Clean Solid Biofuel Production from High Moisture Content Waste Biomass Employing Hydrothermal Treatment

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Abstract

Our society currently faces three challenges, including resource depletion, waste accumulation and environmental degradation, leading to rapidly escalating raw material costs and increasingly expensive and restrictive waste disposal legislation. This work aims to produce clean solid biofuel from high moisture content waste biomass (bio-waste) with high nitrogen (N)/chlorine (Cl) content by mild hydrothermal (HT) conversion processes. **The newest results** are summarized and discussed in terms of the mechanical dewatering and upgrading, dechlorination, denitrification and coalification resulting from the HT pretreatment. Moreover, both the mono-combustion and co-combustion characteristics of the solid fuel are reviewed by concentrating on the pollutants emission control, especially the NO emission properties. In addition, the feasibility of this HT solid biofuel production process is also discussed in terms of “Energy Balance and economic viability”. As an alternative to dry combustion/dry pyrolysis/co-combustion, the HT process, combining the dehydration and decarboxylation of a biomass to raise its carbon content aiming to achieve a higher calorific value, opens up the field of potential feedstock for lignite-like solid biofuel production from a wide range of nontraditional renewable and plentiful wet agricultural residues, sludge and municipal wastes. It would contribute to a wider application of HT pretreatment bio-wastes for safe disposal and energy recycling.

Keywords: hydrothermal treatment, waste biomass utilization, coalification, denitrogenation, dechlorination

34 **Graphical abstract**

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69 1. Introduction

70 Until now, the fossil fuel, which is regarded as non-renewable and the main energy source all over
71 the world, is diminishing fast [1, 2]. At the same time, the worldwide fuel demand keeps increasing
72 dramatically (29.75 billion barrels oil in 2011 and projected to be 34.90 billion barrels in 2030 [3])
73 and correspondingly the fossil fuel reserve (about 1653 billion barrels oil at the end of 2011 [3])
74 decrease rapidly [4, 5]. These historical and anticipated increases in primary energy consumption
75 have amplified concerns about the environmental consequences of continued fossil fuel extraction
76 and use [6]. Therefore, more and more attention has been given to extract energy from the alternative
77 cheap and renewable energy resources with little or no environmental impact [7]. The
78 status/challenge of energy demand, development of the renewable energy and environment of the
79 global and some specific countries or region have been summarized by many researchers, including
80 Dincer [8], Kaygusuz [9], Omer [10], Asif [11], Panwar [12], Bugaje [13], Chang [14],
81 Budzianowski [15-17], etc. They clearly show that among renewable energy, biomass energy seems
82 to be one of the most efficient and effective solutions to energy shortage and some energy-related
83 problem, e.g. CO₂ emission reduction because of its carbon-neutral nature.

84 However, the heterogeneity of biomass causes difficulties in energy recovery technologies such as
85 anaerobic digestion and combustion [18]. **Direct combustion** and co-combustion of biomass with
86 low rank coals **is widely accepted as less risky**, less expensive, time-saving options to utilize
87 biomass energy [19]. Several experts indicated that direct combustion is not so satisfying because of
88 some inherent drawbacks of biomass, including the high moisture and oxygen contents, and high
89 alkaline earth metal content [19-21]. Moreover, biomass are always of low bulk densities (~150
90 kg/m³), which accounts for its low volume-based heating value, requirement of huge storage,
91 expensive transportation, feeding control [19]. On the other hand, the intensified use of biomass

from crops is limited because the finite agricultural land would generate competition between food supply and bioenergy production [22-24], finally resulting in increasing in food prices or even food shortage [18]. Therefore, comprehensively considering the challenges—resource depletion, waste accumulation and environmental degradation, energy recycling from biomass waste (bio-waste) has received more and more **attractive** recently because it provides a large volume reduction, **hazard** reduction, and heavy metals controlling and the release of the environmental burden. Just taking sewage sludge as an example, the publications related on sewage sludge utilization have been grown exponentially in Elsevier from 2000 (**S1**).

These wastes are generally generated from industrial activities such as sewage sludge from wastewater treatment plants, mycelia wastes from medicine production, empty fruit bunches (EFB) from the production of palm oil, and distilled spirits lees from beverage production or agricultural residual such as driftwood, or material from households, like kitchen residues and garden cuts [18, 25], as well as waste from municipal, including the municipal solid waste (MSW), hospital wastes. However, these bio-wastes are usually of high moisture content (around 56 wt.% for MSW and 80 wt.% for sewage sludge), high nitrogen (N) (e.g. sewage sludge: 1.0–10.0 wt.% at dry basis (db) [26-31]; mycelial waste: 2.0–9.0 wt.% (db) [32]; distilled spirits lees: about 3 wt.% (db) [33]) or chlorine (Cl) content (as high as 1.6 wt.% (db) for MSW because of the existence of plastic [34]) [33]. Direct incineration encounters various problems, such as hard to ignite, unsteady and unstable combustion, incomplete combustion, and huge amount of gaseous pollutants due to the high moisture content. Besides, the N and sulphur (S) contained in feedstock will be finally converted into NO_x and SO_x causing a secondary pollution, such as photochemical smog, acid rain, greenhouse emission and ozone depletion [35-39]. High S and Cl contents would **cause corrosion** problems, subsequently reducing the combustion facilities' lifetime and increasing the operating cost [40]. The Cl contents can also increase the risk to emit toxic dioxins and furans [40, 41]. Alkaline metal, such as potassium (K), is also **a concern for** furnace corrosion and lowers the **ash** melting temperatures, which therefore causes severe fouling and agglomeration inside boilers [18, 35, 42-46]. For other thermal conversion technologies, such as pyrolysis and gasification, a pre-drying process is necessary to improve the thermal efficiency, which would therefore significantly increase the operating cost and become unacceptable, especially for the developing countries [47-52]. Thus, a pretreatment is **essential to** upgrade the biomass feedstock (such as improving energy density, removing K and Cl prior to final utilization) to homogenize different biomass into high value-added products, including biodiesel, alcohol, biogas, bio-solid fuels and animal feed in order to utilize them cost-efficiently and environment-friendly.

Recently, hydrothermal (HT) treatment (**wet torrefaction, hot compressed water, or hot water pretreatment**) has been introduced and applied in the field of wastes to energy (WTE). Some works focusing on specific issue have been done to investigate the feasibility of **solid biofuel (hydrochar)** production from bio-waste by employing the HT pretreatment and the combustion characteristics of solid biofuel [2, 34, 53-75]. However, the research and development of applying the HT in solid biofuel production, especially in the clean solid biofuel, has not been summarized. This review will mainly focus on the clean solid biofuel production from bio-waste to realize “3R” rule (reduce, reuse and recycle) by employing HT pretreatment. It concentrates on the water removal, N and Cl

transformation behavior during the HT pretreatment, the biofuel combustion characteristics, and the economic variability of the HT solid biofuel production process. Moreover, the disadvantages, challenges this technology is facing, and the expected future improvements are also discussed aiming to provide some clues for further study. The paper is organized as follows: Section 2 provides a brief introduction of potential bio-wastes using sewage sludge, MSW and EFB as representatives. A short research progress in applying HT as a pretreatment method in bio-waste dewatering and upgrading is given in Section 3. Section 4 concentrates on fuel upgrading, the N and Cl transformation behavior, and coalification during the HT treatment. Section 5 discusses the mono-combustion and co-combustion characteristics in terms of pollutants emission in order to investigate the technical feasibility of solid biofuel production by HT treatment, and finally in Section 6, a mass and energy balance analysis was carried out and the economic feasibility of the HT solid biofuel production process was evaluated by comparing to conventional thermal drying. Moreover, to provide an objective view, results from theoretical calculation and simulation by other researchers are also discussed and presented.

2. Source of waste biomass (bio-waste) and its energy potential

2.1 Sludge

2.1.1 Sources

Treatment of municipal wastewater results worldwide in producing large amounts of sewage sludge. The sludge treatment and disposal has been a severe environmental problem because of this huge yield. In China, about 20.76 million tons sludge with 80% water content has been produced in 2010 [52, 76]. Moreover, this amount will be much higher according to the China's 12th Five-Year Construction Plan for National Urban Wastewater Treatment and Recycling Facilities [52]. Table 1 summarizes the sludge production of some typical countries. It is organizationally, technically, and economically hardly possible to prevent or strongly reduce the amount of municipal wastewater because of the urbanization, industrialization, and growth in population [77]. Sludge volumes will grow in the view of worldwide as countries grow in population and become wealthier. Theoretically, if the coverage and rate of wastewater treatment of some other middle-income countries, such as Brazil, China, reach the same level as high-income countries, the annual sludge production could be highly increased from 410,000 tons to over 4.4 million tons for Brazil and 3.2 million tons to 31 million tons for China according to *Lux Research* [78]. Also, the quality of the produced sewage sludge will not change significantly because a large part of these toxic pollutants originates from diffuse sources. Therefore, sewage sludge will remain a permanent waste problem that requires an appropriate solution [79]. Energy recovery from sewage sludge employing some technologies would be promising in terms of cost and environmental impact.

Table 1 Sludge production of some typical countries ($\times 10^6$ kg/year), data derived from refs.[52, 80-82].

2.1.2 Energy potential

S2 shows some typical chemical composition and properties of untreated/digested sludge. Sewage sludge typically consists of a significant amount of nontoxic organic compounds, in general a

combination of primary sludge and secondary (microbiological) sludge [52, 77]. It is highly heterogeneous and comprises a mixture of various organic and inorganic compounds. Sludge combustion has received worldwide attention and has been widely applied in some developed countries because it provides a large volume reduction, toxicity reduction, and heavy metals controlling of sludge treatment with energy recovering [83, 84]. In a research focusing on the energy potential of non-plantation biomass resources in selected Asian countries, Bhattacharya *et al.* [85] has pointed out that the energy potential of wastewater in 2010 was to be 102, 200, 0.35 and 7.8 PJ ($\times 10^{12}$ MJ) for China, India, Sri Lanka and Thailand, respectively. Li *et al.* [86] also reported the same result when assessing the sustainable energy potential of non-plantation biomass resources in China.

On the other hand, sludge also contains variable quantities of other elements, including heavy metals. During thermal conversion, and especially gasification, most of the gaseous compounds of N, S, and Cl, appear as H_2S , NH_3 , and HCl due to the reducing conditions applied. In the case of sludge exploitation for energy production through thermochemical processes, it is important to ascertain the mobility of these contaminants as they can potentially appear in all the three products formed (gas, char, tar) [87]. However, after HT pretreatment, the toxic element will retard in the solid part and part of organic hazardous elements, such as N, S, Cl, can be removed or converted into inorganic part. During combustion, the harmful gaseous emission was reduced and the toxic element was remained in the ashes portion [76]. Thus, it would be environmentally friendly to produce an alternative fuel from sewage sludge by controlling the sludge moisture content with HT pretreatment.

2.2 Municipal solid wastes (MSW)

2.2.1 Sources

MSW represents a major source of biomass. Its production keeps increasing because of the rapid economic development, continuous urbanization, and improvements in the living standards. Its disposal is one of the vital issues in China due to the rapid urbanization [86]. Comparing to other biomass, MSW has an immediate advantage as a feedstock in that it is already collected at sites around the country and disposed in landfills. S3 shows general sources of MSW generated by households, commercial establishments, institutions, and municipal services etc. It consists of significant perishable organic wastes, glass, paper, plastics, metals etc. Table 2 provides data and projections from 1980 to 2030 for municipal waste generation of the Organization for Economic Co-operation and Development (OECD) and China mainland. It is estimated that in 2030 the mean municipal waste generation will be 1.8 kg/(capita·day) in the OECD region, about 0.75 kg/(capita·day) in the BRICS (an association of emerging national economies: Brazil, Russia, India, China and South Africa) countries, and about 0.9 kg/(capita·day) for the rest of the world (ROW). Total annual waste generation in 2030 is projected under the Baseline to be about 900 million tons for OECD countries, about 1 billion tons for the BRICS countries, and around 1.1 billion tons for the ROW [88]. Actually, some BRICS countries have already exceeded the estimated mean value of 0.75 kg/(capita·day). For China, although the generation rate in rural areas is largely unknown, it is already over 1.2 kg/(capita·day) in cities [88]. It is estimated that in 2030 the urbanization rate will

be 68.7% in China; in India, the corresponding value is about 39.8% [89]. The annual MSW generation is expected to be at least 485 million tons (up 214% from 2004) for China, and around 250 million tons (up 130% from 2001) for India [89]. Recently, the European Topic Centre on Resource and Waste Management (ETC/RWM, 2007) also projects that the MSW generation within the EU15 will increase by 33% to 2030 [88]; whereas it will grow by about 66% to 2030 for the new EU member. The non-OECD area is expected to produce about 70% of the world's municipal waste, mainly due to rising incomes, rapid urbanization, and technical and economic development [90]. In a word, huge amount of MSW requires disposal and is available for the fuel production process discussed. Moreover, it should be mentioned that the MSW does not include construction or demolition debris or automobile scrap in this study.

Table 2 MSW generation within the OECD area and China mainland ($\times 10^6$ kg/year)

2.2.2 Energy potential

Recycling components of MSW is worthwhile if it confers economic advantage to purchasers of recycled materials or products, saves more fuel, and brings about environmental benefits or has lower cost than alternative methods of waste management [91, 92]. As indicated in Fig.1, about 50% of components in MSW are combustible matters. The heating value of MSW can vary according to its composition (depending on the social habits and the economy of the region from which it is collected), the mean lower heating value is around 8 MJ/kg [50, 91-93]. Table 3 also shows fuel properties of MSW within some typical Asian countries, such as China, Japan and India. It indicates that the MSW are of high volatiles with a mass-based heating value higher than 15 MJ/kg. It would be possible to utilize it with some thermal disposal methods, including combustion, pyrolysis and gasification, providing great benefits over traditional methods of disposing MSW. Moreover, its utilization has proved to be an effective option for reducing greenhouse gas emissions and has opened an era for co-utilizing wastes like sewage sludge, waste tyre, etc. Besides, the fuels produced from MSW can be very well used in many applications and replace some part of fossil fuels. It is projected that the energy potential of MSW is 91, 219, 47, 4.8 and 21.3 PJ for China, India, Philippines, Sri Lanka and Thailand in 2010, respectively [85]. However, some technical barriers need to be overcome in order to accelerate the clean, efficient use of MSW [56].

Fig.1 Typical composition of MSW, (a) United States, data adapted from U.S. EPA [94]; (b) by region, data derived from [95] “The World Bank, 2012, source: <http://data.worldbank.org/>”

Table 3 Fuel properties of MSW within some typical countries.

2.3 Palm oil Empty Fruit Bunches (PEFB)

2.3.1 Sources

Crude palm oil production is reaching 52.31 million tons per year globally in 2012 and Southeast Asia is the main contributor, with Indonesia accounting for 48.94%, Malaysia 36.19%, and Thailand 3.10% [96]. Oil palm is a multi-purpose plantation and it is also an intensive producer of biomass. After harvesting fresh fruit bunches from oil palm tree, these bunches are sterilized in a horizontal steam sterilizer to inactivate enzymes present in pericarp and loosen fruits from bunches. The sterilized bunches are fed into a rotary drum thresher in order to remove the sterilized fruit from

bunches. These bunches without fruit are called EFB which are conveyed to the damping ground, whereas the sterilized fruits are further used as feedstock for palm oil production in palm oil extraction process by means of screw type press. The effluents from screw type press are nuts and fibers, which are separated from each other by cyclone. After this separation, nuts are cracked into shells and kernels. The former are solid waste and left unused, the latter are sent to the kernel oil mill [97]. Accompanying production of 1 kg of palm oil, about 4 kg of dry biomass waste are generated, including 1/3 of palm oil empty fruit bunch (PEFB) and the other 2/3 of oil palm trunks and fronds [98, 99]. It was reported that Palm oil production in Malaysia reached 17.9 million tons in 2009, following Indonesia's record of 22 million tons [100]. Meanwhile, about 2.3 million tons of palm kernel cake (PKC) and 30 million tons of EFB and waste fruit fiber were simultaneous generated as by-products. Old palm trees are cut down and replaced by young trees at an interval of 25 years. Consequently, a large quantity of cut-down old palm trees is generated at times. It would be expected that the EFB will be one of the main bio-wastes.

2.3.2 Properties

Although the quantity of EFB available is in the sixth rank of all biomass, the energetic quality is high due to its high heating value and it is not yet mainly used as alternative fuel due to its high moisture (typically 60% w.b.) [101, 102] and volatile matter with low ash melting temperature [103]. Table 4 shows the proximate and ultimate analysis of EFB from typical countries, such as Indonesia, Malaysia and Thailand. It is obvious that the EFB can be used as fuel after removing the water. Yuhazri *et al.* [104] produced briquettes from EFB and waste paper and reported that the product is very durable, which makes it suitable for the end application of the briquettes requiring high durability during handling, transportation and storage. Jamari *et al.*, and Yuliansyah *et al.* [105, 106] employed HT to upgrade EFB waste to produce exportable fuel and stated that the carbon value has been increased after the HT process. Although total energy produced from combustion of this solid biofuel was less than that of raw material, the use of this fuel still offers some other benefits. It is likely that HT will be widely applied to recover energy from EFB because of its high water removal ability in the near future.

Table 4 Proximate and ultimate analysis of EFB from Thailand, Indonesia, and Malaysia. Data adapted from ref. [102] for Indonesia, ref. [97] for Thailand, and ref. [103] for Malaysia.

2.4 Other resources

Considering widespread depletion of fossil fuels and gradually emerging consciousness about environmental degradation, the energy supply in the future has to come from renewable sources of energy. Although wastes are still largely under-utilized in most of the countries all over the world, their use is increasing rapidly; whilst costs (in real terms) drop significantly, resulting in as much as 15-18% contribution to national energy needs [107]. Biomass resources include wood and wood wastes, agricultural crops adapted their waste byproducts, MSW, animal wastes, waste from food processing and aquatic plants and algae [107]. Currently, the bio-waste disposal is a growing worldwide problem. Using bio-waste as feedstocks for bioenergy conversion processes is of particularly important because of its dual functions of waste reduction and energy production [108]. Potential bio-waste discussed in this study contain agricultural production wastes, agricultural

processing wastes, crop residues, urban wood wastes, mill wood wastes, mycelial waste, distilled spirits lees, **distiller grains, manure waste**, paper sludge, **algae**, and urban organic wastes etc., **which** are typically of high moisture content and low heating value. Most of these wastes could be used for energy production through incineration and other process. Taking manure waste as an example, **U.S. agricultural lands currently produce 35 million dry tons of sustainable animal manures [109, 110]. After conversion processing, an annual 5.3 million tons of swine manure could replace about 6.0 million barrels of petroleum-based fuels, equivalent to 2.1% of the annual consumption of petroleum in the U.S [110, 111]. For China, India, Philippines, Sri Lanka and Thailand, the energy potential of manure wastes** in 2010 is estimated to be 2095, 374, 4.9, 6.5 and 13 PJ respectively [85].

In the near future, it can be expected that bio-waste management and research related to innovative treatment methods will focus on three aspects: recovery and reuse of valuable products from waste, a complete solution to the disposal problem of waste, especially regarding the toxics, and acceptable costs. In this respect, it can be expected that the recovery of sustainable energy from bio-waste will become more and more of interest. Clean solid biofuel production from bio-waste with high moisture content employing HT pretreatment would be a technical feasibility and economical way to realize the 3R of waste treatment and disposal.

3. Hydrothermal (HT) treatment

HT, **a process** to treat biomass in water at temperature and under sufficient pressure to keep the water in either liquid or supercritical state [7, 112-114], offers significant advantages for biomass conversion, such as avoiding an energy-extensive drying process, high conversion efficiency and relatively low operation temperature among thermal methods [19, 115, 116]. It also offers a number of potential advantages over other biofuel production methods, including high throughputs, high energy and separation efficiency, the ability to use mixed feedstock like wastes and lignocellulose, the production of direct replacements for existing fuels, and no need to maintain specialized microbial cultures or enzymes. Moreover, it has unique possibilities in coordination with other biofuel processing techniques, including as a pretreatment step or post-fermentation reforming. In addition, the produced biofuels would be free of biologically active organisms or compounds, including bacteria, viruses, and even prion proteins because of the high temperatures involved [7].

In the aspect of energy efficiency, it obviates the need (capital, energy and time) for feedstock dewatering and drying as **needed** for other conversion methods such as gasification and pyrolysis [117]. It allows for integrated energy recovery because: (1) the high temperature effluent stream can be used to preheat the feedstock [118], (2) value-added products can be produced under a relative moderate condition [46, 113, 119-122]. Effective dehydration occurs in the presence of **hot** water [123, 124], which can serve as a solvent, a reactant, and even a catalyst or catalyst precursor [118]. In contrast to standard high-temperature carbonization reactions (e.g. pyrolysis), the HT process is an exothermic process and more energetically favorable [123, 125], as it liberates about a third of the combustion energy through dehydration at the same time forming condensed products [126]. Furthermore, the final carbonaceous product (hydrochar or solid biofuel) can easily be separated from the reaction solution, avoiding complicated drying schemes and costly isolation procedures. Depending upon the process conditions adopted, the carbon efficiency of HT can be very high, i.e.

331 most of the starting carbon stays bound in the final solid product. In a word, application of the HT to
332 WTE (waste to energy) **is** an attractive and effective way to minimize waste from the view point of
333 energy consumption and mitigating greenhouse gas emissions [118, 123, 125, 127, 128]. This can be
334 verified by the annually published research articles which grow exponentially as indicated in S4.

335 With the HT, liquefaction and gasification can be **minimized at a comparably** low temperatures
336 ranging from 160 to 250 °C in order to increase the yield of a solid material termed solid biofuel
337 [129-132]. This HT carbonization process can be used to convert a variety of feedstock to a solid
338 fuel with **carbon** content similar to lignite at mass yields from 35 to 60%. Currently, many biomass
339 substrates, including cellulose [133], lignocellulosic biomass [134, 135], microalgae [136, 137],
340 anaerobically digested maize silage [138], municipal solid waste [66, 72, 112, 139], distiller's grains
341 [140], agricultural residues [141], and black liquor [142], have been applied in HT to gain fuels or
342 materials. HT treatment of biomass generates liquid [30, 143-145], gaseous (mainly carbon dioxide),
343 aqueous chemicals, and solid biofuel. Currently, most attention is paid to the liquid and gaseous
344 products and many processes have been developed and optimized to improve the quality and yields
345 of the target products [27, 143, 146-148]. However, further upgrading is still required because of its
346 high acidity and complex composition [46]. Some others also focused on the biochar—a byproduct
347 during waste biomass liquefaction, or gasification [46, 62, 112, 133, 149]. To investigate the
348 properties of biochar derived by HT carbonization, the bio-waste feedstock were replaced with the
349 pure biomass including glucose and cellulose. The results show that the biochar generated by HT
350 carbonization exhibit some unique physicochemical properties compared to that produced by
351 conventional carbonization. As such, they have been applied in several value-added applications [46,
352 113, 119-122].

353 Undoubtedly, the HT treatment is a promising way to upgrade the biomass. Most of the works in
354 the current literatures focused on the solid (hydrochar), liquid (oil), gas (hydrogen) fuel production at
355 a relative high temperature and high pressure. In the case of bio-waste, they used model compounds
356 (lignin, xylose, glucose and cellulose, etc) to investigate the reaction mechanisms and made great
357 contribution to fully understand this technology. Interested readers can refer these excellent works [7,
358 113, 119, 120, 123, 124, 133, 134, 144, 147, 150-155]. In the field of WTE, some works have been
359 done to investigate the feasibility of solid biofuel production from bio-waste and the fuel combustion
360 characteristics [2, 34, 53-75, 156].

361 **4. Biomass upgrading**

362 As discussed, the high moisture content is the main obstacle for energy recovering from **some**
363 **bio-wastes**, because it would directly reduce the heating value when using bio-waste as fuel supply.
364 Water removal **is** therefore the first and also the key step for the utilization of these high moisture
365 content bio-wastes. Normally, the method for water removal includes the mechanical dewatering
366 (press filter, centrifuge, belt etc.) and forced evaporation with heat source; and the mechanical
367 dewatering is much cheaper and simpler compared to the thermal forced evaporation. Hence, the
368 most promising way is to pretreat the bio-wastes with some physical, chemical or thermal methods
369 to improve the mechanical dewaterability and then remove the water with mechanical dewatering.
370 Accordingly, three “bio-wastes to solid fuel” technologies, including combination of the thermal

drying and physical mixing [84, 157], chemical conditioning [158, 159] and thermal pretreatment [18, 34, 46, 52, 60, 62, 63, 65, 67, 102, 113, 156, 160-163], were proposed to produce solid fuel from sewage sludge, MSW etc.

Fig.2 presents a conceptual schematic of clean solid biofuel production from the high moisture content bio-wastes by HT and conventional thermal drying. As indicated in this figure, the main difference is the way to remove water, determining the cost of solid biofuel. Zhao *et al.* and Namioka *et al.* [52, 63] reported that the energy needed for the HT process was only about 30 wt.% of that consumed in the conventional thermal drying process. Details about the economy of the HT technology will be discussed in [section 4](#).

Fig.2 A conceptual schematic of clean solid biofuel from bio-wastes

As shown in **Fig.2**, the process of clean solid biofuel production by HT is mainly composed of the HT pretreatment, mechanical dewatering and natural drying. Sometimes, a washing process is also used to remove the harmful elements to meet the requirement of environmental policy. The high moisture bio-waste was first pretreated with a HT treatment. During this process, the dewaterability of the parent materials **is** improved and some of the N and Cl would be transformed from organic to inorganic state due to the hydrolysis, dehydration, decarboxylation, aromatization, and condensation polymerization etc., happening in the HT as discussion in section 3. Following with a mechanical dewatering procedure, most of the water contained in the parent raw materials and the water soluble harmful element **are** moved out from the solid part. The water content of the product **is** largely reduced from about 80 wt.% to 50 wt.% (sewage sludge, paper sludge and kimchi etc.) and 50 wt.% to 20 wt.% (MSW) with a significant improvement in the energy density. After a thermal drying or natural drying within a few days, the powder coal-like solid biofuel can be recovered. Because the HT has removed a part of the harmful elements and also affected the transformation paths of N during the combustion resulting in reducing the NO emission, the solid biofuel produced from this process **is** called “clean solid biofuel”. The effect of the HT on the dewaterability and the behavior of some typical harmful elements such as N, Cl will be discussed in the following sections.

4.1 Dewatering and upgrading

The moisture distribution within a wet material shows strong correlation the bound water and the performance of many processes. **Conceptually**, the water existing in the wet materials was divided into four **categories**: free water, interstitial water, surface water and bound water [164]. **The** simplest definition is to divide into two parts: the “bound water”, which is chemically or physically bounded **to** the bulk, and the “free water”, which is the water same as the bulk water and is easily removed by mechanical methods [165]. The basic principle for improving the dewaterability is to force the “bound water” transformation into “free water” by conditioning. The thermal conditioning or thermal pretreatment has been known for many years to give an improvement in the sludge dewaterability [166]. Fisher and Swanwick reported that the sludge dewaterability was largely improved at a temperature above 150 °C [167] and could be further improved at a temperature above 180 °C [166]. After surveying a quantity of literature, Neyens and Baeyens [166] concluded that thermal pre-treatment methods are able to improve the dewaterability of both the undigested and digested sludge. The water content of the sludge cake can be reduced down to about 50 wt.% by a

mechanical dehydration [168-172]. With a natural drying of 24 h, it can be further reduced to about 20 wt.% to produce the coal-like product. Two parameters, the temperature and holding time, were thought to be the most important factors affecting sludge dewaterability in sludge thermal conditioning [173]. As Fig.3 indicated, the moisture content of the dewatered HT product keeps decreasing with both the temperature and holding time. However, the optimal conditions were a little different from each other, for example 180 °C and 60 minutes by Zhao *et al.* [173], 190 °C and 30 minutes by Jiang *et al.* [168], 200 °C and 5 minutes [63], 170 °C and 90 minutes [174] and temperature of 175 °C (holding time, not reported) [166], which could be attributed to the versatile composition of sludge. Our previous results also showed that the optimal temperature for paper sludge mechanical dewatering was 220 °C while that was 200 °C for the sewage sludge. It was because the main component of the sewage sludge was protein and polysaccharide existing in flocs and cellular tissues while the fibers were the main composition of paper sludge. The flocs and cellular tissues were broken and released the bound water under a relative lower temperature (eg. 180 °C) by the thermal energy and pressure during the HT treatment [175, 176], resulting in the denaturing and destroying of the protein. While the optimal conditions for converting the fibers (rice bran) to protein and acid was about 200 °C and 30 minutes [177].

Fig.4 shows an overall dewatering performance (including the mechanical dewatering and the thermal evaporation) of the HT pretreated product. It clearly implies that the mechanical dewatering has been largely improved by the HT. Under a filtration pressure of 0.6 MPa, the moisture content of the HT pretreated paper sludge was reduced from about 85 wt.% to 60 wt.% within only 15 minutes. If increasing the pressure, the moisture could be lower than 50 wt.%. It is also visible that the thermal drying performance has also been improved by the HT. Zhao *et al.* [179, 180] investigated the drying performance of the HT pretreated and untreated paper sludge with an air duct dryer at an air temperature of 30.4 ± 0.4 °C and velocity of 1.34 ± 0.04 m/s. The results show that the drying process mainly took place in the falling rate period and was mainly controlled by the diffusion properties of the inner structure of the product. The drying rate of the HT pretreated samples was twice that of the untreated paper sludge because of the improvement of the diffusion properties. Comprehensively considering the mechanical dewatering and the drying performance, the HT pretreatment was a promising method to remove water from the high moisture content bio-wastes.

Fig.3 Effect of the operating parameters on the sewage sludge dewatering: (a) Holding time; (b) Temperature. (References: Fisher and Swanwick [167], Jiang *et al.*, [168] Zhao *et al.* [173] and Xun *et al.* [174] focusing on the sewage sludge; Areeprasert *et al.* [161] using paper sludge and Zhang *et al.* [163] using mycelial waste) (SRF: specific resistance to filtration)

Fig.4 Overall dewatering performance of the hydrothermal pretreated paper sludge (including the mechanical dewatering and thermal evaporation). Data from (Zhao, unpublished data)

The water removal from the high moisture bio-wastes would directly improve the gross heating value, thus increasing the possibility and quantity of energy recovery. Guo *et al.* [181] applied HT to upgrade the Victorian brown coal with a moisture of around 60–70 wt.% at a temperature ranging from 200 to 300 °C and reported the solid concentration was highly improved from below 30 wt.% to 60 wt.%. The heat value was also improved with an increase in carbon content and decrease in

volatile matters. The results indicated that the HT pretreatment could not only improve the mechanical dewatering of parent materials, but also improve the fuel quality, such as the carbon content and energy density [60, 66, 182, 183]. It is feasible for not only high moisture bio-wastes [46, 62, 66, 75, 106, 161, 162], but also for the low rank coal [60, 181-184]. Fig.5 gives the variation of the calorific value of the HT pretreated product with the HT temperature. It can be also regarded as the variation of the mass based energy density with the temperature. It is evident that the heating value keeps increasing with the HT temperature independent of type of the raw materials. This upgrade became more significant especially in the high temperature zone of 220–380 °C. However, the solid fuel recovery ratio, which was defined the proportion of the dry solid fuel (char) yield to the amount of the raw material, would also decrease with the temperature. To realize the maximum energy production, both the fuel yields and the heating value of the solid biofuel should be taken into account to optimize the operating conditions. Observing these curves, the results from Sakaguchi *et al.* [184] and Guo *et al.* [181] showed the same trend vs the HT temperature under the same holding time of 30 minutes, verifying that the HT pretreatment could upgrade the low rank biomass and coal.

Furthermore, the collection and transportation of biomass is another hindrance for biomass utilization. Transportation costs largely depend on the distance travelled and the energy density, e.g. MJ/m³, of the biomass being transported [185]. The similar issue applies to the utilization of the bio-wastes with high moisture and low energy density. However, the HT pretreatment has bright perspective with three main merits: 1) largely improving the dewaterability; 2) dramatic reduction in volume, especially for the MSW, sawdust, sewage sludge and leaves, thus improving the energy density; 3) energy densification. The volume based heating value of MSW has reported to be improved around 6.4–9.0 times in the HT conversion of the Japanese MSW, India MSW and Chinese MSW [66]. Similar results were also obtained by deriving the data present by Prawisudha *et al.*, [62, 186] indicating that this volume based energy density was improved around 4–5 times after the HT pretreatment. As this data came from a long term running test in a commercial plant, it would be more reliable and significant than the previous one (Lu *et al.* [66]) for the optimization and design of the commercial plant. In the case of production of pellets of biochar from wood by the HT, Reza *et al.* [187] reported that the products exhibited favorable properties, including increased hydrophobicity, abrasion resistance, energy density, and mass density compared to pellets produced from raw pine or dry torrefied pine. Under a HT temperature of 260 °C, the pellets produced had a volumetric fuel value of 70% greater than pellets produced from untreated pine (38.8 MJ/m³ vs. 22.8 GJ/m³), a mass density of 1468 kg/m³, and a higher heating value (HHV) of 26.4 MJ/kg. Liu *et al.* [46] also stated that the energy densification increased with HT temperature, from a low value of 1.34 to 1.66 and from 1.33 to 1.55 for coconut fiber and eucalyptus leaves derived solid biofuel, respectively. The highest energy yield was achieved at the lowest temperature used.

Solid decomposition was significantly affected by reaction temperature more so than reaction time. Higher temperature resulted in lower hydrochar yields [188]. In Danso-Boateng's study, the equilibrium solid hydrochar (solid biofuel) yields (relative to the original dry mass used) were 74%, 66%, 61% and 60% for primary sewage sludge (PSS) at 140, 170, 190 and 200 °C respectively, and 85%, 49%, 48% and 47% for synthetic faeces (SF) at 140, 160, 180 and 200 °C respectively. Energy contents of the solid biofuel from PSS carbonized at 140–200 °C for 4 h ranged from 21.5 to 23.1

MJ/kg, and increased following carbonization [188]. Most recently, He *et al.* [156] employed HT to convert sewage sludge, with a moisture content of 85.7%, to solid fuel at a temperature of 200 °C without prior drying. Elemental analysis showed that 88% of carbon was recovered while 60% of N and sulfur was removed after the HT carbonization process. Due to dehydration and decarboxylation reactions, oxygen/carbon atomic and hydrogen/carbon ratios reduced to 0.39 and 1.53, respectively. Besides, longer carbonization time seemed to decrease oxygen containing functional groups while carbon aromaticity structure was increased, thereby rendering hydrochars highly hydrophobic.

With the HT treatment, the energy-intensive drying in conventional thermochemical treatment of bio-wastes due to its high moisture content could be avoided. The HT pretreatment of biomass with chemical addition may have desirable properties when co-fired in existing coal boilers. Recently, Kang *et al.* [142] indicated that formaldehyde was an effective additive in HT carbonization of black liquor. In his study, formaldehyde was utilized as a polymerization agent to perform HT carbonization of black liquor to produce solid fuel at a temperature around 220–285 °C. The solid fuel produced in the presence of a 2.8 wt.% formaldehyde solution had 1.27–2.13 times higher yield, 1.02–1.36 times HHV, 1.20–2.31 times higher carbon recovery efficiency, 1.20–2.44 times higher total energy recovery efficiency, 0.51–0.64 times lower sulfur content, and 0.48–0.89 times lower ash content, compared to that prepared without formaldehyde. The HHV of solid fuel produced in the presence of formaldehyde ranged from 22 to 30 MJ/kg, while the HHV of solid fuel produced at 285 °C with and without formaldehyde was 1.90 and 1.57 times greater than that of the raw black liquor solid. These considerable improvements indicated that formaldehyde was an effective additive in HT carbonization of black liquor. Lynam *et al.* [189] also found that the addition of Ca chloride and Ca lactate could increase the HHV of solid product and decrease the pretreatment pressure in the HT treatment of loblolly pine. In any case, although the HT leads to some loss of volatile matters, the energy density is improved by the HT to some extent. In conclusion, the HT is an effective way of densifying the energy content independent on the feedstock. It can upgrade the quality of bio-waste by improving the dewaterability and the energy density of the products due to dehydration and decarboxylation.

Fig.5 An illustration of the upgrading of some typical and low rank coal. Data derived from these typical references: Liu *et al.*[46] Cocout and Eucalyptus leaves (holding time: 30 minutes), Mursito *et al.*[60] Indonesia tropical peat (holding time: 30 minutes), Sagakuchi *et al.*[184] Australia Loy Yang coal (holding time as 30 minutes: Brown coal-1 and 180 minutes: Brown coal-2), Yuliansyah *et al.*[106] Oil palm waste, such as Trunk and Frond (holding time: 30 minutes), Guo *et al.*[181] Victorian Loy Yang coal (holding time: 20 minutes), Lu *et al.*[66] Indonesia MSW, Chinese MSW and Japanese MSW at 220 °C and 30 minutes, Hwang *et al.*[75] Paper, Dog food and Wood, Ge *et al.*[162] Japanese sewage sludge (holding time: 1, 30 minutes and 2, 45 minutes), Areeprasert *et al.*[161] Thailand paper sludge (holding time: 30 minutes) and Prawisudha *et al.*[62] Japanese MSW (holding time: 90 minutes).

4.2 Dechlorination

The previous section has discussed the effect of the HT on the dewatering performance and upgrading of these high moisture content bio-wastes such as the sewage sludge, paper sludge, and

MSW. This section will mainly focus on the effect of the HT on the removal of the Cl, which is known to promote clogging, corrosion, and serve as a Cl source for dioxin formation in a furnace. Therefore, dechlorination treatment is necessary for chemically recycling chlorinated waste. Current established Cl removal technologies are mostly focused on inorganic Cl removal by high temperature leaching [190] and chlorite ions elimination by reduced sulfur compounds [191, 192], and ferrous ions [193, 194], or by granular activated carbon, which focuses on the removal of organic Cl from water [195-197]; therefore, the use of other methods, such as hydrothermal treatment, is still promising to solve the Cl problem in plastic impregnated MSW [34, 55, 62, 186].

Kubátová *et al.* [198] employed HT to dechlorinate aliphatic organics without catalyst or other additives. The dehydrohalogenation was reported to occur at temperature as low as 105–200 °C for 1,1,2,2-tetrachloroethane, lindane and dieldrin. Complete loss of the parent compounds was achieved in less than 1 h at 150, 200 and 300 °C for 1,1,2,2-tetrachloroethane, lindane and dieldrin, respectively. The reaction of polyvinyl chloride (PVC) at 300 °C for 1 h was recorded to generate aromatic hydrocarbons ranging from benzene to anthracene and char residue with carbon-to-hydrogen molar ratio of 1:1. The Cl content of the residue was less than 1 wt.%, much smaller than that of the original polymer, which was 57 wt.%. All compounds, including lindane, dieldrin, tetrachloroethane, trichloroethene, and PVC, were shown to yield chloride ion as the major product (at higher temperatures), indicating that complete dechlorination of some aliphatic organochlorines by the HT could be viable. Fig.6 presents the Cl transformation of two kinds of chlorinated Japanese MSW during the HT process. It clearly indicates that the HT was effective to convert the organic Cl into inorganic Cl. Results from Mikata *et al.* and Takeshita *et al.* [199, 200] also showed that the pyrolysis of polyvinyl chloride PVC in the range of 200–300 °C emitted HCl gas dissolving into water due to the dehydrochlorination, which is in accordance with that shown in Fig.6. At a condition of relative low temperature and short holding time, the Cl transformation from the organic (insoluble) to inorganic (soluble) was not so effective by the HT. A very limit conversion was observed at a HT condition of 234 °C for 5 minutes, especially for the Cl in the form of PVC existing in wood [75]. A considerable quantity of organic Cl was converted into the inorganic one as the HT temperature or holding time is increased. Both the temperature and the holding time were significant for this conversion reaction as indicated by the result of “210 °C and 90 minutes” and “225 °C and 30 minutes” in Fig.6. A longer holding time for MSW over 210 °C or a higher temperature for MSW over 90 minutes promoted the dehydrochlorination, enhancing the generation of soluble Cl compounds. Under a HT temperature of 295 °C and pressure of 8 MPa, all the Cl in the form of PVC was converted into inorganic one within only 5 minutes [75].

Fig.6 The Cl behavior during the HT process. Data adapted from ref.[62].

Most of the Cl will remain in the solid part with some shifting to liquid products (eg. bio-oil) regardless of the operating parameters. More than 85 wt.% of Cl originating from PVC was reported to stay in the char independent of the conditions, which were “234 °C and 3 MPa” and “295 °C and 8 MPa” [75]. However, most of the Cl atoms remained in char in the form of soluble compounds, indicating that dehydrochlorination played more important role in the Cl conversion. It could be attributed to: 1) the generation of HCl dissolved in moisture at the surface and in the pores of char particles; 2) the Cl atoms were chemically combined by alkali metals existing in char to produce

573 salts [75, 201]. As above mentioned, the dechlorination process occurred readily and the
574 hydrochloric acid as a water-soluble Cl species was generated during the HT process. Accordingly,
575 the alkali or ammonia was usually added to promote the Cl transformation from the organic to
576 inorganic [68, 202-207]. It is suggested that with an alkali additive, the hydrochloric acid produced
577 because of the dechlorination in HT process reacted with alkali to produce inorganic salts, which can
578 be easily removed from the solid phase by washing process [68].

579 In clean fuel production from straw, the water washing has been utilized to reduce the amount of
580 K and Cl [208, 209]. Many studies on biomass or coal cleaning have shown that a large portion of
581 the Cl could be released by water-washing [190, 210, 211]. About 90% of the Cl was released from
582 biomass char within 20 min in this way [211]. Hwang *et al.* [212] reported that approximately 85
583 wt.% of easily water-soluble Cl was leached out from MSW char after the first washing procedure.
584 Akimoto *et al.* [203] reported that the organic chlorides in fuel oil could be dechlorinated by pure
585 water above 100 °C. Indrawan *et al.* [34] investigated effect of the washing parameters, including
586 the ratio of water to sample, the mixing time, washing temperature and mixing intensity, on the Cl
587 removal efficiency of HT pretreated MSW. Results show that the inorganic Cl removal efficiency
588 was significantly enhanced with the ratio of water to sample and the washing temperature. Up to
589 96% of inorganic Cl was removed only by one time washing under a washing temperature of 40 °C
590 with a water to sample ratio of 32:1, mixing 5 minutes with a mixing speed of 400 rpm. However, a
591 huge amount of water was required in the water washing. It would be possible to save water
592 consumption by reusing the washed water. Fig.7 presents some experimental results relating to the
593 water reuse times under three kinds of water to sample ratio. It clearly indicated more Cl could be
594 removed by reusing the washed water, especially at a water to sample ratio of 1:1. The Cl removal
595 efficiency of sample at water to sample ratio of 1:1 with one time reuse was higher than that of
596 sample at water to sample ratio of 2:1 with one time washing. Therefore, it is feasible to save the
597 water consumption by reusing the washed water in a commercial plant.

598 Fig.7 Feasibility of the water reuse during washing process. Data adapted from refs.[34, 68].

599 4.3 Denitrification

600 Nitrogen oxides (NO_x) are formed as a result of the thermal oxidation of biomass wastes with high
601 N content. It is formed primarily in two ways: (1) high temperature thermal fixation of N in the
602 combustion air with excess oxygen, producing thermal NO_x; and (2) conversion of N₂ that is
603 chemically bound in the fuel, producing fuel NO_x. The amount of NO_x formed depends on flame
604 temperature, the fuel N content, quantity of excess air used for combustion, the degree of turbulence,
605 and the residence time at high temperature. An increase in any of these factors results in increasing
606 in NO_x formation. The NO_x contributes to a variety of environmental problems, including acid rain
607 and acidification of aquatic systems, the greenhouse effect, photochemical smog, and visibility
608 degradation [36-38]. As a result, the viability of applying new technologies to extract energy from
609 biomass with high N content in the future [213], to a large extent, will be determined by the NO_x
610 emissions properties [33].

611 Generally, the NO_x control technologies can be categorized as: (a) pre-combustion controls
612 (physical fuel cleaning and fuel switching blending), (b) combustion controls (low NO, combustion,

613 furnace sorbent injection, fuel or gas re-burning, decoupling combustion (DC, the complex
 614 reactions during the combustion process are separated and reorganized to enhance the
 615 beneficial interactions, thus inhibiting the undesired interactions), fluidized bed combustion
 616 (FBC) and pressurized fluidized bed combustion (PFBC)), and (c) post-combustion controls
 617 (selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR)). Intensive studies
 618 on the NO_x emission and reduction during coal combustion have been carried out and air- and
 619 fuel-staging technology, SCR, PFBC, the thermal DeNO_x process and the DC were usually used to
 620 reduce NO_x emissions [214-221]. The DC as a new low NO_x emission technology for coal was
 621 originally developed in dual-bed model and then applied in circulating fluidized bed (CFB)
 622 combustor [215, 220]. It has been verified as an effective NO_x emission control technology for coal
 623 combustion. Chen *et al.* [33] investigated the variability of applying DC to reduce NO emission from
 624 the combustion of some typical industrial biomass wastes, such as mycelial waste and sewage sludge,
 625 with high N content. The result implies that the DC was promising to reduce the NO emission. At a
 626 combustion temperature of 1,073 K, up to 40% NO emission can be reduced. Moreover, the DC
 627 shows a good stability for NO emission versus the total gas velocity and O₂-fuel ratio at 1,073 K
 628 compared to the conventional combustion. There are many excellent researches focusing on the fuel
 629 N conversion, emission and controls. Interested reader can refer to these excellent works [222-228].

630 This section will mainly focus on the precombustion control by concentrating on the N behavior
 631 during the HT. The word “denitrification” is used here to represent this N removal by the HT. Wang
 632 and Wang [229] reported that the organic N primarily existed in the suspended solid part in the
 633 sewage, accounting for about 94% of the total N. Denitrification increases with increasing the HT
 634 temperature and the holding time because of the dissolution and the hydrolysis of the protein.
 635 Correspondingly, both the total N and the organic N in the liquid was increased. Moreover, because
 636 the hydrolysis of the protein generated polypeptide, dipeptide and aminorganic acid, which would be
 637 further hydrolyzed to produce organic acid, ammonia and carbon dioxide [230]; the concentration of
 638 the NH₄⁺-N was also improved with the holding time or the HT temperature. At 210 °C with 75
 639 minutes, the dissolving ratio of suspended solids and protein reached 60.02% and 47.21%,
 640 respectively. This dissolution and hydrolysis of the protein/extracellular polymeric substances was
 641 also the main reason that the HT pretreatment could improve the anaerobic digestion of sewage
 642 sludge [166]. Fig.8 shows the effect of the HT temperature on the N content in the solid product with
 643 regard to some typical high moisture and N content bio-waste, such as the sewage sludge, paper
 644 sludge and mycelial waste. As the temperature was lower than 220 °C, the N contained in solid kept
 645 decreasing with the temperature. However, when the temperature was too high (higher than 220 °C),
 646 the N contained in solid would increase with the temperature for paper sludge. Similar results were
 647 also observed in hydrothermal carbonization of wheat straw, poplar wood and olive oil residues at a
 648 relative low temperature (180–230 °C) but long holding time (8 h), where the N content is
 649 significant increased with increasing the HT temperature [231]. This could be attributed to these two
 650 main reasons: (1) some N was absorbed by the char or colloid generated in the HT process, (2) the
 651 polymerization under severe reaction would reduce some carboxyl and hydroxyl groups,
 652 correspondingly increasing the N relative content in the solid biofuel. It was reported that some of
 653 the fragments formed from the degradation of biomacromolecules due to the HT were highly

reactive. The unsaturated compounds, which were easily polymerized, were being created by the elimination of carboxyl and hydroxyl groups [123]. In the case of (highly reactive) lignin fragments, polymerization has been reported to be completed within several minutes above 300 °C [232, 233]. Falco *et al.* [234] stated that this co-condensation could be strengthened by increasing the amount of monosaccharide glucose when synthesized the nitrogen-doped carbon materials from the microalgae by the HT.

Fig.9 presents the distribution and mass balance of N (wt.%) in mycelial waste under several HT conditions. It clearly indicated that the N in solid was dramatically reduced by the HT pretreatment, especially when the HT temperature was lower than 200 °C. Zhang *et al.* [163] reported that over 45% of N in the raw antibiotic mycelial waste was removed by the HT via the conversion of non-Kjeldahl organic N into Kjeldahl organic N. Akimoto *et al.* [203, 204] investigated the feasibility of water and aqueous solutions of metal salts and hydroxides for the denitrogenation of the fuel oil generated by the hydrothermal processing of municipal-waste-plastics under sub- and supercritical conditions. The N removed at around 25-250 °C was ascribed to the removal of NH_4^+ , benzonitrile, and ϵ -caprolactam through extraction by and/or the reaction with water. The hydrothermal denitrogenation of organic N compounds by pure water was reported to occur above 275 °C [203]. After replacing the pure water with the aqueous solutions of alkaline and alkaline earth metal salts and hydroxides, it shows the pH value of the aqueous solution plays a significant role in the HT removal of the organic N. The N content was decreased markedly as increasing or decreasing the pH of the reaction condition, indicating the HT denitrogenation occurred readily under acidic or basic conditions [203]. Among the alkaline, alkaline earth metal compounds and the alkaline metal hydroxides, the last one was found to be the most effective for the hydrothermal denitrogenation. Moreover, more N could be removed with increasing the basicity of the alkaline metals. This is because water can act as a catalyst, a reactant and participates in the conversion of organic compounds at higher temperature. Its reactivity is often reinforced in the presence of acids, bases, or solid acid catalysts [7]. Therefore, it could be suggested the HT dechlorination mainly occurred through hydrolysis, whereas the HT denitrogenation occurred primarily via an ionic reaction path catalyzed by OH^- ions in aqueous alkaline solutions.

Fig.8 Nitrogen content varying with the HT temperature. Data adapted from refs.[112, 161, 163, 229, 235].

In the case of some other detrimental elements, Reza *et al.* [236] converted corn stover, miscanthus, switch grass, and rice hulls with HT at 200, 230, and 260 °C for 5 min, in order to investigate the fate of inorganics during HT carbonization. The results show that the solid fuel yield was as low as 41% of the raw biomass, and decreased with increasing the HT temperature; while the HHV was improved up to 55%. Moreover, all heavy metals were reduced by HT treatment; up to 90% of calcium, magnesium, sulfur, phosphorus, and potassium were removed with HT treatment, which was possibly due to hemicellulose removal. At a temperature of 260 °C, some structural Si was removed. The slagging and fouling indices are consequently reduced with HTC treatment relative to that of raw materials. The Cl content was reduced to a low slagging range after the HT temperature above 230 °C, and Alkali index was medium for raw biomass but decreased by HT

treatment. All these works suggested that the HT was a promising pretreatment technology to convert moist bio-wastes into clean solid biofuel without prior drying.

Fig.9 Distribution of nitrogen following the HT temperature. Data adapted from ref.[163]

4.4 Coalification

Fig.10 shows a Van Krevelen diagram [237] for the solid fuel production from some typical biomass and biomass wastes by the HT. The quality of solid fuels produced by the HT could be compared to the lignite or even sub-bituminous coal, depending on the reaction severity. Both the atomic ratio of H/C and the O/C kept decreasing with the HT temperature; yet, the degree is relevant to both the HT conditions and the material used. It has been reported that the char from lignin tends to have a lower hydrogen content [238] and char from cellulose tends to achieve a higher carbon content [123, 239]. All the HT products exhibit lower H/C and O/C ratios than the initial materials, owing to the evolution of H₂O and CO₂ in the dehydration and decarboxylation reactions. Mass balance analyses indicated that carbonization of the feedstock retained a significant fraction of carbon in the solid char [112]. Due to the decrease in the number of low energy H/C and O/C bonds and increase of high energy C-C bond, the energy density of biomass feedstock was improved, as discussed in section 4.1.

Chemical dehydration significantly carbonizes biomass by lowering the H/C and O/C ratios [123]. According to the composition of the produced hydrochar from municipal wastes, Berge *et al.*[112] concluded that both the dehydration and decarboxylation occurred during carbonization, resulting in structures with high aromaticity. Previous studies indicated that the decomposition of the cellulose was mainly attributed to the dehydration according to reaction R1 as [123]:

The evolution of the H/C and O/C atomic ratios follows essentially the path of a dehydration process, similar to that previously observed for the hydrothermal transformation of saccharides such as glucose, sucrose or starch [127]. Significant decarboxylation only appeared after plenty of water has been generated [123]. There has been little effort to explain the fundamental chemistry, but these experimental results from the HT pretreatment of mycelial waste, paper sludge, kimchi, cellulose and sewage sludge also show that dehydration can be achieved without significant decarboxylation at low reaction severity (as indicated in Fig.10) [69, 125, 151, 161-163]. It is largely unknown to which extent biomass can be carbonized without major decarboxylation. However, the rate of dehydration was thought be much higher than decarboxylation during common hydrothermal carbonization [123].

Fig.10 Van Krevelen diagram for the solid fuel production from bio-wastes by the HT at different temperatures in comparison with other solid fuel. Data adapted from Ge *et al.* [162] Japanese sewage sludge (holding time: 30 minutes), Liu *et al.* [46] Cocout (holding time: 30 minutes), Mursito *et al.* [60] Indonesia tropical peat (holding time: 30 minutes), Zhang *et al.* [163] mycelial waste (holding time: 30 minutes), Areeprasert *et al.* [161] paper sludge (holding time: 30 minutes), Gao *et al.* [151] cellulose (holding time: 30 minutes), Wiedner *et al.* [231] wheat straw, poplar and olive oil residues

(holding time: 8 h), Yuliansyah *et al.* [106] Oil palm waste-trunk and Frond (holding time: 30 minutes), Liu *et al.* [46] Cocout (holding time: 30 minutes), Kim *et al.* [69] Kimchi and paper (holding time: about 30 minutes) and Berge *et al.* [112] MSW and anaerobic digested sludge (holding time: about 50 h).

Dehydration is generally explained by elimination of hydroxyl groups, while decarboxylation is the thermal cracking of the long chain carboxylic acids. Fig.11 shows a conceptual dehydration and decarboxylation reactions. They are two major reactions that can remove oxygen heteroatom in the form of H₂O and CO₂, respectively [146]. As for the source of water, the dehydroxylation and condensation reaction are also regarded as the possible paths. Early studies stated that the dehydroxylation of catechol was worked as a path for water formation during the cleavage of phenolic and alcohol groups above 150 °C and 200 °C respectively in the case of HT conversion lignin [123]. As for the CO₂, it was reported that the carboxyl and carbonyl groups were rapidly degrade above 150 °C, releasing CO₂ and CO, respectively. Early observations conclude that the HT decomposition of the formic acid, which is formed in significant amounts during the cellulose degradation, yielding primarily CO₂ and H₂O, was one likely source for CO₂ formation [240]. Other possible sources include the condensation reactions as well as the cleavage of molecular bonds. Due to destruction of colloidal structures, gas formation, less hydrophilic functional groups, and a lower viscosity of water, physical dewatering is enhanced significantly under hydrothermal conditions [166]. Some of these effects are reversible; the combined mechanical/thermal dewatering technology has therefore been developed and widely applied to dewater a range of biomaterials [241-246].

Fig.11 Dehydration of D-fructose to 5-hydroxymethylfurfural [247] and decarboxylation stearic acid to diesel products [248].

Many reaction mechanisms would contribute to this coalification during the HT, whereas more detailed reaction pathways and kinetics are largely unknown with the exception of the HT degradation of glucose. Funke and Ziegler [123] have summarized and discussed these possible chemical mechanisms occurring in the HT process. According to previous studies on hydrochar formation mechanisms [120, 122, 129, 132, 156, 249-252], the carbonaceous particles can be obtained via three main reaction pathways: (1) direct solid-solid conversion of biomass materials (termed “char”) undergoing devolatilization, condensation, dehydration and decarboxylation; (2) polymerization of dissolved intermediates degraded from the original biomass towards polyfurans; (3) carbonization *via* further inter-molecule (named “coke”). Briefly, carbohydrates bio-wastes were hydrolyzed to glucose or fructose which was converted to 5-hydroxymethylfurfural (HMF) via dehydration under the HT condition. The derived HMF was polymerized to primary particles followed by aggregation and carbonization via further intermolecular dehydration to form carbonaceous spheres (coke) [252]. The coke accumulated along with longer carbonization time while a part of the HMF was dissolved in the liquid phase. Simultaneously, amino acids derived from hydrolysis of proteins in bio-waste subsequently interacted with sugars to form N-containing ring compounds via Mailard reaction [250]. The brown color and characteristic odor of hydrochars were the evidences of Mailard reaction [156]. Based on the aforementioned pathways, mechanism for solid biofuel from bio-wastes with HT treatment is summarized in Fig.12. It should be mentioned that the pathways are proposed according to the HT conversion of pure carbohydrates, such as

glucose, xylose, maltose, amylopectin, hemicellulose, cellulose and lignin. To approach the underlying chemistry occurring in the HT conversion of bio-waste, more works should be done focusing on the kinetics and process simulation. Moreover, for HT conversion of a specific bio-waste, the contribution of each pathway would be different and should be further investigated.

Most recently, Danso-Boateng *et al.* [188] reported that the decomposition kinetics of PSS and SF could be modeled by first order kinetics with Arrhenius law. The activation energy was 70 and 78 kJ/mol, and the pre-exponential factors were 4.0×10^6 and $1.5 \times 10^7 \text{ min}^{-1}$, for solid decomposition of PSS and SF, respectively. Reza *et al.* [253] investigated the reaction kinetics of hydrothermal carbonization of loblolly pine. They proposed and validated that both hemicellulose and cellulose decomposed in parallel first-order reactions. The activation energy was 30 kJ/mol for hemicellulose and 73 kJ/mol for cellulose. At a short holding time, they observed both the reaction and diffusion effect during the hydrothermal carbonization of loblolly pine. The activation energy of sludge was close to that of cellulose but much higher than that of hemicellulose. This was attributed to the difference existing in their component and composition.

Fig.12 schematic clean solid biofuel formation pathways in HT of bio-wastes

5. Fuel combustion characteristics

5.1 Mono-combustion

Ohki *et al.* [254] upgraded the Indonesian low-rank coal by employing the HT at 200–350 °C and studied the combustion characteristic of the hydrothermally treated coal with a thermogravimetric analysis (TGA). It was reported that the ignition temperature (T_i) shifts to a high temperature; whereas the change of the temperature (T_m), at which the maximum combustion rate occurs, is not remarkable. The combustion rate was largely improved, representing about 2–3 times higher than the untreated one. For the T_i and combustion rate, similar results was observed in our study concentrating on the combustion characteristics of the hydrothermally treated sewage sludge at 200 °C for 30 min [255]. However, the results for the T_m presents a little different, which relates to the heating rate of TGA. The difference of T_m between the treated and untreated sludge was negligible when the TGA was operated under a slow heating rate lower than 30 °C/min; while the T_m of the hydrothermally treated sludge (HTS) was about 9.3% lower than that of the raw sludge (RS) when the heating rate was 40 and 50 °C/min. The HT pretreatment has caused substantial changes in the TG and DTG profiles [126]. According to Parshetti *et al.*, [126] all the combustion parameters, such as the T_i , T_m , and the burnout temperature T_f detected based on the mass stability, keep increasing with increasing the HT temperature. The maximum weight loss rate keeps decreasing with increasing the HT temperature, which is opposite to our previous results, indicating the HT enhanced the devolatilization rate of sewage sludge [76]. The thermogravimetric analysis by He *et al.*, [156] also showed that the DTG profile altered from a single peak for raw sludge to two peaks for solid biofuel. The combustion reaction was best fitted to the first order for both raw sludge and solid biofuel. The combustion of solid biofuel is expected to be easier and more stable than raw sludge because of lower activation energy and pre-exponential factor. However, the combustion of solid biofuel produced from PEFB at a low HT temperature (<250 °C) takes place in two stages (devolatilization and combustion), whereas the hydrochar produced at 350 °C shows only one major

combustion stage (combustion temperature ranging from 310 to 590 °C) [126]. Lu *et al.* [66] explored the combustion characteristics of HT pretreated Japanese MSW, Indian MSW, and Chinese MSW by comparing with three standard samples such as rice, cellulose, and polypropylene through TGA. The results show that before HT, the combustion behavior was determined by the composition of MSW, whereas after HT, it was considerably affected by the intrinsic characteristics of the MSW—both and its properties will control the combustion behaviors.

Indrawan *et al.* [68] investigated the chlorine transformation during the combustion of the HT pretreated MSW with/without water washing under 500, 700 and 900 °C and stated that the major part of the chlorine in the unwashed HT MSW was transferred to the ash portion; whereas it was mainly shifted to the exhaust gases portion for the washed HT pretreated MSW because of the removal of the inorganic chlorine by the water washing. It could be concluded that the organic chlorine is mainly emitted in exhaust gases, while the inorganic part mainly shifted to the ash. To detect the effect of the combustion temperature on the shift of inorganic chlorine, thermal degradation of several alkali-chlorine salts, such as KCl, NaCl and CaCl₂, was conducted with TGA. The results indicated that the water washing could be avoided if the combustion temperature is higher than 800 °C because most of the inorganic chlorine will go to the ash part. Therefore, the HT product can be utilized for co-combustion with low-rank coal or the combustion of briquetting products itself without water washing at a temperature below 800 °C. However, a water washing is suggested to remove the inorganic chlorine which will transfer to the exhaust gases at a temperature higher than 850 °C.

Erlach *et al.* [256] employed HT carbonization to pretreat wood to produce a coal-like substance being suitable for entrained flow gasification. They found that the gasification of solid biofuel is more efficient than the gasification of wood, but the losses and auxiliary energy consumption of the HT process lead to a lower overall efficiency of the conversion from wood to clean syngas. The carbon capture rate was found to be 73% in the gasification of hydrochar, which is lower than that of direct wood gasification. This was attributed to the carbon loss associated with the gaseous and liquid byproducts in the HT process. Tremel *et al.* [257] stated that the pulverization of solid biofuel is found to be much less energy intensive compared to wood. In a following gasification experiment, they found that the carbon conversion of solid biofuel at a residence time of 1.0 s is higher than 84% at a temperature of 1000–1400 °C. The results show that the HT pretreatment process has improved biomass properties like energy density, grindability and particle shape and could be utilized to produce a standardized fuel. The HT pretreatment was feasible to produce this new fuel for entrained flow gasification.

Limited information is known about the impact of HT pre-treatment on the pollutants emission characteristics during the combustion. In a recent study, we investigated the NO_x emission behavior of HT pretreated and untreated sewage sludge employing five combustion modes, including conventional combustion (CC), decoupling combustion (DC), separated combustion (SC) and air-staging combustion (AC) with two operating modes, at a temperature of 800 °C [76]. The result shows the amount of NO₂ and N₂O was usually lower than 8 ppm for all experiments; the main component of the NO_x is the NO. Fig.13 shows the NO emission from the raw sludge (RS) and HT sludge (HTS) for different combustion modes (AC-A and AC-B represents different operation conditions in the AC). It is evident that the NO emission from the HTS was lower than that from the

RS independent on the combustion mode employed. This was more notable for the CC and AC-B, where the NO emission of the HTS was only 49.3% and 43.6% of that from the RS, respectively. The NO emission from HTS in DC, SC and AC-A were 96.9%, 92.1% and 56.2%, respectively, of that from RS. Both DC and AC were effective to reduce NO emission from coal and/or biomass combustion [214, 215, 258-260]. Compared with the NO emission from RS in CC, it was reduced to 39.4%, 37.0% and 72.8%, respectively, by employing DC, AC-A and AC-B in the current study. The result in DC was in accordance with that from Chen *et al* [33]. It was reported the NO reduction efficiency can reach 70.0%, 72.0%, and 52.2%, respectively, for mycelia waste, Chinese sewage sludge, and Thailand sewage sludge at a combustion temperature of 1173 K in their study. Moreover, they also stated that in the range of 873-1073 K, a high temperature favors the NO reduction for biomass wastes combustion in DC. Considering the difference in the initial fuel-N content of RS (6.6% d.b.) and HTS (6.2% d.b.), the NO reduction ratio $NO_{reduction}$ by the HT pretreatment in CC, DC, SC, AC-A and AC-B was 50.7%, 3.1%, 7.9%, 43.8% and 56.4%, respectively.

Only considering the NO reduction efficiency of HT pretreatment and DC/AC-B, the HT pretreatment is less effective to reduce the NO emission. However, as illustrated in the introduction, the sludge dewatering was regarded as an essential step for sludge thermal utilization because the high moisture content was one of the main obstacles. The HT pretreatment has been widely accepted to be one of the most effective methods to improve the sludge dewaterability [63, 166, 261]. It was reported that the energy consumption for removing the water from sewage sludge by thermal pretreatment was only about 30% of that consumed in conventional drying process [52, 63]. Moreover, the treated sludge could be combusted to recover energy with a relative lower NO emission in a conventional combustion facility. No extra investment is required to construct a special incinerator or to modify combustors to prevent the possible secondary pollution resulting from the high moisture/N content. Therefore, although the reduction ratio of the HT pretreatment was a little smaller than that of DC and AC, the HT pretreatment could still be a powerful method to lower NO emission from sludge combustion.

To investigate the reason for NO reduction by the HT pretreatment, the X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared (FTIR) and TGA were conducted to detect the nitrogen functional group in sludge with or without HT pretreatment. It shows the main functional group of nitrogen within sludge was the N-C bond in amide or amine at a binding energy of around 400 eV and the N-H bonds in ammonia or protonated amine at a binding energy of about 402 eV {Zhao, 2013 #2153}. The TGA data indicated that the weight loss rate (combustion rate) of HTS was much higher than that of RS. The maximum combustion rate of HTS was around 1.3-2.3 times more than that of RS. Most of the organic matters in HTS have been volatilized over the temperature range of 170-300 °C at a heating rate of 20 °C·min⁻¹, whereas the corresponding temperature range was 170-375 °C for RS. These results verified that the HT pretreatment has promoted the devolatilization properties of sludge and consequently increased the NH₃ release rate in HTS combustion. Taking the previous results from Miyamae *et al.* [262] and Kamabara *et al.* [217] into account, Zhao *et al.* [76] stated that the main reason for HT reducing NO emission was that the HT has improved the NH₃ release rate and amount, enhancing the reaction of NO with NH₃ similar to

the DeNO_x or SNCR process according to the reaction R2 and R3 [36]. Moreover, because the amount of N₂O was very small (<8 ppm), the R3 was supposed to be the main reaction occurred in the HTS combustion [76].

Fig.13 Comparison of NO emission from RS and HTS for different combustion modes [76, 235]. RS: raw sludge; CC: conventional combustion; DC: decoupling combustion; SC: separated combustion; AC: air-stage combustion

5.2 Co-combustion

To improve the stability and remove the pathogenic bacteria and odorous substances, the HT was utilized to pretreat sewage sludge to produce the CSWS (coal-sludge-water slurry). Park *et al.* [175] studied on the stability and dispersibility of this slurry fuel and reported that the HT pre-treatment of sewage sludge at 200 °C enhanced the coal slurry rheological properties, such as the stability and dispersibility; the viscosity and solid content of the CSWS remained the same after 72 h stability testing, whereas those of the coal-water decreased by ca.1000 cP and 3.3%, respectively. It is anticipated that positive synergistic relationships would be achieved when **combusting** the HT products with coal. The HT conversion of high moisture content wastes **by** co-combustion with coal would be a viable waste disposal solution from the viewpoint of suppressing the environmental pollution as well as saving coal consumption. Several studies have been conducted to investigate the co-combustion characteristic of the HT pretreated products, such as MSW, **and** PEFB [54, 56, 66, 72, 126]. Parshetti *et al.* [126] conducted co-combustion of hydrochar in three different blending ratios of 5%, 10%, and 20% with coal to detect the interactive effect of hydrochars obtained at various HT temperatures on combustion characteristics of low rank Indonesian coal. The combustion was characterized by only **one stage with TGA profile** regardless of the blending ratios and the HT temperature. For all samples, the T_i of the blended fuels was reduced and followed the weighted percentage of hydrochar, thus exhibiting an additive behavior. A higher blending ratio will lower T_i resulting in a potential fire hazard, and the fuel may consequently get burnt ahead of a point where it is expected to. Therefore, in the co-combustion, attention should be paid to ensure that the reduction in T_i is within the allowable range for the currently available facilities [56]. The T_f of the blended fuels increased with increasing in the blending ratio [54, 56, 126]. Muthuraman *et al.* [54] first compared the co-combustion characteristics of Indian coal with wood and the HT pretreated Japanese MSW and stated that the devolatilization properties of coal could be improved by blending of both wood and MSW. The ignition temperature was significantly reduced by co-combustion of the HT pretreated MSW with coal. Moreover, this effect became more prominent with increasing the blending ratio of HT pretreated MSW resulting from its high volatile matter content. The results indicated that blending of HT pretreated MSW improves the reactivity of low reactive char combustibles leading to a reduction in unburnt carbon (UC). However, the co-combustion characteristics would not depend on the properties of the HT product, but also **those of the fuel co-combusted with the HT products.**

In a subsequent study, Muthuraman *et al.* [56] investigated the co-combustion characteristics of the HT pretreated MSW with different rank coals, including Indian, Indonesian and Australian coals, with a TGA at a temperature ranging from ambient to 700 °C under the heating rate of 10 °C·min⁻¹, aiming to find how the parameters, such as the heating value, volatiles and ash contents affect the ignition characteristics. The results indicated that the blending of HT pretreated MSW improves devolatilization properties of coal. However, the co-combustion characteristics of HT pretreated MSW and coal blend cannot be predicted only from the pyrolytic and/or devolatilization phenomena because other **factors**, such as the coal quality, also play a significant role in co-combustion characteristics. If the fuel co-combusted has a very low volatile content and very high amount of fixed carbon, the ignition temperature would not be considerably affected by blending of HT pretreated MSW because higher activation energy was required to initiate combustion. In a drop tube reactor (DTR), Lu *et al.* [139] studied the co-combustion behaviour of HT pretreated MSW with three kinds of low rank coals, including peat, lignite and sub-bituminous coal, at a blending ratio of 20 wt.%. The results indicated that the coal characteristics significantly affect the properties of gaseous emission and UC. Blending of HT pretreated MSW would exert negative effects on the CO oxidation during co-combustion with high volatile matter content coal. It also contributes to the NO reduction for coal with low fixed carbon content; the lower the fixed carbon content is, the more effective the introduction of HT pretreated MSW will be on the NO reduction. Jin *et al.* [72] stated the NO emission will be always reduced by co-combustion of HT pretreated MSW with coal, and for the NO_x precursors, the introduction of the HT pretreated MSW encourages the conversion of HCN to NH₃. Long **residence** time (RT) would help **reduce** the NO emission, whereas the excess air ratio (ER) exerts little effect on the NO reduction [139]. Jin *et al.* [72] tested both the effect of blending ratio and combustion temperature on the combustion efficiency to verify to which extent coal can be replaced with the MSW in terms of gaseous emissions and UC in fly ash (FA) in a bubbling fluidized bed (BFB). At low blending ratio (< 20%), the CO emission of co-combustion was much lower than that of coal combustion. The high CO emission of coal combustion was attributed to its high ash content, which would form an ash layer surrounding the FC [19]. In the case of high ER, RT was also a dominant parameter for CO oxidation [139]. Due to a low S content of MSW, the SO₂ emission of co-combustion of coal with HT pretreated MSW kept decreasing with the addition of HT pretreated MSW and also rising in combustion temperature. However, the HCl emission increased with the HT pretreated MSW percentage because of the high Cl content in MSW. In addition, the combustion efficiency was enhanced by adding the HT pretreated MSW so that the UC content decreased at the mixing ratio below 30% at low temperature [139]. Thus, it is acceptable to substitute coal with 30% of HT pretreated MSW in a coal-fired combustor without major modification. The co-combustion of HT products with coal using currently facilities is a viable and cost-effective way to release the environmental protection stress and to achieve WTE.

6. Energy Balance and Economic viability

Namioka *et al.* [63] evaluated the energy consumption of solid fuel production from dewatered sewage sludge employing HT pretreatment by comparing with that of conventional thermal drying process. The proposed clean solid biofuel production process is composed of HT pretreatment, **water removal by mechanical dewatering**, concentration, and thermal drying. The assumption is that after

975 HT, the moisture content of the sludge was reduced from 80 wt.% to 50 wt.% by pressure
976 dewatering and then further decreased to 20 wt.% with a thermal drying; the separated liquid was
977 first concentrated to 50 wt.% with a multi-effect evaporator and then dried to 20 wt.% with a
978 procedure same as treating the solid parts. Moreover, the HT temperature was 200 °C . Based on this
979 assumption, the energy consumption of the proposed process was estimated to 2 thirds of that
980 consumed in the conventional thermal drying. The result indicates that the HT pretreatment is an
981 energy-saving process to control the sludge water content to produce solid biofuel. However, this
982 estimation did not consider the thermal efficiency of all the facilities, solid recovery ratio, and
983 energy density of products, etc., so that the reference value was weakened to some extent.

984 Prawisudha *et al.* [62, 186] employed the HT to produce solid biofuel from MSW in a
985 commercial-scale plant and calculated the energy efficiency of the HT process to verify its
986 self-sustainability in waste recycling. The capacity of this plant is 705 kg/h, running by steam with a
987 temperature of 215 °C and pressure of 2 MPa. During evaluating the energy efficiency of HT, the
988 dry basis heating value of the raw MSW was assumed to be 100%. The energy loss to the condenser
989 and the water content in the product were also calculated based on the product's temperature. The
990 heat loss was obtained from the difference in the total energy balance. The estimated result **indicates**
991 **that** the energy required to treat MSW **is** approximately one-ninth (11.3%) of the energy contained in
992 MSW in this system. If **it is** assumed that all the energy was provided by combustion of the
993 generated solid fuel, about 46.5% of the energy can be recovered by the HT. This **implies that** HT
994 can utilize its own product as energy source to run the process and at the same time to produce net
995 solid fuel products. Because these parameters come from a real plant, it is more meaningful for plant
996 design. However, this calculation considers only the input and output of the HT process, but not
997 including the other important parameters, such as the energy recovery ratio, dewatering performance,
998 and solid recovery ratio, etc. Therefore, these results are not sufficient for the process optimization
999 and large-scale commercialization. To achieve that, an overall estimate is necessary to take the effect
1000 of operating conditions on the carbon distribution, calorific value and recovery ratio of solid fuels,
1001 and the performance of mechanical dewatering and thermal drying into account.

1002 Recently, a detailed energy and mass balance has been worked out for capacity of 1000 kg/batch
1003 in sewage sludge [162]. This estimate considers the effect of the HT temperature and holding time
1004 on the mechanical dewatering performance, solid recovery ratio, and fuel properties of the solid
1005 product. **The calculation is based on the schematic diagram shown in Fig.2.** The thermal efficiency
1006 of the HT solid biofuel production is evaluated compared with the traditional sludge combustion
1007 technology – combination of thermal drying with combustion. **Fig.14** presents a typical energy and
1008 mass balance of solid fuel production from dewatered sewage sludge by employing HT (200 °C and
1009 30 minutes). Under this condition, the solid recovery ratio was about 91 wt.% and the dry basis
1010 heating value of the product is 19.8 MJ/kg. **Fig.14** shows that the energy required running this fuel
1011 production process was 1.3 MJ/kg, whereas it is 3.2 MJ/kg for the conventional drying. The energy
1012 consumption of the HT solid fuel production process is only 40% of that consumed in conventional
1013 thermal drying. Zhao *et al.* [52] also reported that the energy consumption of solid fuel production
1014 by steam explosion was only 22% that of the conventional drying system to produce solid fuel from
1015 sewage sludge. **The energy consumption of the current process was higher than that consumed** in the

steam explosion. It is because that after mechanical dewatering, the residual water was assumed to be removed by forced thermal drying. In the real plant, the waste heat could be used as a heat source for the thermal drying as the drying performance has been improved by the HT pretreatment [180]. Then, the energy consumption could be further saved. Fig.14 also shows that the HT solid biofuel production process is an energy-self-sustainable system. About 52.4% of heat from fuel combustion was sufficient to support this process and another 47.6% can be recovered in terms of heat and electricity, etc. However, the thermal drying is an endothermic process, in which additional fuel is required to run the process. It indicated the high moisture (untreated) sewage sludge needs more heat for drying than it has available by combustion. The co-combustion of untreated sewage sludge with coal is not cost-effective.

Fig.14 Energy balance of solid fuel production by HT pretreatment (200 °C for 30 minutes)

In the case of PEFB in Malaysia, Stemann *et al.* [102] employed the HT to produce hydrochar and evaluated its **economics**. The investment, operating, and total production cost are calculated based on results from the simulation results from *Aspen plus V7.1*. Two different plant sizes were analyzed: one has a processing capacity of 5.7 t/h EFB while the other one has a processing capacity of 13.8 t/h EFB. The results show that the production cost is 19% lower for the bigger plant because of economy-of-scale effects. The biggest cost component by far are the carrying charges (**including the total capital investment, collecting, taxes and insurances**) (52–57%), followed by transportation fee (15–18%), maintenance costs (11–12%), and cost of EFB (5–7%). The total cost of the HT solid biofuel, including shipping from Malaysia to Europe, is about 7.94 and 9.67 €/GJ HHV for these two plants simulated. It is **similar** to the cost of industrial wood pellets, which is 114–140 €/t between 2007 and 2010 [263], corresponding to 6.54–7.96 €/GJ HHV. Compared with bituminous coal (about 2.6 €/GJ HHV), these solid biofuel are not price-competitive. However, if considering environmental protection, sustainable development, and public policy incentives, such as carbon certificates, the solid biofuel production is still a cost-effective and promising way in the case of recycling EFB and releasing environmental stress. Moreover, because the cost of HT solid biofuel is in the same range as industrial wood pellets, their use for co-combustion will be economically viable under the same circumstances. **For the economic evaluation, it remains large uncertainty with regard to HT performance and cost.** Further optimization of the design and operating parameters based on a commercial plant is required and may well yield higher efficiencies and lower production costs.

Conclusions

The conversion of waste biomass (bio-waste) into chemicals and energy can be used in order to protect our environment and achieve sustainable development. Hydrothermal (HT) treatment requires the application of heat and pressure to treat biomass in an aqueous medium. It is widely considered as a promising means for converting wet biomass into value-added products (such as biofuels and chemicals) because it obviates the need (capital, energy and time) for feedstock dewatering and drying. This work **reviewed** the clean solid biofuel production from bio-waste with high moisture, N/Cl content. **The results show that the HT processing is a cost-effective pretreatment. It offers many advantages including: 1) dewaterability can be largely improved and water can be removed cost-effectively; 2) the process does not require the addition and recovery of chemicals**

different from water; 3) simple and economical operation; 4) free of pathogens because of the high temperature. For these reasons, the HT processing can be considered an environmental friendly WTE process for high moisture content bio-wastes.

The main findings are summarized as followings:

- (1) Some bio-wastes have high moisture, N and/or Cl content, low heating value, low energy density, and **may be** harmful to human beings, causing severe environmental and health-related issues. To dispose these bio-wastes safely and cost-effectively, it is necessary to pretreat or upgrade them prior to final utilization to homogenize different feedbacks into high value-added products;
- (2) Hydrothermal (HT) pretreatment improves the hydrophobicity of **a** solid, thus enhancing the mechanical dewaterability of high moisture bio-wastes. As a result, the water, which is one of the main obstacles for bio-wastes utilization and disposal, can be easily and cost-effectively removed by a following mechanical (belt pressing, centrifugal, filtration, etc.) dewatering, **which** directly improves the gross heating value, thus decreasing the volume and increasing the quality of bio-wastes, which make it possible for fuel production. Therefore, HT can upgrade the quality of bio-wastes by improving the water removal ability and the energy density of the products;
- (3) HT is effective to convert organic Cl into inorganic Cl, thus reducing the potential **for** clogging, corrosion, and dioxin formation occurring in the combustion of bio-wastes with high Cl content. Moreover, during combustion of the solid biofuel production from high chlorine bio-wastes by HT, water washing process could be avoided when the combustion temperature is higher than 800 °C because most of the inorganic Cl will go to the ash part;
- (4) A small part of N can be removed by HT in terms of NH_4^+ and water-soluble N. HT dechlorination and denitrogenation mainly occur through hydrolysis, whereas HT denitrogenation occurs primarily via an ionic reaction path catalyzed by OH^- ions in aqueous alkaline solutions. Moreover, the HT pretreatment can **result in** largely **reducing** the NO_x emission from solid biofuel combustion in current coal-fired facilities. The transformation of protein nature and reduction of the binding energy between chemical bonds, have improved the **NH_3 releasing rate and amount during combustion** of solid biofuel, thus enhancing the reaction of NO with NH_3 similar to the De NO_x or SNCR process, which is identified as the main reason that the HT dramatically reduced the NO emission from solid biofuel combustion;
- (5) The quality of solid fuels produced by the HT could be compared to the lignite or even sub-bituminous **coal**, depending on the reaction severity. Both the atomic ratio of H/C and the O/C kept decreasing with the HT temperature; yet, the degree is relevant to both the HT conditions and the material used. The evolution of the H/C and O/C atomic ratios follows essentially the path of a dehydration process, significant decarboxylation only occurs after plenty of water has been generated. Therefore, it would be feasible to increase the water ratio to enhance the carbonization to improve the fuel quality in HT.
- (6) HT pretreatment improves the combustion or co-combustion performance in terms of ignition temperature, pollutants emission, combustion completeness, and reduction in unburnt carbon (UC). It was also found to encourage the conversion of HCN to NH_3 in the solid biofuel combustion. In co-combustion, the final combustion performance of the blending fuels depends

on the properties of HT solid fuel, the fuel co-combusted, and also the blending ratio. It is viable to substitute coal with 30% of HT solid biofuel (from MSW) in a coal-fired combustor without major modification.

(7) The energy consumption of the HT solid biofuel production process is about 40% of that consumed in conventional thermal drying. About half the energy from fuel combustion was sufficient to support this HT solid fuel production process and the rest can be recovered for heat and electricity, etc. Therefore, HT pretreatment for biofuels production from bio-wastes seems to have great potential, especially when considering uses of bio-wastes as alternative fuels in existing plants without significant modification.

Future developments

However, HT solid fuel production systems still face some challenges in real application [124]. Firstly, the corrosion, resulting from the yield of acid or alkali, reduces the life of reactor, thus increasing the cost, especially for catalytic HT in super-critical conditions; Secondly, it is necessary to treat the liquid from HT due to its high content of COD and undesirable elements; Thirdly, it is essential to recover heat (by heat exchangers) in order to reduce the operation cost, while it is difficult to realize; Fourthly, because of the good solid-liquid separation property of the HT product, its transportation was another barrier because of the potential blockage pipeline; Fifthly, the safety issue resulting from the operating pressure would increase the capital costs of reactor.

Therefore, more works focusing on these following aspects should be done in the near future:

- There are technological barriers in the large-scale application of thermo-conversion processes. In order to overcome the technological limits and to develop a more economically competitive as well as environmentally sound technology, process scale up, pollutants reduction and cleaning bio-fuels production are subjects requiring additional research, investigation and study. For technical implementation of HT solid biofuel production and application, plans should base on a comprehensive management concept, which should address the feedstock properties and collection, treatment of by-products and recovery of nutrients. Any comparisons or modifications must consider the current substantial costs and environmental impacts of the alternative collection and treatment processes in use currently;
- HT pre-treatment can improve the drying performance and shorten the sludge drying time. The mechanism is still unclear. Future works should concentrate on the impact of the HT pre-treatment on the water distribution, particle size distribution, porosity and rheological properties of sludge, and bound energy of the water, to explore this mechanism. Also, the effect of other operating parameters, such as the HT temperature, holding time, air temperature, velocity, humidity and sample thickness, on the drying behaviors will be studied to reveal how the HT pre-treatment affect the drying behaviors;
- It is important to optimize the design and operation of HT from an overall viewpoint, which considering the solid fuel recovery ratio, energy density, treatment of by-products, and performance of mechanical dewatering and thermal drying, etc. An economic evaluation taking all aspects from feed handling to reactor design, heat recovery, environmental impacts, product separation, and auxiliary processes for by-product treatment into account should be done to

1136 provide some theoretical basis for HT commercialization;

1137 ➤ Even though a preliminary work indicated that the HT reducing NO emission could be ascribed to

1138 the reason that the HT has improved the NH₃ release rate and amount, enhancing the reaction of

1139 NO with NH₃ similar to the DeNO_x or SNCR process, the underlying chemistry involving in the

1140 combustion of HT solid biofuel combustion is still unclear. Due to the complexity and

1141 particularity of the bio-wastes, it is difficult to characterize and specify the reaction mechanism in

1142 its combustion. Therefore, the gaseous emission characteristics of solid biofuel derived from other

1143 kinds of bio-wastes should be further investigated to check if the HT pretreatment can always

1144 reduce the gaseous emission from bio-waste combustion. It is **necessary to identify** some model

1145 compounds to produce HT solid biofuel and investigate its combustion to fully understand the

1146 reaction mechanism of HT reducing gaseous pollutants. Furthermore, the impact of HT

1147 pretreatment on the transformation characteristics of trace metals and some undesirable elements

1148 should be investigate to utilize the solid biofuel in the real plant;

1149 ➤ In the aspect of the co-combustion characteristics, the synergistic effect and reaction mechanisms

1150 should be investigated to improve combustion performance and optimize process design.

1151 Moreover, based on our experiences, the trace metals and heavy metals **are mainly** in the solid fuel.

1152 Therefore, the behavior of heavy metals during fuel combustion is one of the topics **for further**

1153 **research**.

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1745 Biographies

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Dr. Kunio Yoshikawa is a professor of Frontier Research Center, Tokyo Institute of Technology, Japan, from where he received his PhD in 1986. His research areas are energy conversion, thermal engineering, combustion, gasification, waste treatment technologies and atmospheric environmental engineering, and he wrote more than 300 papers. He was awarded the AIAA Best Paper Award in 1999, ASME James Harry Potter Gold Medal in 2001, JSME Environmental Technology Achievement Award in 2006 and the Fellow of JSME in 2008.

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Peitao Zhao is working as a visiting scholar in the field of Waste to Energy (WTE) in Prof. Kunio Yoshikawa's laboratory at Tokyo Institute of Technology (Japan), founded by the State Scholarship Fund of China and supported by a Strategic China-Japan Cooperative Program from 2011. He obtained his B.S. degree (2008) on Process Equipment and Control Engineering from Tianjin University of Science & Technology (PR China). He combined his master's and doctoral courses (2009) and started his PhD in the field of WTE at Southeast University (PR China) from 2010. His main research interests are solid waste recycling and

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Figures's captions

Fig.1 Typical composition of MSW, (a) United States, data adapted from U.S. EPA [94]; (b) by region, data derived from [95] “*The World Bank, 2012, source: <http://data.worldbank.org/>”*

Fig.2 A conceptual schematic of clean solid biofuel from bio-wastes

Fig.3 Effect of the operating parameters on the sewage sludge dewatering: (a) Holding time; (b) Temperature. (References: Fisher and Swanwick [167], Jiang *et al.*, [168] Zhao *et al.* [173] and Xun *et al.* [174] focusing on the sewage sludge; Areeprasert *et al.* [161] using paper sludge and Zhang *et al.* [163] using mycelial waste) (SRF: specific resistance to filtration)

Fig.4 Overall dewatering performance of the hydrothermal pretreated paper sludge (including the mechanical de watering and thermal evaporation). Data from (Zhao, unpublished data)

Fig.5 An illustration of the upgrading of some typical and low rank coal. Data derived from these typical references: Liu *et al.*[46] Cocout and Eucalyptus leaves (holding time: 30 minutes), Mursito *et al.*[60] Indonesia tropical peat (holding time: 30 minutes), Sagakuchi *et al.*[184] Australia Loy Yang coal (holding time as 30 minutes: Brown coal-1 and 180 minutes: Brown coal-2), Yuliansyah *et al.*[106] Oil palm waste, such as Trunk and Frond (holding time: 30 minutes), Guo *et al.*[181] Victorian Loy Yang coal (holding time: 20 minutes), Lu *et al.*[66] Indonesia MSW, Chinese MSW and Japanese MSW at 220 °C and 30 minutes, Hwang *et al.*[75] Paper, Dog food and Wood, Ge *et al.*[162] Japanese sewage sludge (holding time: 1, 30 minutes and 2, 45 minutes), Areeprasert *et al.*[161] Thailand paper sludge (holding time: 30 minutes) and Prawisudha *et al.*[62] Japanese MSW (holding time: 90 minutes).

Fig.6 The CI behavior during the HT process. Data adapted from ref.[62].

Fig.7 Feasibility of the water reuse during washing process. Data adapted from refs.[34, 68].

Fig.8 Nitrogen content varying with the HT temperature. Data adapted from refs.[112, 161, 163, 229, 235].

Fig.9 Distribution of nitrogen following the HT temperature. Data adapted from ref.[163]

Fig.10 Van Krevelen diagram for the solid fuel production from bio-wastes by the HT at different temperatures in comparison with other solid fuel. Data adapted from Ge *et al.* [162] Japanese sewage sludge (holding time: 30 minutes), Liu *et al.* [46] Cocout (holding time: 30 minutes), Mursito *et al.* [60] Indonesia tropical peat (holding time: 30 minutes), Zhang *et al.* [163] mycelial waste (holding time: 30 minutes), Areeprasert *et al.* [161] paper sludge (holding time: 30 minutes), Gao *et al.* [151] cellulose (holding time: 30 minutes), Wiedner *et al.* [231] wheat straw, poplar and olive oil residues (holding time: 8 h), Yuliansyah *et al.* [106] Oil palm waste-trunk and Frond (holding time: 30 minutes), Liu *et al.* [46] Cocout (holding time: 30 minutes), Kim *et al.* [69] Kimchi and paper (holding time: about 30 minutes) and Berge *et al.* [112] MSW and anaerobic digested sludge (holding time: about 50 h).

Fig.11 Dehydration of D-fructose to 5-hydroxymethylfurfural [247] and decarboxylation stearic acid to diesel products [248].

Fig.12 schematic clean solid biofuel formation pathways in HT of bio-wastes

Fig.13 Comparison of NO emission from RS and HTS for different combustion modes (RS: raw sludge; CC: conventional combustion; DC: decoupling combustion; SC: separated combustion; AC: air-stage combustion)

Fig.14 Energy balance of solid fuel production by HT pretreatment (200 °C for 30 minutes)

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Tables

Table 1 Sludge production of some typical countries ($\times 10^6$ kg/year), data derived from refs.[52, 80-82].

Countries(regions)/years	2005	2010	2020
United Kingdom (UK)	1,545(2006)	1,640	1,640
EU-27 total	10,135(2006)	11,564	13,047
Japan	2,227	2,300	–
United States	7,600	8,100	–
China mainland ^a	2,104	4,150	6,457(2015)

^a Data for China was calculated according to the statistics data of Chinese sewage drainage. Assuming that treatment every 10,000 of sewage will produce 2 kg of sewage sludge. Source: <http://www.mep.gov.cn/zwgk/hjtj/>[82] Data for 2015 was calculated according to the China's 12th Five-Year Construction Plan for National Urban Wastewater Treatment and Recycling Facilities, indicating that the daily domestic sewage treatment rate would be improved to 85%. During this calculation, the amount of sewage drainage was assumed as the same as that of 2010, referring to ref.[264].

Table 2 MSW generation within the OECD area and China mainland ($\times 10^6$ kg/year)

Regions/years	1980	1995	2000	2005	2015	2020	2030	Increase rate
OECD total	3,950	5,610	6,240	6,530	7,540	8,000	9,000	1.3%
(kg/capita/year)	376	476	512	522	576	600	658	
OECD Pacific	120	150	160	170	190	200	220	1.1%
OECD Asia	550	680	690	740	840	880	970	1.1%
OECD Nafta	1,640	2,420	2,720	2,840	3,260	3,470	3,890	1.3%
OECD Europe	1,700	2,360	2,670	2,790	3,280	3,520	4,000	1.5%
United States	1,211(1970)	2,173	2,425	2,527	2,499(2010)	–	–	4.7% ^a
China mainland	310	690(1990)	1,200	1,580	1,800	2,100(2015)	4,850	8-10%

OECD: Organization for Economic Co-operation and Development, Nafta: North American Free Trade Agreement, data for United States comes from United States Environmental Protection Agency (U.S. EPA) [94]. Data for OECD and China mainland comes from Cheng *et al.* and European Environment Agency (Source: OECD Environmental Outlook Baseline) [50, 90].

Table 3 Fuel properties of MSW within some typical countries.

Items/Composition (% db)	Plastics	Food	Paper	Wood	Textiles	Inert	Total (%)
Chinese MSW	13.0	58.8	12.8	9.1	4.4	1.9	100
Japanese MSW	6.8	35.9	42.9	9.0	4.4	1.0	100
Indian MSW	4.0	0	27.2	40.8	5.7	22.3	100
<i>Fuel properties</i>							
Items/properties	Density ^a (kg/m ³)	M_w^a (%, wt)	M_{vm} (%, db)	M_{fc} (%, db)	M_{ash} (%, db)	Mass based HV (MJ/kg, db)	Volume based HV (MJ/m ³ , db)
Chinese MSW	110	30.4	80.1	8.3	11.6	17.6	1,936
Japanese MSW	110	32.0	85.3	4.5	10.2	16.1	1,771
Indian MSW	120	30.2	77.2	9.2	13.6	15.7	1,884

a: as received; M_w , moisture content; M_{vm} , volatile matters; M_{fc} , fix carbon; M_{ash} , ash content; HV, heating value. Data derived from ref.[66].

Table 4 Proximate and ultimate analysis of EFB from Thailand, Indonesia, and Malaysia. Data adapted from ref. [102] for Indonesia, ref. [97] for Thailand, and ref. [103] for Malaysia.

Items/sample origins	Thailand	Indonesia.	Malaysia
<i>Proximate analysis</i>			
Moisture (wt. %)	8.34 ^a	0.65 ^b	8.75 ^a
Volatile matter (wt.%)	73.16	77.41	79.65
Fix carbon (wt.%)	12.2	17.42	8.6
Ash (wt.%)	6.3	4.52	3.0
<i>Ultimate analysis (dry ashes free, daf, %)</i>			
C	46.74	51.51	50.30
H	6.62	7.33	7.56
O	45.51	40.42	41.42
N	0.47	0.67	0.00
S	0.10	0.07	0.70
Others	0.57	0.0	0.02
Heating value (MJ/kg)	19.24	21.33	18.96

^a air dried basis

^b Mean water content of empty fruit bunches after steam sterilization

Captions for Support Information

S1 Paper relating to energy recovering from waste in Elsevier [265]

S2 Typical chemical composition and properties of untreated/digested sludge, data adapted from ref.[266, 267].

S3 General source of MSW and types of wastes [268]

S4 Annually published research articles on the application HT carbonization or upgrading [269]
(source: Elsevier, <http://www.elsevier.com/>)

Support Information

S1 Paper relating to energy recovering from waste in Elsevier [265]

S2 Typical chemical composition and properties of untreated/digested sludge, data adapted from ref.[266, 267].

Item/Sludge type	Primary sludge		Digested primary sludge		Activated sludge
	Value range	Typical	Value range	Typical	
PH	5.0–8.0	6.0	6.5–7.5	7.0	6.5–8.0
Solid content	2.0–8.0	5.0	6.0	12.0	0.83–1.16
Grease and fats (% db)					
Ether soluble	6–30	–	5–20	18	–
Ether extract	7–35	–	–	–	5–12
Protein (% db)	20–30	25	15–20	18	32–41
Nitrogen (% db)	1.5–4.0	2.5	1.6–6.0	3.0	2.4–5.0
Phosphorous (P ₂ O ₅ , % db)	0.8–2.8	1.6	1.5–4.0	2.5	2.8–11.0
Potash (K ₂ O, % db)	0–1	0.4	0.0–3.0	1.0	0.5–0.7
Cellulose (% db)	8.0–15.0	10.0	8.0–15.0	10.0	–
Iron (not as sulfide)	2.0–4.0	2.5	3.0–8.0	4.0	–
Silica (SiO ₂ , % db)	15.0–20.0	–	10.0–20.0	–	–
Alkalinity (mg/L as CaCO ₃)	500–1500	600	2500–3500	–	580–1100
Organic acid (mg/L as HAC)	200–2000	500	100–600	3000	1100–1700
Volatile (% db)	60–80	65	30–60	40	59–88
Heating value (MJ/kg, db)	23–29	25.5	14–18	16	16–23

S3 General source of MSW and types of wastes [268]

Sources	Typical waste generators	Types of solid waste
Residential	Single and multifamily dwellings	Paper, cardboard, food wastes, plastics, textiles, glass, metal ashes, special wastes (bulky item consumer electronics, batteries, oil and tires) and household hazardous wastes, etc.
Commercial & Institutional	Stores, hospitals markets, Schools, restaurants, etc.	Paper, wood, cardboard, food wastes, plastics, metals, glass, special wastes, hazardous wastes, wood residues, etc.
Municipal services	Street cleaning, garden, parks, beaches, recreational areas, etc.	landscape and tree trimmings, Street sweeping, generation wastes from park, beaches and other recreational areas, etc.
Component	Description	
Food wastes	The animal, fruit, or vegetable residues (also called garbage) resulting from the handling, preparation, cooking and eating of foods. Because food wastes are putrescible, they will decompose rapidly, especially in warm weather.	
Rubbish	Combustible and non-combustible solid wastes, excluding food wastes or putrescible materials. Typically combustible rubbish consists of materials such as paper, cardboard, plastics, textiles, rubber, leather, wood, furniture, and garden trimmings. Non- combustible rubbish consists of items such as glass, crockery, tin cans, aluminum cans, ferrous and non-ferrous metals, and construction material.	

Sources: <http://www.unep.org/ietc/InformationResources/Publications/tabid/56265/Default.aspx#WastePubTop>

S4 Annually published research articles on the application HT carbonization or upgrading [269]
(source: Elsevier, <http://www.elsevier.com/>)