Comparative evaluation of conventional and microwave hydrothermal carbonization of human biowaste for value recovery

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Abstract

This paper compares conventional and microwave hydrothermal carbonization (HTC) of human biowaste (HBW) at 160°C, 180°C and 200°C as a potential technology to recover valuable carbonaceous solid fuel char and organic-rich liquor. Also discussed are the influence of HTC heating methods and temperature on HBW processing conversion into solid fuel char, i.e. yield and post-HTC management, i.e. dewaterability rates, particle size distribution and the carbon and energy properties of solid fuel char. While HTC temperatures influenced all parameters investigated, especially yield and properties of end products recovered, heating source effects were noticeable on dewatering rates, char particle sizes and HBW processing/end product recovery rate and, by extension, energy consumed. The microwave process was found to be more efficient for dewatering processed HBW and for char recovery, consuming half the energy used by the conventional HTC method despite the similarity in yields, carbon and energy properties of the recovered char. However, both processes reliably overcame the heterogeneity of HBW, converting them into non-foul end products, which were easily dewatered at <3 seconds/g total solids (c.f. 50.3 seconds/g total solids for a raw sample) to recover energy-densified chars of ≈17MJ/kg calorific value and up to 1.4g/l of ammonia concentration in recovered liquor.

Keywords

Bioenergy, chars, conventional heating, hydrothermal carbonization, microwave, sewage sludge

1. Introduction

The need for more innovative approaches to ameliorate the pervasive consequences of poor sanitation in low- and middle-income countries cannot be over-emphasized, as 2.4 billion people still lack access to safe sanitation. An estimated 1 billion tons of faecal matter is generated annually (Sobsey, 2006). In low- and middle-income countries, more than 90% of faecal waste generated is discharged untreated (Langergraber and Muellegger, 2005). Current approaches such as manual pit emptying, incineration, and disposal to landfill present significant environmental problems related to public health, environmental pollution, greenhouse emissions and contamination of soil and water resources (WHO/UNICEF, 2014; Strauss and Montangero, 2002; Samolada and Zabaniotu, 2014). Environmental regulations for disposal, meanwhile, are becoming increasingly severe and call for more effective solutions and management strategies. The potential for integrating novel sanitation transformative technologies to address the challenges of poor sanitation is gaining international attention and relevance. This interest also lies with their being potentially more environmental friendly, aligning with the concepts of sustainable ecological sanitation, and favouring valuable resource recovery and bioenergy generation (Esrey, 2001; Samolada and Zabaniotu, 2014). Essentially, sanitation technologies should not only treat human faecal wastes without any health or environmental impacts and recover valuable (energy) end products, but should also be scalable to address rapid increases in population and urbanization, without violating environmental regulations and standards for faecal management.

The hydrothermal carbonization (HTC) process, sometimes referred to as 'wet pyrolysis', represents an effective sanitation technology that can be used to address both issues, i.e. poor sanitation and bioenergy needs. HTC can be used to process human biowaste (HBW) – untreated excrement, faecal sludge, primary and secondary sewage sludge – into a sterilized safe form, while also recovering usable and valuable organic carbon, nitrogen and energy end products. HTC is a thermochemical process that involves heating biowaste at sub-critical water conditions between 160°C and 220°C under autogenous pressure in the absence of oxygen, to convert biowaste organics into valuable end products – a carbonaceous (coal-like) solid, i.e. char, and organic-rich liquor (Libra et al., 2011; Peterson et al., 2008; Basso et al., 2016). HTC is distinguished by the use of wet feedstock, obviating the need for energyintensive drying before or during the process (Libra et al., 2011); essentially, this makes HBW, which is characterized by high moisture content of up to 95% (w/w), fit the HTC spectrum. Further, the capacity for handling the heterogeneous nature of HBW pathogen kill (due to the high temperature associated with the technology), and the potential recovery and recycling of valuable nutrients, energy and other inorganic chemicals (in ionic forms), strengthens the HTC technology (Libra et al., 2011; Peterson et al., 2008).

Heating source/method and processing efficiencies are very important considerations for any waste processing technology. A variety of heat sources used for HTC processing have been reported. Conventional HTC (C-HTC) processes usually involve the use of electrically heated high-pressure stainless steel vessels/reactors where heating is achieved via temperature gradients, with conduction and convection as the main heat-transfer mechanisms (Ramke et al., 2009; Berge et al., 2011; Makela et al., 2015). Microwave HTC (M-HTC), i.e. heating via the electromagnetic interaction of microwave with dipolar materials (mainly water content in HBW), has also been acknowledged (Guiotoku et al., 2009; Afolabi et al., 2015; Elaigwu and Greenway, 2016). Absent from the literature, however, is an assessment of how both heating methods compare under similar HTC temperature ranges and how they affect the whole HBW processing/conversion into solid char fuel. More specifically, there are knowledge gaps in comparative char yield (and energy consumed during both HTC processes); post-HTC processes, including dewaterability rates of processed HBW, particle size distribution of char solids, as well as their carbon and energy properties; and ammonia recovery and other HTC liquor properties. These knowledge gaps informed the present study as part of our continued research under the Bill and Melinda Gates Foundation 'Re-invent the Toilet' project, which centres on the development of an HTC-based sanitation facility/toilet that collects HBW, and treats and converts it into safe and usable products.

2. Materials and methods

2.1 Primary sewage sludge (SS)

Primary sewage sludge (SS), the closest alternative to fresh human faeces, is used for this study as representative of a HBW sample. This was obtained from the primary sedimentation holding tank at Wanlip Sewage Treatment works, Leicester, UK. The SS derives from a catchment area serving a population of 0.5 million people, with mixed domestic and industrial effluent. The SS was obtained in a container that was vented to prevent gas build-up. Once sealed, the SS was transported for storage in the cold room of the Civil Engineering Water Laboratory throughout the experimental period. The characteristics of the SS used for this study are summarized in Table 1.

Table 1 Characteristic of sewage sludge (SS) used in this study

Parameters		Primary sewage sludge (SS)
Elemental (%)	Carbon, C	36.6 ±0.4
	Hydrogen, H	5.7 ±0.04
	Nitrogen, N	5.1 ±0.03
	Oxygen, O*	52.6 ±0.5
Proximate (%)	Moisture content, MC (%)	95.6 ±0.2
	Total solids, TS (%)	4.4 ±0.1
	Volatile solids (of TS)	71.4 ±0.2
	Fixed solids (of TS)	28.6 ±0.2
pH		5.5 ±0.3
Energy content (MJ/Kg)		15.8±0.2
Density# (g/cm^3)		1.1
Capillary suction time, CST (Seconds)		389.9 ± 28.9

*Determined by difference, i.e. [100 – {C+H+N}]%

#Provided by the waste treatment plant

2.2 Hydrothermal carbonization methods

2.2.1 Microwave hydrothermal carbonization (M-HTC)

The M-HTC was set up as reported in a previous study (Afolabi et al., 2015) using Anton Paar Multiwave Microwave Labstation (Anton Paar Ltd, Austria) at 2.45 GHz frequency, 900 W at 10A pulse-controlled power output. Raw SS (total weight 160g) was equally divided in four replicates and poured into pre-weighed cylindrical PTFE-TFM reactor vessels of 260°C and 60 bars rating. Weighing was by mass to improve reproducibility during each carbonization experiment. The reactor vessels were loaded symmetrically on the microwave carousal to enhance temperature and pressure reading accuracy during the carbonization process. Microwave energy supplied to the reactor vessels was controlled by wireless sensors, which monitor internal temperature and pressure inside the vessels and also prevent overheating. In addition, an infrared sensor at the base of the microwave cavity measured the temperature in all the reactor vessels and maintained the reactor vessels at ±2°C of set reaction temperature during the M-HTC process.

2.2.2 Conventional conduction hydrothermal carbonization (C-HTC)

C-HTC process was conducted using a high-pressure reactor (Berghof Ltd, Germany) with a temperature and pressure rating of 300°C and 200 bar. The reactor comprised a 300ml PTFE reactor vessel placed in a stainless steel jacket, surrounded by a thermo-insulated heater (DAH-3) block mount. The stainless steel jacket was seated on a (BLH-800) electric heating plate (of a similar microwave power rating), which supplied heat to the reactor vessel by conduction. Raw SS (total weight 160g) was poured inside the pre-weighed PTFE vessel and loaded into the stainless steel jacket. Weighing was also done by mass. The reaction temperature was measured via a thermocouple placed centrally within the PTFE reactor vessel and connected to a BTC-3000 regulator, which maintained a set reaction temperature during the C-HTC process. A PT-100 pressure sensor also measured autogenously generated pressure inside the vessel.

2.2.3 Experimental work-up

Raw SS was processed under both the M-HTC and C-HTC processes at three peak temperatures: 160°C, 180°C and 200°C. The process pressure was autogenous and correlated with the carbonization temperature used. Guided by preliminary experiments and existing literature (Chen et al., 2012; Guiotoku et al., 2011; Funke and Ziegler, 2010; Lu et al., 2012, Basso et al., 2015; Neyens and Baeyens, 2003), 30mins was used as residence time for the M-HTC process, while 3hrs was used for the C-HTC process to ensure enough contact time to achieve carbonization during each experiment. The experiments were conducted in triplicate. Using a wattmeter connected between the mains and each item of carbonization equipment, the energy consumed per gram of SS solids ($\mathrm{Wh.g^{-1}}$ TS) processed during each M-HTC and C-HTC processes were estimated for each HTC temperature investigated. After the completion of each carbonization experiment, the reactor vessels were cooled to room temperature. Carbonized materials were filtered using a 63µm mesh sieve size. The solid fraction, i.e. the wet char, was subsequently dried at 105°C for 18–24hrs for further analysis. The char yield on a dried basis was estimated using equation 1:

$$Char\ yield_{\,(\mathrm{db})}\ (\%) = \frac{\mathit{Dried\ char\ recovered,g}}{\mathit{Dried\ SS,g}} \text{ x } 100\% \qquad \text{Equation 1}$$

The liquor fraction recovered was analyzed immediately after each carbonization experiment to minimize volatile losses.

2.3 Analysis and characterizations

2.3.1 Solids analysis

Raw SS samples and chars produced from both HTC methods were analyzed for moisture (MC), total solids (TS), volatile solids (VS) and fixed solids (FS) according to Standard Methods 2540G (APHA, 2005).

2.3.2 Dewaterability rate

The dewaterability rate was measured as capillary suction time (CST) according to Standard Method 2710G (APHA, 2005) using a CST apparatus (Triton–Type 165, Triton Electronic Ltd, England). The experiment was conducted with a minimum of seven replicates, before estimating their mean values and standard deviations.

2.3.3 Particle size distribution (PSD) analyses

PSD analysis of dried and uniformly grounded solids of raw SS and chars from each experiment was conducted by the laser diffraction method on a Malvern Mastersizer 2000 (Malvern Instruments Ltd, UK) adopting Standard Method ISO 13320:2009. Depending on reproducibility of scattered particle patterns, a minimum of seven replicates were conducted and the size distribution averages were analyzed using the PSD analyzer.

2.3.4 Elemental analysis

Raw SS samples and the chars recovered from each carbonization process were analyzed for their carbon (C), hydrogen (H) and nitrogen (N) contents using a CHN analyzer (CE-440 Elemental Analyzer, Exeter Analytical Inc., UK) adopting the ASTM D5373 Standard Test Method. Analyses were conducted in triplicate, with mean values and the standard deviation estimated for each sample respectively.

2.3.5 Energy content

Calorific values, i.e. higher heating values (HHVs), of all dried solids (raw SS and chars recovered from each carbonization process) were measured using a bomb calorimeter (CAL 2K, Digital Data Systems, South Africa) based on the ISO 1928:2009 Standard. Tests were conducted in triplicate and mean values used as the energy value of the samples.

2.3.6 Recovered HTC liquor analyses

The chemical oxygen demand (COD) of the HTC liquor recovered after separating solids was measured using standard test kits on a COD analyzer (Photometer 8000, Palintest Ltd, UK) according to Standard Methods 5229D (Close Reflux Calorimetric method) (APHA, 2005). Total organic carbon (TOC) was determined by the high-temperature combustion method using a TOC analyzer (DC 190 Rosemount Dohrman, USA) according to Standard Methods 5310B (APHA, 2005). An analysis of ammonia and volatile fatty acids (VFA) was conducted using standard test kits on an automatic spectrophotometer (Hach Lange DR 3900) adopting Standard Methods 4500-$NH_{3,}$ Phenate Method and Spectrophotometric Method respectively (APHA, 2005). The pH was measured using an electronic pH meter (Mettler Delta 340), calibrated against freshly prepared solutions of known pH 4.0 and 7.0. All analyses were conducted in triplicate, with their mean and standard deviation estimated. These tests were conducted for comparative assessment of recovered liquor characteristics from both HTC methods.

3. Results and discussion

3.1 Physical and sensory assessment

The smell and colour of the carbonized SS recovered from both processes were very similar. Foul odour, a characteristic of raw SS, was completely eradicated and replaced with a coffee-like smell and a coal-like black colouration. These observations are consistent with previous studies involving thermochemical conversion/transformation processes at temperature ranges similar to those used in this study. For example, using a paar reactor supplied with heat from a muffle furnace, Wilson and Novak (2009) observed a caramel-like odour and tea-colouration of processed primary and secondary wastewater sludges processed at 130–220 °C. Other studies involving HTC processing of biowastes using plug flow reactors (Peterson et al., 2010), autoclave (Lu et al., 2011) and microwave pyrolysis (Masek et al., 2013) have all reported similar organoleptic changes. These changes are due to intermediate reactions associated with HTC processing at temperatures ≥160°C, including Maillard reaction (occurring between amino acids monomers and carbonyl radicals of reducing sugars; both resulting from thermal hydrolyses of protein and carbohydrates components of SS during HTC processing) and caramelization reactions (a non-enzymatic browning effect on reducing sugars in biowastes) (Nurtsen, 2005; Wilson and Novak 2009; Peterson et al., 2010). Effectively, the similarities in organoleptic properties of end products recovered from both HTC methods in this study compared to previous studies suggests that both processes converted SS to a more pleasant end product. Additionally, smell and colour transformations tend to occur regardless of type/source of heating source used, with reactions associated with HTC temperature processing playing a crucial role in eradicating the foul odour of HBW.

3.2 Dewaterability of processed HBW

CST quantifies the time required for sludgy water content drawn by capillary forces to wet a piece of adsorbent chromatography filter paper. A greater CST value indicates that it is more difficult for sludgy water to be drawn out by capillary forces, and implies higher resistance to filtration or poor dewaterability. As shown in Table 2, dewaterability of carbonized HBW material is feasible using both the M-HTC and C-HTC process. Both processes indicated significant improvement in dewatering rates when compared to raw SS at all temperatures investigated.

Table 2: CST (seconds) and specific CST* (seconds/g TS) of processed SS under both HTC processes

	CST (seconds)		Specific CST (seconds/g TS)	
Raw SS	389.9 ± 28.9		50.3±3.7	
	M-HTC	C-HTC	M-HTC	C-HTC
160°C	10.6±0.5	15.8±0.8	2.3±0.1	3.4±0.4
180°C	9.3±0.6	11.4±0.6	2.2±0.2	2.9±0.1
200°C	8.2±0.4	10.5±0.5	2.1±0.2	2.8±0.2

$$* \, Specific\ CST\ (\text{seconds/g}\ TS) = \frac{\text{CST values (seconds)}}{\text{Total solids of sludgy material (dried weight, g)}}$$

Furthermore, dewaterability was even improved over the HTC carbonization temperature ranges used for both processes – the net effect being that the dewaterability rate of carbonized SS actually decreased with increasing temperature of carbonization. Comparatively, CST values for carbonized products by the M-HTC process at all temperature ranges examined were shorter than C-HTC – indicating a higher dewaterability. This effect, i.e. the improvement in dewaterability of M-HTC compared to the C-HTC method, was most significantly at 160°C (by 32.8%), but reduced towards 180°C and 200°C (<12%). These comparatively observed improvements are similar to those reported in a previous study: 13.8%

and 17.8% improvements in dewatering rates of microwave pre-treated sewage sludge compared to those of conventionally heated sludge at 60°C and 65°C respectively (Pino-Jelcic et al., 2006). Solid concentration/distribution also affects CST values, because larger solid particles tend to block movement of water, which is driven through capillary forces (APHA, 2005). Specific CST (S-CST) was estimated, which allows the dewaterability of samples having various solid concentrations to be compared to understand the net effect of the HTC process on dewaterability. Effectively, M-HTC yields solid char that dewaters at ≤ 2.3 seconds/g TS, while the C-HTC yields at ≤ 3.4 seconds/g TS at temperatures above ca. 150°C (c.f. raw SS at 50.3 ± 3.72 $s.g^{-1}$ TS).

While both processes improved dewaterability of processed SS for char recovery, HTC temperature and heating methods can be implied to have influenced dewaterability. The aqueous phase of sludgy materials is generally described as free water and bound water; however, bound water requires higher energy to be released (Neyens and Baeyens, 2003). Fundamentally, raising the temperature of sludgy materials decreases their viscosity and facilitates filterability. This explains the net improvement in dewaterability rates observed under both processes as temperature (more energy) is raised from 160°C to 200°C. The thermal hydrolysis that occurs under both processes activates sludge flocs (which serve as repositories for water) to improve dewaterability however under different mechanisms. Heat transferred through conduction and convection during C-HTC process disintegrates sludgy flocs (Xun et al., 2008). The C-HTC process relies on thermal gradients (from source of heating to the heated sludge) to dislodge larger sludge flocs, degrade the sludge floc structure and release bound water. However, sludge dewaterability under M-HTC process can be attributed to both the thermal and athermal effects of microwave heating (Wojciechowska, 2005; Eskicioglu et al., 2007), and possibly explains the relatively lower CST values obtained when compared with the C-HTC process. Thermal effects result from direct coupling of electromagnetic energy with water molecules and other polar organics in sludgy biowaste, causing rapid volumetric heating. Athermal effects, meanwhile, i.e. those not related to temperature, are attributed to the vibrational effects of microwaves on the hydrogen bonds in sludgy cell walls through the alternation of the electric field of water (polar substance), causing overall weakening; this may facilitate the breaking of chemically bound water in sludgy biowaste (Solymon et al., 2011). At all temperature investigated, both (thermal and athermal) effects selectively energize polar substances within biowaste and chemically bound water in the cells of SS. This subsequently leads to rapid disruption and disintegration of sludge flocs and bound water, rupturing of the cell walls and membranes, accompanied by chemical dissociation and release of bound water.

In essence, improvements in dewaterability during M-HTC over C-HTC are due to the highly selective nature of the dielectric heating mechanism. Understanding of the degree/extent to which both effects (thermal and athermal) influence dewaterability is still developing, but may explain why M-HTC is slightly better than the C-HTC in this study.

3.3 Particle size distributions of recovered char fuel

The cumulative volume weighted distribution (%) profiles of particle sizes of both raw and carbonized chars produced from M-HTC and C-HTC at the different carbonization temperatures used are presented in Figures 1 and 2 respectively.

As shown in Figure 1, particle sizes in raw SS span a range up to 1700μm, whereas chars produced at the three carbonization temperatures from the M-HTC process produce a smaller and narrower percentage cumulative volume distribution of less than 300μm at 180°C and 200°C; 160°C gave a range slightly above 1000 μm. Similar behaviour was obtained with the C-HTC process (see Figure 2). However, for temperatures below 200°C under the C-HTC process, average particle size distribution extended up to 1200μm. When comparing the profile of raw SS to that of char obtained at 160°C from both processes, a striking difference – characterized by a '*swelling effect*' – can be seen. The effect is consistent with the disintegration/ fragmentation of solids, as observed in previous studies (Chen et al., 2011; Chen et al., 2012). Subsequent increases in temperature to 180°C and 200°C show the cumulative volume distribution profiles shifting towards a proliferation of smaller and finer particles – characterized by a '*swell-rupture effect*'. Comparatively, however, M-HTC appears to result in an increase in solid fragmentation and solubilization compared to C-HTC, especially at 180°C. This further supports results obtained during dewaterability studies. These data further illustrate an increase in fragmentation of raw

SS solids with increasing temperature, indicating that increased solid particle solubilization is a function of reaction temperature.

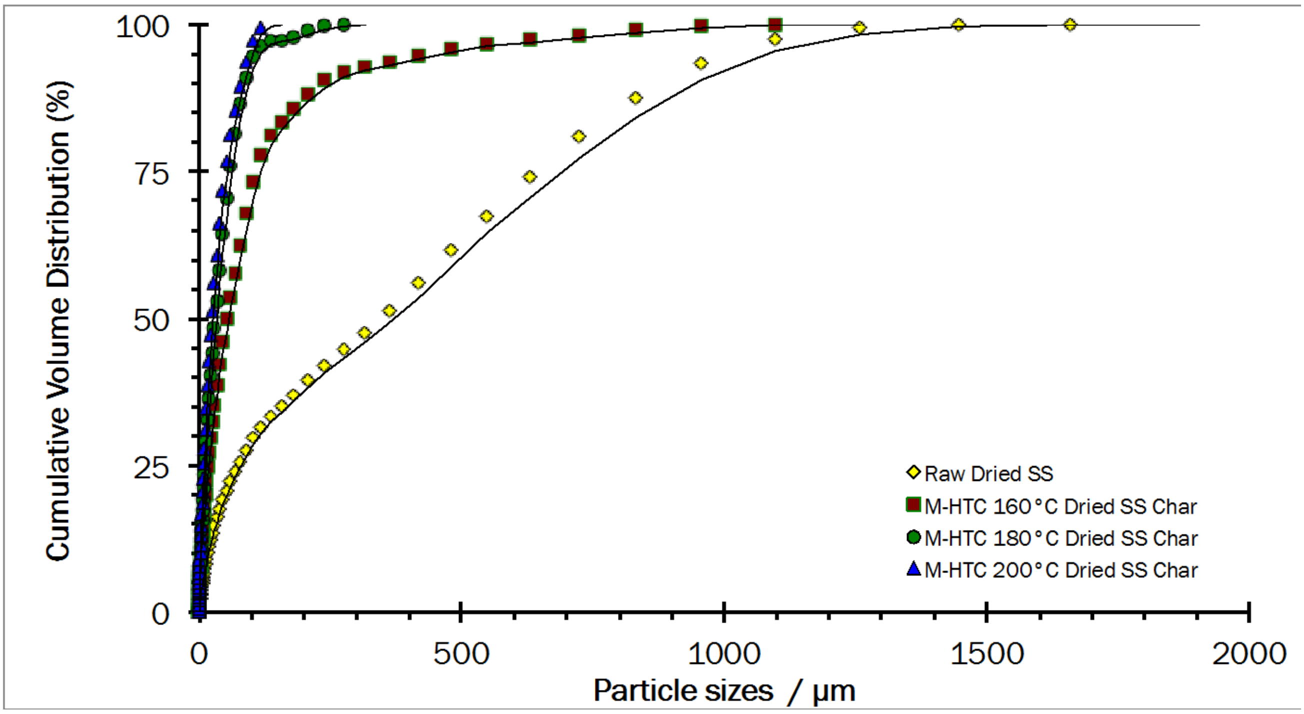

Figure 1 Particle size distribution profiles of raw SS and chars from the M-HTC process

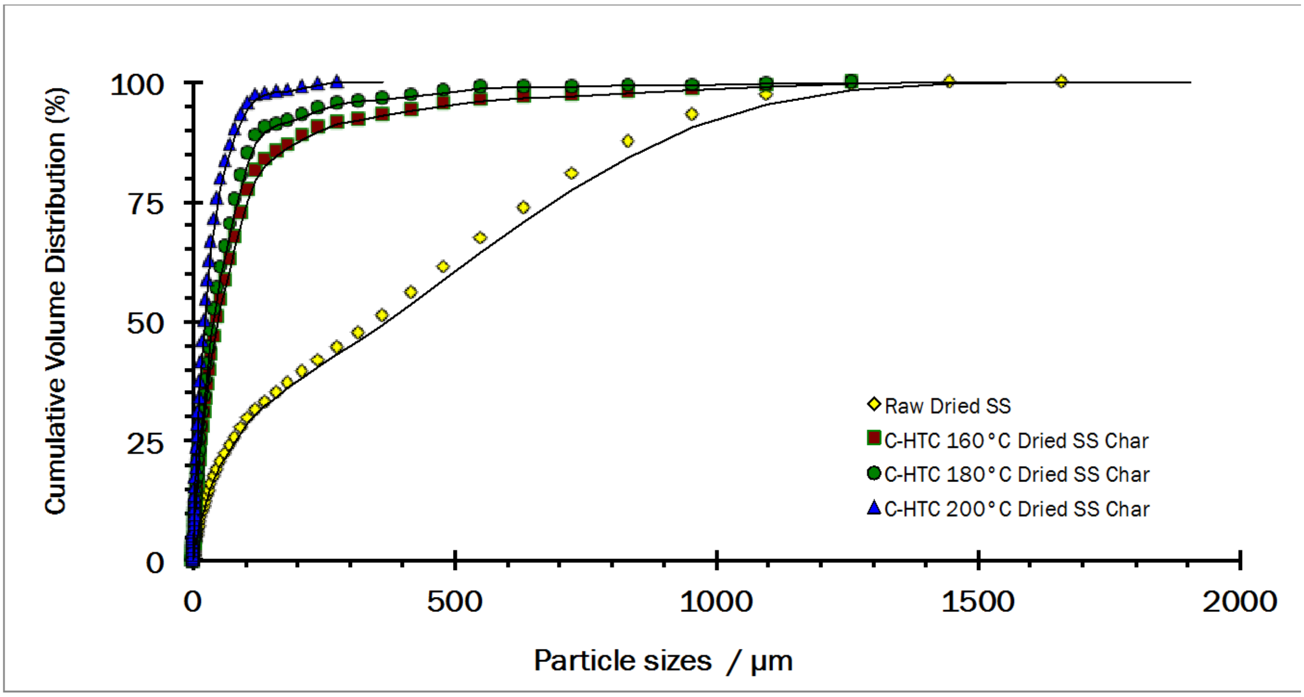

Figure 2 Particle size distribution profiles of raw SS and chars from C-HTC process

The significant reduction in particle size from both processes with increasing temperature when compared with raw SS is made clearer by the D10, D50 and D90 distribution of chars recovered at the three HTC temperature ranges compared to raw SS, as shown in Table 3.

Table 3: D10, D50 and D90 distribution of raw SS and carbonized chars from both HTC processes

	Diameter size (μm)		
Sample description	D10	D50	D90
Raw SS	17.1	347.4	875.8
M-HTC 160°C dried SS char	4.8	52.7	232.2
M-HTC 180°C dried SS char	3.9	31.9	88.2
M-HTC 200°C dried SS char	2.3	19.8	78.7
C-HTC 160°C dried SS char	4.2	44.3	227.3
C-HTC 180°C dried SS char	3.5	36.6	129.3
C-HTC 200°C dried SS char	3.3	25.2	80.9

Where:

D10 – represents the particle size **(μm),** where 10% of sample particle sizes are less (smaller) than this value and 90% are greater (larger) than this value

D50 – represents the median particle size **(μm),** where 50% i.e. half of sample particle sizes are less (smaller) than this value and the other half are greater (larger) than this value

D90 – represents the particle size **(μm),** where 90% of sample particle sizes are less (smaller) than this value and 10% are greater (larger) than this value

Using the cut-off diameter D90, raw SS was 876μm compared to those obtained from M-HTC and C-HTC at 160°C of 232μm and 227μm respectively. This correlates with CST values of raw SS and CST values for chars obtained at 160°C. At 180°C and 200°C, D90 values decreased significantly to <90μm and <130μm for the M-HTC and C-HTC process respectively, in contrast to raw SS and chars obtained at 160°C. This further illustrates why dewaterability was promoted by temperatures greater than 160°C, although there appears to be no substantial benefit of raising the temperature above 180°C. The same trends were observed at D10 and D50 respectively across the two HTC processes, and at all other temperatures used. Comparatively, M-HTC indicated lower D50 and D90 values for char recovered at 180°C and 200°C than those from the C-HTC process.

Effectively, both C-HTC and M-HTC heating methods behaved similarly; i.e. they initiated breakdown of solid aggregates and facilitated the removal of smaller particles of solids, while increasing HTC temperature further enhanced the fragmentation and solubilization of solid aggregates. This explains why the carbonized solids from both processes are more friable and easily ground into homogeneous powders after drying than the dried starting materials. Hence, both processes can convert raw SS into chars amenable to grinding and powdering for moulding into high-density pellets for fuel, for example.

However, the particle size distribution profiles of chars from both HTC methods suggest fragmentation, and particle size reduction/re-distribution largely affected by the HTC temperature used. The microwave heating mechanism though may have accounted for the increased fragmentation, smaller and finer particles observed for chars recovered from the M-HTC process, as exposure to increasing energetic microwave irradiation tends to make particles become smaller and smaller due to the continuous frictions/attrition occurring between molecules of already degraded/disrupted sludge flocs and broken sludge cells structure (Chang et al., 2011).

3.4 Value recovery and consumptive energy audit

Table 4 shows the char yield, concentration of ammonia in recovered liquor and energy consumption by both processes. Generally, depending on the type and characteristics (among other factors) of the feedstock, an average 50–80% in char yield is typical of HTC processes within temperature ranges of 180–250°C, regardless of the heating source (Libra et al., 2011; Funke and Ziegler, 2010). Different yields are also characteristic of different feedstock properties, with moisture content and percentage solid loading being crucial (Ramke et al., 2009; Masek, et al., 2013). Char yield recovered from both processes in this study are within these range as shown in Table 4. The effects of carbonization temperature on char yield from both processes are similar, i.e. char yield from both processes decreased with increasing temperature of carbonization. This supports the proposition fragmentation and solubilization during HTC process increase with carbonization temperature, while char yield decreases. Net decreases in char yield over the temperature investigated were 10.8% and 14.1% for the M-HTC and C-HTC processes respectively.

Up to 1.4 g/l of ammonia was recovered from both processes. The concentration of ammonia recovered was observed to increase with temperature and this result is similar to previous studies (Sun et al., 2013; Lian-hai, 2006; Wilson and Novak, 2009). Basically, protein and other nitrogenous compounds are the primary sources of nitrogen in the raw HBW. At temperatures greater than 150°C, these compounds are hydrolyzed and decomposed to amino acids, organic-N and ammonium compounds. With increasing temperature (≥ 180°C), deamination and hydrolysis of amino acids into short-chain volatile fatty acids, ammonia and carbon IV oxide occurs (Sun et al., 2013; Lian-hai et al., 2006), which further illustrates the increasing concentration of ammonia recovered as temperature increased to 200°C. Comparatively, while both processes tend to produce similar char yields, the C-HTC recovered a slightly higher concentration of ammonia at 180°C and 200°C than the M-HTC process. This may be due to the longer residence of the C-HTC process. The level of ammonia in the liquor phase from both processes supports the proposition that this may be used as liquid fertilizer. Ammonia recovery may be seen as an apparent additional economic benefit from HBW management using the HTC process. However, the direct use in agriculture requires further assessment and other factors, such as endocrine-disrupting exogenous compounds and heavy metals, which are beyond this study, ought to be considered.

When the overall energy required for processing raw SS into value-added char and ammonia in recovered liquor is taken into account, the C-HTC process consumed significantly more energy than the M-HTC process, as shown in Table 4. Energy required to process raw SS solids using the C-HTC process at every other temperature considered almost doubles that required for M-HTC, despite the relatively small differences in the char recovered and ammonia in recovered liquor from both processes. Additionally and as expected, energy consumption increased with increasing temperature; however, the C-HTC process consumed more with increasing temperature than M-HTC. For example, increasing temperature from 160 to 200°C for SS increased energy consumption by 19.73 Wh.g^{-1} TS for M-HTC and 84Wh.g^{-1} TS for the C-HTC process.

Table 4: Comparative energy consumption and char yield from both HTC methods

Temperature (°C)	Energy consumed (Wh.g^{-1}TS)		Char yield (%)		Ammonia in recovered liquor (g/l)	
	M-HTC	C-HTC	M-HTC	C-HTC	M-HTC	C-HTC
160	103.6±0.6	194.9±0.1	61.3±1.2	60.2±1.8	0.7±0.04	1.1±0.02
180	114.2±0.4	267.6±0.3	54.4±1.6	52.4±1.1	0.9±0.05	1.2 ±0.03
200	123.3±0.1	279.3±0.5	50.5±0.9	46.1±0.8	1.2±0.03	1.4±0.04

The higher energy consumption associated with the C-HTC process as compared with M-HTC is due to the average processing time (hrs)[1] required for the each process to achieve carbonization. Based on

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[1] In this study, average processing time includes the warming time to peak temperature and residence time at that temperature. The M-HTC process takes 15mins to attain peak temperature and 30mins as minimum residence times to achieve carbonization; hence the 0.75hrs average processing/conversion time from raw SS to chars. The C-HTC process takes 2hrs to attain peak temperature and a minimum of 3hrs to ensure enough contact time for carbonization to occur.

average processing time involved to achieve carbonization from both processes in this study, the average raw SS solids processing rate, g (TS)/hr, were 9.39 and 1.41 for M-HTC and C-HTC respectively. Hence the M-HTC process has a higher process-conversion efficiency of raw SS into valuable char by a factor of six and consumes less energy when compared with the C-HTC process. This is similar to the conclusion of previous studies (Chang et al., 2011; Gronnow et al., 2013) that have identified the microwave process as being more efficient for converting biomass into chars.

These data clearly demonstrate that both HTC temperature and heating method affect raw SS process-conversion efficiency to char. While both processes behaved similarly in terms of char yield and concentrated ammonia recovered in liquor with increasing carbonization temperature, the disparities in SS conversion/processing rate and energy consumption can be attributed to differences in the heating mechanisms between the processes. The C-HTC process transfers heat energy to material by convection and conduction from the heating source via thermal gradients to the core of the processed material inside the reactor. By contrast, the M-HTC process occurs at the molecular level via direct interaction of high frequency electromagnetic radiation with dipolar molecules (water, proteins and other liquids constituent of wet HBW), which cause dielectric heating from molecular rotation and vibrations. This in effect leads to enhanced selectivity, homogenous and volumetric heating throughout the raw SS inside the microwave reactor, which consequently leads to a faster process via novel reaction pathways, potentially due to reduced activation energy (Sobhy and Chaouki, 2010; Yin, 2012). The merit of the shorter processing time of raw SS and higher recovery rate of chars associated with microwave processing further implies higher throughputs potential, and this may represent a significant advantage over the C-HTC process in terms of biowaste processing for value-added products recovery.

3.5 Chars and recovered liquor properties

The proximate, elemental analysis of carbon, hydrogen, nitrogen and oxygen, and the energy properties of chars and recovered liquor properties recovered at each carbonization temperature from both HTC processes is presented in Table 5.

Table 5: Properties of chars and liquor recovered from both HTC process

			M-HTC			**C-HTC**		
			160°C	180°C	200°C	160°C	180°C	200°C
SOLID CHAR	Proximate analysis (%)	TS	10.8±0.1	11.4±0.3	12.9±0.2	10.3±0.2	10.9±0.1	12.7±0.2
		VS	65.5±2.1	62.6±1.1	58.6±0.7	67.1±0.3	62.9±0.9	59.2±0.0
		FS	34.5±1.9	37.4±1.3	41.4±0.6	32.9±0.2	37.1±0.7	40.8±0.8
	Elemental Analysis (%)	C	38.1±0.4	38.0±0.1	38.2±0.2	39.2±0.1	38.8±0.3	37.9±0.7
		H	5.2±0.04	5.1±0.02	5.0±0.02	5.5±0.09	5.1±0.04	4.8±0.05
		N	3.6±0.03	3.2±0.1	2.6±0.03	3.4±0.08	3.0±0.02	2.8±0.01
		O*	53.1±0.5	53.7±0.2	54.2±0.2	51.9±0.3	53.1±0.4	54.5±0.8
	Carbon properties	C_{DF}[1]	1.04	1.03	1.04	1.07	1.06	1.04
		C_{RW}[2]	61.4	54.4	50.7	62.0	53.5	45.9
		CSF[3]	0.23	0.21	0.19	0.25	0.22	0.19
	Energy properties	HHV (MJ/kg)	16.8±0.6	16.4±0.2	16.8±0.3	16.7±0.1	16.2±0.4	16.3±0.3
		EEF[4]	1.06	1.04	1.06	1.06	1.03	1.03
		E_Y (%)[5]	64.9	56.6	53.5	63.8	53.9	47.4
LIQUOR	pH		4.39	4.81	4.86	4.85	4.91	5.07
	TOC (g/l)		9.3±0.2	9.7±0.1	10.3±0.4	9.6±0.3	10.3±0.5	9.9±0.4
	COD (g/l)		30.8±0.8	31.5±0.5	32.3±0.6	34.1±0.4	35.6±0.1	36.8±0.6
	VFA (g/l)		7.1±0.01	6.2±0.02	5.7±0.3	7.0±0.1	5.3±0.2	4.9±0.2

*Determined by difference i.e. [100 – {C+H+N}]%

[1] Carbon densification factor, $C_{DF} = \frac{\%\ carbon\ in\ dried\ char\ solids}{\%\ carbon\ in\ dried\ raw\ SS}$

[2] %Weighted carbon retained in chars from raw, $C_{RW} = \frac{(\%\ carbon\ in\ dried\ char\ solids * mass\ of\ dried\ char\ recovered)}{(\%\ carbon\ in\ dried\ raw\ SS * mass\ of\ dried\ raw\ SS)}$

[3] Carbon storage factor, $CSF = \frac{Mass\ of\ carbon\ in\ char}{Mass\ of\ dried\ raw\ biowaste}$

[4] Energy enrichment factor, $EEF = \frac{HHV\ of\ dried\ chars\ solids}{HHV\ of\ dried\ raw\ SS}$

[5] Energy yield, E_Y (%) $= EEF\ x\ Char\ Yield\ (\%)$

The total solids (TS) of chars are greater than of raw SS (4.4%), this being consistent with decreased moisture content. Higher TS in chars is a typical characteristic of the HTC process, from the re-distribution of solids during the process. TS of chars were also observed to increase as carbonization temperature increased. The volatile solids (VS) and fixed solids (FS) of chars recovered from both HTC processes were similar in range: 59% to 67% and 32% to 41% respectively. While VS decreased with increasing carbonization temperature, fixed solids (FS) appeared to increase with increasing carbonization temperature. The carbon content of chars recovered at each HTC temperature investigated was fairly stable at 38%, representing less than 3% increase over raw SS. The carbon densification factor, which indicates the ratio of carbon concentrated in chars (dry basis) compared with raw SS, was greater than 1 in all cases. Literature values for carbon densification range between 1 and 1.8 (Servill and Fuertes, 2009a; Servill and Fuertes, 2009b; Lu et al., 2013). Between 45.9% and 62% of carbon from starting SS was retained in recovered chars, and this range was similar to previous study findings on the carbon distribution in solid chars recovered from municipal waste and lignocellulosic substrates (Lu et al., 2012; Berge et al., 2011; Hoekman et al., 2011). However, carbon retained in recovered char decreased with increasing HTC temperature investigated due to C-content solubilization. The amount of carbon sequestered in chars after HTC was estimated as the carbon storage factor (CSF). CSF represents the mass equivalence of carbon remaining in char solids per unit dry mass of raw feedstock after biological decompositions in a landfill (Barlaz, 1998). This factor provides a means for a relative comparison of sequestered carbon. Table 5 shows that CSF values ranged between 0.19 and 0.25 from both methods. CSF was also observed to decrease slightly as the temperature increased from 160°C to 200°C. Previously reported CSF values for paper, food, municipal solid waste (MSW) and anaerobic digested wastes were 0.18, 0.34, 0.23 and 0.14 respectively (Lu et al., 2012). Comparatively, these ranges are very similar to those reported in this study. High CSF values could imply a potentially long-term stability of carbon sequestered in chars if disposed or used in agriculture; however, this is still largely unknown and requires further investigation.

The higher heating value (HHV), is one of the most important characteristics of chars regarding their potential use as solid fuel. The calorific value also enables the estimation/assessment of key energetic parameters such as energy densification and energy yield for comparative assessment with both raw SS and conventional fuels. The effect of HTC temperature and heating methods on raw SS was observed to generate chars with calorific value improvement up to 16.8 MJ/kg, greater than low-rank fuels such as peat (13.8–15.4 MJ/kg), comparable to lignite (16.3–16.9 MJ/kg) and close to some grades of bituminous coal (17 MJ/kg) (Speight, 2005; Haykiri-Açma et al., 2002; Haykiri-Açma and Yaman 2010;). Similar observations have been reported in many studies, with many substrates and heating sources (Parshetti et al., 2012; Hoekman et al., 2011; Chen et al., 2012). The energy content of chars recovered from wastewater sludge ranges from 14.4 to 27.2MJ.kg^{-1} (Berge et al., 2012; Ramke et al., 2009; Ozcimen and Ersoy-Mericboyu, 2010; Lu et al., 2011). These are comparable to the HHVs obtained for all chars recovered in this study. During HTC carbonization, the solid mass decreases due to solubilization and this results in energy densification – as indicated by the energy enrichment factor (EEF) i.e. ratio of the HHV of char to raw SS. In Table 5, the EEF of all chars recovered from raw SS was greater than 1 in all cases. Both processes yield energy densification factors comparable to previous-reported HTC studies specifically run to enhance energy densification on a variety of feedstocks (Roman et al. 2012; Hwang et al., 2012). This is evidence that both HTC processes appear to promote energy densification in chars. Energy yield provides a means for assessing the energy recoverable from chars. Consistent with similar studies, energy yields decreases gradually with increasing carbonization temperature – primarily due to reducing char yield. Increasing temperature from 160 to 200°C resulted in a corresponding decrease in energy yield by 11% and 16% from the M-HTC and C-HTC processes respectively. Measured independently, carbon densification and energy enrichment factor values are in agreement, which reflect the relationships between carbon content and heating value of the chars. N-content in raw SS decreased when compared to those recorded in recovered chars as seen in Table 5 due to thermolytic flushing of N-content in raw SS into the liquid phase during the HTC process. This increased with increasing temperature and was consistent with the increase in ammonia concentration in liquor recovered. The low N-content in chars will further reduce the amount of unwanted nitrogen oxides during combustion, reducing environmental impact.

The properties of liquor measured across the temperature ranges studied in this work suggest similarity in values and trends for both HTC methods, with HTC temperature largely affecting measured values. The pH of the liquor was generally slightly acidic and increased slightly with increasing HTC temperature. This is consistent with volatile fatty acid (VFA) values, which decreased with increasing temperature. Increasing decomposition of organic acids or volatilization of intermediate organic compounds with increasing temperature may be responsible for observations associated with decreasing VFA values. Similarly, both total organic compound (TOC) and chemical oxygen demand (COD) values generally tend to increase with increasing temperature for both HTC methods. This is because in the presence of sub-critical water, polysaccharides (the primary source of C-content in HBW) are broken down and enhanced in dissolution rates into the liquid phase as HTC temperatures increases. This ultimately aids the absolute carbon loss per unit mass of raw HBW to the liquid phase, as revealed by the COD values.

4. Conclusion

The potentials of conventional and microwave HTC processes (under three temperature regimes) for treating/processing HBW, while recovering value-added solid char fuel and liquor rich in ammonia, is demonstrated and comparatively evaluated in this paper. No doubt, both parameters i.e. HTC source of heating and temperature investigated are important for the conversion of HBW and recovery of valuable end products. While both processes compare in yield, carbon and energetic properties of char and recovered liquor, differences were observed in dewaterability, particle size distributions and energy use. They both produced chars of lower particle size distribution, 70–130μm (using D90 as the cut-off diameter) when compared with raw SS, yet with improved CST values corresponding to improved sludge dewaterability. Based on this study, the potential merits of M-HTC over the C-HTC process in terms of biowaste-processing efficiency include:

- faster processing times, due to rapid volumetric heating;
- higher processing rates, due to the relatively lower residence time required;
- a better dewaterability rate, due to the thermal and athermal effects of microwave heating;
- the lower energy requirement to convert SS into valuable end products (chars and ammonia liquor) at all temperatures; and
- potential recovery of char yields slightly higher than for the C-HTC process, despite higher energy consumption and processing time.

Acknowledgements

The authors would like to thank The Bill & Melinda Gates Foundations for funding Loughborough University, UK, on the 'Reinvent the Toilet Challenge' project. The views expressed in this paper are of the authors. Mr Geoff Russell is greatly appreciated for his assistance in collection of primary sewage sludge from the wastewater treatment plant.

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