany in 2014, Tech. rep., Fraunhofer Institute for Solar Energy Systems ISE (2014).

[14] K. J. Mościcki, Ł. Niedźwiecki, P. Owczarek, M. Wnukowski, Commoditization of biomass: dry torrefaction and pelletization-a review, Journal of power technologies 94 (4) (2014) 233–249.

[15] R. Walton, B. Bommel, A complete and comprehensive overview of torrefaction technologies, Tech. rep., E-EnergyMarket, http://www. e-energymarket. com/mall/market-reports-and-studies. html (2011).

[16] J. Koppejan, S. Sokhansanj, S. Melin, S. Madrali, Status overview of torrefaction technologies, Tech. rep., IEA Bioenergy Task 32 (2012).

[17] D. R. Nhuchhen, P. Basu, B. Acharya, A comprehensive review on biomass torrefaction, International Journal of Renewable Energy & Biofuels 2014 (2014) 1–56.

[18] J. Shankar Tumuluru, S. Sokhansanj, J. R. Hess, C. T. Wright, R. D. Boardman, A review on biomass torrefaction process and product

properties for energy applications, Industrial Biotechnology 7 (5) (2011) 384–401.

[19] L. Nunes, J. Matias, J. Catalão, A review on torrefied biomass pellets as a sustainable alternative to coal in power generation, Renewable and Sustainable Energy Reviews 40 (2014) 153–160.

[20] P. Basu, C. Kefa, L. Jestin, Boilers and burners: design and theory, Springer Science & Business Media, 2012.

[21] P. Basu, Combustion and gasification in fluidized beds, CRC press, 2006.

[22] K. Rayaprolu, Boilers for power and process, CRC Press, 2009.

[23] D. A. Tillman, D. Duong, B. Miller, Chlorine in solid fuels fired in pulverized fuel boilers—sources, forms, reactions, and consequences: A literature review, Energy & Fuels 23 (7) (2009) 3379–3391.

[24] D. Mudgal, S. Singh, S. Prakash, Corrosion problems in incinerators and biomass-fuel-fired boilers, International Journal of Corrosion 2014.

[25] K. Hein, Operatinal problems, trace emissions and by-product management for industrial biomass co-combustion, Tech. rep., Institute of Process Engineering and Power Plant Technology, University of Stuttgart (1999).

[26] Bisyplan web-based handbook, [Accessed 24 december 2014]. (2012).
URL http://bisyplan.bioenarea.eu/html-files-en/

[27] F. Rosillo-Calle, J. Woods, The biomass assessment handbook: bioenergy for a sustainable environment, Earthscan, 2012.

[28] A. Broch, U. Jena, S. K. Hoekman, J. Langford, Analysis of solid and aqueous phase products from hydrothermal carbonization of whole and lipid-extracted algae, Energies 7 (1) (2013) 62–79.

[29] A. T. Mursito, T. Hirajima, K. Sasaki, Upgrading and dewatering of raw tropical peat by hydrothermal treatment, Fuel 89 (3) (2010) 635–641.

[30] A. Funke, F. Ziegler, Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering, Biofuels, Bioproducts and Biorefining 4 (2) (2010) 160–177.

[31] J. R. Pels, P. Bergman, TORWASH: proof of principle, phase 1, ECN, Energy Research Centre of the Netherlands, 2006.

[32] W. Yan, T. C. Acharjee, C. J. Coronella, V. R. Vasquez, Thermal pretreatment of lignocellulosic biomass, Environmental Progress & Sustainable Energy 28 (3) (2009) 435–440.

[33] A. Funke, F. Ziegler, Heat of reaction measurements for hydrothermal carbonization of biomass, Bioresource technology 102 (16) (2011) 7595–7598.

[34] W. Yan, J. T. Hastings, T. C. Acharjee, C. J. Coronella, V. R. Vásquez, Mass and energy balances of wet torrefaction of lignocellulosic biomass, Energy & Fuels 24 (9) (2010) 4738–4742.

[35] M. T. Reza, W. Yan, M. H. Uddin, J. G. Lynam, S. K. Hoekman, C. J. Coronella, V. R. Vásquez, Reaction kinetics of hydrothermal carbonization of loblolly pine, Bioresource technology 139 (2013) 161–169.

[36] H. A. Ruiz, R. M. Rodriguez-Jasso, B. D. Fernandes, A. A. Vicente, J. A. Teixeira, Hydrothermal processing, as an alternative for upgrading agriculture residues and marine biomass according to the biorefinery concept: a review, Renewable and Sustainable Energy Reviews 21 (2013) 35–51.

[37] S. G. Allen, L. C. Kam, A. J. Zemann, M. J. Antal, Fractionation of sugar cane with hot, compressed, liquid water, Industrial & Engineering Chemistry Research 35 (8) (1996) 2709–2715.

[38] L. Deng, T. Zhang, D. Che, Effect of water washing on fuel properties, pyrolysis and combustion characteristics, and ash fusibility of biomass, Fuel Processing Technology 106 (2013) 712–720.

[39] J. Koppejan, S. Van Loo, The handbook of biomass combustion and co-firing, Routledge, 2012.

[40] A. Saddawi, J. Jones, A. Williams, C. Le Coeur, Commodity fuels from biomass through pretreatment and torrefaction: effects of mineral content on torrefied fuel characteristics and quality, Energy & Fuels 26 (11) (2012) 6466–6474.

[41] M. Cocchi, L. Nikolaisen, M. Junginger, C. S. Goh, J. Heinimö, D. Bradley, R. Hess, J. Jacobson, L. P. Ovard, D. Thrän, C. Hennig, M. Deutmeyer, P. P. Schouwenberg, D. Marchal, Global wood pellet industry market and trade study, Tech. rep., International Energy Agency (2011).

[42] B. Erlach, B. Wirth, G. Tsatsaronis, Co-production of electricity; heat and biocoal pellets from biomass: A techno-economic comparison with wood pelletizing, in: World Renewable Energy Congress-Sweden; 8-13 May; 2011; Linköping; Sweden, no. 57, Linköping University Electronic Press, 2011, pp. 508–515.

[43] A. M. Shulenberger, M. Wechsler, Device and method for conversion of biomass to biofuel (2010).

[44] B. Wirth, J. Mumme, Anaerobic digestion of waste water from hydrothermal carbonization of corn silage, Applied Bioenergy 1 (1).

[45] A. Funke, J. Mumme, M. Koon, M. Diakite, Cascaded production of biogas and hydrochar from wheat straw: energetic potential and recovery of carbon and plant nutrients, Biomass and bioenergy 58 (2013) 229–237.

[46] I. Oliveira, D. Blöhse, H.-G. Ramke, Hydrothermal carbonization of agricultural residues, Bioresource technology 142 (2013) 138–146.

[47] A. Funke, F. Reebs, A. Kruse, Experimental comparison of hydrothermal and vapothermal carbonization, Fuel processing technology 115 (2013) 261–269.

[48] M.-M. Titirici, A. Thomas, M. Antonietti, Back in the black: hydrothermal carbonization of plant material as an efficient chemical process to treat the co 2 problem?, New Journal of Chemistry 31 (6) (2007) 787–789.

[49] S. Chang, Z. Zhao, A. Zheng, X. Li, X. Wang, Z. Huang, F. He, H. Li, Effect of hydrothermal pretreatment on properties of bio-oil produced from fast pyrolysis of eucalyptus wood in a fluidized bed reactor, Bioresource technology 138 (2013) 321–328.

[50] M. T. Reza, J. G. Lynam, M. H. Uddin, C. J. Coronella, Hydrothermal carbonization: fate of inorganics, Biomass and Bioenergy 49 (2013) 86–94.

[51] J. E. White, W. J. Catallo, B. L. Legendre, Biomass pyrolysis kinetics: a comparative critical review with relevant agricultural residue case studies, Journal of Analytical and Applied Pyrolysis 91 (1) (2011) 1–33.

[52] J. Stemann, A. Putschew, F. Ziegler, Hydrothermal carbonization: process water characterization and effects of water recirculation, Bioresource technology 143 (2013) 139–146.

[53] S. K. Hoekman, A. Broch, C. Robbins, B. Zielinska, L. Felix, Hydrothermal carbonization (htc) of selected woody and herbaceous biomass feedstocks, Biomass Conversion and Biorefinery 3 (2) (2013) 113–126.

[54] M. T. Reza, E. Rottler, L. Herklotz, B. Wirth, Hydrothermal carbonization (htc) of wheat straw: Influence of feedwater ph prepared by acetic acid and potassium hydroxide, Bioresource technology 182 (2015) 336–344.

[55] M. H. Uddin, M. T. Reza, J. G. Lynam, C. J. Coronella, Effects of water recycling in hydrothermal carbonization of loblolly pine, Environmental Progress & Sustainable Energy 33 (4) (2014) 1309–1315.

[56] W. Tirler, A. Basso, Resembling a "natural formation pattern" of chlorinated dibenzo-p-dioxins by varying the experimental conditions of hydrothermal carbonization, Chemosphere 93 (8) (2013) 1464–1470.

[57] X. Lu, B. Jordan, N. D. Berge, Thermal conversion of municipal solid waste via hydrothermal carbonization: comparison of carbonization products to products from current waste management techniques, Waste management 32 (7) (2012) 1353–1365.

[58] N. D. Berge, K. S. Ro, J. Mao, J. R. Flora, M. A. Chappell, S. Bae, Hydrothermal carbonization of municipal waste streams, Environmental science & technology 45 (13) (2011) 5696–5703.

[59] C. He, A. Giannis, J.-Y. Wang, Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: hydrochar fuel characteristics and combustion behavior, Applied Energy 111 (2013) 257–266.

[60] Solid biofuels — fuel specifications and classes. part 1 general requirements (2014).

[61] A. Zheng, Z. Zhao, S. Chang, Z. Huang, K. Zhao, G. Wei, F. He, H. Li, Comparison of the effect of wet and dry torrefaction on chemical structure and pyrolysis behavior of corncobs, Bioresource technology 176 (2015) 15–22.

[62] H. S. Kambo, A. Dutta, Comparative evaluation of torrefaction and hydrothermal carbonization of lignocellulosic biomass for the production of solid biofuel, Energy conversion and management 105 (2015) 746–755.

[63] Q.-V. Bach, K.-Q. Tran, Dry and wet torrefaction of woody biomass—a comparative studyon combustion kinetics, Energy Procedia 75 (2015)

150–155.

[64] M. Pala, I. C. Kantarli, H. B. Buyukisik, J. Yanik, Hydrothermal carbonization and torrefaction of grape pomace: A comparative evaluation, Bioresource technology 161 (2014) 255–262.

[65] W.-H. Chen, S.-C. Ye, H.-K. Sheen, Hydrothermal carbonization of sugarcane bagasse via wet torrefaction in association with microwave heating, Bioresource technology 118 (2012) 195–203.

[66] M. Wnukowski, P. Owczarek, et al., Wet torrefaction of miscanthus–characterization of hydrochars in view of handling, storage and combustion properties, Journal of Ecological Engineering 16 (3) (2015) 161–167.

[67] D. Basso, F. Patuzzi, D. Castello, M. Baratieri, E. C. Rada, E. Weiss-Hortala, L. Fiori, Agro-industrial waste to solid biofuel through hydrothermal carbonization, Waste Management 47 (2016) 114–121.

[68] X. Lu, P. J. Pellechia, J. R. Flora, N. D. Berge, Influence of reaction time and temperature on product formation and characteristics associated with the hydrothermal carbonization of cellulose, Bioresource technology 138 (2013) 180–190.

[69] M. Pronobis, Evaluation of the influence of biomass co-combustion on boiler furnace slagging by means of fusibility correlations, Biomass and Bioenergy 28 (4) (2005) 375–383.

[70] B. Jenkins, L. Baxter, T. Miles Jr, T. Miles, Combustion properties of biomass, Fuel processing technology 54 (1-3) (1998) 17–46.

[71] E. Sermyagina, J. Saari, J. Kaikko, E. Vakkilainen, Hydrothermal carbonization of coniferous biomass: Effect of process parameters on mass and energy yields, Journal of Analytical and Applied Pyrolysis 113 (2015) 551–556.

[72] V. Benavente, E. Calabuig, A. Fullana, Upgrading of moist agro-industrial wastes by hydrothermal carbonization, Journal of Analytical and Applied Pyrolysis 113 (2015) 89–98.

[73] E. Erdogan, B. Atila, J. Mumme, M. T. Reza, A. Toptas, M. Elibol, J. Yanik, Characterization of products from hydrothermal carbonization of orange pomace including anaerobic digestibility of process liquor, Bioresource technology 196 (2015) 35–42.

[74] J. Poerschmann, B. Weiner, H. Wedwitschka, A. Zehnsdorf, R. Koehler, F.-D. Kopinke, Characterization of biochars and dissolved organic matter phases obtained upon hydrothermal carbonization of elodea nuttallii, Bioresource technology 189 (2015) 145–153.

[75] M. Sevilla, J. A. Macia-Agullo, A. B. Fuertes, Hydrothermal carbonization of biomass as a route for the sequestration of co 2: chemical and structural properties of the carbonized products, Biomass and Bioenergy 35 (7) (2011) 3152–3159.

[76] E. Danso-Boateng, G. Shama, A. D. Wheatley, S. J. Martin, R. Holdich, Hydrothermal carbonisation of sewage sludge: effect of process conditions on product characteristics and methane production, Bioresource technology 177 (2015) 318–327.

[77] T. Keipi, H. Tolvanen, L. Kokko, R. Raiko, The effect of torrefaction on the chlorine content and heating value of eight woody biomass samples, Biomass and Bioenergy 66 (2014) 232–239.

[78] M. Deutmeyer, D. Bradley, B. Hektor, R. Hess, L. Nikolaisen, J. Tumuluru, M. Wild, Possible effect of torrefaction on biomass trade, in: IEA bioenergy task, Vol. 40, 2012.

[79] B. Batidzirai, A. Mignot, W. Schakel, H. Junginger, A. Faaij, Biomass torrefaction technology: Techno-economic status and future prospects, Energy 62 (2013) 196–214.

[80] M. Svanberg, I. Olofsson, J. Flodén, A. Nordin, Analysing biomass torrefaction supply chain costs, Bioresource technology 142 (2013) 287–296.

[81] Handbook for the certification of wood pellets for heating purposes v 2.0„ published by European Pellet Council (2013).

[82] G. Christa, P. Wilfried, G. Michael, H. A. HFA, Hygroscopicity of wood pellets test method development–influence on pellet quality–coating of wood pellets, in: Proceedings of the 2nd World Conference on Pellets, 2006.

[83] H. M. Künzel, Indoor relative humidity in residential buildings–a necessary boundary condition to assess the moisture performance of building envelope systems, Download: http://www.hoki. ibp. fraunhofer. de/ibp/publikationen/fachzeitschriften/wksb%20Raumluftfeuchte1_E. pdf.

[84] G. J. Jenkins, et al., The climate of the United Kingdom and recent trends, Exeter: Met Office Hadley Centre, 2007.

[85] T. C. Acharjee, C. J. Coronella, V. R. Vasquez, Effect of thermal pretreatment on equilibrium moisture content of lignocellulosic biomass, Bioresource technology 102 (7) (2011) 4849–4854.

[86] W. Yang, T. Shimanouchi, M. Iwamura, Y. Takahashi, R. Mano, K. Takashima, T. Tanifuji, Y. Kimura, Elevating the fuel properties of humulus lupulus, plumeria alba and calophyllum inophyllum l. through wet torrefaction, Fuel 146 (2015) 88–94.

[87] W. Yan, S. K. Hoekman, A. Broch, C. J. Coronella, Effect of hydrothermal carbonization reaction parameters on the properties of hydrochar and pellets, Environmental Progress & Sustainable Energy 33 (3) (2014) 676–680.

[88] Z. Liu, A. Quek, R. Balasubramanian, Preparation and characterization of fuel pellets from woody biomass, agro-residues and their corresponding hydrochars, Applied Energy 113 (2014) 1315–1322.

[89] M. T. Reza, M. H. Uddin, J. G. Lynam, C. J. Coronella, Engineered pellets from dry torrefied and htc biochar blends, Biomass and Bioenergy 63 (2014) 229–238.

[90] S. K. Hoekman, A. Broch, A. Warren, L. Felix, J. Irvin, Laboratory pelletization of hydrochar from woody biomass, Biofuels 5 (6) (2014) 651–666.

[91] Solid biofuels - determination of mechanical durability of pellets and briquettes - part 1: Pellets (2015).

[92] U. Svedberg, J. Samuelsson, S. Melin, Hazardous off-gassing of carbon monoxide and oxygen depletion during ocean transportation of wood pellets, Annals of occupational hygiene 52 (4) (2008) 259–266.

[93] X. Kuang, T. J. Shankar, X. T. Bi, S. Sokhansanj, C. Jim Lim, S. Melin, Characterization and kinetics study of off-gas emissions from stored wood pellets, Annals of Occupational Hygiene 52 (8) (2008) 675–683.

[94] S. Gauthier, H. Grass, M. Lory, T. Krämer, M. Thali, C. Bartsch, Lethal carbon monoxide poisoning in wood pellet storerooms—two cases and a review of the literature, Annals of occupational hygiene 56 (7) (2012) 755–763.

[95] W. Emhofer, K. Lichtenegger, W. Haslinger, H. Hofbauer, I. Schmutzer-Roseneder, S. Aigenbauer, M. Lienhard, Ventilation of carbon monoxide from a biomass pellet storage tank—a study of the effects of variation of temperature and cross-ventilation on the efficiency of natural ventilation, Annals of Occupational Hygiene 59 (1) (2014) 79–90.

[96] Eh40/2005 workplace exposure limits, published by Health and Safety Executive (United Kingdom) (2011).

[97] C. H. Medina, H. Sattar, H. N. Phylaktou, G. E. Andrews, B. M. Gibbs, Explosion reactivity characterisation of pulverised torrefied spruce wood, Journal of Loss Prevention in the Process Industries 36 (2015) 287–295.

[98] A. Boskovic, P. Basu, P. Amyotte, An exploratory study of explosion potential of dust from torrefied biomass, The Canadian Journal of Chemical Engineering 93 (4) (2015) 658–663.

[99] C. H. Medina, B. MacCoitir, H. Sattar, D. J. Slatter, H. N. Phylaktou, G. E. Andrews, B. M. Gibbs, Comparison of the explosion characteristics and flame speeds of pulverised coals and biomass in the iso standard 1m 3 dust explosion equipment, Fuel 151 (2015) 91–101.

[100] D. M. Boylan, G. K. Roberts, B. Zemo, J. L. Wilson, Torrefied wood field tests at a coal-fired power plant, in: Pulp and Paper Industry Technical Conference, Conference Record of 2014 Annual, IEEE, 2014, pp. 101–107.

[101] Accessed September 2015. [link].
URL https://www.ecn.nl/news/item/successful-test-with-innovativ

[102] Accessed September 2015. [link].
URL http://biomassmagazine.com/articles/10027/dutch-power-plant-successfully-tests-torrefiedbiomass-pellets

[103] N. Padban, First experiences from large scale co-gasification tests with refined biomass fuels, in: Central European Biomass Conference. 17th January, 2014.

[104] Hard coal — determination of hardgrove grindability index (2015).

[105] Accessed September 2015. [link].
URL http://www.businesswire.com/news/home/20121122005340/en/HTC-1-Industrial-Planthydrothermal-carbonization-Worldwide-AVACO2#. Vf7pr5eoPhp

[106] Accessed September 2015. [link].
URL http://www.suncoal.de/en/technology/htc-pilotplant.