An Investigation into Human Biowaste Management using Microwave Hydrothermal Carbonization for Sustainable Sanitation

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STATEMENT OF ORIGINAL AUTHORSHIP

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DEDICATION

*To **HIM** and the **great people** that have supported me in my life's journey so far. I am greatly indebted and will forever be grateful for your invaluable input*

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ABSTRACT

The prolonged challenges and dire consequences of poor sanitation, especially in developing economies, call for the exploration of new sustainable technologies. These need to be: capable of effectively treating human faecal wastes without any health or environmental impacts; scalable to address rapid increases in population and urbanization; capable of meeting environmental regulations and standards for faecal management; and competitive with existing strategies. Further and importantly, despite its noxiousness and pathogenic load, the chemical composition of human biowaste (HBW) indicates that it may be considered to be a potentially valuable, nutrient-rich renewable resource, rather than a problematic waste product. This doctoral study therefore investigated microwave hydrothermal carbonization (M-HTC) as a sanitation technology for processing HBW – to convert it into a safe, pathogen-free material, while also recovering inherent value and providing an economic base to sustain the technology. To this end, the products of M-HTC treatment of sewage sludge, human faecal sludge, synthetic faecal simulant and human faeces were characterized with a suite of techniques and tests to demonstrate pathogenic deactivation, and the intrinsic value of the resultant solid char and liquor.

M-HTC was found to process the four HBW substrates effectively, eradicating foul odour with complete pathogenic deactivation, yielding Class A Biosolids that conformed to relevant international guidelines for the treatment of HBW. Microstructural and combustion analyses indicated that M-HTC produces energy densified chars (carbonaceous solids), with up to 67% yield and improved calorific value recovered (19MJ.kg^{-1} to 26MJ.kg^{-1}), making them suitable candidates for solid-fuel or soil-conditioner applications. The liquor contained up to 80% ammonia concentrate – a suitable candidate for fertilizer application. M-HTC was significantly faster than current conventional approaches (30min. vs. 6hr.) and used up to 50% less energy. Additional advantages were noted to be a potential for higher throughput capacity and improvements in dewaterability. M-HTC appears to be a sustainable and lower-cost capable candidate technology for treating and recovering value from HBW.

Keywords: Sanitation, developing economies, human biowaste, microwave, hydrothermal carbonization, value recovery

PUBLICATIONS, CONFERENCES AND PRIZES

Publications

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Prizes

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AD	anaerobic digestion
BET	Brunauer-Emmett-Teller (analysis)
BT	burnout temperature
CFU	coliform forming units
CHN	carbon, hydrogen, nitrogen analyser
C-HTC	conventional hydrothermal carbonization
COD	chemical oxygen demand
CSF	carbon storage factor
CST	capillary suction time
Da	Dalton: 1k Da = 1000g.mol^{-1}
DTG	derivative thermogravimetric analysis
E. coli	*Escherichia coli*
EEF	energy enrichment factor
EPA	United States Environmental Protection Agency
eV	Electron-volt; 1eV = 10^{-19} joules
FAO	Food and Agriculture Organization
FC	faecal coliforms
FS	fixed solids
FSS	faecal sludge simulant
FTIR	Fourier Transform Infrared (spectrometry/ spectra)
GHG	greenhouse gas
HBW	human biowaste
HF	human faeces only
HFS	human faecal sludge
HHV	higher heating value
HMF	hydroxymethylfurfural
HTC	hydrothermal carbonization
HTL	hydrothermal liquefaction
HTG	hydrothermal gasification
IC	inorganic carbon
ICP	Inductively coupled plasma (spectrometry)
IR	infrared
L/g cap^{-1}.day^{-1}	litres/grams per capita per day
Kt.day-1	kilo tonnes per day
MC	moisture content

M-HTC	microwave hydrothermal carbonization
$Mg.l^{-1}$	milligram per litre
$MJ.kg^{-1}$	mega joules per kilogram
MPN	most probable number
MSW	municipal solid waste
ppm; ppb	part per million = $1mg.l^{-1}$; part per billion = $1\mu g.l^{-1}$
PSD	particle size distribution
Pt/Co	platinum/cobalt scale
SEM	scanning Electron Microscope
SS	primary sewage sludge
TC	total carbon/ total coliforms
TG	thermo-gravimetric
TGA	thermo-gravimetric analysis
TOC	total organic carbon
TS	total solids
TSS	total suspended solids
UN	United Nations
UNICEF	United Nations Children's Fund
VFA	volatile fatty acids
VS	volatile solids
WC	water closet
WHO	World Health Organization
$Wh.g^{-1}$	watt hour per gram solid of HBW treated
Wt. %	percentage weight

CHAPTER 1 INTRODUCTION

'Sanitation is more important than independence' – Mahatma Gandhi

1.1 BACKGROUND

Poor sanitation is one of the greatest challenges of this century. Based on recent figures from the World Health Organization (WHO), 2.5 billion people currently lack access to improved sanitation facilities, while 1.1 billion still practice open defecation (1). Approximately 500kt.day^{-1} of human faeces goes uncollected and some result in faecal contamination of water resources (2; 3). Combined with this, more than 700 million people still lack ready access to safe drinking water, and an estimated 1.8 billion people drink faecally contaminated water (1). This profile encapsulates the developing world, where the scourge of poor sanitation is most critical. For example, half the people in Asia are without adequate sanitation (2). Shocking statistics like this are similar for Sub-Saharan Africa, Latin America and other developing economies, as shown in Fig. 1.1.

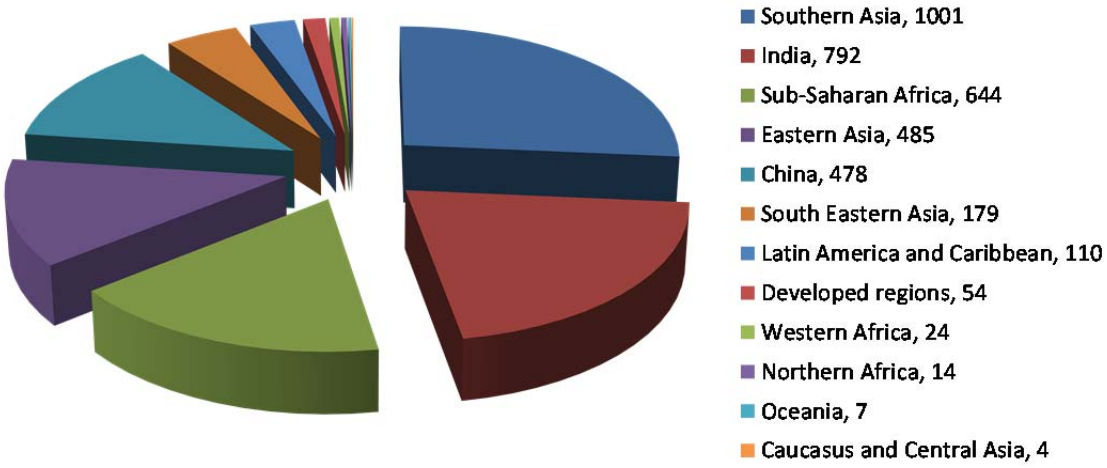

Fig.1.1 Global distribution of people (number in millions) without access to improved sanitation facilities, as at 2012 [adapted from (1)]

According to WHO and the Centre for Disease Control and Prevention (CDC), poor sanitation and contaminated drinking water resources cause more than 80% of all disease in the developing world (4; 5). For example, the reported global incidence of diarrhoea is approximately 4 billion cases per year (2) and, while adults also suffer, 700,000 children die per year from this (6). In fact, diarrheal disease alone is

responsible for 15% of deaths worldwide among children under age five (7). For millions of people across the developing world, restricted access to adequate sanitation, hygiene and potable water affects their nutritional status, health and quality of life, and is ultimately reflected in the reduced life expectancies, characteristic of such impacted communities. Apart from the health impacts, poor sanitation also has pervasive societal effects, such as increasing the rates of school drop-outs for young women and girls who cannot attend schools without the adequate sanitation facilities they need to manage their personal hygiene during menstruation (8). Poverty and poor sanitation are also intertwined (9). For example, nursing the sick that contract diseases due to poor sanitation adds to the financial strain on many already living below the $1.25 per day benchmark, while also reducing their ability to earn incomes. This in effect promotes a cycle of continuous poverty.

Since the 19th century, the dominant solution for managing human bio-waste (HBW) is still the water closet (WC), linked to a sewerage system that facilitates its transportation to centralized wastewater treatment plants, but often terminating in cesspits or other forms of storage, or discharged directly without treatment (10; 11). The introduction of the WC made it possible to separate and contain HBW from polluting drinking water, thereby protecting water resources and supply. While the WC in combination with sewerage systems represents one of the greatest achievements and improvements in hygiene and public health protection, it has over time been subject to evolving environmental criticisms. WCs use clean water of high quality. Despite the introduction of low-flush toilets, WCs still use between 3 and 5L per flush, depending on type, old style single flush WCs can use up to 12L per flush (12). In addition, the minimum daily water requirement of a WC linked with sewered toilets/septic tanks is estimated to be 7.5l.cap^{-1}.day^{-1}, depending on occupation and users' behaviour (13). This is particularly problematic given the global challenge of drinking water scarcity needed to meet increasing population and urbanization demands. This inevitable need for increasingly scarce water resources to clean, flush and transport HBW is a key issue that questions the sustainability of the WC–sewerage system. At the same time, wastewater treatment plants have also been criticised for their intensive capital and energy requirements (14) and this may present a financial challenge for their adoption and transfer in low-income economies in particular.

Generally, for many regions and neighbourhoods across the world, sanitation is characterized by (15):

- a few urban institutions, i.e. a few commercialized/industrialized areas, and a fraction of domestic users (consisting of the small percentage of people who can afford the costs) with sewerage connections and onsite sanitation, e.g. septic tanks, pit latrines etc.; and
- for many, open defecation.

The majority of all properties in Europe (92%) and North America (96%) are connected to a sewerage system, compared to 18% in Africa, and less than 45% for Asia and Latin America (2). In poorly developed areas without sanitation facilities, open defecation becomes the norm, creating at-risk groups that account for an estimated 70% of the population in many economically disadvantaged communities across the world. This burden appears to fall heaviest on the 'rural–poor' (16).

Aside from the non-technical issues such as poor regulatory framework, sanitation-related institutions, capacities and financial constraints, most approaches to onsite sanitation in economically disadvantaged regions may be viewed as being labour intensive, crude and ineffective. Such approaches are little more than 'bucket and chuck it', and fail to address basic structural, environmental and ecological needs (16; 17). A typical scenario is the widespread practice of manually emptying slurry-pits with the accompanying bailing-out/pumping/draining, storage, transportation and disposal of faecal waste (Figs. 1.2 and 1.3 illustrates such activities). These activities create hazardous exposure to pathogens for all concerned, and often lead to uncontrolled and indiscriminate disposal of the bio-waste slurry into drains, canals and open places (see Figs. 1.4 to 1.6). Consequently, this impacts economically deprived communities, where disposals take place near slums and shantytowns characterized by poor road networks, traffic congestion and a lack of properly managed dumps/landfill sites (18). Such practices aggravate further the health impacts of exposure to untreated faecal bio-waste.[1]

Without appropriate infrastructure, the burden of providing effective onsite sanitation becomes financially onerous and unaffordable for the people and communities at risk. The fees for effective, safe and responsible pit emptying are driven by haulage, transportation and collection/disposal costs at designated dumpsites (15). The consequences are non-virtuous cycles of poor sanitation/bio-waste management, and societal impacts that include serious public health risks, pollution of the environment, contamination of drinking/freshwater resources and further impoverishment.

[1] The author has personal experience of suffering from cholera as a consequence of poor sanitation.

Fig.1.2 Manual pit emptying [adapted from (19)]

Fig.1.3 Emptying trucks to dispose of HBW slurry [adapted from (19)]

Figs. 1.2 and 1.3 illustrate the labour-intensive nature of manual pit emptying in developing economies. In most cases, a toilet emptier goes inside the pit without gloves, boots or other safety gear to manually collect (using buckets) and/or position pipes connected to pumping device to pump faecal sludge. This is accompanied by the use of trucks, which collect, store and transport for final disposal. Aside the labour-intensive nature, these practices are costly and represent serious health risks to workers, the public and environment.

Fig.1.4 Sewer pipe vandalization and release of slurry into immediate environment [adapted from (20)]

Fig.1.5 Indiscriminate dumping of waste in an open place [adapted from (19)]

Fig.1.6 Potential discharge of HBW to waterways [adapted from (19)]

Figs. 1.4 to 1.6 Illustrate examples of how some existing sanitation solutions have failed to address the structural and environmental needs of basic sanitation. In order to deal with blockages or filled pits, sewer pipes are easily vandalized, discharging slurry into the immediate environment (Fig. 1.4). Indiscriminate dumping of waste by some toilet emptiers/trucks in open places poses serious health risks to the public, the environment and workers who have to clean up drains (Fig. 1.5). Indiscriminate disposal in poorly designed drains contributes to the contamination water resources (Fig. 1.6).

Despite long-standing international programmes and strategies led by, among others, the United Nations and the World Bank, which specifically address improving sanitation in at-risk communities, there is a strong imperative for better approaches to sanitation (1). Such approaches need to embody effective, affordable and sustainable technologies, which can substitute/complement the current approaches to onsite sanitation. Over the years proposed solutions have included:

- Biological processes such as settling tank/sedimentation beds, unplanted natural air-drying beds, wetlands and composting.
  These are ineffective, as they cannot generate pathogen-free stabilized biosolids. Odour nuisance, parasitic helminth (which tends to concentrate in settled or floating solid [18]) and *E. coli,* for example, characterize the end products of these processes (21).
- Biochemical approaches such as aerobic or anaerobic digestion.

Aerobic and anaerobic digestion technologies require significant construction investments, can take up to three weeks to process human waste and do not ensure pathogen destruction (22; 23).

- Thermochemical treatment, including: incineration, gasification and dry pyrolysis (24; 25).

  Incineration is also capital intensive and generates dioxins and other toxic air pollutants, which pose risks to public health (24). Furthermore, such processes are limited to dry substrate as starting material, requiring high-energy input with significant greenhouse gas emissions (26).

- Composting.

  Characterized by significant pathogenic residues due to the low temperatures (<50°C) involved. Direct exposure to faecal matter during the compositing process also represents a health risk (27; 28).

These approaches are also difficult to implement in dispersed rural settlements and poorly developed urban settings with high-occupation rates (slums). The large construction footprints, longer conversion times, greenhouse gas emissions, along with air pollutants, all raise further barriers to their transfer/adoption in economically deprived areas. Consequently, there is an enduring need to develop better technologies, or remodel and optimize existing ones that are sustainable and effective at managing HBW. Such developments must be viable for adoption by all the world's citizens and, most importantly, able to be scaled to meet the needs of an increasing population that is undergoing rapid urbanization. This need forms the basis for this doctoral study.

1.2 CONTEXT OF THE RESEARCH STUDY: SUSTAINABLE AND RESOURCEFUL POTENTIALS OF HBW

Although HBW is bio-hazardous, its composition and in particular its nutrient content reviewed in detailed in Section 2.1 suggest it can be viewed *as a significant nutrient resource* that can be beneficially exploited, rather than as a problematic *waste product* as it is conventionally viewed. The Water Supply and Sanitation Collaborative (WSSC) recommendations in Vision 21 (29) emphasised this potential of HBW. Some studies have also suggested (but not demonstrated using actual faecal material) its use for energy production (24; 26), nutrient recovery as fertilizer and carbon sequestration, as well as the recovery of valuable organic compounds (30). They have been explored extensively for agriculture use (31; 32; 33). Consider, for example, *Terra preta do Indio,* also called Amazonian Dark Earth (ADE) – highly fertile and productive black soils found in the Amazon Basin region, which are reported to result from the prolonged use of soil

ameliorants derived from HBW (34; 35). Direct excretion of urine and faeces onto agricultural land in Thailand to supplement fertility has also been reported (36). The direct application of urine for horticulture is a common practise that, in Nepal, has been scaled up so that diverted urine stored in urine banks may be either applied directly to soil, used in aquaculture or used to produce struvite (a phosphorous-rich, powdery compound derived from the addition of magnesium to urine banks), which is subsequently applied as fertilizer (37). Furthermore, the fertilizer equivalent of human excreta (Table 1.1) suggests plant nutrients from human excreta produced by one person in a year can meet the fertilizer requirements of 250kg of cereal.

Table 1.1 The fertilizer equivalent of human excreta (38)

Nutrient (kg)	In urine ($500l.yr^{-1}$)	In faeces ($50l.yr^{-1}$)	Total	Required for 250kg of cereal
N	4.0	0.5	4.5	5.6
P	0.4	0.2	0.6	0.7
K	0.9	0.3	1.2	1.2

With a generation rate of 120g–400g.cap^{-1}day^{-1} of wet human faeces and 1–1.2l.cap^{-1}.day^{-1} of urine, HBW represent a huge (280MTonne.day^{-1}), nutrient-rich, sustainable and under-exploited resource.

1.2.1 Research focus

This research focuses on:

- the investigation of an alternative technology for the processing HBW to address the challenges of poor sanitation; and
- the realization of the value inherent in HBW (energy and plant fertilizer, for instance) to provide an economic base to sustain the technology.

This premise is based on the fact that a large proportion of the nutrients in food are present in urine and faeces, and that HBW contains valuable resources that include but not limited to: water, urea, minerals, salts and energy. Two primary components that can be viably recovered from HBW are nutrients (primarily N, P, K) and energy (carbon). Nevertheless, the pathogenic content of HBW presents a serious challenge, both for treatment and resource-recovery purposes. Additionally, HBW may also contain residues of many complex engineered chemicals/synthetic products, hormones, antibiotics and food additives, for example. Some of these compounds pose further environmental risks due to their poor biodegradability. The challenge, therefore, is to develop the technological ways and means needed to provide safe and affordable sanitation to 2.5 billion people in a manner that is pleasing to use, publically acceptable and that

effectively removes human waste from the environment, while also recovering recyclable valuables from it. This is to be achieved without additional financial burden or the need for piped water or sewerage systems.

1.2.2 Scope of the research

Microwave hydrothermal carbonization (M-HTC) was investigated in this doctoral study as a novel and scalable technological process for managing HBW. The proposition is that M-HTC may be used to convert HBW into harmless, pathogen-free material with intrinsic value. The features, suitability and technical considerations for this approach are discussed in more detail in Chapters 2 and 3. This work studied: human faecal sludge, a synthetic variant of human faecal sludge and sewage sludge as representative HBW substrates. Lignocellulose materials such as plant-based waste or aquaculture waste were not involved in the study. The products of M-HTC treatment of each substrate were characterized using a suite of techniques and tests to demonstrate pathogenic deactivation, and the intrinsic value of the resultant solid char and liquor. Operational parameters, including energy consumption, process time and throughput capacity, were also assessed to enable comparative evaluation against existing methods.

1.3 RESEARCH AIMS AND OBJECTIVES

Primarily, this research is centred on the exploration and evaluation of the M-HTC process as an alternative and efficient sanitation technology. As well as benchmarking M-HTC against existing conventional HTC technologies, the research also aims to provide information essential for the design, scaling and operation of an M-HTC based sanitation system for faecal sludge treatment and resource recovery for prototype development. The key objectives of the research are to:

1. characterize the thermochemical decomposition of human-related biomass and recovery of recyclable resources such as solid chars, nutrients and minerals by the M-HTC technology;
2. optimize the process parameters for the microwave carbonization of HBW, pathogen kill, as well as post-carbonization processes e.g. dewaterability;
3. describe the effect of process parameters (temperature and residence time) of the M-HTC process on the properties of the products (for example, the solid-particle solubilization, recovered liquor properties and char properties, such as energy value and carbon enrichment/efficiency, and further relate the characterized char properties to relevant uses);
4. establish operational figures of merit that relate to energy use, process time and throughput capacity in comparison with existing conventional HTC process; and

5. establish the technical specifications for translating the outcomes of this study to potential prototype systems suitable for decentralized faecal sludge processing applications.

1.4 RESEARCH CONCEPTUAL FRAMEWORK

The research proposition is that M-HTC is a novel process with the potential to achieve the objectives of this doctoral research, as outlined in Section 1.3. The key research questions, gaps and hypotheses forming the scope of this work, and how these justify the materials and methods employed for this study, are summarized in Table 1.2.

Table 1.2 Research gaps, questions and hypotheses

Research gaps and questions	Research hypotheses	Research objectives addressed
HBW is heterogeneous and of multiple variations. It has not been explored for HTC. Can M-HTC overcome this heterogeneous nature to produce consistent and stabilized end products?	M-HTC can not only be used for new feedstock in HBW, but can also overcome its heterogeneity to generate carbonaceous solids – i.e. char and liquor rich in nutrients	1 & 3
Can the process ensure pathogen destruction? Can the process generate safe by-products?	Microwave irradiation during the HTC process can ensure pathogen kill below regulatory standards	2
Unprocessed faecal sludge is not easily dewatered nor settled by sedimentation.	It is hypothesized that the M-HTC process will improve dewaterability more than the conventional process	2 & 3
How will the M-HTC process fair with existing conventional process in terms of: **1. Char yield** **2. Physico-chemical properties including carbon content, calorific content, odour nuisance, liquor nutrient** **3. Processing time and energy consumption (kWh.g^{-1} Total solids processed)**	The hypotheses are: 1. Char and carbon yield obtained from the M-HTC method are higher than those from the conventional HTC process 2. Chars obtained from the M-HTC method are of better chemical compositions, physical and chemical properties 3. The process is both time and energy efficient compared to the conventional method, due to its novel reaction kinetics	1, 4 - 5

1.5 RESEARCH VISION AND IMPACT

The vision driving this work is a fast sanitation process that requires minimal energy input and directly treats and valorises human faecal sludge within a household or communal dwelling. Removing the need for sewerage networks and substituting an environmentally beneficial process that is less expensive to operate, will liberate many from the costs associated with central sewage connections and water distribution networks. Success will protect many from the consequences of failures in HBW treatment and management. Potentially, the process could be integrated with existing onsite sanitation in different capacities. For example, due to the smaller footprint, it could substitute the conventional emptying/disposal system with a mobile faecal biowaste processor.

The potential for the recovery and recycling of carbonized material of intrinsic value is of significant importance. Success in the generation of value from the process holds the possibility of an economic model that provides the financial leverage to sustain HBW management. Other significant benefits of the solid end product include carbon sequestration and soil regeneration, contributing to an environmentally friendly, globally sustainable development.

1.6 THESIS OUTLINE

The thesis is organised as follows: Chapter 2 reviews literature on the fundamentals of human biowaste and existing biowaste technologies, outlining the gaps and challenges associated with their transfer to low-income resource settings. The underlying science, principles and technological considerations of the M-HTC process are also deliberated. Chapters 3 and 4 detail the materials and methodology adopted to investigate the hypotheses outlined, while Chapter 5, 6 and 7 discuss the findings from the research. A conclusion, contribution to knowledge and recommendations for future work are deliberated in Chapter 8.

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CHAPTER 2 M-HTC: A NOVEL SANITATION TECHNOLOGY FOR HBW MANAGEMENT

2.1 OVERVIEW

This chapter begins with a general review of human biowaste (HBW) in Section 2.2 with a focus on its composition, nutrient content and generation rates. Existing and potential transformative biowaste processing technologies as they relate to HBW management are discussed in Section 2.3. Sections 2.4 and 2.5 narrow down to feature the novel technology forming the basis of this thesis i.e. microwave hydrothermal carbonization (M-HTC). The suitability of the process, technological considerations and comparison with existing methods, along with the underlying principles of the microwave–carbonization process, including the chemistry, reaction mechanisms and energetics as they relate to HBW processing are also reviewed in these sections.

2.2 WHAT IS HUMAN BIOWASTE?

Human biowaste (HBW) (see Table 2.1) is generally taken to refer to:

- all human excreta;
- associated sanitary waste;
- unclassified wastes;
- accidental; and
- other liquid cleaning/disinfection products.

In short, these are materials typically found at and in onsite sanitation facilities – such as pit latrines, wash blocks, mobile toilets, septic tanks, aqua privies, dry toilets and open-defecation sites. The focus of this study is HBW in the form of faeces, excreta (faeces and urine) or faecal sludge. This study also extends to wastewater mixtures transported through sewerage networks, i.e. sewage sludge.

Table 2.1 Compendium of HBW forms and description [adapted from (1; 2)]

Key terms	Definition and description
Urine	Liquid waste excreted by the body comprising mainly water, urea and other components. Urine serves to balance liquids and salts in the body and excesses are filtered from the blood by the kidneys (3).
Faeces	Semi-solid excrement produced without urine or additional water. Consists of undigested materials from the digestive system, mixed with extracts from the blood stream or sheds from glands and intestine, mucus and bile (4). Faeces also contain pathogenic load comprising bacteria, viruses, helminths and parasitic protozoans.
Excreta	Mixture of urine and faeces not mixed with any water. Mixture could be soft, semi-solid and watery.
Anal cleansing water	Water used for cleaning after urinating and/or faecal excretion. Volume of water collected for anal cleaning ranges from 0.5 to 3L per cleaning.
Sanitary cleansing materials	Materials used to aid personal hygiene, such as: absorbent paper; feminine hygiene products, such as pads, napkins and tampons; disposable nappies; and incontinence pads.
Unclassified waste	This is other waste commonly found in HBW, which may include: alternative cleaning materials such as rags or corncobs; accidental waste such as stones, phones and food debris; and household cleaning products including detergents, deodorising and/or disinfectant formulations.
Flushwater	Water (which can be freshwater, rainwater and/or greywater) used to move excreta through sanitary facilities.
Blackwater	Mixtures of urine, faeces, flushwater, anal cleansing water and/or dry cleansing water.
Greywater	Total volume of domestic wastewater (e.g. from baths, kitchen sinks, laundries) with minimal or no input of human excreta.
Faecal sludge	A general term that encompasses mixtures of fresh, unprocessed or partially digested excreta present in slurry or semi-solids within pipework or storage tanks. May also contain blackwater, with or without greywater. Composition varies and depends largely on factors that include water content, storage medium and temperature. Faecal sludge is usually more concentrated in suspended and dissolved solids than wastewater.
Treated sludge	Partially digested or fully stabilised faecal sludge, i.e. sludge that has undergone some degree of treatment, with substantial decrease in pathogenic content.
Brownwater	Consists ideally of faeces and flushwater only, with urine produced during excretion diverted into another compartment. However, not all urine is diverted as up to 15% of urine can be in brownwater.
Dried faeces	Dried excreta, usually in a friable/powdery form but still rich in organics and considered a biohazard

2.2.1 Sensory impacts of HBW

Foul odour characterises HBW and this represents a nuisance with environmental, public health and even financial implications (5; 6). In a UN/Food and Agriculture Organization (FAO) report, odour control was specifically mentioned as probably the most important public acceptability dimension in the beneficial reuse of treated HBW (7). Foul odours have an instantaneous, unpleasant impact, causing considerable distress to the public and workers during handling, storage and/or transportation of HBW. Different approaches are used to control odour. These include odour suppressants such as potassium permanganate (a strong oxidising agent) and the use of specialized equipment and vehicles for handling, storage and transportation of HBW; all of these have financial implications (8). In addition, the health risks linked to foul odours have been extensively reviewed (9). While the toxicological effects of foul odours are yet to be proven (10), there have been reported cases of illness/symptoms associated with exposure to malodorous faecal sludges (3; 11).

2.2.2 Pathogenic content of HBW

From a health perspective, exposure to untreated HBW is always hazardous due to the potential presence of pathogenic bacteria, viruses, parasitic protozoa and helminths (see Table 2.2 and Fig. 2.1).

Faeces contain most of the pathogens associated with human excreta (12), with the bacteria of greatest concern being *Shigella*, *Vibrio cholera*, *Salmonella typhi* and *E.coli.* Infections by these organisms are responsible for the distressingly high prevalence of diarrhoea, cholera and typhoid wherever economically disadvantaged communities have restricted access to safe sanitation and/or have consumed agricultural crop produce following the use of untreated or partially digested biosolids as fertilizers (13). Typically, human faeces contain a pathogenic load in the range 10^6–10^{10} faecal coliforms ml^{-1} (14).

Enteric viruses are reported as the cause of the majority of gastrointestinal infections (15). Those enteric viruses of greatest concern commonly associated with human faeces are: Hepatitis A; rotavirus; poliovirus; and enterovirus (13). Parasitic protozoan *Giardia intestinalis* and *Cyptosporidium spp*. are the most prevalent parasitic causes of diarrhoea in the developing world (16). Hookworm disease, schistosomiasis and other infections caused by the helminthic parasites (see Table 2.2) are well-documented outbreaks and reportedly prevalent in tropical and subtropical regions of the developing world where water and sanitation facilities are inadequate (17; 18). The infectivity

associated with helminth pathogens is partly due to the potentially large number of helminthic eggs found in human excreta derived from infected individuals, which varies between ≤ 20 to 60,000l^{-1} (19; 20), combined with their resistance to poorly designed or poorly implemented treatment processes. These organisms will survive storage of excreta and become of serious concern when they contaminate untreated or partially digested biosolids applied to soil for food crops (13; 21).

Urinary-borne pathogens of concern include: *Leptospira interrogans; Salmonella typhi;* and *Schistosoma haematobium* (excreted eggs), which cause leptospirosis, typhoid fever and schistosomiasis respectively. The risk of pathogen transmission via urine is generally considered insignificant, as urine excreted from a healthy human is sterile. Contaminated urine is usually linked with faecal contamination of undiverted faeces or, in few cases, where the host is infected (1; 13).

Untreated HBW is hazardous and a risk to public health. Any treatment method must address such risks and conform to WHO guidelines on *E.coli* and helminth eggs, due to their prevalence in most wastewater treatment facilities and their propensity to end up in the biosolids generated by wastewater treatment (13). Consequently, the levels of these organisms in treated bio-waste are used as health/safety indicators.

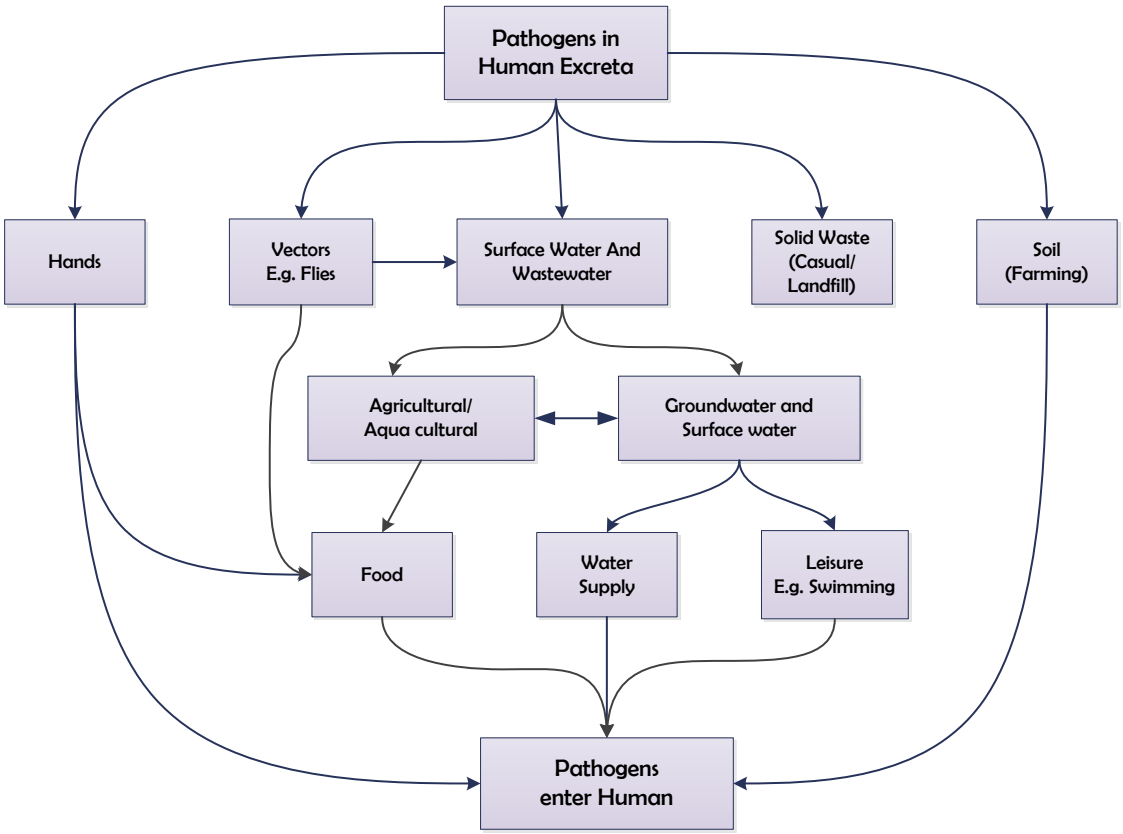


Fig. 2.1 Transmission pathways of pathogens in human excreta

Table 2.2 Pathogens in human excreta [adapted from (13; 22)]

Group	Pathogens	Present in		Diseases caused and common symptoms
		Faeces	Urine	
Bacteria	*Escherichia coli*	x	x	Enteritis (diarrhoea)
	Salmonella typhi/paratyphi	x	x	Typhoid/paratyphoid fever – headache, fever, anorexia, malaise, cough
	Vibrio cholera	x		Cholera – watery diarrhoea, which is lethal if severe and untreated
	Aeromonas spp.	x		Enteritis
	Campylobacter jejuni/coli	x		Campylobacteriosis – diarrhoea, cramps, fever, arthritis
	Salmonella spp.	x		Salmonellalosis – diarrhoea, fever and abdominal cramps
	Shigella spp.	x		Shigellosis – dysentery (bloody diarrhoea), vomiting, cramps, fever
	Yersinia spp.	x		Yersiniosis – Fever, abdominal pains, diarrhoea
	Leptospira interrogans		x	Leptospirosis
Viruses	Hepatitis A, E	x		Hepatitis – fever, jaundice, nausea, anorexia
	Poliovirus	x		Poliomyelitis – fever, vomiting, nausea, paralysis
	Rotavirus	x		Enteritis
	Echovirus	x		Aseptic meningitis, encephalitis, paralysis
	Enterovirus types 68–71	x		Meningitis, encephalitis, paralysis
	Cytomegalovirus, polyomaviruses		x	Usually excreted with urine
Parasitic protozoa	*Giardia intestinalis*	x		Giardiasis – diarrhoea, abdominal cramps, malaise, weight loss
	Entamoeba histolytica	x		Amoebiasis – dysentery, fever, chills
	Crytosporidium parvuum	x		Cryptosporidiosis – watery diarrhoea, abdominal cramps
	Microsporidia	x	x	Usually associated with HIV virus
Helminths	*Schistosoma spp.* (Blood fluke)	x	x	Schistosomiasis, bilharzia
	Ascaris lumbricoides (Round worm)	x		Ascariasis – generally no or few symptoms; coughing, fever, wheezing
	Ancylostoma duodenale/Necator americanus (Hookworm)	x		Itch, rash, cough, anaemia
	Taenia solium/saginata (Tapeworm)	x		Taeniasis
	Trichuris trichiura (Whipworm)	x		Trichuriasis

2.2.3 Physiochemical composition of HBW

HBW is heterogeneous and highly variable in content, consistency, quantity, composition and concentration (21). Physical and chemical properties of HBW are determined by many factors, with the principal ones including: the health of the individual(s), levels of hydration and nutrition, the quantity of food consumed, the nature of diet, phenotype(s), as well as environmental factors (22).

Human faeces may be characterized as a complex mixture of water, micro-organisms (viruses, bacteria, helminths and protozoa); nutrients in the form of undigested macromolecular organics (i.e. protein, lipids and polysaccharides); inorganics and mineral matter (12; 13; 23–27; see Table 2.3). The presence of exogenous compounds, including radioisotopes, antibiotics, food additives and heavy metals, has also been reported with special reference to excreta derived from hospitals or patients under radiopharmaceutical treatment (28).

Table 2.3 Main components of human faeces [adapted from 4; 25; 27]

	Components	Percentages (%) (Reference 25)	Percentages (%) (Reference 4; 27)
Chemical compositions	Fat content/lipids	5–25	10–20
	Protein	10–15	2–3
	Carbohydrates	10–30	30
	Minerals (K, Ca & P)	5–8	Inorganic matter
	Nitrogenous materials	<2–3	10–20
	Bacterial debris	10–30*	30–33
Moisture content		65–85	75
Solid content		15–35	25

*Another study reported that bacterial content of human faeces could be up to 50% (29)

Studies conducted on urine indicate that it is composed of water (up to 96%), urea (up to 1.3%), organic acids (uric acid, citric acids), electrolytes, solubilized metabolites, hormones, vitamins, ammonium salts, nitrogenous compounds and inorganic salts (24; 30). Micro-organisms are sometimes found in urine, as discussed in Section 2.2.2.

2.2.4 Structural and elemental composition of human excreta

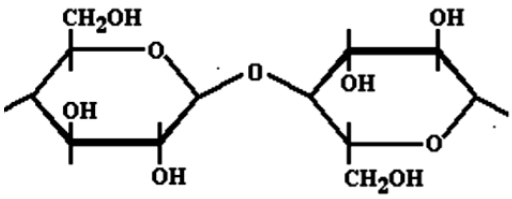
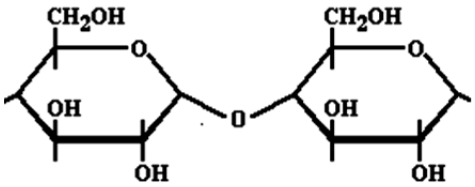
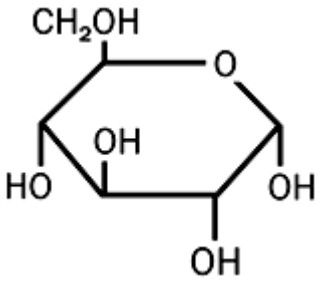
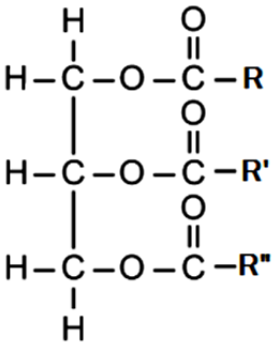
A study derived the empirical structure for dried faeces to be (31):

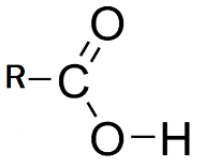
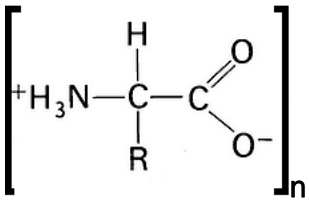
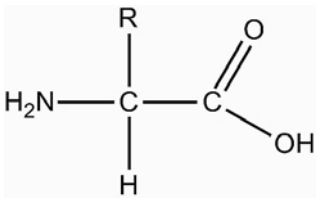
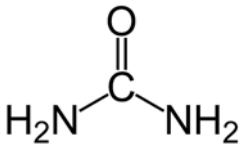
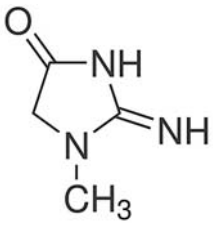
$$C_1 H_{1.87} O_{1.11} N_{0.2}$$

No empirical formula currently exists for urine; however, the structures of its key components, such as urea and creatinine (as shown in Table 2.4), are well reported (24; 27). As shown in Table 2.4, while sugars form the building block of polysaccharides, fatty

acids and amino acids monomers form the macromolecular structures of the fat and protein contents in human faeces.

Table 2.4 Structure of important components of human excreta [(27; 32; 33)

Component	Chemical formula of typical monomers	Structural information
Cellulose	$(C_6H_{10}O_5)_n$ 	Formed from straight-chained glucose anhydride monomers. Crystalline structure, not soluble in water. n ≈ 500–10,000; β (1–4) Linkages between glucose residues
Starch	$(C_6H_{10}O_5)_n$ 	Also composed of glucose monomer; however, in ranges between 250 and 300units form helical shape. It is, composed of branched chain and soluble in water, unlike cellulose. α (1–4) Linkages between glucose residues
Glucose	$C_6H_{10}O_6$ 	Main monomer block forming most polysaccharides in HBW
Fats	RCOO $CH_2CH(R'COO)CH_2$ R''COO 	RCOO; R'COO; R''COO are fatty acids with ester linkages to a glycerol backbone

Fatty acids	**RCOOH** 	R is an alkyl group, typically of 12–20 carbons with 0–4 double bonds e.g. butanoic acid
Proteins	**$[NHCH(R)C(OO)]_n$** 	Monomers are amino acids residue with various (R) groups $n \approx 500–2000$
Amino acids	**$H_2NCH(R)COOH$** 	R is the side group which varies from H to heterocyclic groups
Urea	**H_2NCONH_2** 	Ranges between 4800 $mg.l^{-1}$ to 23,000 $mg.l^{-1}$
Creatinine	**$HNC(=NH)N(CH_3)CH_2C=O$** 	Between 240 $mg.l^{-1}$ and 2000 $mg.l^{-1}$

In decreasing order of abundance, the major and minor elements found in human excreta can be grouped into three (34; 35):

- Category 1: Carbon (C), oxygen (O), hydrogen (H), nitrogen (N), phosphorus (P), potassium (K) and sulphur (S) – present in significant amounts
- Category 2: Calcium (Ca), magnesium (Mg) and zinc (Zn) – present in smaller but significant amounts
- Category 3: Trace elements such as copper (Cu), nickel (Ni), cadmium (Cd), lead (Pb), mercury (Hg)

Ca, Mg, Zn, Cu, Ni, Cd, Pb and Hg are mainly discharged in faeces, while N, P, K, and S are found in urine (26). Generally, the amount of heavy metals in human excreta coming from ingested food is quite low (13). For example, 9–16mg Zn, 1.4–1.5mg Cu, 0.3mg Ni, 0.02–0.03mg Cd, 0.07–0.14mg Pb and 0.01mg Hg were reported as ranges found in human excreta $cap^{-1}.day^{-1}$ from a study conducted in Southern Thailand (26). These are low when compared with other waste streams such as industrial effluents (34; 36).

2.2.5 Plant-available nutrients in human excreta

The key plant nutrients in human excreta are nitrogen (N), phosphorus (P) and potassium (K). The exact nature and quantity of these nutrients in human excreta arise mainly from the nature/type of food (diet) consumed and, as such, this determines, among other factors, their generation rates (see Table 2.5). Some studies have related the distribution of these nutrients in food consumed into human faeces in the following proportions: 10–20% N, 20–50% P and 10–20% K respectively (3; 23; 37; 38). About 20% of N content in human faeces is in the form of ammonia, which has undergone biochemical degradation from large macromolecular organics of protein, peptides and ammonia acids; others are found in dead bacteria and enzymes (23). Human urine contains the largest proportion of plant nutrient of all forms of HBW (38; 39), with N being the predominant nutrient. The total amount of N excreted is closely related to the amount of protein consumed. With a high-protein intake, up to 90%, and with a protein-free diet, 50–60% of N content in urine is in the form of urea (23). P and K in urine are excreted in ionic forms that are the same as those found in chemical fertilizers (40).

Based on empirical studies, an estimate of N and P in excreta from food consumed can be determined using the relationships (41):

$$N(\text{ in excreta}) = 0.13\ x\ TFP \qquad 1.1$$

$$P\ (\text{in excreta}) = 0.011\ x\ (\ TFP + VFP) \qquad 1.2$$

Where $TFP\ and\ VFP$ are total food protein and vegetal food protein respectively, estimated from FAO statistics on food supply (41)

Table 2.5 Generation rates of N, P and K in human excreta

	Generation rates ($g.cap^{-1}.day^{-1}$)			Basis	References
HBW	N	P	K		
Faeces	0.3–1.7	0.2–1.3	0.3–0.4	Study conducted on 21 adults	(42)
	0.9–2.8	0.3 – 0.8		Study conducted on 24 adults	(43)
	1.5	0.5	1.0	Averages reported in Sweden	(38)
Urine	6.9–11.8	1.1–2.7	2.5–2.7	Ranges reported in Sweden	(23; 28)
	5.5–10.9			Average of $500l.yr^{-1}$ of urine	(1)
Excreta	7.6–7.9	1.6–1.7	1.8–2.7	Ranges reported in Southern Thailand	(26)
	~10–12	~ 2	3		(44)
	12.3–12.6	1.6	3.8		(38; 39)

2.2.6 Generation rates of human excreta

Generation rates vary largely and depend on many factors such as sex, age, occupation, geographical location, climate, water consumption and diet (22; 26). Direct measurement has been employed in many studies to estimate generation rates. A study reported a range of 130 to $520g.cap^{-1}.day^{-1}$ of faeces generated in developing countries and 100 to $200g.cap^{-1}.day^{-1}$ for European and North American countries (12). A higher generation rate of 500 to $900g.cap^{-1}.day^{-1}$ was reported in another study conducted in eastern Nigeria (45). The conclusion from most studies suggests generation rates are largely dependent on the fibre and protein content of diet (12; 22; 25). Adults fed with a mixed diet in a survey generated an average 170g of faeces as compared to 350g generated by adults fed with a high-fibre content diet (46). This partly explains why developing countries tend to have higher generation rates than developed countries, due to their higher fibre consumption. The amount of urine generated is largely dependent on water consumption rate, temperature and humidity defining the geographical location considered. Generally, urine-generation rates range between $0.6–1.2l.cap^{-1}.day^{-1}$ (12; 22). Table 2.6 summarizes generation rates of human excreta $cap^{-1}.day^{-1}$ obtained from across the world.

Table 2.6 Generation rates of wet human excreta (faeces and urine), $cap^{-1}.day^{-1}$

Site of study	Faeces (g)	Urine (l)	References
Developing countries	130–520	1–1.2	(12)
- India	255–311	-	(47 & 48)
- Peru (rural)	325	-	(49)
- Rural Malaysia	477	-	(50)
- Rural Uganda	470	-	(51)
- Kenya	520	-	(52)
- Eastern Nigeria	500–900	-	(45)
China and Japan	116–209	-	(50)
Thailand (Southern)	120–400	0.6–1.2	(25)
Vietnam	130–140	0.82–1.2	(53)
Europe and North America	100–200	1.2	(12)
- Sweden	140	1.5	(38)
- Denmark	170	-	(54)
	95–132	1.27–2.11	(27)
Other studies	150	0.6–1.2	(55)
	170–350	-	(25)

2.3 REVIEW OF BIOWASTE PROCESSING TECHNOLOGIES

Technology for processing HBW must overcome the intrinsic heterogeneity of the matrix, destroy pathogens, eradicate odour to acceptable levels and also recover value-added resources. Alongside these technical aspects, other selection criteria (see Fig. 2.2) include the economics (purchase costs, running and maintenance costs), environmental factors (size, noise, compatibility within the dwelling, greenhouse gas emissions, air pollution) and also social and cultural factors (56).

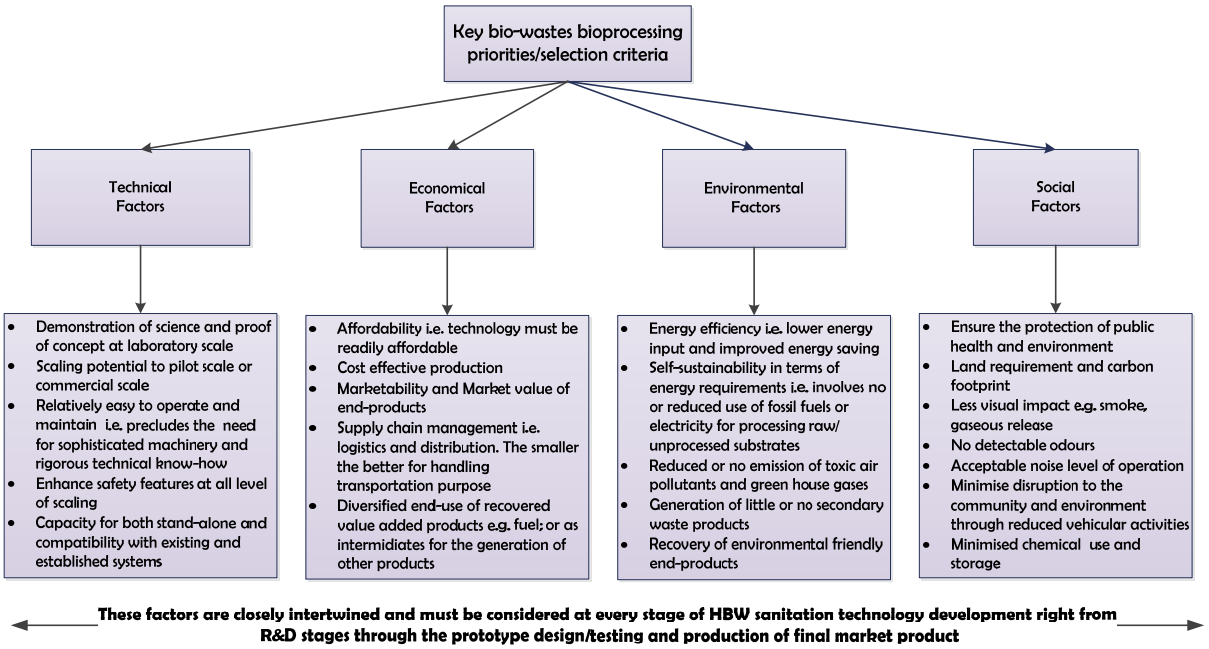


Fig. 2.2 Key biowaste processing selection factors

Generally, the technology for recovering value from biowaste may be placed into one of four categories (see Fig. 2.3):

- thermal,
- thermochemical,
- biological/biochemical, and
- mechanical/mechanical-chemical processes.

2.3.1 Thermal processes

Thermal processes involve heating biowaste to high temperatures (650 to 1100°C) in the presence of air (oxygen) to ensure the partial/complete destruction of its components through the oxidation of its organics and inorganics (57). Examples include incineration, or co-incineration systems, as well as partial combustion systems such as rotary kilns used to make charcoal. Thermal processes usually require feeding dried biowaste into a refractory chamber, where complete combustion generates CO_2, water and ash; in the case of incomplete combustion, charcoal particles are produced. Energy recovery, in the form of heat/electricity generation, is the main end use for thermal processes (58; 59).

Thermal processes are mostly found in highly-resourced communities due to the capital-intensive nature of the technology (high-temperature reactors are expensive) and the energy required for dewatering and drying biowaste before incineration (57; 60). In addition to considerations of capital, gaseous pollutants such as dioxins and greenhouse gases also have to be addressed, accounting for the relatively low public acceptance of the technology (61). Thermal processes are effective in reducing waste volume and, latterly, residual wastes from incineration, such as ash and slag, have been maximised to make building and constructions materials (62), while charcoal is extensively used for different purposes (63).

2.3.2 Biochemical processes

Biochemical processes use micro-organisms to convert the organic content in biomass/biowaste into fuels and other useful materials (64). Biochemical conversion can be achieved with anaerobic or photosynthetic micro-organisms decomposing biowaste organics to generate liquid (alcohols) and gaseous fuels, while the slurry residue can be used to condition land/soil (65). Anaerobic digestion represents a key process in this class of technology, which has been widely explored for the generation of biogas from biowaste similar to HBW, such as livestock manure, sewage sludge and municipal wastes (66; 67; 68). Biochemical processes are widely employed in sewage/wastewater treatment plants as well.

A disadvantage of biochemical processes is the time required to process biowaste, which can range from days to weeks or even months (65). Other problems include malodour, greenhouse gas emissions, the need to accommodate large facilities and the inevitable reliance on microbial culture or feed that is susceptible to toxic pollutants in the feedstock. Also, biochemical processes are not guaranteed to deliver pathogen destruction. For example, the highest temperature range of anaerobic digestion, i.e. the thermophilic range, is 45–60°C (66) – too low for pathogenic inactivation.

2.3.3 Thermochemical processes

Thermochemical processes such as flash carbonization, dry pyrolysis, gasification and dry liquefaction have been studied for solid, liquid and gaseous fuel recovery from biowastes including swine manure, sewage sludge, chicken litters and lignocellulose-based substrates (63; 69; 70; 71). Thermochemical processes heat the biowaste to 180°C for hydrothermal processes, or higher – up to 1000°C – for gasification process, usually in the absence of oxygen to inhibit oxidation and limit the production of undesirable gaseous components such as nitrogen (N_2), water vapour and carbon monoxide (CO) (72). The high temperatures decompose and reform organic components in biowaste to form volatile gases, oxygenated bio-oil and a solid char residue. The volatiles are usually a mixture of hydrogen (H_2), CO, carbon dioxide (CO_2), N_2, water vapour, hydrocarbon gases such as methane (CH_4), ethane ($C_2H_{6)}$ and tars (63; 65). The exact balance of these products depends on the operating parameters, which typically include peak temperature, operating pressure, vapour residence time, heating rate and residence time (71; 73) (Table 2.7). Other factors that affect not only the thermochemical processes but also reflect the characteristics of the end products include the nature, source, type, composition and moisture content of the biomass feedstock (73; 74).

Table 2.7 General operating conditions of thermochemical processes and potential end products (75)

Desired end product of thermochemical process	Process/operating conditions required	Example of process/remark
Liquid	Low temperature High heating rate Short gas residence time	Pyrolysis is the main process for achieving this
Gas	High temperature Low heating rate Long gas residence time	Gasification produces more gaseous products, small quantity of char and ash Pyrolysis usually used as an indirect gasification process, although with less gaseous component recovery
Solids (Char/Charcoal)	Low temperature Low Heating rate No gas residence time	Pyrolysis, flash carbonization, hydrothermal carbonization

As well as the complex engineering required for thermochemical processing, there are other challenges (59). With the exception of hydrothermal processes, dried feedstock is required as a starting material, so introducing an additional energy requirements and costs. This is especially true when considering HBW, which can contain up to 95% moisture. The emission of greenhouse gases (although low) and dioxins has also been associated with pyrolysis processes (76). However, thermochemical processes can ensure pathogen destruction, involve short processing times (in the region of minutes), require a small footprint and can achieve mass reduction of biowaste by up to 40%. They can achieve conversion of biowaste into desired end products and also promote recovery of other valuable resources such as coagulants and phosphates, as well as fuel resources (69; 76).

2.3.4 Mechanical or mechanical–chemical processes

These methods are in most cases used as stand-alone processes to recover specific components such as proteins and enzymes from biowaste, or as a complementary process, normally with anaerobic digestion (56). The ultra-sonication process, an example of technology in this category, has been used to recover certain proteins from primary sewage sludge (SS) (77). For example, a study reported recovering 3177.5mg.l^{-1} of intracellular protein from activated sludge (initially at 5330mg.l^{-1}) (78). Enzymes such as dehydrogenase, catalase and protease recovered via membrane filtration or ultra-sonication may be used in enzymatic hydrolysis processes to recover biofuels, e.g. bioethanol, biodiesel (66), or to enhance the biodegradation and digestibility of biowaste, e.g. sludge for biogas production – especially with respect to anaerobic digestion (79).

However, this technology is susceptible to fouling/clogging of membranes, requires high-energy inputs and is capital intensive. Additionally, the potential for pathogen inactivation has not been demonstrated.

The freeze-thawing low temperature storage process involves short (hours) to mid-term (up to 30 days) storage of biowaste such as sewage sludge at temperatures between -25 °C and -7 °C, with the aim of reducing pathogenic load, notably of *E-Coli* (80; 81). The principle is that freezing-thawing cycles damage pathogenic cells via intracellular freezing and osmotic effects. These effects dehydrate cells due to the osmotic pressure difference between the concentration of solute within the cell and extracellular solution around the cell of the pathogen (82; 83). However, the method has recorded little success in terms of pathogen deactivation, as thawed sludge falls short of the Class B Biosolids requirement of $2x10^6$ MPN g^{-1} dry solids (83). Also, the process is highly selective and economic for cold regions, but impractical for most economically disadvantaged communities, which are characterized by relatively high ambient temperatures. The process also requires high-energy input due to the inevitable low temperature requirement for freezing. Apart from the inability to destroy pathogens, this process has yet to recover any valuable end product.

2.3.5 Summary

The main drawbacks in common with most of these reviewed technologies, which make them unsuitable for HBW treatment, are:

- The need for dried feedstock, which has energy (and cost) implications for HBW that is typically high in moisture content. Drying HBW prior to conversion would require a large footprint, while odour nuisance also constitutes a health risk.
- Secondary environmental pollution and contamination of soil and water resources may result.

These drawbacks form the basis for the investigations into the hydrothermal carbonization process, seeking to address these issues.

Technologies	Thermal	Thermochemical					Biochemical		Mechanical or mechanical-chemical		
Method Process	Incineration/ complete combustion	Pyrolysis	Gasification	Flash Carbonization	Super-critical water oxidation	Hydrothermal Carbonization	Anaerobic digestion	Aerobic and other microbial/ enzymatic/ processes	Freeze-thawing	Membrane Technology	Ultra sonication
Form of biowaste prior processing	Dry				Wet, but must be pre-thickened	Wet and dry (but must be immersed in water)	Wet				
Potential end products	Heat, CO_2, ash	Bio-oil, ash, char, fuel gas,	Syngas, fuel gas	Heat, char, fuel gas	Phosphorus, energy, coagulant	Char, nutrient-rich liquor, energy	Biogas, fuel gas	Compost, H_2 gas, bio-plastic, methanol/ethanol,	Nutrient-rich sludge	Nutrients, enzymes, H_2O	Bio-diesel, H_2 gas, enzymes, proteins
End uses	Process heat, power generation, building or construction materials	Process heat, fuel resource, recovery of heavy metals	Process heat, Power generation, alternative natural gas	Process heat, power generation	Potential for building and construction materials	Solid char fuel, biogas generation from liquor, liquor as commercial fertilizer, carbon sink	For heat and power generation	Use as fertilizers, power generation fuel cells	As fertilizer, but pathogenic load need careful consideration	Potential reuse of water, recycling of nutrients	Potential uses as fuel, power generation
Costs and energy requirements	High-energy inputs and high (initial and running) costs					Low / moderate	Moderate		High		
Technological maturity/ development stage	Well established and applied at full scale	Successful at pilot scales and potentially nearing full scale			Laboratory stage. Challenges with pilot scaling	Still at laboratory and experimental pilot scale	Well established and applied at full scale		Development stage	Successful at pilot scales	Development stage
Socio-environmental factors, e.g. public health, land requirements, GHG emissions	Poor public acceptance, GHG emissions/air pollution, moderate land requirement	Moderate to large land requirement depending on scaling Potential GHG emissions Minimal to moderate chemical use, transport			Effective odour management Complete reduction in GHG emissions Very small footprint due to reduced reactor sizes		Odour nuisance Emission of GHGs, phosphates and ammonia during process Largest footprint, i.e. large land requirement		Not fully assessed, but may require moderate to large land use	Secondary waste generation, e.g. fouling waste and unwanted fractions from sonication Small land requirement	
Potential for decentralization and remarks	Cannot be decentralized for household applications due to process conditions, e.g. high temperatures and pressures associated with the process				Very complex and high temperature ranges, can't handle heterogeneous feed	Can be decentralized as stand-alone. Minimal temperature regimes	Cannot be decentralized to household level and microbial feed makes it impractical		Potentially suitable, but challenges with handling/ transportation/ storage	Not fully assessed, but potential suitable	

Fig. 2.3 Summary of biowaste processing technologies (currently in use or viable) for resource recovery (56; 65; 76)

2.4 HYDROTHERMAL CARBONIZATION PROCESSES

2.4.1 A proposition for the treatment of HBW?

'Carbonization' is the decomposition of organic materials to form solid residues (i.e. chars) characterized by high-carbon content (84). When this process is carried out in the presence of sub-critical water (32), it is called 'hydrothermal carbonization'. Therefore, hydrothermal carbonization (HTC) can be defined as a thermochemical process that involves the immersion of organic material in sub-critical water (throughout the reaction time) heated to between 160°C and 220°C in the absence of oxygen at pressure (10–20 Bar) (74), for the conversion of biomass organics into a carbonaceous (coal-like) solid i.e. char and organic–rich liquor. For almost a century, HTC has been used as an artificial coalification process for organic materials. Friedrich Bergius reportedly conducted the first HTC experiment in 1913, involving the hydrothermal transformation of cellulose into coal-like materials (85; 86). Subsequent experimental investigations by Berl and Schmit, in 1932 studied the production of similar coal-like material by the HTC process from other biomass sources (85). Contemporary studies and interest in HTC processes and technology have resulted from: the increasing need for alternative energy resources (85; 87); soil fertility improvement/reclamation studies, driven by the discoveries of Amazonian soils and the role played by chars (88; 89; 90; 91); the need and recent strategies for carbon sequestration/CO_2 neutral technologies (92; 93); and production of catalytic, sorbents and other innovative materials (74; 94).

HTC is distinguished by the use of wet feedstock, obviating the need for energy-intensive drying before or during the process (65; 74). This makes HTC a candidate for the carbonization of HBW, which is characterized by high-moisture content of up to 95% (w/w), and other related wet biowaste streams such as livestock wastes. Further, the potential recovery and recycling of nutrients and other inorganic chemicals (in ionic forms) from the final liquor strengthens the HTC proposition.

Recent studies have demonstrated solid-fuel generation with different feedstocks, including sewage sludge (95), agricultural waste (86) and municipal solid wastes (96), using HTC. Other studies have also demonstrated its potential for the recovery of carbon particles with surface functionalities for sorption studies (85; 94; 97). HTC can also pasteurize biowaste, eliminating pathogen hazards while thermally degrading and/or transforming pharmaceutically active compounds (69; 98; 99). The process can also transform smell and colour of biowaste, see Table 2.8. Other factors supporting the HTC proposition include: the capacity for handling heterogeneous feedstock or blends; preclusion of microbial cultures; the absence of fugitive gas emissions; short processing times; and smaller footprint (compared with biochemical processes (65; 74).

Table 2.8 Smell and colour changes of HTC products reported in literature

Description of work	Odour change reported	Colour change	References
Primary sewage sludge samples on a bench-scale (Parr) hydrothermal reactor at 180°C–240°C and different reaction times	Coffee-like	Black	(100)
Dewatered sewage sludge samples at 200°C and different process times using a non-stirred Parr reactor	Nut-like smell	Brown colouration	(101)
Subjected dewatered sewage sludge, rice husk and a mixture of rice husk and sewage sludge to steam at 200°C, using a stirred reactor using a band type electric heater	While the dewatered sewage sludge produced a scorched smell, the mixture of sewage sludge and rice husk was reported to produce an aroma of roasted coffee beans	Dark brown	(102)
Municipal solid wastes from three different countries were subject to hydrothermal treatment at 220°C for 30mins. in an autoclave reactor	Not mentioned	Darkish brown colour	(95)
Glucose (model carbohydrate compound) and glycerine (model protein compound) were subjected to 250°C, 10 bar in a continuous plug flow reactor	Nutty odour	Dark brown	(103)
Primary and secondary wastewater sludges were processed in a Parr reactor supplied with heat from a muffle furnace from 130-220°C for 30mins.	Like caramel	Tea-coloured liquid	(104)
Pine sawdust and α-cellulose were processed hydrothermally in the presence of citric acid in a microwave at 200°C for 30mins.	Not mentioned	Colour gets darker as concentration of catalyst increased	(105)

However, HTC is an immature technology, with unknown factors and incomplete theories, particularly associated with reaction pathways or kinetics (32; 99). This makes enthalpy-based predictions of heat yields challenging. HTC also requires construction materials strong enough to withstand the temperature and pressure conditions generated, as well as those that are resistant to the potentially corrosive environment of hydrothermal media. Material optimization and specification for HTC reactors is an area that requires further research.

2.4.2 The role of water during HTC

Hydrothermal conditions are created when water is held at temperatures below its critical temperature of 374˚C and at pressures higher than its vapour pressure for such a temperature, see Fig. 2.4. The kinetics of sub-critical water as it relates thermochemical decomposition have been reported in many studies (106; 107; 108; 109; 110). At sub-critical conditions, water promotes ionic chemistry and supresses free radical reactions (107). Sub-critical water is characterised by unique and enhanced properties, such as lower density and dielectric constant, higher ion product and diffusivity (110). With increasing temperature, the ionic product of water at sub-critical conditions increases while its dielectric constant decreases, resulting in a significant change in its viscosity and increased diffusion coefficient, which causes it to behave like an hydrolytic agent at that phase (106; 107; 109). Consequently the organic compounds within biowaste are rapidly extracted from the matrix into the sub-critical water within an HTC process, where degradation and solubilization take place, yielding water-soluble species/compounds occurring in both organic and inorganic ionic forms (111). However, the water-content of biowaste effects the distribution of the end products into solid–liquid–gaseous phases and their subsequent dissolution into the aqueous liquor media (112).

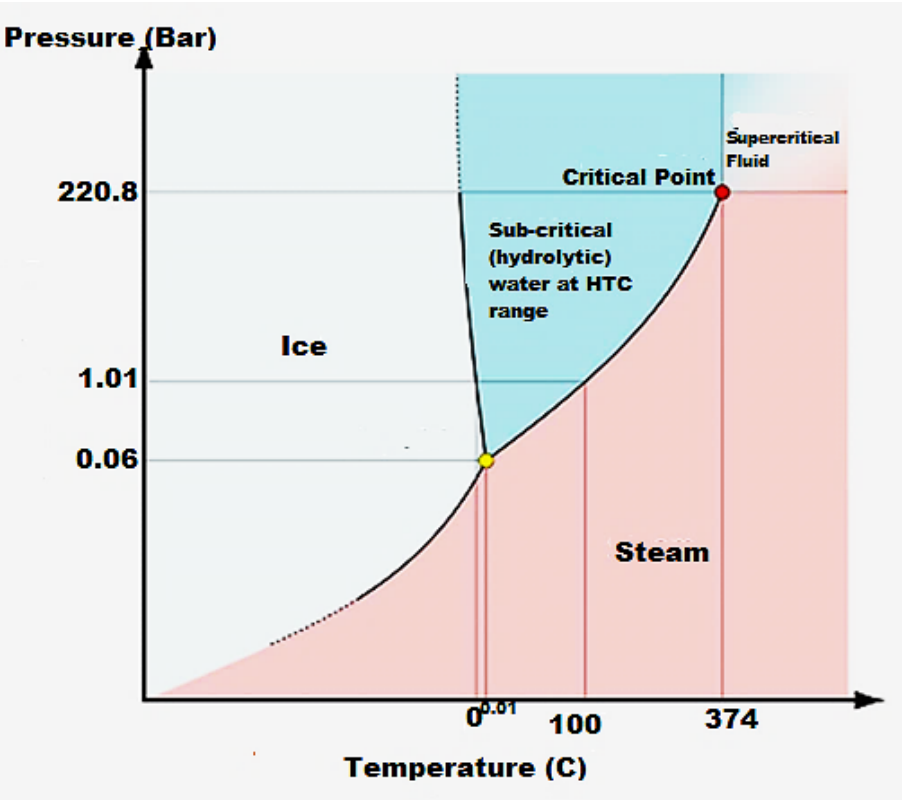


Fig. 2.4 Hydrothermal conditions of subcritical water

2.4.3 Process conditions/parameters of the HTC technology

Key conditions crucial for the HTC process include the following (74; 113):

- HTC processing must be limited to sub-critical conditions within a liquid water phase;
- peak temperature must be >100°C, as significant hydrolysis starts above this regime;
- optimum residence time is required, to ensure process 'completion', i.e. carbonization of biowaste; and
- reaction pressure which is autogenously generated, and dependent on the range of temperature involved.

Temperature has been reported to be the most important HTC factor (113; 114). HTC is promoted at temperatures between 180 and 200˚C and 10–15 bar pressure. Under these HTC conditions, gas yields from substrates are about 5%, while up to 20% of organic carbon in the substrates ends up in the liquor with the rest converted into solids. Increasing the process temperature and pressure above these ranges promotes hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG), with no appreciable production of solid char (32; 74). At 300°C, and 20 bar pressure, liquid hydrocarbons (known as 'bio-oil') and gases are generated via HTL (115). Further increases in temperature and pressure to more than 350°C and 20 bar results in HTG, with the production of methane and hydrogen in the presence of super-critical water (74).

In addition to the role of sub-critical water, heating at elevated temperatures can increase reaction rates and promote the hydrolysis of biowaste components. Other important factors that may affect the HTC process include residence time (which varies from 1 to 72 hours), feedstock characteristics, i.e. nature and composition of the biowaste such as moisture content (and in effect percentage solid loading), and pH. All these factors determine the product characteristics and distribution into the solid, liquid and gaseous phases – see Table 2.9 (74; 113).

2.4.4 Chemistry and reaction pathways of the HTC process

Knowledge of the reaction pathways and kinetics associated with HTC is incomplete (99). However, the current consensus proposes that the reaction pathways of HTC are similar to those associated with dry pyrolysis processes and include: hydrolysis, decarboxylation, aromatization, polymerization and, recondensation (74; 32; 85; 113; 116). Another study stressed that HTC reaction pathways and mechanisms were largely dependent on the substrate characteristics involved (112). Essentially, hydrothermal conditions initiate a network of chain reactions, with the consequence that carbonization processes are more rapid than coalification due to the concurrent nature of many of the reaction pathways.

Sub-critical water during HTC initiates hydrolysis of organic bio-macromolecules in biowaste, which consequently leads to different chemical reactions pathways and (intermediate and/or final) products (32; 117). Using cellulose as a model substrate, a study reported cellulose hydrolysed during the HTC process to short-chain glucose monomers (116). Subsequent dehydration and/or fragmentation formed soluble intermediates products – including 1, 6-anhydroglucose, eryhtrose, furans and furfurals, short-chain volatile fatty acids (VFA) and aldehydes (116). This is similar to other studies conducted using glucose and fructose as other carbohydrate-based substrates during the HTC process (117; 118). The net effects of these reaction mechanisms are sometimes characterised as the transfer of carbon, hydrogen and oxygen as steam and CO_2 from the biomass feedstock into the end products (119).

2.4.5 Energetics of the HTC process

The feasibility of any conversion process is determined by its energetics, where the amount of energy generated or consumed depends, among other factors, on the nature of feedstock and the temperature and time involved (120). HBW cannot be regarded as a well-defined or pure reactant due to its chemical complexity and heterogeneous nature, and as such providing reliable predictions of energetics is problematic. Some studies (85; 120) have discussed the energetics associated with HTC. HTC is regarded as an exothermic reaction and energetically more advantageous than other thermochemical processes, such as dry pyrolysis, particularly for feedstock of high-moisture content (121; 122). No literature currently exists on the energetics associated with HBW. Models have been used to provide insight. With cellulose, heat of reaction associated with HTC was estimated to be -1.6 $MJ.kg^{-1}$ (74), while another study reported a range of values of -1.08 to -0.76 $MJ.kg^{-1}$ (120). Using anaerobically digested sewage sludge, a study reported a range between -2.62 and -0.68$MJ.kg^{-1}$ as the net heat of reaction (96). The overall net reaction of the HTC process is exothermic and recovering the heat energy lost during the process could potentially make the process nearly self-sustainable. However, initial phases during HTC – especially during hydrolysis – are reported to be endothermic, as confirmed for studies conducted on cellulose (123). It is necessary, however, to conduct further investigations in this area, particularly on heat recovery during the HTC process.

2.4.6 Technological comparison with other thermochemical processes

Table 2.9 provide a comparison of the hydrothermal carbonization process with some current state-of-the-art thermochemical processes. HTC is relatively simpler when compared with a complex process like gasification, and is more suitable for heterogeneous wet biowaste with moisture greater than 50% (74) as, unlike other processes, it does not need preliminary separation and pre-drying, with the associated

costs. In terms of processing parameters, the HTC process uses relatively lower and mild temperature ranges (180–220°C) when compared to pyrolysis (300°C) and gasification (up to 1000°C) processes (124; 99; 74). The implications are lower energy input and cost implications. The reactor design can be suited to lower temperatures and pressures, removing the need for the expensive safety engineering and controls associated with high-temperature and pressure processing. Importantly, the operating conditions for HTC indicate integration with toilet/sanitation facilities, which may be feasible and acceptable for use within dwellings and communal settings.

Table 2.9 Technological comparison of key thermochemical processes on end products (74; 125; 126)

Process	Operating parameters	Percentage (%) by weight distribution of end products		
		Gas	Liquid	Solid char
Slow pyrolysis	~ 400˚C, hours to weeks (low heating rates, long vapour residence time)	35	30	35
Intermediate pyrolysis	~ 500˚C; 10–20 seconds	30	50	20
Fast pyrolysis	~ 500˚C for less than 1 second (high heating rate and short residence time)	13	75	12
Gasification	~ 800˚C; 10–20 seconds	85	5	10
Hydrothermal carbonization process (with conventional heating)	~ 180–250˚C; 5–24# hours	2–5	5–20	50–80
Combustion	300–700˚C	n/a	n/a	33+
Torrefaction	~ 290˚C, 10–60 min.			61–84*
Flash Carbonization	300 – 600˚C, Pressure 10–20 bar and > 30min.	-	-	37*

Up to 72 hours have been reported (113)
* Figures obtained for dried wood stock (125)
+ Conventional charcoal production; average yield at 500˚C and with 75% carbon content (126)

Further, HTC processes are self-contained, requiring smaller reactor sizes, and hence reduced carbon footprints, than their larger biological-based alternatives. HTC results in water-soluble products and generates little or no greenhouse gases (GHGs), and thereby contributes to GHG mitigation (65; 69). In terms of process conversion, HTC has been reported to both have higher yields of solid char (up to 84%, see Table 2.9) and also higher carbon retention in their chars (up to 90%) when compared with combustion (0%), fermentation (66%) or anaerobic digestion (50%) processes (85).

2.4.7 Challenges with heating under conventional HTC process

Heating source and efficiency are probably the most important considerations of any biowaste conversion technology. There are varieties of heat sources that can be used for biowaste processing. Most conventional heating processes usually involve the use of electrically heated, high-pressure stainless steel vessels/reactors. Heating is achieved via temperature gradients, with conduction and convection as the main heat-transfer mechanisms. Autoclave and the use of pressurized steam (vapothermal heating) have also been reported (127). The challenges with existing heat sources include:

- poor heating efficiency, i.e. poor coupling of heat sources with heated materials;
- relatively longer residence/processing times; at least 12 hours is needed for most conventional HTC processes involving conduction heating (up to 72hrs have been reported (113)) to ensure enough contact time to achieve carbonization; and
- longer processing times imply in high energy-input requirements and associated costs.

The implementation of efficient heating within the HTC process was identified as a core priority of this research, and to this end the use of microwave heating is a logical next step in the development of HTC processes for use in domestic settings.

2.5 MICROWAVE TECHNOLOGY FOR HTC APPLICATION

Microwave technology is an acknowledged and widely accepted heating source, and has been used in place of 'conventional' heating processes in many applications. For example, microwave heating is used for the accelerated synthesis of materials for the production of valuable intermediates/compounds and other nanostructure materials or materials with special surface functionalities (128; 129; 130; 131). In food processing, it has been used for enzyme inactivation and retention of antioxidants in food (132), and widely for the digestion of environmental samples (133). Recently, microwave heating has been reported for: biomass refinery applications (134; 135); sludge disintegration (136); heavy metals stabilization (137); and pre-processing substrates for anaerobic digestion (138). Until the current project study, microwaves had not been studied (to the best of our knowledge) for treating or processing of actual human excreta or faecal sludge.

2.5.1 Basics of microwave technology

Within the electromagnetic spectrum (Fig.2.5), microwaves occupy the wavelengths from 1mm to 1m with a corresponding frequency range of 0.3GHz–300GHz (139). They are non-ionizing radiation that is also used in cellular phones, radar, television, satellite communication and, more commonly, in microwave ovens (140). Heating processes use

two microwave frequencies, 0.915GHz and 2.45GHz, although higher frequencies are used for other applications such as satellite communications (140; 141). For most domestic and laboratory microwave reactions, the 2.45GHz frequency heats dielectric materials (142). At this frequency, the energy of the microwave photon is 0.0016eV; this is too low to break chemical bonds such as H-OH, which is 5.2eV (143) (see Table 2.10 for more comparisons) and cannot ionize human living tissue, as compared with the ~33eV energy released per ionization radiation of x-rays/gamma rays (144). This implies that microwaves cannot induce chemical reactions, nor can they affect users of the technology within necessary safety limits.

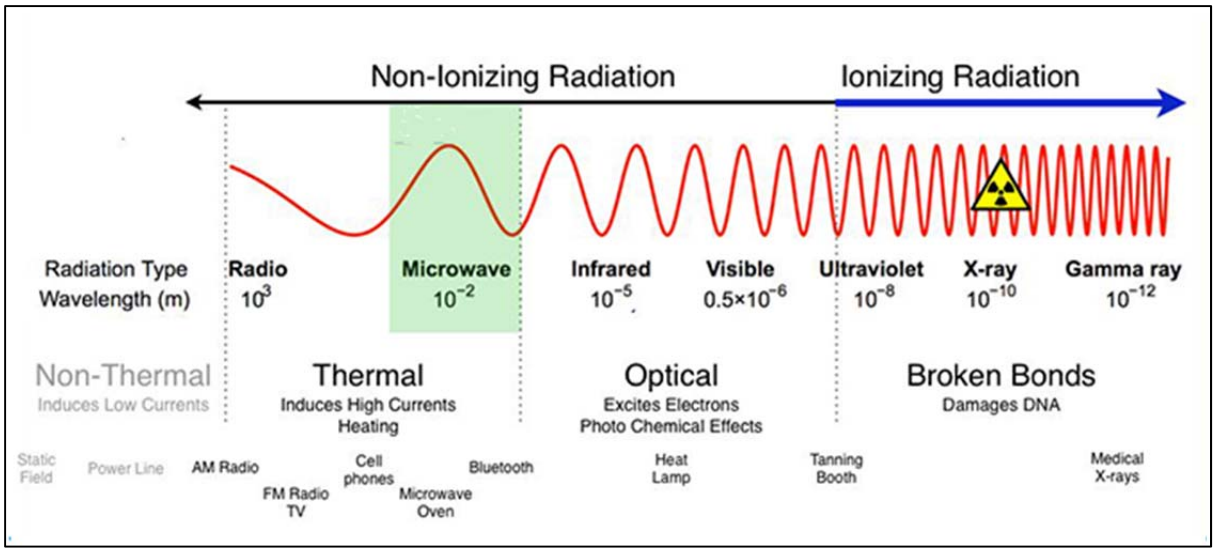


Fig. 2.5 Microwave waves within the electromagnetic spectrum

Table 2.10 Comparing microwave energy with the energies of common chemical bonds [adapted from (144; 145)]

Examples of bonds	Energy 1eV = 10^{-19} joules
Van Der Waal bonds	0.044eV
Ionic bonds	0.17 – 0.3eV
Hydrogen bonds	≈ 0.2eV
Single covalent bonds	≈ 2 to 5eV
Double bond between two carbon atoms in a molecule	6.6eV
Triple bond between two carbon atoms in a molecule	8.8eV
Energy required for a single bacterial cell to replicate	10^6eV
Energy in food consumed by average person per day	1.2 x 10^7 joules
Microwave energy photon	10^{-3} to 10^{-5}eV
Ionising radiation energy photon	33eV

2.5.1.1 Microwave generation, transmission and application

A microwave system has three main features: microwave generation, transmission and application. Microwaves are usually generated in a vacuum tube, commonly referred to as a magnetron or a magnetron tube (140). Magnetrons are composed of a metallic

cathode rod placed within a vacuum chamber of an anode tube held in an orthogonal magnetic field, as shown in Fig. 2.6. The anode tube is made of resonating cavities designed to operate at the specific frequency.

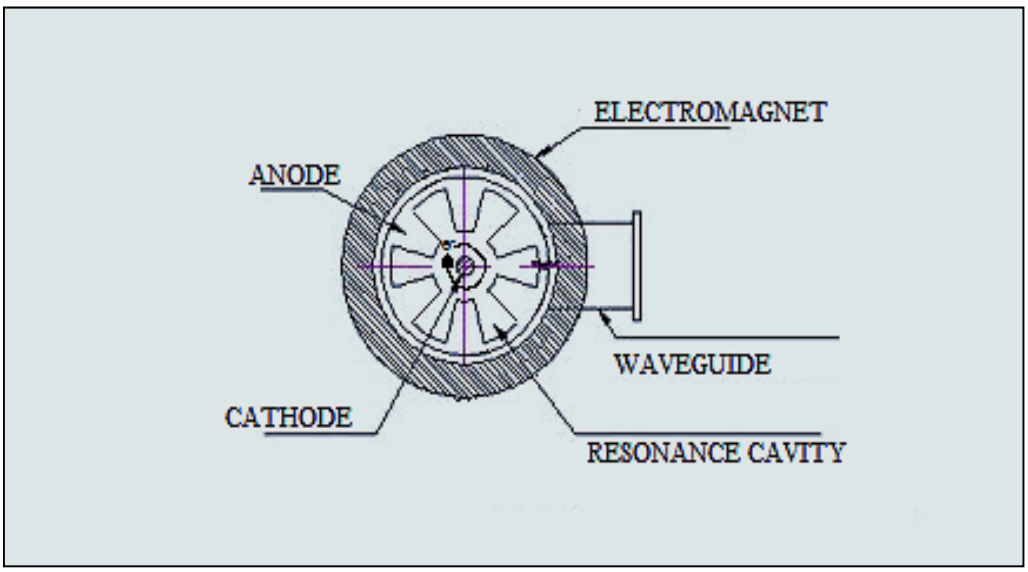


Fig.2.6: Schematic diagram of a microwave magnetron (145)

The cathode rod is usually composed of heating a filament, which emits electrons when a voltage is applied, and the electrons accelerate toward the anode cavity tube in a spiral due to the external orthogonal magnetic field from the electromagnet placed on the anode tube (139). The net effect of the spiral directional movement is a cloud of electrons swirling around the anode resonating cavities. As the cloud of electrons passes through these resonance cavities, the cavities initiate an oscillatory effect on the electron cloud. The continuous effect of the electron cloud swirling around the cavities and the consequent oscillatory effect generates microwaves at a specific frequency within the anode resonating cavities. The frequency of the oscillations in the electron cloud of the microwaves generated is largely dependent on the sizes of the cavities (140). Microwaves are then coupled from one of the resonance cavities for transmission through a waveguide to the point of application (see Fig. 2.6). Microwave waveguides are usually hollow tubes. More details on the types, shape and the mode of microwave propagation are provided in references (146; 140; 141). Microwave applicators are the direct window between transmitted microwaves and the materials to be heated, i.e. they channel microwave energy to heated dielectric materials. Basically, there are single mode cavities and multi-mode cavities applicators and the type of applicator used depends on the type of dielectric material to be heated and the purpose of the heating (140).

Single mode cavities focus microwave energy of one wavelength to generate a heated target volume within the dielectric material. Multi-mode cavities use more than one wavelength to produce multiple hot–volumes for more uniform heating in dielectric materials (147). This project used a microwave system with a multi-mode cavity applicator with a turntable carousel (see Chapter 4 for more details) to deliver uniform heating in biowaste material and prevent localized overheating. The moving turntable carousel passes reactors containing biowaste to be heated through the focussed zones to achieve a time-average uniform heating in the materials under study.

2.5.1.2 Microwave and materials to be heated

For heat to be generated within a material by microwaves, it must be partially transparent to microwave radiation while absorbing the microwave energy. The ability of a material to absorb microwave energy is determined by the dielectric properties of its dielectric constant (ε') and dielectric loss (ε''). The dielectric constant of a material quantifies its capacitive property, in other words the ability of the molecules of the material to be polarized by an electric field. Dielectric loss measures a material's conductive ability, in other words the efficiency of converting microwave energy to heat as the dielectric loss indicates the amount of input microwave energy that will be lost to the material by being dissipated as heat (140; 143). The complex dielectric constant (ε^*) is used to describe the total dielectric properties of any material, and is expressed as:

$$\varepsilon^* = \varepsilon' \pm j\varepsilon'' \qquad 2.1$$

Where the real part, ε', represents the ability of the material to be polarized by an external electric field, and the imaginary part, jε", is the effective loss which quantifies the efficiency with which the electromagnetic energy is converted to heat (146).

Furthermore, both parameters are related by a term called tangent loss, $\tan(\delta)$, where the angle δ measures the phase difference between the electric field and the polarized material (142). Essentially, the tangent loss ($\tan(\delta)$) is used to measure the dielectric response of any materials, i.e. to measure the overall efficiency of any material to absorb microwave energy and convert the heat at a specific frequency and temperature, and hence is also called the dissipation factor of materials (142). This tangent loss, tan (δ), is defined as:

$$\tan(\delta) = \frac{\varepsilon''}{\varepsilon'} \qquad 2.2$$

$tan\,(\delta)$ is used to characterize the microwave-absorbing potentials of materials (see Table 2.11 for examples) as: transparent/insulators (i.e. not sensitive to microwave energy, as they can pass through with little or no attenuation e.g. glass, Teflon, quartz, ceramic); reflecting/opaque materials (i.e. materials that do not allow microwaves to penetrate through them and react by reflecting microwaves (e.g. metals and other very good conductors); and receptors/dielectrics (i.e. very good absorbers of microwaves, depending on their dielectric properties (e.g. activated carbon, water, common electrolytes) (148; 149).

Table 2.11 $tan(\delta)$ of some materials and solvents at 2.45GHz and 20˚C relevant to M-HTC [adapted from (143; 150)]

Materials/solvent	$\boldsymbol{tan(\delta)}$
Ethanol	0.941
Acetic acid	0.174
Ethylene glycol (used in faecal simulants)	1.350
Water	0.123
Acetone	0.054
Activated carbon (from coconut)	1.646
Char from oil palm empty fruit bunch	0.134
Ceramic F-66	5.5×10^{-4}
Borosilicate glass	1.06×10^{-3}
Polyethylene	3.1×10^{-4}
Fused Quartz	6×10^{-5}
Teflon PFA	1.5×10^{-5}

Materials with tan δ > 0.5 are usually referred to as good microwave absorbers, while those with Tan δ between 0.1 and 0.5 and those < 0.1 are considered to be medium and low-microwave absorbers respectively (143). However, a low Tan δ material can be blended with materials with a high Tan δ to improve its overall microwave absorptive capacity (143; 115).

2.5.1.3 Microwave dielectric heating mechanisms

Microwave heating, also known as dielectric heating, occurs when microwave radiation interacts with dipolar molecules, such as water. There are two main mechanisms behind microwave heating: thermal effects due to dipolar rotational effect and athermal effects caused mainly by ionic migration, as illustrated in Fig. 2.7.

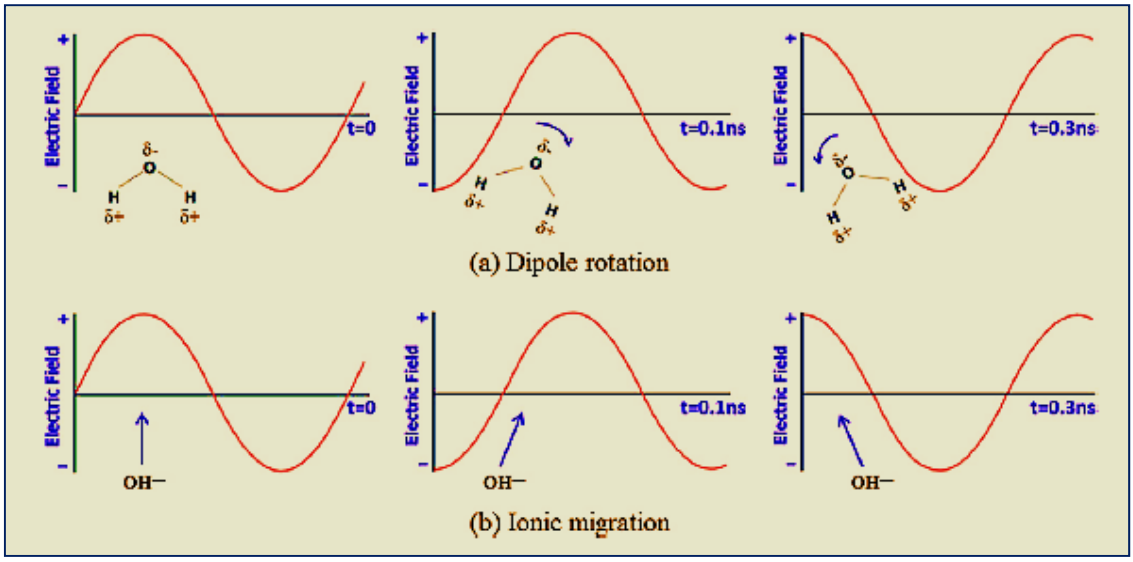


Fig. 2.7 Phase diagram of microwave heating mechanism [adapted from (143)]

Thermal effect of dipolar polarization

Dipolar polarization is the primary heat-induction mechanism of the microwave dielectric heating, which results from the direct coupling of molecular dipoles with electromagnetic microwaves. Dipolar materials are highly sensitive to electric fields, as their local charges tend to move in response to an applied electric field (140). Dipolar polarization results from the interaction of incident microwave irradiation with molecular dipoles, such as moisture in HBW, causing the dipoles to respond by rotating in order to re-align in the direction of the applied electromagnetic field. As the dipole re-orientates to align itself with the field, the field is already changing (as depicted in Fig. 2.7), creating a phase difference between the orientation of the field and the dipole. This phase difference causes energy to be lost from the dipoles through random collision/frictions at a frequency of 2.45GHz, causing dielectric heating. In other words, dipole polarization lags behind an applied electric field due to the internal forces and/or bond resistance of re-aligning dipolar molecules, and this lag results in molecular friction or dielectric loss – characterized by energy loss dissipated in the form of heat (139; 146; 151). The ability of irradiated material to become heated is directly related to the ability of its dipoles to change orientation in the direction of the electromagnetic field, and this behaviour defines the dielectric properties of the material (140; 148). At high frequencies, dipoles rotating do not have enough time to re-align and hence no heating will occur. However, under low frequencies, dipoles have sufficient time to undergo rapid realignment to the applied electric field. While energy is gained by the dipolar molecule rotating in order to re-align, energy is also lost as heat by their constant and continuous friction/collision, although this causes a net heating effect. Frequencies 0.915 and 2.45GHz are within the optimum range to achieve heating (148).

Athermal effect

Athermal effects, i.e. those not associated with temperature increase, have been attributed to the net effect of the continuous realignment of polarised dipoles to the electric field, and ionic migration which occurs when an applied electrical field causes dissolved ions of positive and negative charges of heated dipolar materials to move towards oppositely charged regions of the field, as shown in Fig. 2.7. This results in net collisions of dipoles and possible weakening of the hydrogen bonds within water molecules of heated biowaste material (152; 153).

2.5.1.4 Microwave heating factors

There are three key factors that determine the overall efficiency of microwave heating, namely: power absorbed per unit volume of irradiated materials; penetration depth in the materials; and heat absorption rate within irradiated material. These parameters are largely dependent on the dielectric properties of the materials irradiated with microwaves (141; 148; 154).

Power absorption of materials, P_v

Power absorption relates the amount of transmitted power absorbed by heated materials from the electromagnetic microwave distribution. This is usually estimated as:

$$P_v = 2\pi f \varepsilon_0 \varepsilon' \tan(\delta) |E|^2 \qquad 2.3$$

Where

P_v: Power absorbed per unit volume of feedstock (W.m^{-3})

f: Frequency of microwave in Hz

ε_0: Permittivity of free space

ε': Dielectric constant

$\tan(\delta)$: Tangent loss

E: Electric field (V.m^{-1})

If heating is uniform as a result of an evenly distributed electric field, the P_v can be simplified as:

$$P_v = 2\pi f \varepsilon'' |E|^2 \qquad 2.4$$

Where ε" = Dielectric loss = ε' tan δ (from equation 2.2)

Penetration depth, Dp

Penetration depth is the distance at which transmitted power drops to $e^{-0.368}$ from its value at the surface. Beyond this depth, volumetric heating due to microwave energy is

insignificant (140; 148). This parameter is particularly important for determining the uniformity of heating in a material. It follows that if the penetration depth of incident microwaves is less than the thickness of the sample, only the surface of the material will be heated, while the rest will heated by conduction (140). Penetration depth is estimated as:

$$D_p = \frac{3\lambda_0}{8.686\pi \tan\delta \left(\sqrt{\frac{\varepsilon'}{\varepsilon_0}}\right)} \qquad 2.5$$

Where λ_0 = Incident wavelength of microwave (m)

The penetration depth is also related to frequency of microwave operation, using the equation:

$$D_p = \frac{c\,\varepsilon^0}{2\pi f \varepsilon''} \qquad 2.6$$

Where c = speed of light ($m.s^{-1}$)

It follows from Equations 2.5 and 2.6 that penetration depth is dependent on the frequency of microwaves and the dielectric properties. Higher frequencies and larger dielectric properties will produce low penetration depth and cause on-surface heating of the material, while lower frequencies and smaller dielectric properties of a material will promote volumetric heating (148).

Heating rate

Heating rate measures the amount of power absorbed that is converted to heat within the material. This is estimated as:

$$\frac{\Delta T}{\Delta t} = \frac{P_v}{\rho C_p} \qquad 2.7$$

Where

ΔT = Change in temperature
Δt = Residence time involved
ρ = Density of the material
C_p= Heat capacity of the material
P_v = Power absorption of material

2.5.2 Comparison of microwaves with conventional heating

The main difference between microwave and conventional heating processes is in their heating mechanisms, as summarized in Table 2.12. Specifically, microwave heating causes selective and rapid volumetric heating and faster reaction rates, which make it superior to conventional heating (155; 156). As illustrated in Fig. 2.8, the conventional

heating process is characterized by an external supply of heat transferred by thermal gradients to heated material, i.e. the heat supplied penetrates from the surface towards the core of heated material, causing the outer region of heated components (i.e. reactor vessels and material surfaces) to be hotter than their inner regions. This is slow and inefficient when compared with what occurs during microwave heating. When microwaves heat materials, selective heating of dipoles occurs throughout the heated material, causing a uniform and volumetric heating effect. As a result, the inner regions of the heated material become hotter and this reduces the chance of surface drying/degradation, which is commonly associated with conduction heating (157). In addition, since most microwave handling components are good insulators e.g. quartz or glass, this causes a reverse thermal gradient – i.e. a higher temperature at the core and lower temperature at the surface, as shown in Fig. 2.8 (148). Also, in conventional heating, heating is slower because (source energy such as electric) energy is first converted into heat energy, before being introduced into sample material from the conducting surface to the material. In microwave heating, heat is induced within the core of the material through the direct conversion of microwaves into calorific heat, thereby turning the material into a heat source. As a result, microwave heating provides faster and more energy-efficient heating. This feature has been linked with the accelerated reaction rates microwave heating offers, because turning the heated material to a heat source can lead to an alteration of reaction kinetics (135; 158). Conventional processes also tend to make biowaste processing equipment in-situ. Using microwave heating can overcome this problem due to it lower footprint (135; 151; 158). Reactor vessels used for conventional processes are usually thick-walled metallic conductors, which must withstand pressurized conditions and sometimes the corroding environment of the HTC process. This may have cost implications, especially when scaling the process (111). However, with microwave heating, this can be avoided as metals are poor microwave conductors, hence cheap and readily available insulators such as ceramic and other refractory materials can be used to make reactor vessels.

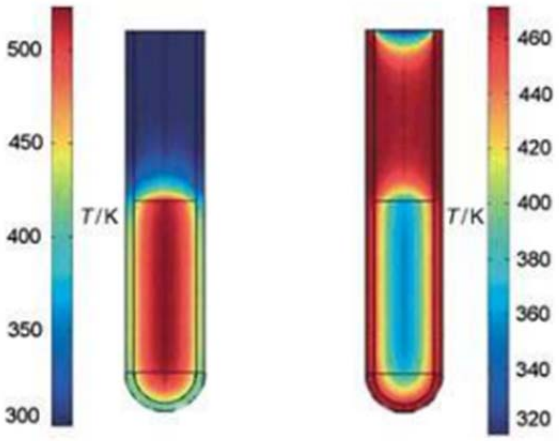


Fig.2.8 Microwave heating vs. conventional heating [adapted from (150)]

Fig. 2.8 compares the temperature profiles of a reaction mixture heated by microwave irradiation (left) and when it was heated in an oil bath. Microwave irradiation raises the temperature of the whole mixture uniformly (i.e. volume heating), while in the oil-heated tube, the reaction mixture in contact with the reactor vessel wall is heated first (i.e. heating via temperature gradients) (150).

Table 2.12 Microwave vs. conventional heating for human biowaste (HBW)

Process parameters	Microwave heating	Conventional heating
Energy	Conversion of energy from electromagnetic to heating	Transfer of heat associated with thermal gradients
Heating	1. In-core volumetric and uniform heating, simultaneously heating materials due to energetic coupling at molecular level 2. Non-contact heating	1. Superficial heating via conduction /convections 2. Need for contact between heating source and heated biowaste
Rate	Rapid and efficient rate of heating due to molecular interaction at a very high frequency. Hence with microwave desired peak temperature can be reached quicker	Slow, inefficient, limited by material thermal conductivity
Selectivity	Very selective for polar substances, but poor for non-polar materials	Non-selective
Hotspots	Localized hotspots due to in-homogeneities of microwave electric field concentration or due to dielectric properties within material. This causes arcing, i.e. temp within materials to be higher than bulk temp of materials	No hotspots
Dependence on nature of heated materials	Highly dependent on dielectric properties of the material	Less dependant
Heating control features	Enhanced control and process monitoring features. Precise on/off power and temperature controls. Energy input can be stopped abruptly.	Poor controllable nature
Cooling rate	Faster cooling rates due to enhanced cooling units	Longer cooling rates
Particle size	Not sensitive to particle size	Very sensitive to particle size in terms of enhancing heating rate

2.5.3 Technological considerations and suitability of microwave technology for the hydrothermal processing of HBW

M-HTC simply involves the use of microwave heating to process HBW, render it safe and recover value-added products. The idea behind this approach stems from the efficient coupling of microwave electromagnetic waves with molecular dipoles, i.e. the water abundantly present in HBW, to initiate dielectric heating. Other considerations include:

- Consistent sterilization of HBW. Microwaves can kill pathogens efficiently, thereby making products safe to handle. With microwave irradiation, at least 70°C is reported as the optimum temperature needed for pathogen inactivation (156; 159).
- The high-moisture content (up to 95%) that characterizes HBW makes it fit the dielectric heating spectrum. This triggers very rapid and volumetric heating, promotes novel reaction pathways and enhances reaction rates (135).
- Microwave irradiation also has the capacity to diminish hazardous product formation and prevent emission of fugitive or greenhouse gases, hence making it environmentally friendly (156).
- The highly selective nature of microwave heating targeting dipoles may lead to molecular and structural changes in processed biowaste sludge solids. This could potentially have the effect of dewatering and drying HTC solid products i.e. chars (151; 135).
- Enhanced reaction rates present an opportunity to develop higher throughputs.
- The process can ensure the digestion of biowaste sludge for the recovery of valuable organics and inorganics, e.g. ammonium and others ionic species

Microwave technology is not without its limitation, however. For example, a lack of data on the dielectric properties of materials such as human faeces or urine in the microwave frequency ranges, and at different HTC temperature regimes, hampers the opportunity of determining key parameters, as highlighted in section 2.5.1.4 – i.e. the optimum heating rate, power absorption and the penetration depth – crucial for enhancing microwave heating efficiency (154). Determination of the dielectric properties depends on many factors such as temperature changes, frequency of microwave, moisture content, chemical composition of material, density of material and physical characteristics of material (homogeneity and particle size distribution) (154; 140; 160), and this presents a significant developmental challenge for highly-heterogonous and variable HBW. Additionally, the presence of mineral components and other impurities has been reported to generate hotspots, especially when heating pure reactants (161). Since HBW is not a pure reactant, this may not have a significant impact on the kinetics of the biowaste processing. The challenges of precise temperature measurement within the core of heated the material during the microwave process have also been highlighted in a few reports (161; 134). Most measurements are conducted externally via infrared pyrometers. More work on system designs, development and performance improvement, especially for scaling purposes (i.e. outside laboratory applications), are needed for the

microwave technology (155; 162). Finally, empirical studies with this material are physiologically and psychologically challenging, so there are welfare considerations that demand experimental designs are efficient, and exposure to faecal impacts are minimized.

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CHAPTER 3 HUMAN BIOWASTE TEST MATERIALS

3.1 INTRODUCTION

The test materials used in this research as feedstock were selected with the following factors in mind:

- relevance to the *Reinvent the Toilet* project (1) – they needed to be representative of human biowaste (HBW);
- rich in organic components, with water, urea, salts and minerals at levels found in HBW (1,2);
- the quantities of material for study were to reflect the generation rates of HBW (untreated excreta and faecal sludge) (3); and
- the test materials were to be previously unstudied, providing new and relevant data in this research area.

No work to date has been published involving real HBW as a test material for thermochemical conversion associated with either treatment purposes or other related scientific investigations (4). Most work has been limited to sewage sludge, chicken litters, dog and monkey faeces, and lately faecal simulants (5) as representative samples. Human faecal sludge is different in composition, water absorption properties, chemical and physical properties to such mixtures (4, 6). Adoption of HBW as a test material was novel and offered the opportunity to address knowledge gaps in this field. Further, the hydrothermal treatment reaction, chemistry and resultant products are sensitive to the type and nature of the feedstock used (4), as different materials have different reaction kinetics and behaviours within the hydrothermal process. HBW was consequently selected for use in these studies.

This material requires careful preparation, handling and storage. Storage was within the cold room at the Water Laboratory, Civil Engineering Department, Loughborough University at 4 to 5°C. Storage at this temperature range minimises microbiological decomposition of solids and the subsequent loss of volatiles. However, samples were brought to room temperature for all experiments and/or analyses. This was important to ensure a consistent viscosity (which is higher at cold room temperatures) and hence handling and measurement reproducibility.

3.2 HUMAN BIOWASTE FEEDSTOCK

The HBW samples used were:

- Primary sewage sludge (SS)
- Faecal sludge simulant (FSS)
- Human faeces (HF) – without urine, flush water or sanitary products
- Human faecal sludge (HFS) – including faeces, urine, flush water and tissue paper

3.3 PRIMARY SEWAGE SLUDGE (SS)

Primary sewage sludge (SS) has been used widely as a HFS substitute. The SS used for the present study 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.

SS was obtained by sampling specialists in a container that were 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. Protective measures, including wearing protective covers, safety glasses and single-use gloves, were taken while obtaining the samples for use due to their bio-hazardous nature. Also, the sampling/storage areas and equipment used were thoroughly cleaned after each sampling process. Wastes generated during handling and sampling were disposed in designated bins appropriately.

The moisture content of SS was observed to fall between 95 to 96% by mass, determined by drying at 105°C for 18 to 24hrs. (See Chapter 4 Section 4.4.2 for more details). SS is black with a foul in smell (due to its high-organic matter) – see Fig.3.1; the pH falls in the range 5.5 to 6.1, while the density is approximately 1.1g.cm^{-3}.

Fig.3.1 Primary sewage sludge: black, slightly acidic and foul smelling slurry

3.4 FAECAL SLUDGE SIMULANT (FSS)

Faecal sludge simulant (FSS) is an artificial faecal sludge; it is prepared from a formulated recipe (6) to replicate the chemical composition, water absorption capacity and rheology of real human faeces. This study modified the recipe, however (see Table 3.1), to better mimic the HFS generated by flushing from a WC toilet.

Human faeces are excreted with a water content in the range 65%–85% by mass (6) in an admixture of urine, typically excreted at 1 to 1.2L.cap^{-1}.day^{-1} (7; 8; 9), and 3L of flushwater per flush. The moisture content of the FSS produced by the recipe was adjusted to about 96% by carefully weighing each constituent of the faecal simulant components and mixing uniformly with water to represent an after-flush scenario from a toilet (see Fig. 3.2). One litre (1L) of freshly prepared FSS sample was always used for the carbonization experiments. In order to ensure homogeneity and reproducibility of samples, many replicates were performed and tests were carried out to ensure moisture content was between 95 and 97%, i.e. 3–5% solids – similar to sewage and actual faecal sludge. This was to ensure consistent solid loading in the experiments.

Table 3.1 Modified faecal sludge simulant (FSS) recipe

Components	Mass (%)	Constituents
Fats	15	Oleic acid
Protein	35	Yeast (20%) and miso (15%)
Carbohydrates	30	Bran flakes (5%), psyllium (15%) and cellulose (10%)
Inorganics	5	Potassium chloride (KCl) (2%), calcium chloride (CaCl) (1%), sodium chloride (NaCl) (1%)
Polyethylene glycol	10	Polyethylene glycol
Toilet tissue	5	Toilet tissue

Fig. 3.2 presents a photograph of an FSS formulation being prepared. The brownish yellow colour was due to the psyllium and miso components of the recipe. The final pH of the simulant usually used for carbonization was between 4.8 and 5.0 and, unlike sewage sludge and human faeces, there was no foul smell.

Fig.3.2 Faecal sludge simulant (FSS) during mixing

3.5 HUMAN FAECES (HF)

The human faeces (HF) (without urine or sanitary products) used in this study were provided by at least three volunteer participants throughout the experimental period. The same participants were used throughout, and were instructed to separate urine from faeces at the point of defecation. Polythene bags provided to the donors were used to collect faeces. Before use, the faecal specimens were examined to ensure no urine or sanitary products were present. Before the faeces were used in carbonization, tests to establish moisture content and percentage solids were performed.

Abnormal faeces were not used in the study. Abnormality was determined through a physical examination and evaluation against the Bristol stool chart (see Fig. 3.3). Only faecal types 3 and 4 were used (10). Types 1 and 2 are considered to be indicative of constipation, while type 5 is typically low in fibre and types 6 and 7 are due to diarrhoea. These grouped types have abnormal properties – such as transit time in the human body, diameter and shape configuration, rheology, and chemical and biological compositions, which make them different from the normal human faeces defecated daily (10).

HF were prepared for carbonization experiments by mixing them with[2] distilled water to form a slurry with a solid content of 3% to 4% by mass (Fig. 3.4). The slurry was used immediately for carbonization experiments. Remaining samples were covered with film and stored in enclosed containers at 5˚C (to reduce loss of volatile organics) and used within 24 hours; any samples remaining after this were disposed of in the toilet.

The HF slurry was brown and foul smelling due to nitrogenous and sulphur compounds such as indole, skatole and hydrogen sulphides (11). Bio-hazard precautions included wearing protective covers, clothing, safety gear and gloves, accompanied by a thorough washing and disinfection routine after each experiment. Wastes generated during the handling process were disposed of in designated bins.

[2] The faecal samples were found to contain ca. 30% solids, and this was too thick for the carbonization experiment. Further uniform loading of the microwave vessel reactors with unprocessed HF was problematic.

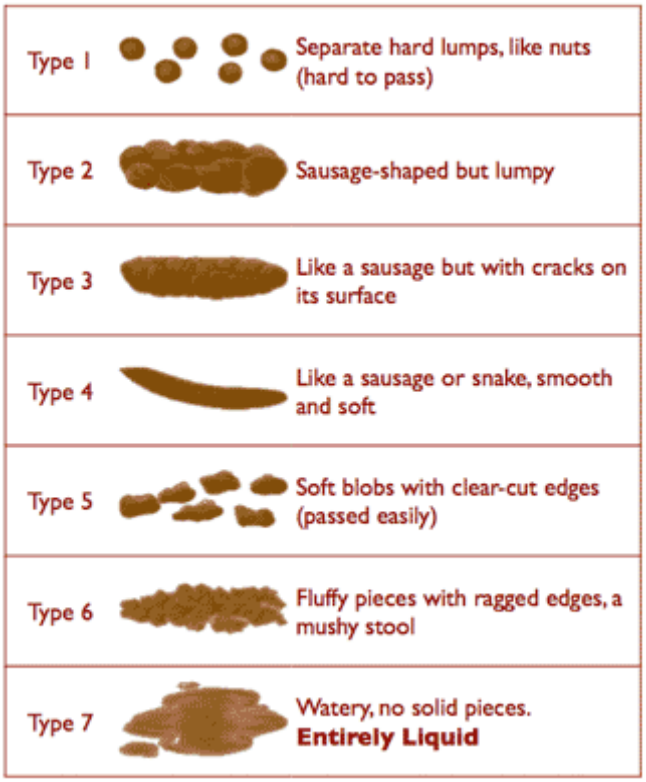

Fig.3.3 Bristol stool chart (10)

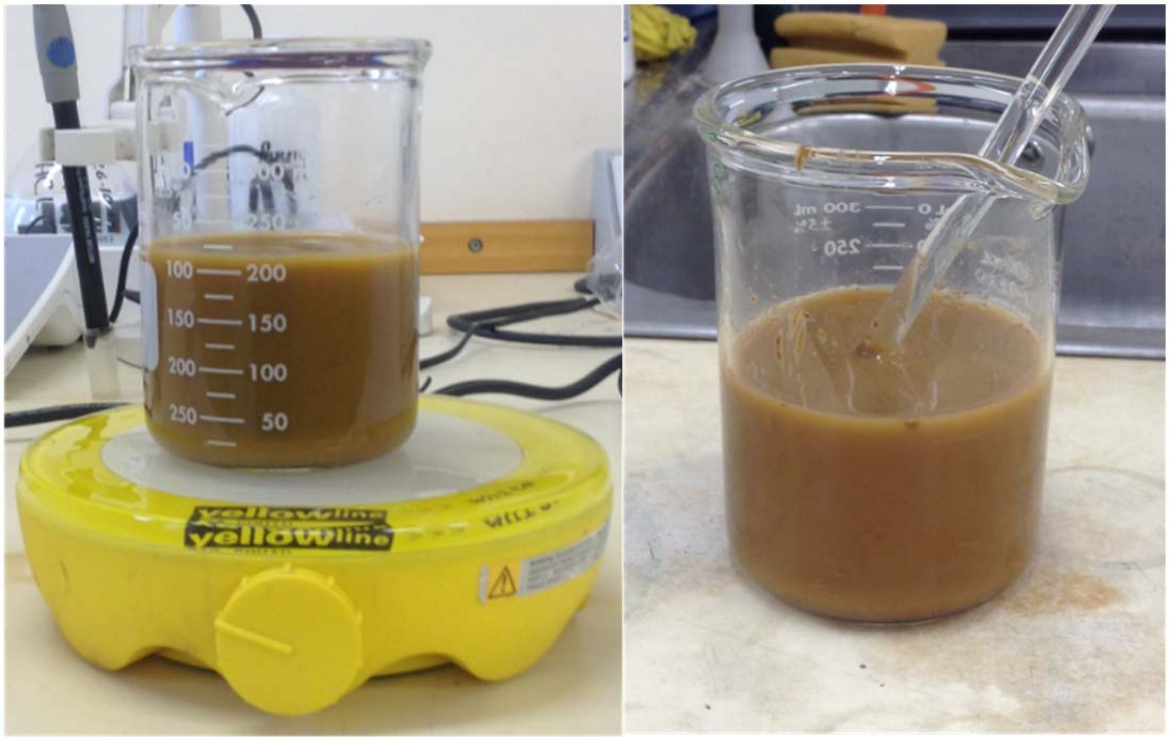

Fig. 3.4 Slurry of human faeces without urine or sanitary products

3.6 HUMAN FAECAL SLUDGE (HFS)

Fresh human faecal sludge (HFS) samples were collected from anonymous donors. A portable mobile toilet (Porta Potti), shown in Fig. 3.5, was placed in a designated toilet to collect HFS samples. On average, two to four donors provided human faecal sludge each day over the sampling campaign. The mobile toilet works like a conventional WC system. It has two main compartments: a 15L reservoir for flush water and a 21L waste storage tank. Other features include a tissue paper holding unit, a manually operated piston pump for flushing, a valve connecting the toilet seat bowl to the waste storage tank and a drainage pipe connected to the waste storage for the removal of faecal sludge.

Fig.3.5 Features of the mobile (Porta Potti) toilet

Conventionally, deodorising (smell reducing) and/or disinfectant chemicals are added to the waste storage tank of the portable toilet to disinfect, and sometimes to accelerate degradation of the collected HFS. In this work, no chemical was added, as the effects of such chemicals on the carbonization process were not known. Hence, chemical addition was not considered for the intended use, i.e. carbonization of collected HFS. The portable toilet was filled with 15L flush water, toilet tissue paper and a small amount of water (about 1L) in the waste storage tank to prevent faecal material from sticking to the base and to ease the removal of faecal sludge. The quantity of HFS produced per user varied,

determined mostly by the amount of water that was used for flushing, which in this case was dependent on user behaviour.

Before use, the HFS samples were homogenised by maceration (see Fig. 3.6). Literature values indicate that the average generation rate of wet human faeces is 120g–400g.cap^{-1}.day^{-1}, urine is 0.6–1.2 L.cap^{-1}.day^{-1}, with a standard flushing volume of 3L (7–9; 12). These rates were be used to estimate and adjust resultant moisture content of collected HFS to be between 96% and 97%. Samples were then covered with film and stored in enclosed containers at 5°C to minimize loss of volatile organics and reduce decomposition rate. All the procedures – i.e. preliminary tests used with HF, including physical inspections and health and safety measures – were also observed during the HFS sampling campaign.

Fig.3.6 Human faecal sludge after maceration and mixing

Although macerated HFS has the same colour as the HF slurry, there is a distinctive difference in the particle size distribution in the HFS samples due to the sanitary product, i.e. toilet tissue, included in the mix. There were more suspended and colloidal particles in the HFS sample than the HF samples. HFS is brownish and also smells foul.

3.7 SUMMARY OF HBW PROPERTIES

HBW are highly heterogeneous. To minimize variability and further reproducibility during the carbonization experiments, representative samples of each feedstock were always

analysed for moisture and solid contents. The range of values used to ensure consistency in samples is summarized in Table 3.2.

Table 3.2 Properties of HBW substrates*

Parameters	SS	FSS	HF (slurry)	HFS
MC (%)	95–96 (95.2 ± 0.4)	95–97 (96.3 ± 0.2)	96–97 (97.1 ± 0.7)	95–97 (96.6 ± 0.2)
TS (%)	4–5 (4.8 ± 0.4)	3–5 (3.7 ± 0.2)	3–4 (2.9 ± 0.7)	3–5 (3.4 ± 0.2)
VS (%)	73–74 (73.9 ± 0.2)	87–89 (88.3 ± 0.9)	86–87 (86.7 ± 0.3)	79–81 (80.2 ± 0.8)
FS (%)	26–27 (26.1 ± 0.2)	11–13 (11.7± 0.9)	13–14 (13.3 ± 0.3)	19–21 (19.7± 0.8)
pH	5.5–6.1	4.8–5.0	7–7.5	
Colour	Black	Light brown	Brownish	
Smell	Foul	Mild	Foul	
Appearance/Rheology	Viscous	Not viscous	Not viscous	

*Values in bracket are mean values from at least 12 replicates

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CHAPTER 4 EXPERIMENTAL METHOD

4.1 INTRODUCTION

This chapter outlines the experimental design of the research study. Section 4.2 describes the microwave heating equipment used for the present study, including safety features and relevant calibrations conducted on the equipment. Section 4.3 details the experimental set-up, flow process and relevant process parameters of the hydrothermal carbonization (HTC) process. The material work-up, and analytical and characterization techniques adopted to test materials (unprocessed and carbonized) in line with the set hypotheses (Section 1.5) are detailed in Section 4.4, which also includes the characterizations and analytical techniques used to investigate the research hypotheses. All carbonization experiments and analyses were conducted in the Water Laboratory in the Civil Engineering Department, while most characterizations were conducted in the Material Department of Loughborough University. Section 4.5 discusses how the data collected were analysed and, finally, Section 4.6 summarizes the ethical considerations of the research, including the potential challenges encountered.

4.2 THE MICROWAVE HTC SYSTEM

4.2.1 Basic features of the microwave system

Batch M-HTC experiments were carried out using the Anton Paar Multiwave microwave Lab-station (Anton Paar Ltd.) (see Fig. 4.1). The microwave system is a fast and completely closed-vessel digestion reaction system, which makes it suitable for high-temperature and pressure digestion of organic-rich materials such as HBW.

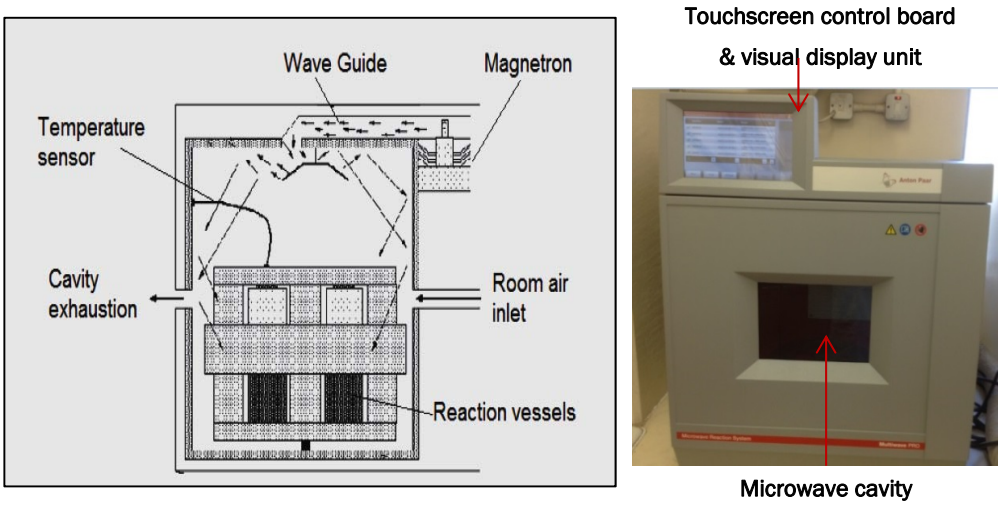

Fig.4.1 Schematic of main features of microwave system *(actual photograph inserted)*

The microwave heating was induced by two 850W-rated magnetrons, while a microwave rotor distributed the energy uniformly throughout the heating cavity. Temperature and pressure probes ensured accurate and reproducible operating conditions. The reaction vessels were rated to withstand temperatures and pressures up to 260°C and 60 bar respectively.

4.2.1.1 Magnetron

Operating at 2.45GHz, the magnetrons were capable of delivering a maximum microwave power of 1500W, un-pulsed over the full power range. Power supplied by the magnetron during the microwaving operation usually depends on the number of reactor vessels used, as more reactor vessels require more microwave energy and hence more power. For this work, power of 900W was used, as recommended by system's manual (1) for the number of reactor vessels used.

4.2.1.2 Temperature and pressure measurement

The challenges associated with accurate measurement of sample temperature inside microwave reactor vessels during microwave processing are well reported (2; 3). In most cases, the surface temperature of samples is used, as measured by an infrared pyrometer. Hotspots, another challenge of microwave heating, affect accurate temperature measurement. Hotspots are sometimes due to impurities or non-uniform heating within the sample, especially at the beginning of the microwave heating process (2).

Temperature differences caused by hotspots can trigger heterogeneous reactions during microwave processing (4), which could be detrimental to the M-HTC process. Hence, additional temperature and pressure monitoring features were adopted to ensure stable and reproducible HTC processing (1; 5). These were:

- a wireless sensor, which controls microwave energies by monitoring internal temperature and pressure inside the reactor vessels;
- an infrared sensor located at the base of the microwave cavity, which measures temperature from the base surface of all the reactor vessels simultaneously (i.e. external measurement) and maintains peak reaction temperature at ±2˚C during the process;
- a hydraulic pressure sensor integrated with the microwave rotor, which measures pressure build up in all reactor vessel simultaneously every 20 milliseconds

during the reaction process (external measurement); this provides for controlled pressure monitoring during the microwave process; and

- a P/T (pressure/temperature) probe inserted into a reference reactor vessel to provide a baseline reading for other vessels, ensuring that their readings were within the measured parameters of the reference vessel.

Appendix 2 further illustrates the stability of reaction temperature and pressure profiles against power supply during the M-HTC process.

4.2.1.3 Rotor (carousel) and reactor vessels

Fig. 4.2 provides schematic diagrams of the rotor and reactor vessel of the microwave system.

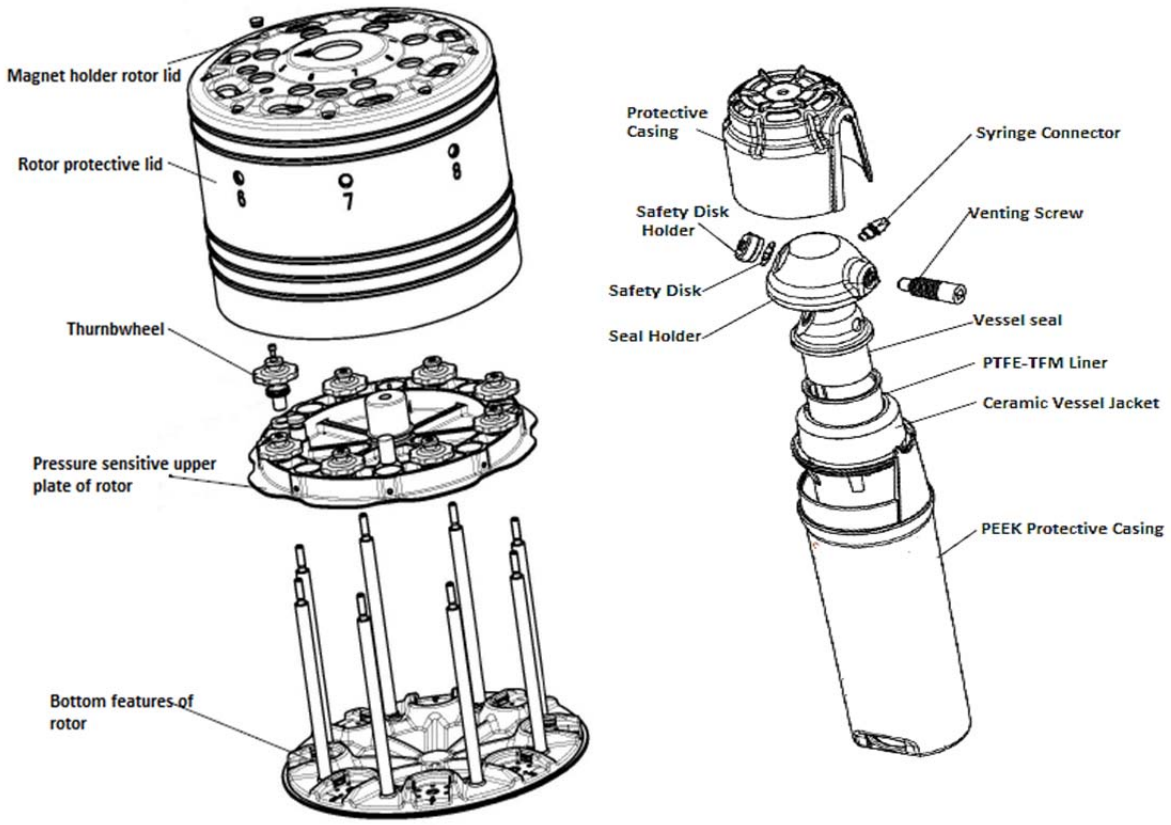

Fig.4.2 Schematic diagram of microwave rotor and reactor vessel (4, 5)

The rotor consisted of an integrated hydraulic pressure sensor, which monitored:

- the average pressure exerted on all reaction vessels when loaded on the microwave rotor (i.e. starting pressure); and
- the pressure increase from all reactor vessels during microwave processing.

The starting pressure was largely dependent on the extent to which the rotor thumbwheels (see Fig. 4.2) were tightened; for the rotor to work the value needed to be between 2 to 10 bar. The reactor vessels (D x H: 390mm x 320mm) were made of chemically inert PTFE-TFM liners placed inside ceramic jackets to provide insulation and thermal stability. The volume of the reactor vessels was 100ml (with half of this as working volume). The vessels were further enclosed by a protective casing and cap, both made of Polyetheretherketone (PEEK) material capable of withstanding high-thermal conditions. Each vessel was fitted with a venting screw and a safety-bursting disk to provide additional safety features. A protective shield used to cover the rotor after loading the reactor vessel into the carousal provided an additional layer of safety.

4.2.1.4 Exhaust and cooling unit

An integrated forced air-cooling and exhaust system cooled the reactor vessels and microwave cavity during and after each heating cycle. It also removed excess reaction heat and escaping gases from the microwave cavity. This enabled faster cooling rates, and was more efficient – eliminating several hours of post-processing cooling associated with conventional heating approaches.

4.2.2 System calibration

Calibrations were conducted on the microwave system to validate performance. The main microwave system components – magnetron power, temperature and pressure sensors, including infrared sensors, probes etc. – were calibrated following the procedures, as set down in the instruction manual (1; 6). All the sensors were calibrated automatically through the system's operating software.

Microwave power was calibrated by placing a glass beaker containing 1kg of water (at approximately 20°C) in the microwave and subsequently heating at 900 W for a specific time, pre-set by the system. The temperatures of the water before and after the short heating cycle were measured with a thermometer (resolution 0.1°C with 14–45°C range). The microwave power was determined by:

$$Calibrated\ Microwave\ Power, W = [T_f - T_I]\ x\ P_f \qquad 4.1$$

Where T_f , T_I , and P_f are final temperature and initial temperature of water in the beaker and microwave power factor (which is estimated and displayed by the microwave after heating the water to a set power) respectively.

Power calibrations were performed in triplicate annually and were consistently found to be within 898 ± 2 W.

4.3 EXPERIMENTAL DESIGN

Table 4.1 provides a summary of the experimental design of this work, matching outlined hypotheses with success criteria for each hypothesis.

Table 4.1 Summary of experimental design

	Hypothesis	Summary of experiments/calculations conducted to test hypothesis	Success criteria
1.	**M-HTC can generate char from biowaste**	Four different biowaste feedstock i.e. SS, HFS, HF and FSS, will be subjected to microwave treatment under different process times, heating rates and peak temperatures	Sensory impacts (smell, colour) and physical observation of carbonized end products in comparison with those produced from C-HTC method
2.	**Solid products, i.e. char, produced have same properties as those produced by C-HTC process**	Char characterization studies e.g. elemental analysis, energy value	Results must be comparable or better than those produced from other HTC methods
3.	**Energy input is reduced for the M-HTC method**	Power monitoring studies and energy consumption calculations	Total power and energy requirements less than those for other methods
4.	**Conversion yield (higher, lower or equivalent)**	Estimation of char yield on dried basis from each biowaste feedstock	Higher conversion efficiency and product yield
5.	**Reduced process time and higher throughput**	Estimation of total process time required for M-HTC and mass equivalent of sample processed in comparison with conventional process	Total process time for M-HTC less than equivalent used by other methods
6.	**Improved separation efficiency**	Capillary suction time (dewaterability test) and particle size distribution analyses (see chap 6)	Lesser specific resistance to filtration of carbonized material

4.3.1 Biowaste sample preparation and experimental set-up

Sections 3.2 to 3.6 of this thesis provide details of the test materials used in the research to test the M-HTC technology. To test each biowaste material, the M-HTC experiment was set up as shown in Fig. 4.3.

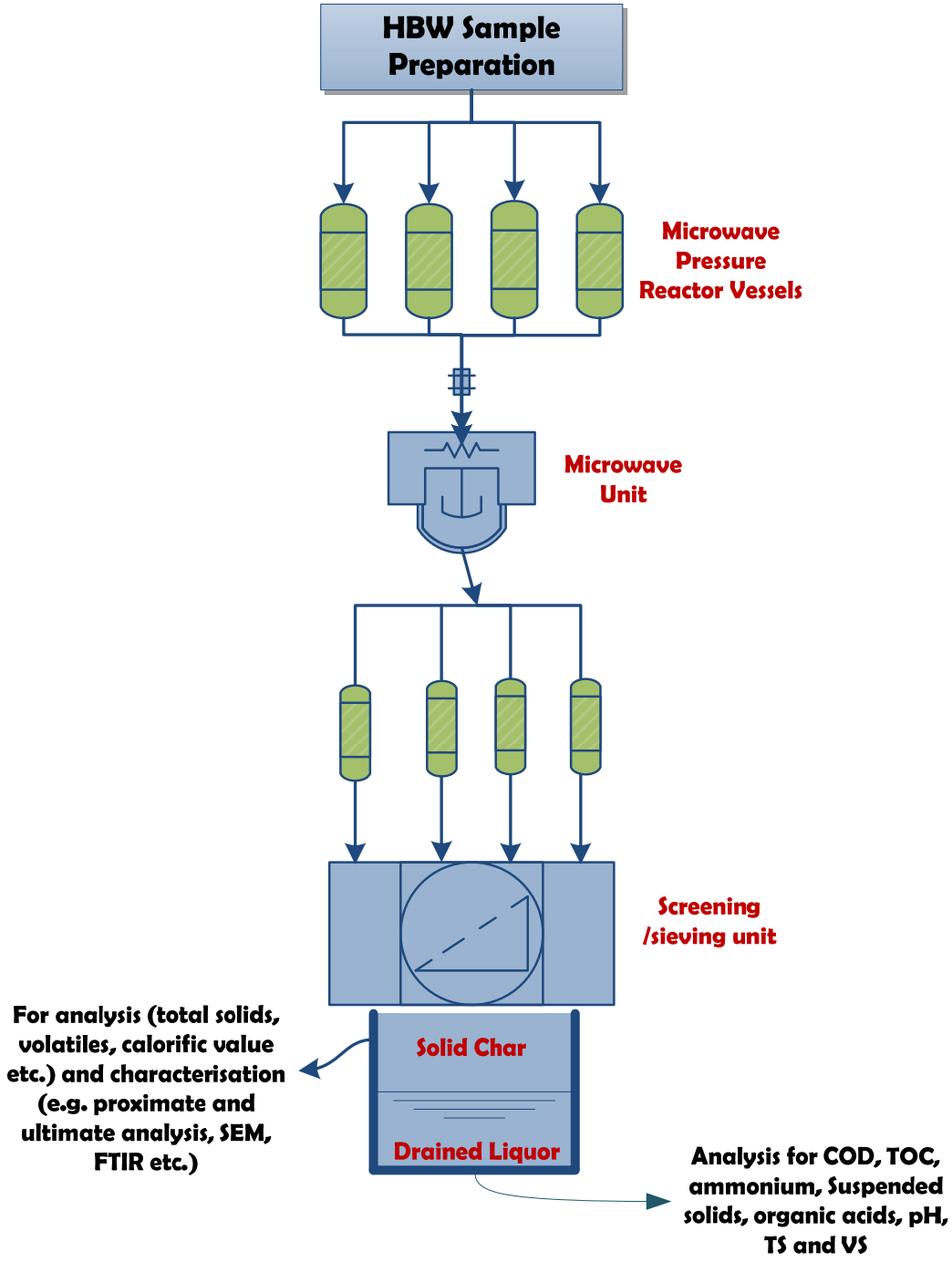

Fig.4.3 Schematic experimental flow of M-HTC process

The experimental workflow was divided into three main stages:

- sample preparation;
- carbonization process parameters; and
- processed material separation into solid and liquid fractions for analysis and characterizations (see Table 4.2).

4.3.2 Sample preparation

The amount of unprocessed HBW samples (ca. 200g) used for all the carbonization experiments was consistent throughout the study. During each carbonization experiment, the samples were equally divided into four replicates and poured into pre-weighed reactor vessels, as shown in Fig. 4.2. Weighing was by mass to improve reproducibility of samples in reactor vessels due to the viscous nature of feedstocks, particularly SS. The vessels were then covered with the vessel cap and placed in a ceramic jacket before being fitted into the protective casing, as shown in Figs. 4.2 and 4.3. The four vessels were loaded symmetrically on the microwave carousal to enhance temperature and pressure reading accuracy during the carbonization process. Finally, the loaded carousal was placed on the rotor plate of the microwave cavity, process parameters were input and the microwave system was supplied with 900W (power) 10A (current) output.

4.3.3 Carbonization process parameters

Primarily, as discussed in Chapter 2, carbonization temperature is the most important process parameter during HTC processing. Other parameters which may influence HTC process kinetics and chemistry include (7; 8):

- percentage solid loading;
- pH of test materials;
- power input;
- initial pressure; and,
- residence time and heating rate.

Table 3.1 shows that the percentage solid loading was maintained at ~ 5% (w/w) for all biowastes; representative of faecal sludge samples. pH of biowastes varied according to the type of feedstock, and the power input was constant at 900W for all experiments. The initial starting pressure was recorded with the hydraulic sensor on the microwave rotor. Pressure build-up during the HTC process was monitored throughout the carbonization process. There are two phases of heating during the M-HTC process:

- warming phase (heating to peak temperature); and,

- residence/holding phase (heating supplied to maintain peak temperature over residence time).

In the warming phase, the heating was ramped to peak carbonization temperature over a period of 15min. During the residence phase, heating was kept constant to maintain peak temperature. Only the effects of peak carbonization temperature (160–200°C) and residence time (holding time at the peak temperature: 15, 30, 60min.) on char yield and properties such as carbon efficiency, chemical compositions and liquor properties, including organics and inorganics, under the M-HTC process of each feedstock were investigated.

4.3.4 Material separation and post-HTC analyses

Following carbonization, the reactor vessels were cooled to room temperature and the carbonized materials removed and filtered with a 63µm mesh sieve size and dried at 105°C for 24hrs. Char yield was estimated using Equation 4.2. Dried char was subsequently characterized according to the methods described in Section 4.4:

$$Char\ Yield_{(\text{dry basis}),,\%} = \frac{Weight\ of\ hydrochar\ after\ drying}{Weight\ of\ dried\ feedstock}\ x\ 100 \qquad 4.2$$

Liquor fraction recovered was weighed and analysed immediately for its organic content, including chemical oxygen demand (COD), total organic carbon (TOC) and ammonia to minimize volatile losses.

4.4 MATERIAL ANALYSES AND CHARACTERIZATIONS

4.4.1 Analytical plan

Table 4.2 outlines analyses/characterizations conducted in this study to investigate unprocessed samples, solid char properties and liquid fractions of carbonized materials after the M-HTC process of each HBW test material. Recommended guidelines published by the International Biochar Initiative (IBI) (9; 10) established standard testing procedures for wastewater (11), and relevant literatures were used to design this analytical and characterization plan.

Table 4.2 Characterization and analytical flow of materials

HBW feedstock		SS	FSS	HF	HFS
Characterization and analytical plan conducted on unprocessed HBW (solid) samples and carbonized chars after the M-HTC process	Proximate analysis (MC, TS, VS, FS)	x	x	x	x
	Elemental analysis	x	x	x	x
	Calorific value	x	x	x	x
	Combustion behaviour	x	x	x	x
	Surface morphology	x	x	x	x
	Heavy metals, & P, K	x	x	x	x
	Surface area and porosity	x	x	x	x
	Surface functionalities	x	x	x	x
	Capillary suction time*	x	x	x	x
	Particle size distribution*	x	x	x	x
Characterization conducted on liquor fractions of carbonized HBW after the M-HTC process	Total organic carbon	x	x	x	x
	Pathogenic deactivation test	x	x	x	x
	Chemical oxygen demand	x	x	x	x
	Volatile fatty acids	x	x	x	x
	Ammonia	x	x	x	x
	Proximate analysis (TS, SS, VS, FS)	x	x	x	x

**Note: CST (See Section 4.4.10) and PSD (4.4.11) were conducted using only sewage sludge (unprocessed and carbonized samples) as representative samples for comparative studies between M-HTC and C-HTC processes during dewaterability studies. These are discussed in more details in Chapter 6.*

4.4.2 Analysis of solids in unprocessed biowaste and carbonized chars

All unprocessed biowastes samples and the chars produced from them after each carbonization experiment were analysed for moisture content (MC), total solids (TS), volatile solids (VS) and fixed solids (FS), adopting Standard Methods 2540G – *Total, Fixed and Volatile Solids in Solid and Semisolid Samples* (11). The definitions of these terms are provided in Appendix 1.

The solids analysis enabled estimates of mass balance, char formation rate under different conditions, and percentage solids enrichment due to the HTC process. Representative samples of feedstock and their char were weighed into evaporating dishes and placed on a water bath to evaporate moisture before subsequent drying at 105°C±2°C for 18–24hrs. They were subsequently dried to a balance temperature in a desiccator and then weighed. Drying was repeated for another hour, with the samples subsequently cooled and weighed. The drying/cooling and weighing cycles were repeated until a constant weight, i.e. change in weight was less than 4%. The final weight was recorded and used to determine MC and TS using Equations 4.3 and 4.4. For the determination of VS and FS, dried residues from the TS were ignited at 550°C for an hour in a furnace. Dishes and their residue after ignition were cooled in the desiccator to balance temperature and then weighed. In order to attain constant weight i.e. less than 4% change in weight, dishes and residues were subsequently ignited for 30mins., cooled

in a desiccator and weighed. The final constant weight was recorded and the VS and FS were estimated using Equations 4.5 and 4.6

$$MC, \% = \frac{(W_C - W_A)}{(W_C - W_B)} \times 100 \quad 4.3$$

$$TS, \% = \frac{(W_A - W_B)}{(W_C - W_B)} \times 100 \quad 4.4$$

$$VS, \% = \frac{(W_A - W_D)}{(W_A - W_B)} \times 100 \quad 4.5$$

$$FS, \% = \frac{(W_D - W_B)}{(W_A - W_B)} \times 100 \quad 4.6$$

Where: W_A = Weight of dried residue + dish (g)

W_B = Weight of dish used (g)

W_C = Initial wet weight of biowaste (or char) + dish (g)

W_D = Residual weight + dish after ignition at 550˚C (g)

These tests were conducted in triplicate and their mean values estimated.

4.4.3 Elemental (CHN) analysis

Elemental analysis, also known as ultimate analysis, is an analytical technique used for the rapid determination of carbon, hydrogen, nitrogen and sulphur in organic matrices and other types of materials (12). This analysis has been used specifically to estimate, among other properties, the heat of combustion, devolatilization behaviour and grindability of fuel materials (13; 14; 15). The basic principle of this technique entails the combustion of sample matrices in a furnace filled with excess oxygen at about 975°C for the determination of CHN (16), or at about 1000°C if sulphur is to be analysed (12). The combustion converts carbon to CO_2; hydrogen to water; nitrogen to nitrogen gas/oxides of nitrogen; and sulphur to sulphur dioxide. These combustion products are carried by helium through the detectors and analytical systems of the analyser. Helium is also used to discharge combustion products out of the system and to purge the whole system. For detection and analysis, combustion products are passed over specialized reagents to ensure complete oxidation of the combustion products and to further remove unwanted by-products including sulphur, halogens and phosphorus. Combustion products are subsequently passed over pure copper wire in a reduction tube to remove excess oxygen and to reduce oxides of nitrogen to elemental nitrogen. After this, the gaseous products are mixed homogenously in a mixing chamber at constant volume, temperature and pressure. The homogenously mixed gases are then released to pass through a series of

high-precision thermal conductivity detectors, each containing a pair of thermal conductivity cells. The cells trap water and CO_2 and relate their concentrations to the elemental hydrogen (H) and carbon (C) in the samples combusted. Elemental N in the sample is measured against a helium reference cell (16).

For this work, the unprocessed HBW samples and their respective chars were analysed for their carbon (C), hydrogen (H) and nitrogen (N) contents using a CHN analyser (CE-440 Elemental Analyser, Exeter Analytical Inc., UK) adopting ASTM D5373 standard testing procedure (17). Sulphur (S) was not determined in this study, as preliminary tests indicate a negligible percentage in unprocessed HBW and char samples. These analyses sought to measure the impact of HTC process parameters on these elements, specifically carbon. The effect of HTC on carbon yield and efficiency makes this test imperative. The CHN analyses quantified the extent of carbonization of the HBW samples and enabled heating values of the char product to be tested. Between 2mg and 3mg of dried and ground samples (feedstock and/or char sample) were used. The CHN analyser was calibrated with benzoic acid, which contains 68.85wt. % carbon, 4.95wt. % hydrogen, 26.20wt. % oxygen and no traces of nitrogen or sulphur. Analyses were conducted in triplicate, with mean values and the standard deviation estimated for each sample respectively.

4.4.4 Energy content

Calorific values, i.e. higher heating values (HHVs), of both feedstock and all char samples were measured using a bomb calorimeter (CAL 2K, Digital Data Systems, South Africa) based on the ISO 1928:2009 Standard (18). The bomb calorimeter determined the heat of combustion (i.e. energy content) of the test materials (such as fuel, polymers, food materials etc.) by igniting the sample in a sealed vessel (usually known as a 'bomb') under a high pressure of oxygen. The energy released as the test material undergoes complete combustion is absorbed within the calorimeter and the resultant temperature rise in the absorbing medium of the calorimeter is noted. To estimate the calorific value (i.e. heat of combustion) of the test material, the temperature change (of the absorbing medium of the calorimeter before and after combustion of test materials) is multiplied by the heat capacity of a standard material such as benzoic acid (19).

This analysis was conducted to measure the energy value of char products and, furthermore, correlate their values with the carbonization parameters to study the effect of the process on the energy value of products. To achieve this, 0.2 g of dried test

sample was placed in the combustion tare. The ignition thread was supplied to the sample in the tare before the assembly was placed in the bomb. The bomb was subsequently covered with its metallic lid, pre-pressurised with 20 bar of pure oxygen and placed in the calorimeter. The sample was ignited and combusted in the bomb. The heat generated during the combustion was detected and the energy value measured automatically. Calibrations were carried out with benzoic acid (HHV, 26.464 $MJ.kg^{-1}$) as the standard material. Tests were conducted in triplicate and mean values used as the energy value of the samples.

4.4.5 Surface morphology using Scanning Electron Microscope (SEM)

Surface morphologies of feedstocks and char samples were examined on a LEO 1530VP Field Emission Gun Scanning Electron Microscope (FEGSEM). Micrographs were taken for different areas of each sample. Imaging was conducted at an accelerating voltage of 5kV primary electron beam current of approximately 200pA. To enhance image resolutions, samples were ground and mounted on an adhesive graphite foil on an aluminium sample holding stud. Mounted samples were subsequently sputter-coated (EMITECH 1750 Sputter Coating instrument) with gold-palladium for 90 seconds using a plasma current of 20mA. This experiment was conducted to further understand the effects of HTC on the structure of processed char materials in comparison with their unprocessed samples.

4.4.6 *Thermal/combustion analysis*

This analysis investigated the thermal decomposition behaviour of chars as a potential fuel. Thermogravimetric (TG) analysis of feedstock and representative char samples was carried out using a thermogravimetric analyser (Q5000IR TGA, TA Instruments, UK). Between 10mg and 30mg of the representative sample was placed in a platinum crucible and heated under atmospheric pressure, with an air flow rate of $50ml.min^{-1}$. Weight loss and the corresponding weight loss rate (also known as DTG, i.e. derivative TG) of the sample were measured continuously under non-isothermal conditions, with a temperature range of 30–900°C at a constant heating rate of $10°C.min^{-1}$. The corresponding DTG curve was plotted at various points on the TG graph. The TG–DTG graphs of each analysed sample were used to estimate peak temperatures at each combustion phase and burnt–out temperature (20).

4.4.7 Brunauer-Emmett-Teller (BET) analysis

The surface area ($m^2.g^{-1}$) and pore sizes (nm) of all the unprocessed HBW and char products generated by the different process conditions were determined using a single

point BET nitrogen adsorption analysis on a Micrometrics Tristar Surface Area and Porosity Analyser. Before analysis, 0.2g to 0.3g of the representative samples were degassed in a vacuum. Analyses of the data and isotherms generated during the analysis were processed by Micrometrics Tristar 3000 (V6.05) software to determine the specific surface area and porosity: pore distribution and pore sizes. The essence of the BET analysis (In conjunction with SEM) in this work stems from the need to investigate the effects created by the M-HTC process on the char samples. The analysis was also carried out in order to classify the char pore sizes based on IUPAC classifications (21) as they relate to potential uses in agriculture, for example.

4.4.8 Surface functionalities

The surface functionalities of the unprocessed HBW and its char products were examined using Fourier Transform Infrared (FTIR) spectrometry (22; 23). The technique characterizes the microchemistry of materials and provides information about the type of functional groups and active surface species that were produced by HTC. This characterization relates to the potential use of chars in adsorption studies, including organic and inorganic removal, water purification and, particularly in agriculture, binding and retaining nutrients for higher bioavailability and uptake in soils (7). The FTIR analysis of all feedstocks and representative char samples was performed using a Shimadzu FTIR-8400S. Samples were run using a Golden Gate diamond ATR (attenuated total reflectance) (Specac Ltd, UK) FTIR spectrometer accessory. The Golden Gate ATR accessory eliminates rigorous sample preparation and offers high-quality spectra data (24). Infrared spectra were collected within the 4000 to 600 cm^{-1} region with a spectra resolution of 2cm^{-1}. To ensure accuracy during this analysis, the background emission spectrum of the infrared (IR) source was recorded and taken into account while collecting the emission spectrum of the IR source from the test material. Background emissions were automatically deducted from each sample emission spectra. Sixty-four (64) scans were collected for each sample.

4.4.9 Metals analysis

Inductively coupled plasma spectrometry (ICP) is both a qualitative and quantitative analytical technique that can be used to detect about 70 elements, particularly at low concentrations in a sample matrix. This technique has an excellent detection limit for most elements in the range 0.1–100 $ng.ml^{-1}$ (25; 26).

The analysis of nutrients such as potassium (K), phosphorus (P); heavy metals; pH and electrical conductivities in HBW and their derivatives, such as chars, is strongly recommended, especially as it relates to their application on agricultural soils (9). The international Biochar initiative (IBI) guide (9) and sludge to land UK regulations (27) were used as references in the design of the analysis of relevant nutrient elements and heavy metals in the chars produced from the M-HTC experiments. SS feedstock and chars under different process conditions were analysed as a representative test material to study the effects of HTC on carbonized samples. For this, 0.5g of dried sample (feedstock and associated char products) was mixed with 5ml of deionized water and 5ml of conc. HNO_3. The mixture was left to stand for 15mins. for pre-digestion before being subjected to 200°C microwave digestions for an additional 15mins., as specified by a procedure for waste activated sludge (28). Digested samples were cooled, filtered and then diluted with distilled water accordingly for analysis. Metals in the samples were determined on an ICPE-9000 Shimadzu with optical emission spectrometer (ICP-OES). The instrument was calibrated for B, Cr, Na, Ni, Cu, K, P, Zn, Cd, Co, Se, Mo, with 0.2, 0.4, 0.6, 0.8, 1.0, 5.0, 10 and 50mg.l^{-1}.

4.4.10 Capillary suction time analysis (CST)

The CST apparatus used to analyse sludge dewaterability (See Chapter 6) was set up as shown Fig. 4.4. It consisted of two plates, three sensors placed on two concentric circles, a CST chromatography filter paper, a sludge reservoir and a timer.

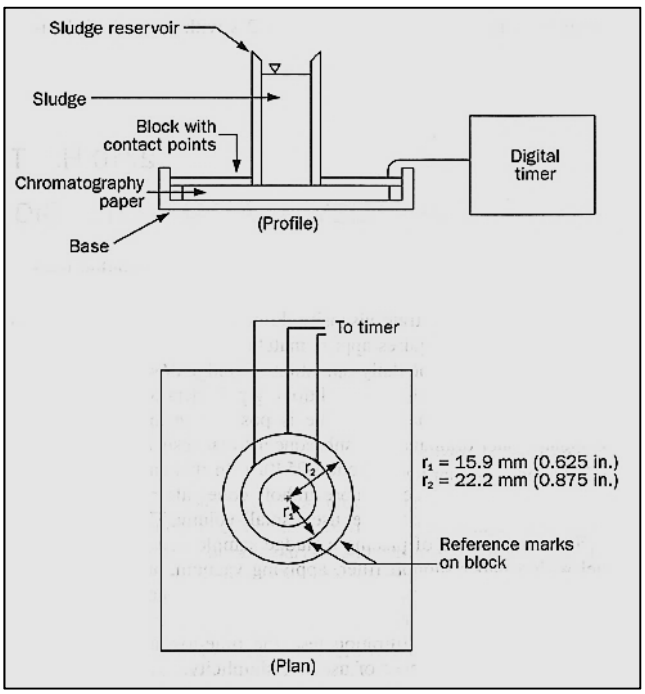

Fig. 4.4 Schematic of CST apparatus (11; 29)

The apparatus measures CST as an indication of filterability by recording the time expended when a chromatography adsorbent filter paper draws filtrate from a sludgy sample by capillary suction. Samples are poured into the reservoir resting on the filter paper. The capillary suction provided by the filter paper draws filtrate progressively to saturate the filter's paper area. When the filtrate touches the first two sensors, there is an increase in electrical conductivity and this triggers the timer. The counting stops when the filtrate touches the second sensor due to a likely change in conductivity with initial sensors. The time taken by the filtrate to move from the first two probes to the second probes is the material's CST value, which reflects its filterability. The lower this CST value, the better the filterability of the material mix (31). During analysis, carbonized materials were continuously stirred before pouring to fill the sludge reservoir, to ensure a homogenous representative mixture of solids and liquid was analysed. The time taken for filtrate migration was recorded off the digital timer. The experiment was repeated for at least seven replicates (until consistency in reading was attained) and their average CST estimated. The experiment was carried out with carbonized materials cooled to room temperature. For the unprocessed sludge, the same procedure was used; however, as temperature affects CST value, unprocessed sludge from the cold storage room (~5°C) was allowed to attain room temperature prior to analysis.

4.4.11 Particle size distribution (PSD) analysis

PSD was conducted by the laser diffraction method on a Malvern Mastersizer 2000 (Malvern Instruments Ltd, UK) adopting Standard Method ISO 13320: Particle Size Analysis – Laser diffraction methods (30). The method is accurate, simple and ensures reproducibility of data (31). The principle behind the laser diffraction method is based on the fact that spatial distribution of scattered light (laser beam) is a function of sample particle sizes. The method uses the spatial distribution of scattered light – i.e. the scattering pattern of a particle, which varies/depends largely on the particle's diameter and wavelength of incident light – to estimate the distribution of sizes obtained in a sample material. More details can be found in reference (33). Importantly, sample particles must be dispersed in a suitable medium, i.e. water.

The procedure for measurement follows thus: The sample is dispersed in water and supplied to the instrument. On passing through a focussed beam of light, different particle sizes scatter the focussed beam of light at characteristic spatial angles. The scattered light patterns, which are also called the scattering patterns of the particles, are

collected by detectors, analysed (using diameter of particle, scattering angle and optical index of the detector) and related to the particle size distribution of the sample.

In this study, following the completion of the HTC processes, recovered solid chars were dried at 105°C for 18–24 hours and were uniformly ground to a powdery form. Unprocessed SS was also treated this way, i.e. dried at 105°C and ground. Before PSD analysis, 2–3g of the samples was uniformly mixed with water as a dispersant before pipetting into the analyser. Depending on reproducibility of scattered particle patterns, a minimum of seven replicates were conducted and the size distribution averages automatically analysed by the PSD analyser.

4.4.12 Recovered liquid analysis: Total solids (TS), fixed solids (FS) and volatile solids (VS)

TS, VS, FS in the liquor recovered from the HTC experiments were determined using standard methods: 2540B – *Total Solids Dried at 103–105^{0}C*; 2540E – *Fixed And Volatile Solids Ignited at 550^{0}C,* respectively (11) (see Appendix 1 for definitions of these terms). Thirty (30) ml of the well-mixed samples from the recovered liquors was poured into pre-weighed evaporating dishes and evaporated to dryness in a steam bath before further drying at 103°C to 105°C for 1hr. to remove remaining moisture. The hot solids were placed in a desiccator to cool before they were weighed. Repeated cycles of drying and cooling in a desiccator were performed until a constant weight was attained (i.e., the difference in weight was less than 4%). For FSandVS, the same procedures described in Section 4.4.2 were used.

The TS, VS and FS in liquor recovered after carbonization were estimated using the following equations:

$$TS\ , mg.l^{-1} = \frac{(W_A - W_B)}{V} \times 1000 \qquad 4.7$$

$$VS, mg.l^{-1} = \frac{(W_A - W_C)}{V} \times 1000 \qquad 4.8$$

$$FS, mg.l^{-1} = \frac{(W_C - W_B)}{V} \times 1000 \qquad 4.9$$

Where: W_A= Weight of dried residue + dish (mg)

W_B = Weight of dish used (mg)

W_C= Residual weight + dish after ignition at 550°C (mg)

V = Volume of sample used (ml)

Analyses were conducted in triplicate and their mean values estimated.

4.4.13 Recovered liquid analysis: Total suspended solids (TSS) and total dissolved solids (TDS)

Standard Method 2540D: *Total Suspended Solids (TSS) Dried at 103°C to 105˚C* (11) was used. In order to prevent clogging of the filter, 10ml of liquor recovered from the HTC experiments was filtered through a pre-washed, dried (at 105°C for 1 hour) and weighed standard 1.2µm glass-fibre filter paper (Fisher Scientific) fitted in a glass-fibre filter disk. Complete rinsing of liquor from its container was ensured, as well as washing of the filter paper at least three successive times with 10ml of deionised water during the suction. The filter papers containing the solids were then removed, placed on aluminium support foils and dried at 103–105˚C for an hour before being cooled in a desiccator. They were then weighed. Constant weight was achieved by using the procedure described in Section 4.4.10. Suspended solids in the recovered liquor were determined using the equation:

$$TSS, mg.l^{-1} = \frac{(W_A - W_F)}{V} \times 1000 \qquad 4.9$$

Where: W_A= Weight of dried solid residue + filter (mg)

W_F= Weight of filter used (mg)

V = Volume of recovered liquor used (ml)

Total dissolved solids (TDS) were determined by:

$$TDS, mg.l^{-1} = TS - TSS \qquad 4.10$$

4.4.14 Recovered liquid analysis: Chemical oxygen demand (COD)

The chemical oxygen demand (COD) is an important parameter for assessing the quality of the recovered liquor after each carbonization experiment, especially for disposal purposes. COD provides an estimate of the oxygen demand of suspended or dissolved chemicals in the recovered liquor if discharged, for example, to natural water bodies; and hence can be used for monitoring and controlling discharge parameters.

For the present study, COD in the recovered liquor was measured using standard test kits on a COD analyser (Palintest 8000 Photometer, Palintest Ltd, UK) in accordance with Standard Method 5220D – *Closed Reflux Calorimetric Method* (11). The methods relate COD values in the samples to the amount of strong oxidizing agent reduced by the samples when digested with strong acid in the presence of a catalyst. The oxidizing agent, acid and catalyst used in this method were potassium dichromate ($K_2Cr_2O_7$), sulphuric acid (H_2SO_4) and silver sulphate, respectively. A photometer was used to

measure the amount of oxidant reduced, based on colour changes of the oxidizing agent caused by the interaction of organics in the samples with the oxidizing agent. During the sample digestion, chromium is reduced in its hexavalent state in $Cr_2O_7^{2-}$ to a trivalent state Cr^{3+}, and both states have unique colours absorbed in the visible region of electromagnetic spectrum. For example, while $Cr_2O_7^{2-}$ absorbs strongly in the 400-nm region, Cr^{3+} absorbs less. Also Cr^{3+} absorbs strongly at about the 600-nm region, while $Cr_2O_7^{2-}$ has almost zero absorption. The photometer used to measure COD in this study used 570nm wavelength, hence measuring the reduced state of chromium Cr^{3+} and relating it to the COD values of the recovered liquor.

Recovered liquor after each carbonization experiment was diluted by 1:10 and 0.2ml of the resultant liquor was pipetted into specialized COD test tubes (COD reagent tube PL 456, with a measuring range of 500–20,000mg of oxygen demand.L^{-1}). The test tubes were then covered and shaken firmly before being heated up in test-tube reactors (Hach Camlab COD reactor) at 150˚C ± 2˚C for 2 hours. Blanks were prepared by adding 0.2ml of deionized water in a COD test-tube and this was heated with the other test tubes as well. This was done in order to factor into the calculation the oxygen demand of the reagent itself. After the completion of the digestion process, the test tubes were removed, gently mixed to combine condensed water and dislodge insoluble matter, and then allowed to cool to room temperature slowly – thereby avoiding precipitation. The test tubes after digestion and cooling must be of a straw/transparent yellow colouration in order to ensure that they are fit for COD evaluation on the photometer. COD values were measured against the blanks and recorded as mg of oxygen demand.L^{-1}. The analysis was conducted in triplicate; mean values and the standard deviation were then calculated.

4.4.15 Recovered liquid analysis: Total organic carbon (TOC)

Total organic carbon (TOC) analysis was conducted to measure the total organic content independent of the oxidation states in the recovered liquor. (Only organic carbon is measured by this method, as other organically bound elements such as H or N are not measured). This analysis was primarily for discharge purposes, as one of the main potential impacts of organics includes serving as nutrient for biological growth. Other uses of this information include assessment of the potential of the liquor as a feedstock for anaerobic digestion.

TOC in recovered liquor was measured on a Total Organic Carbon analyser (Rosemount Dohrmann Dc-190, USA) adopting Standard Method 5229D – *High Temperature Combustion Method* (11). The principle behind the method involves the use of high temperature at 950˚C to break down organic carbon in samples into single molecular forms of CO_2, and then relate their concentration to the TOC in the samples. Due to the high temperature involved, the method can determine organic carbon from samples containing chemically refractory compounds and high levels of suspended organic carbon.

Liquor recovered after the carbonization experiments was diluted by a ratio 1:10 and then filtered with 0.22µm pore size (Elkay filter paper). Filtration before analysis is important in order to avoid clogging of the sample injector and the TOC analyser. Using this method involves the determination of the total carbon (TC) and inorganic carbon (IC) in the samples. The TOC is then determined by calculating the difference between the TC and IC in mg l^{-1}. The IC was determined by measuring out 50µl of the samples with a syringe, and injecting this into the IC chamber via the IC injection port on the TOC analyser. Here the samples were acidified by conc. H_2SO_4. Acidification of the samples causes all the inorganic carbon in them to be converted into CO_2. The concentration of CO_2 is measured separately as the IC content in the sample. Under the acidic conditions in the IC chamber, however, the organic carbon in the samples is not affected – i.e. it is not oxidized under the acidic conditions and hence only IC is measured. The TC was determined by taking 50µl of the samples and injecting this into the TC reaction chamber, which contained an oxidising catalyst, via the TC injection port. In this chamber, water is vaporized and the organic carbon in the sample oxidized into CO_2 and H_2O. CO_2 from the complete combustion and oxidation of the samples – i.e. from both their organic and inorganic content – is transported by streams of carrier gas to be detected and measured by a non-dispersive infrared analyser.

Injections into the IC and TC ports were repeated until measured values were within ±10% variation. The mean of the values was then estimated along with their standard deviations. In order to prevent cross-contamination in samples during the repetitive injections, either during the IC or TC measurements, the syringe injector used was always washed 10 times with deionized water.

4.4.16 Recovered liquid analysis: Ammonia (NH_3)

This test was primarily conducted to measure the concentration of recoverable NH_3, as a potential value-added nutrient product from the M-HTC process. The analysis of ammonia was carried out using standard test kits on an automatic spectrophotometer (Hach Lange DR 3900) adopting Standard Methods 4500-NH_3 Phenate Method (11). The principle of the method is based on the reaction of ammonium ions with hypochlorite ions and salicylate ions in the presence of sodium nitroprusside as a catalyst to form indophenol blue; this is subsequently evaluated photometrically.

The samples were then diluted down to the measuring ranges of the standard kits, with 0.2ml of the samples pipetted into the standard reagent test tube kits and shaken firmly. The mixture was allowed 15mins. to react before the concentration of ammonium ions was evaluated on the spectrophotometer at 694-nm wavelength. The values were recorded in $mg.l^{-1}$ of ammonium – nitrogen as related to the concentration of ammonia. This analysis is time sensitive, hence the test tubes were analysed within a maximum 30mins. duration window after each carbonization experiment. Analyses were conducted in triplicate, with their mean and standard deviation estimated. Ammonia measurements were further validated against the percentage wt. mass balance of N-content removed from the unprocessed substrates into the liquid fractions of carbonized materials.

4.4.17 Recovered liquid analysis: Volatile fatty acids (VFA)

VFA analysis is a useful wastewater assessment parameter. For the present study, VFA in recovered liquor were analysed using standard test kits on an automatic spectrophotometer (Hach Lange, DR 3900). The principle of the test kits is based on the reaction of fatty acids (carboxylic acids) with diols (alcohol) within an acidic environment to form fatty acids esters. The fatty acids esters are then reduced by iron (III) salts to form red-coloured complexes, which are evaluated photometrically on the spectrophotometer at an absorption wavelength of 497nm. Specifically, the standard test kits measures ethanoic acid – CH_3COOH (50–2500 $mg.l^{-1}$) – and butanoic acid – C_3H_7COOH (75–3600 $mg.l^{-1}$) – and presents the sum of their concentrations as the total VFA (mg organic acids/l) in the recovered liquor.

The recovered liquor samples were diluted with distilled water by a ratio 1:10. Then 0.4ml of a standard reagent (LCK 365A) was added to the standard test tube (LCK 356), followed by 0.4ml of the sample. The solutions were then transferred to a thermostat-heating reactor (Hach Lange LT 200) and heated for 10min. After heating, the solution

was cooled to room temperature, before pipetting 0.4ml of other standard reagents (LCK 356B and LCK 356C) respectively. The mixture was mixed by shaking, before pipetting 2ml of another standard reagent solution (LCK 365D) and allowing 3mins. to settle. The concentration of total volatile organic fatty acids in the liquor was then evaluated on the spectrophotometer. Analyses were conducted in triplicate, with their average and standard deviation estimated.

4.4.18 Recovered liquid analysis: pH

The pH of recovered liquor from each of the HTC experiments was measured using an electronic pH meter (Mettler Delta 340), calibrated against freshly prepared solutions of known pH 4.0 and 7.0 on a weekly basis. The measurements were conducted in triplicate, with both the average and standard deviations calculated.

4.4.19 Pathogenic deactivation test

Pathogen destruction tests (using *E. coli* as indicator) were conducted to assess disinfection outcomes for HBW under the M-HTC process. First, 200g of the unprocessed HFS samples were processed by M-HTC at 180°C (residence time, 30mins). A control HFS sample was also processed by C-HTC at 180°C (residence time, 3hr). Tests for total coliforms (TC) and faecal coliforms (FC) were conducted on the liquor recovered from the HTC processes, where supernatant liquor from the carbonized HFS was carefully decanted into prepared sterile bottles. The tests were also repeated on the HFS feedstock, also collected into sterile bottles. TC was tested by membrane filtration according Standard Method 9222B – *Standard Total Coliform Membrane Filter Procedure.* Faecal coliform was tested with the Standard Method 9222D – *Faecal Coliform Membrane Filter Procedure* (11). M-Endo broth culture media and M-FC broth culture media (Scientific Lab Supplier Ltd, UK) were used for the TC and FC tests respectively. During sample preparation, Ringer's buffer solution was used to dilute the recovered liquor samples. Unprocessed HFS was diluted to 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8} and 10^{-9} concentrations, and HTC processed liquor samples were diluted to 10^{-1}, 10^{-2}, 10^{-3} and 10^{-4} concentrations. Fifty (50ml) of the diluted samples were used for membrane filtrations. The tests were conducted in triplicate and averages estimated. Following filtration, TC membranes were incubated at 37°C and FC membranes at 44°C for 18–24hrs. Counting of colony forming units was conducted after 18hrs.

4.5 ANALYSIS OF DATA

Data collected during all procedures involving weighing were properly recorded on appropriate weighing sheets. MS Excel was used to analyse all data, conduct relevant calculations and also to plot graphs. The characterizations data, including those from FTIR, TGA, BET etc., were analysed using their analytical softwares.

4.6 ETHICS AND CHALLENGES

Due to the nature of this work, which involves the collection, handling and use of human samples, ethics approval for the work was required. This was granted. Risk assessments and relevant medications were also conducted. Protection against biological hazards and all laboratory safety ethics were strictly observed.

One of the challenges encountered in this work was lack of published material for validating analytical and characterization data from the HBW materials. The variability of human wastes also makes it challenging to maintain homogenous representative samples. The quality of SS used over the duration of this research may have been affected by seasonal variability in discharges.

Handling and smell of unprocessed HBW meant collection of HFS and HF, manual inspection, sample preparations and most experiments had to be conducted at specific times during the course of this work. In addition, un-estimated health risks of HBW and other laboratory ethics prevented the analyses and characterizations of some HBW substrate properties, such as using HF on particle size analyser or for digestion for ICP analyses. Thus the work was confined to the use of SS in such cases, as a surrogate to simulate the behaviour of HBW for such properties.

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5.1 INTRODUCTION

The studies described in Section 4.4 were undertaken at the Water Laboratory, Civil Engineering Department, Loughborough University and provided the data and materials that were subsequently used to:

- characterize the products of M-HTC treatment of HBW feedstocks (Section 5.2);
- evaluate the efficacy of pathogenic inactivation by M-HTC (Section 5.3);
- estimate end products recovery in the form of solid chars and liquid ammonia concentrate (Section 5.4);
- compare M-HTC with C-HTC processes based on different heat sources, i.e. microwave and conduction heating (Section 5.5); and
- provide benchmark estimates of yield, and process time/throughput and energy consumption for M-HTC (Section 5.4 and 5.5).

5.2 CONVERSION OF HBW DURING M-HTC

5.2.1 Organoleptic assessment of M-HTC products of HBW

5.2.1.1 Sensory impressions

The smell, colour and texture of the M-HTC products from the four feedstocks are summarized in Table 5.1.

Table 5.1 Sensory assessment, before and after M-HTC

Physical parameters	Feedstock	Before M-HTC	After M-HTC	Remarks
Smell	SS HFS FSS HF	Foul Very foul Mild Very foul	Coffee-like Like almond Like burnt oil Like almond	Distinctive smell change, which grows stronger with rise in temperature
Colour (both solid and liquid fractions)	SS HFS FSS HF	Black Brown Brownish-yellow Brown	Light to darkish brown to black colouration, depending on process condition	Carbonized material gets darker with increasing temperature and residence time
Texture (Dried samples)	SS HFS FSS HF	Loosely packed, flake – like, fibrous, lumpy, hard to ground	Easily grounded, Crumby and friable	Carbonized materials appears denser and slightly oily at higher temperature (>180°C)

The foul odour associated with unprocessed SS, HFS and HF was replaced by: a coffee-like smell for SS; an almond-like smell for HFS and HF; and smell characteristic of burnt oil for FSS. The smell of the end products represents a significant improvement when compared to the foul odour of unprocessed biowastes. While the smell of the carbonized material was consistent for all the process parameters, i.e. at the different reaction temperatures and residence times used, the smell intensity was observed to increase with increasing reaction temperature and residence time.

Fig. 5.1 illustrates the differences in appearance of each biowaste feedstock (both wet and dried samples) before and after M-HTC. The colour of both the carbonized solids (and recovered liquor) after the M-HTC process changed from the brown colour associated with human faeces or sludges to a carbonaceous, coal-like colour. SS, which is typically black in colour as shown in Fig.5.1, retained its colour. The colouration of the carbonized biowaste materials also appears to depend on the process parameters used, as both solids and liquid fractions of carbonized end products for all feedstocks get darker with increasing temperature and residence time profile used.

The sensory assessment of the smell and colour of the carbonized end products recovered after the M-HTC process showed them to be similar to those obtained from the C-HTC process used in the work. It would appear that the smell and colour of the products of HTC are similar regardless of heat sources, but dependent on type of feedstock.[3] This is explained in Section 5.2.1.3. These observations are consistent with thermochemical conversion/transformation processes reported in Table 2.8 Section 2.4.1 involving other conventional methods, where a hot plate heater (or something similar) was used (1; 2; 3). Hence, these similarities in the organoleptic properties of smell and colour of the end products from the M-HTC of HBW with existing methods, and the characteristic colour and smell change of end products from the HTC processes, provide preliminary evidence that suggests M-HTC converted HBW to carbonaceous materials.

[3] Other substrates such as orange peel and horse manure were subjected to HTC treatment during preliminary testing of this research. They all produced a black coal-like colour, but with different smells. Orange peel produced a scorched lime smell, while horse manure produced a prune-like smell.

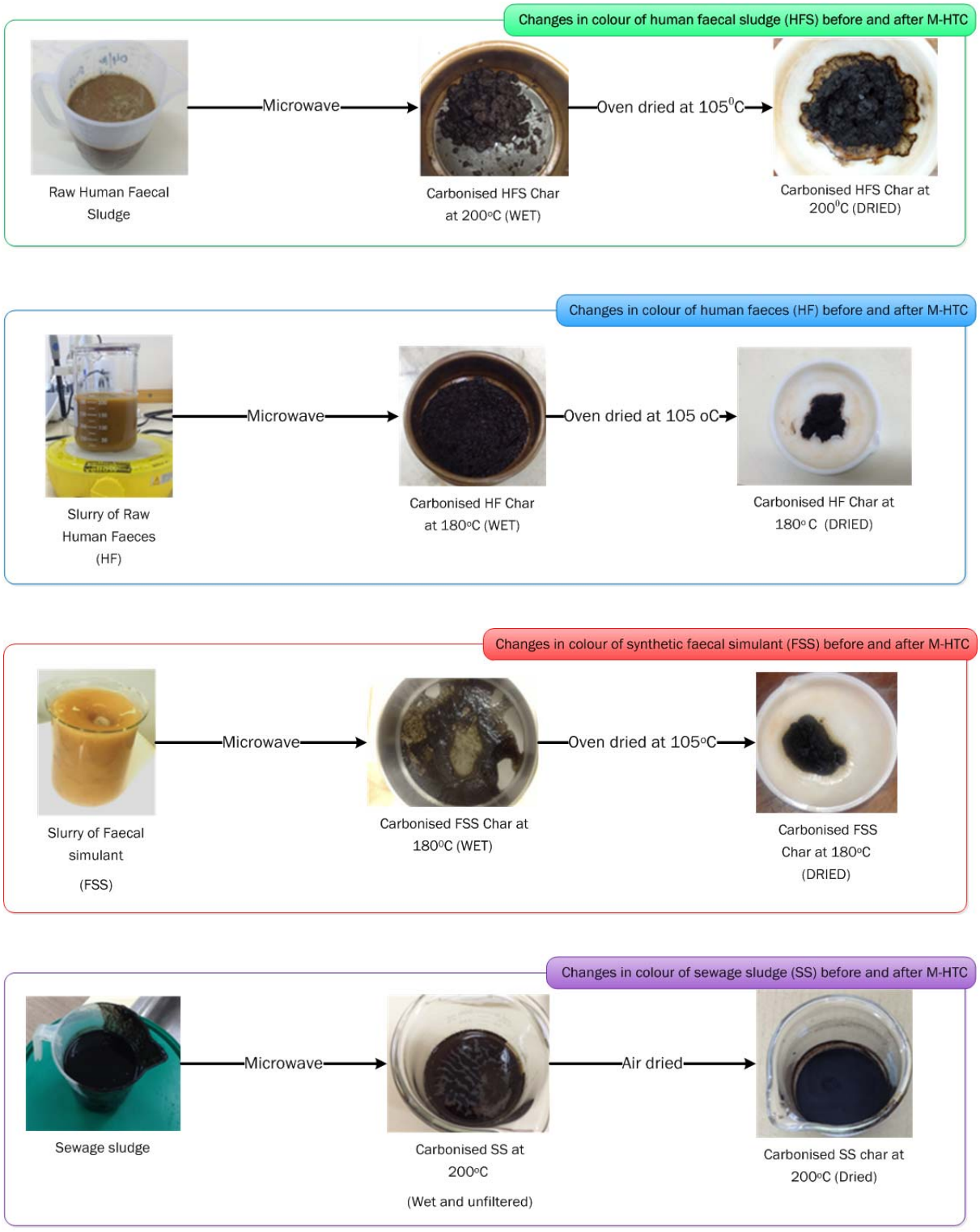

Fig.5.1 Differences in the appearance of M-HTC products of HBW

5.2.1.2 Mechanism behind the colouration of carbonized HBW

The colour changes after M-HTC are evidence of caramelization and/or the Maillard reaction (4; 5; 6). Chapter 2 described the large macromolecular components of human faecal biowastes (proteins [nitrogenous compounds], carbohydrates, lipids [fat content], minerals and bacterial debris in varying proportions) (7; 8). M-HTC subjects these macromolecules to thermal hydrolysis, producing shorter-chain intermediate monomers.

- carbohydrates are broken down into reducing sugars (glucose and fructose);
- protein and fat content are broken down into amino acids and short-chain fatty acids (9; 10).

Under favourable conditions, especially those associated with high temperature, reducing sugars react with amino acids (Maillard reaction, see Fig. 5.2). The reactive C- in the open chain carbonyl radical of reducing sugar is attacked by the lone pairs of the N-terminal amino group to generate the dark-brown coloured complex compounds referred to as melanoidins, which are responsible for the colouration of processed biowaste (5; 11). Apart from caramelization, which is another non-enzymatic browning effect observed on sugars in biowastes processed at elevated temperature (12), the primary mechanism responsible for the dark-brown colour formation during HTC are these melanoidins compounds resulting from the polymerization of mainly low molecular weight intermediates (50–70kDa) of carbohydrates and amino acids during the Maillard reaction (11; 13).

Among other factors, the extent of browning of processed biowaste materials caused by the Maillard reaction correlates with increase in HTC reaction temperature (12; 14). A study measured the colour intensities of sewage sludge subjected to thermal hydrolysis at two different temperatures, i.e. 140˚C and 165˚C, and reported a significant increase in colour intensity from 3837mg.l^{-1} (Pt/Co scale) at 140˚C to 12,667mg.l^{-1} (Pt/Co scale) at 160˚C (11). Another study used known amino acids and sugar concentrations to form synthetic solutions of melanoidins, and indicated that a 10˚C rise in temperature increased the melanoidins formation rate and hence colour formation intensity (15). This may explain why the colour of char from HBW, especially HFS, FSS and HF, gets darker with increasing temperature. For example, FSS was obsevered to change from a very light brown colour at 140˚C to a completely brown colour at 160˚C and a dark brown colour at 180˚C and 200˚C. A similar observation was noted for HF and HFS, as indicated in Table 5.1.

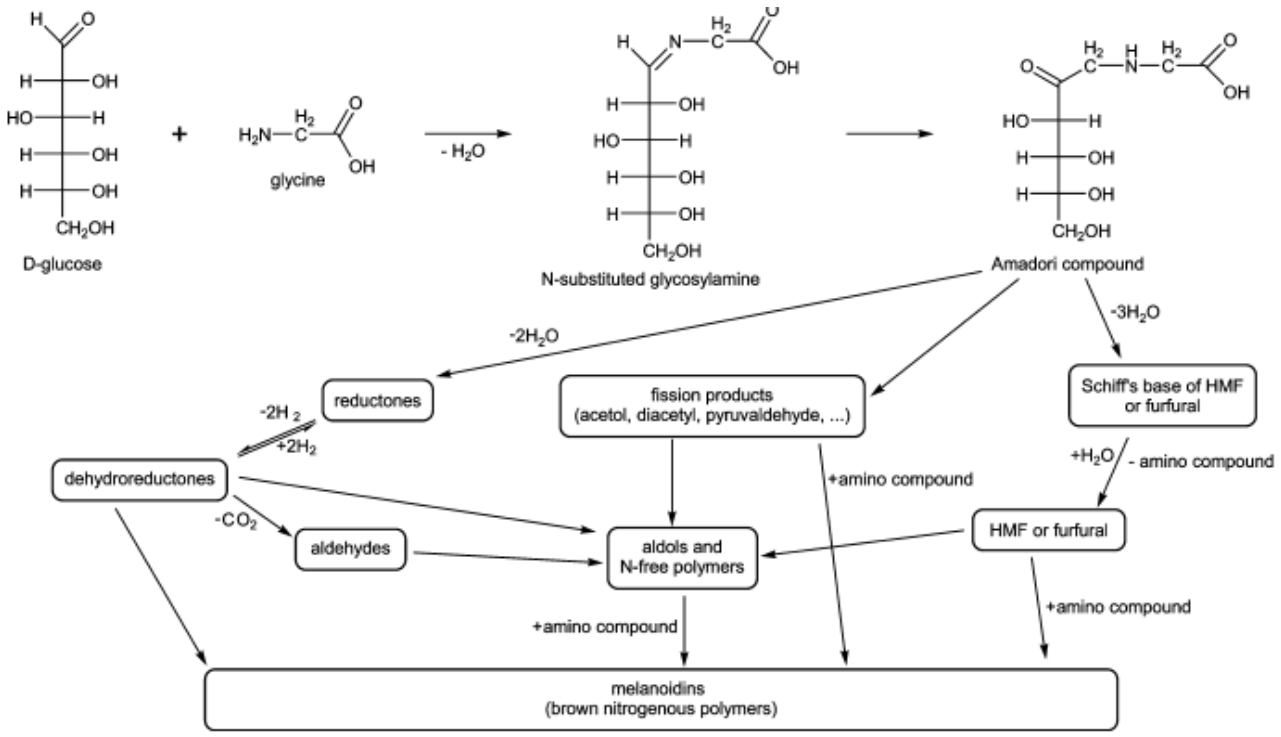

Fig. 5.2 The Maillard reaction: reducing sugars (source of carbohydrates in HBW) react with amino acids (protein source in HBW) [6]

5.2.1.3 Mechanism behind smell changes in carbonized HBW

Nitrogenous benzo pyrrole compounds – notably indole and skatole, hydrogen sulphide, the methyl sulphides and other sulphur-containing compounds – cause the foul odour of HBW (16; 17; 18; 19). Thermal hydrolysis during M-HTC solubilizes these organic components, trapping them in the aqueous phase. Furthermore, the characteristic smell in the products of caramelization and/or the Maillard reaction masks residual odour (9). Solubilizations of sulphur-containing compounds in HBW may also play a role in the reduction of odour in carbonized biowastes (20). A study reported concentrations of dimethyl sulphide (8.1 ppm (v)) and methyl mercaptane (14.2 ppm (v)) in dewatered sewage sludge falling to 11 ppb (v) and 3 ppb (v) in HTC-treated and dried samples respectively (16). Other reactions associated with HTC, including aromatization, may also supress odour (20). In essence, reactive hydrolysis during HTC renders sulphur-containing compounds non-volatile and dissolved into the liquid phase.

Studies of the Maillard reaction mechanism indicate that the type of smell that will be produced in end products after the M-HTC process depends largely, among other factors, on the type and nature of proteins present in the biowaste feedstock (21). Different biowastes with different proteins provide different amino groups, produced during protein hydrolysis (during HTC process), that subsequently enter the Maillard reaction, yielding products with different odours (21; 22; 23). For example, sewage sludge produces char that smells like roasted coffee; char from human faeces smells like almond; char from horse manure and orange peel smells prune-like and scorched lime respectively *[UNPUBLISHED EXPERIMENTAL DATA FROM THIS RESEARCH]*.

In the same manner that colour was observed to intensify with temperature and process time, the odour profile of chars also intensified with incremental changes in process heating time and peak temperature. Increasing odour appears to be correlated with increased browning effect, i.e. melanoidins compounds formation during the Maillard reaction at higher temperature (11). It appears that increasing temperature and process time increases thermal hydrolysis and decomposition and the subsequent dissolution of biowaste components, which in turn increases the concentration and intensity of colour and aroma profile of processed biowaste products (21; 23).

5.2.1.4 Textural changes of carbonized char

Carbonized solids from different waste feedstocks are denser, more friable and easily ground into homogeneous powders after drying than the dried starting materials. M-HTC overcomes the heterogeneous nature of HBW, and converts it into homogenous chars amenable to grinding and powdering for moulding into high-density pellets for fuel, for example. Such properties are due partly to particle size re-distribution during the HTC process (24, 25) (see Chapter 6).

5.2.2 Conversion of HBW into carbonaceous material based on SEM imaging

Scanning electron microscope (SEM) imaging has been used to study potential conversion/formation pathways for char derived from different feedstocks, including glucose and cellulose (26), digested sewage (2) and lignocellulose biomass (27). This technique was also used in this work to study the changes in morphology of the materials before and after M-HTC at 180 °C. SEM micrographs of feedstocks (HFS, HF, SS and FSS) and dried chars were obtained and studied to investigate conversion mechanisms and char formation pathways.

Figs. 5.3 to 5.10 present a series of SEM micrographs of chars recovered from the four biowastes compared with their unprocessed samples. The differences in microstructural morphology are discernible and similar to those obtained in a previous study run at 400°C using conventional heating (28). The information obtained from the SEM micrographs suggests two possible M-HTC char formation pathways from HBW.

5.2.2.1 Direct solid-to-solid conversion pathway

Figs. 5.3 to 5.10 show the microstructure of HF, SS, HFS and FSS respectively. While unprocessed FSS shows some scattered aggregate of long strands (Fig. 5.9), other unprocessed biowastes exhibit undisturbed flat layers with no discernible porosity (see Fig. 5.3 – unprocessed HF; Fig. 5.5 – unprocessed SS; and Fig. 5.7 – unprocessed HFS).

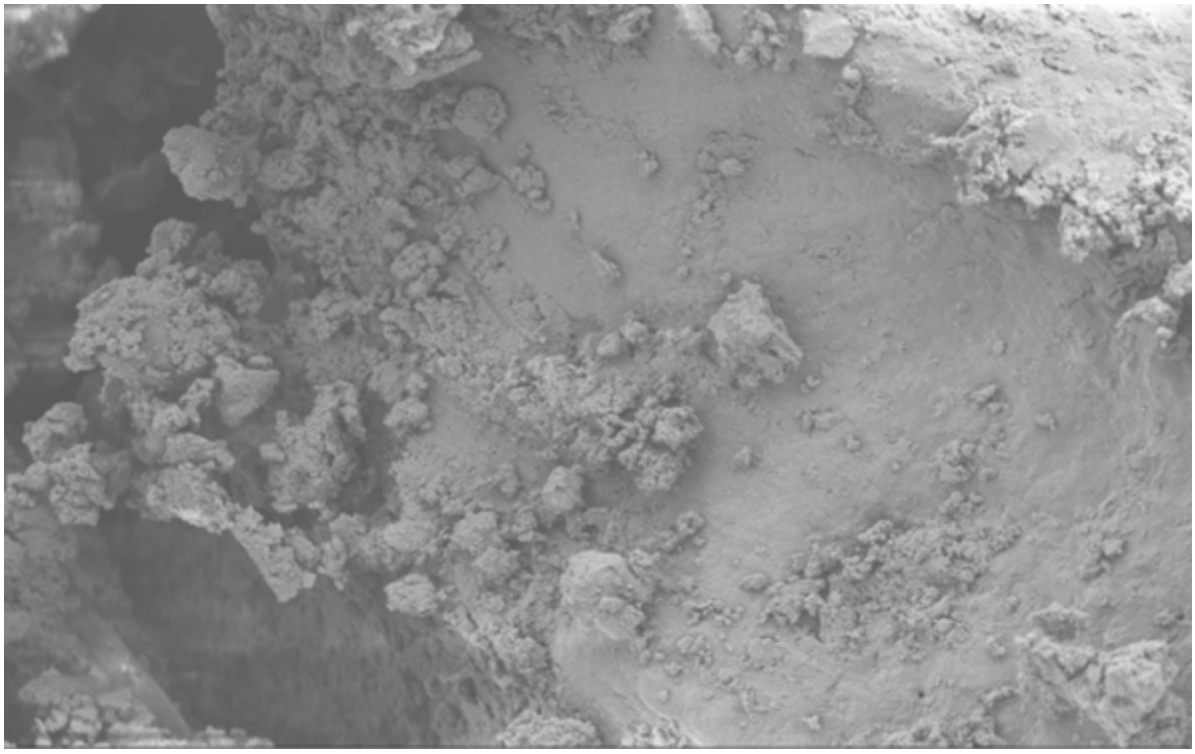

Fig. 5.3 SEM micrograph of unprocessed HF

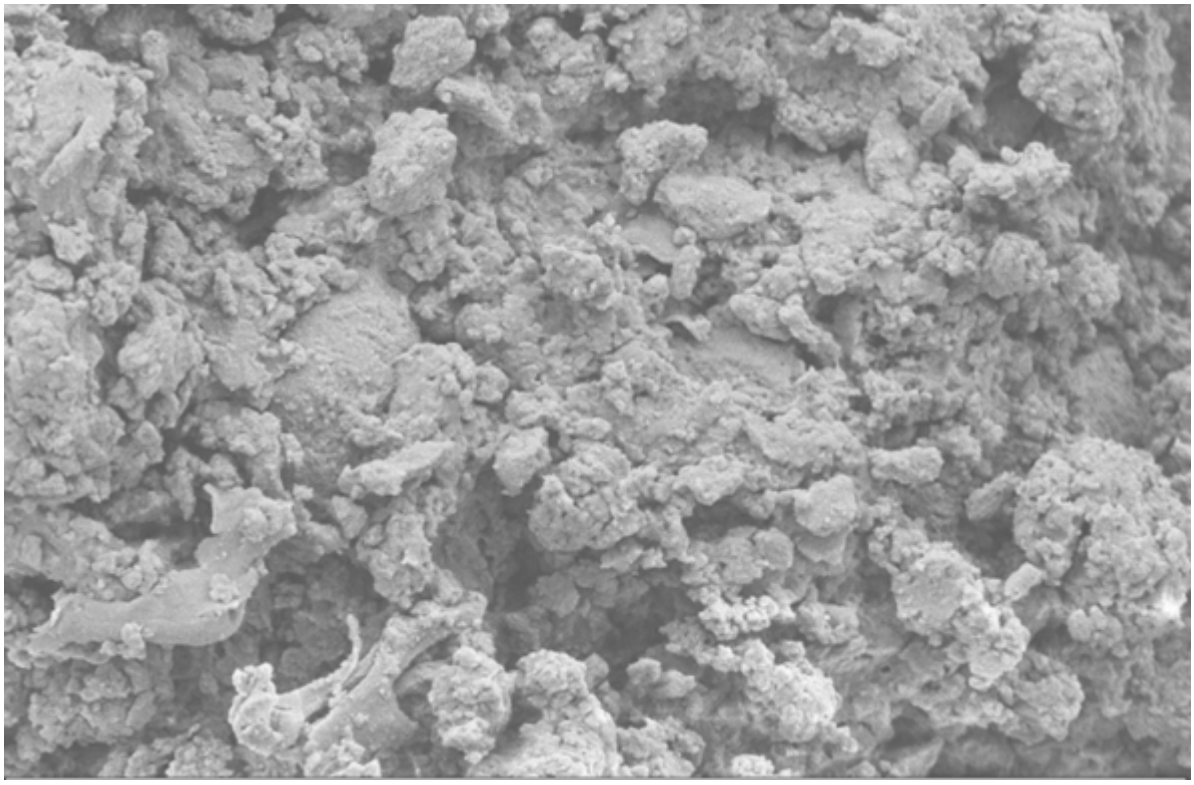

Fig. 5.4 SEM micrograph of HF char

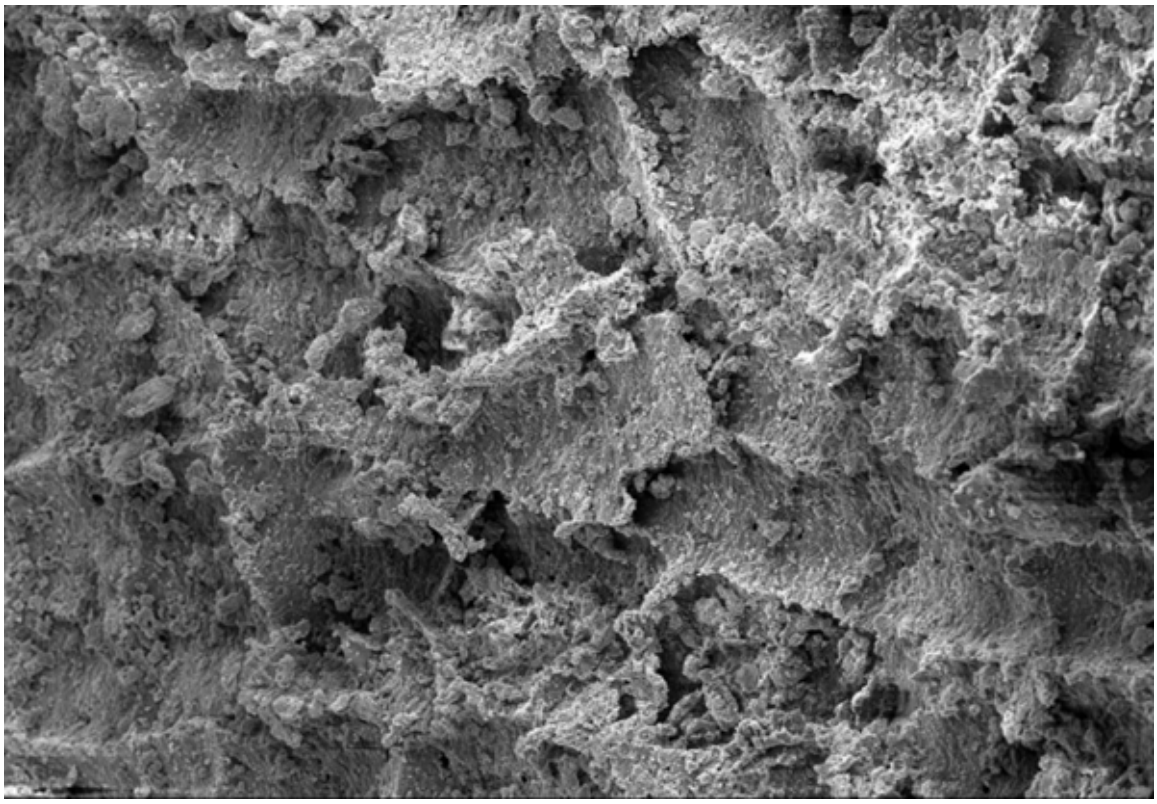

Fig. 5.5 SEM micrograph of unprocessed SS

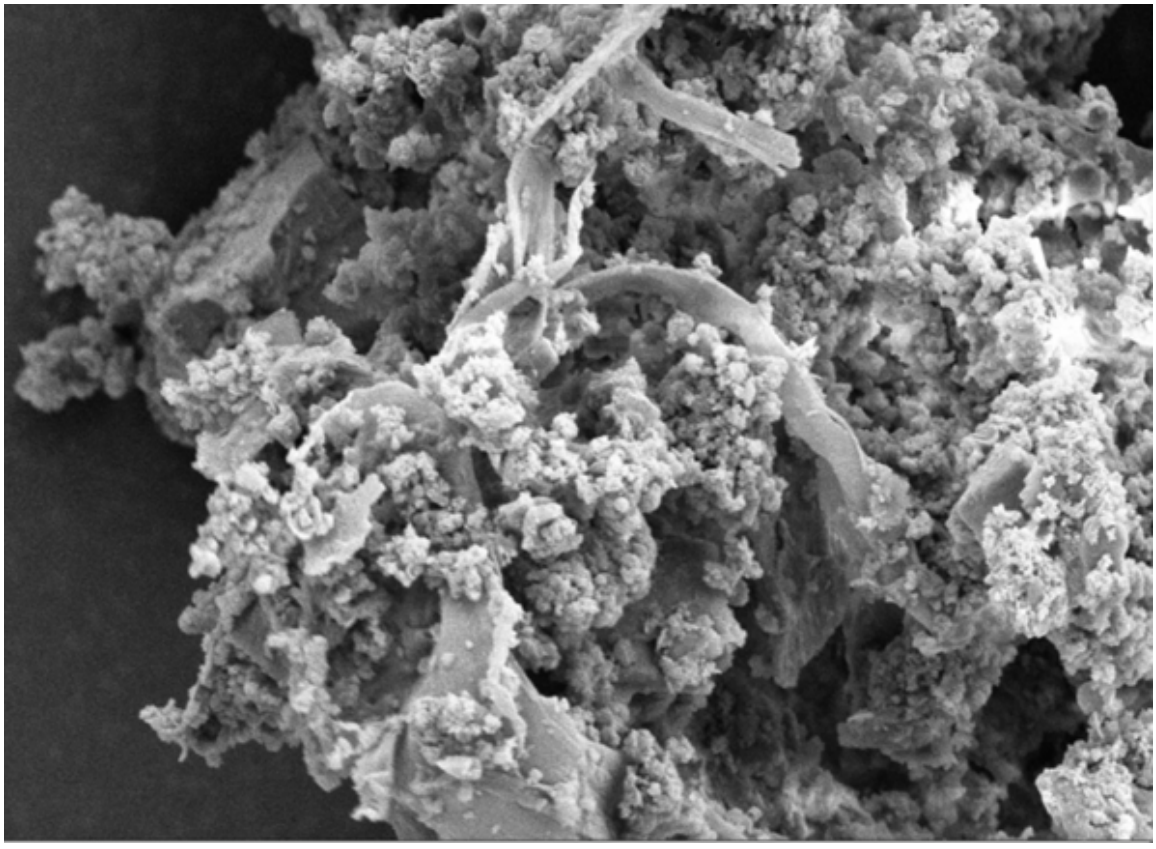

Fig. 5.6 SEM micrograph of SS char

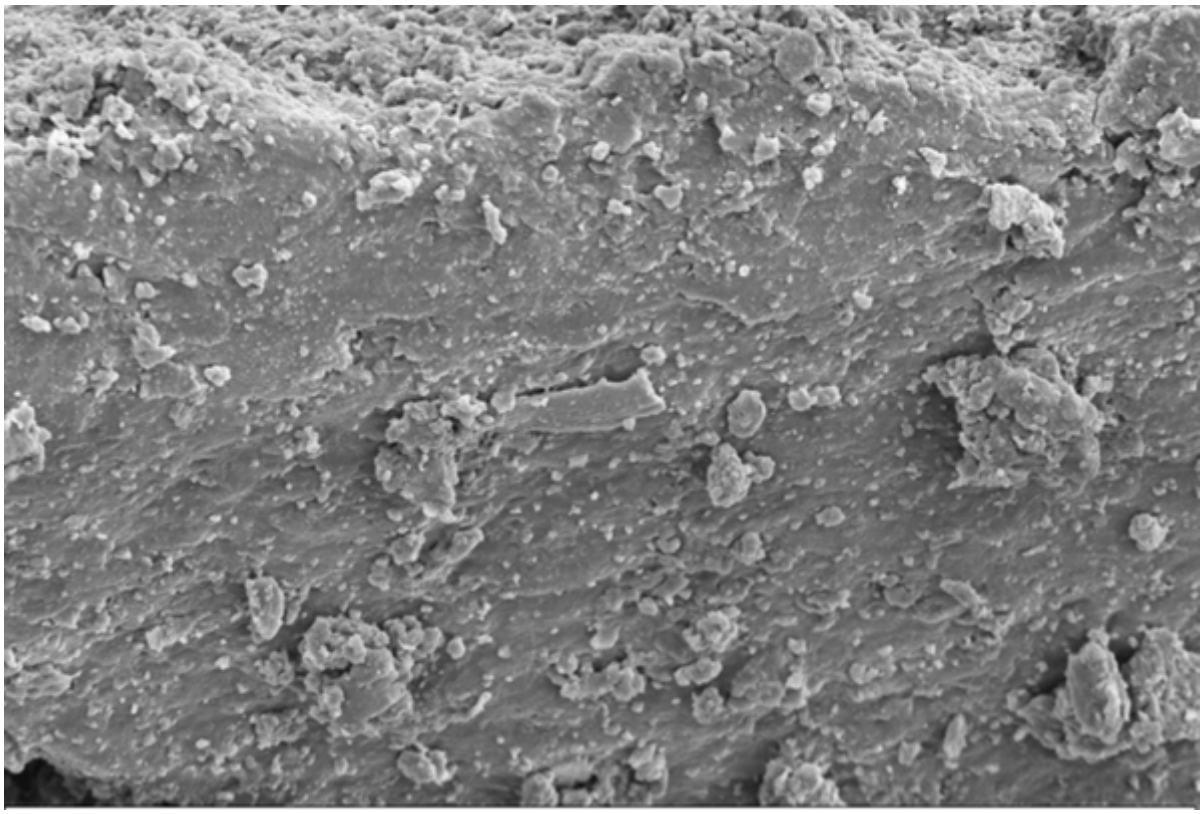

Fig. 5.7 SEM micrograph of unprocessed HFS

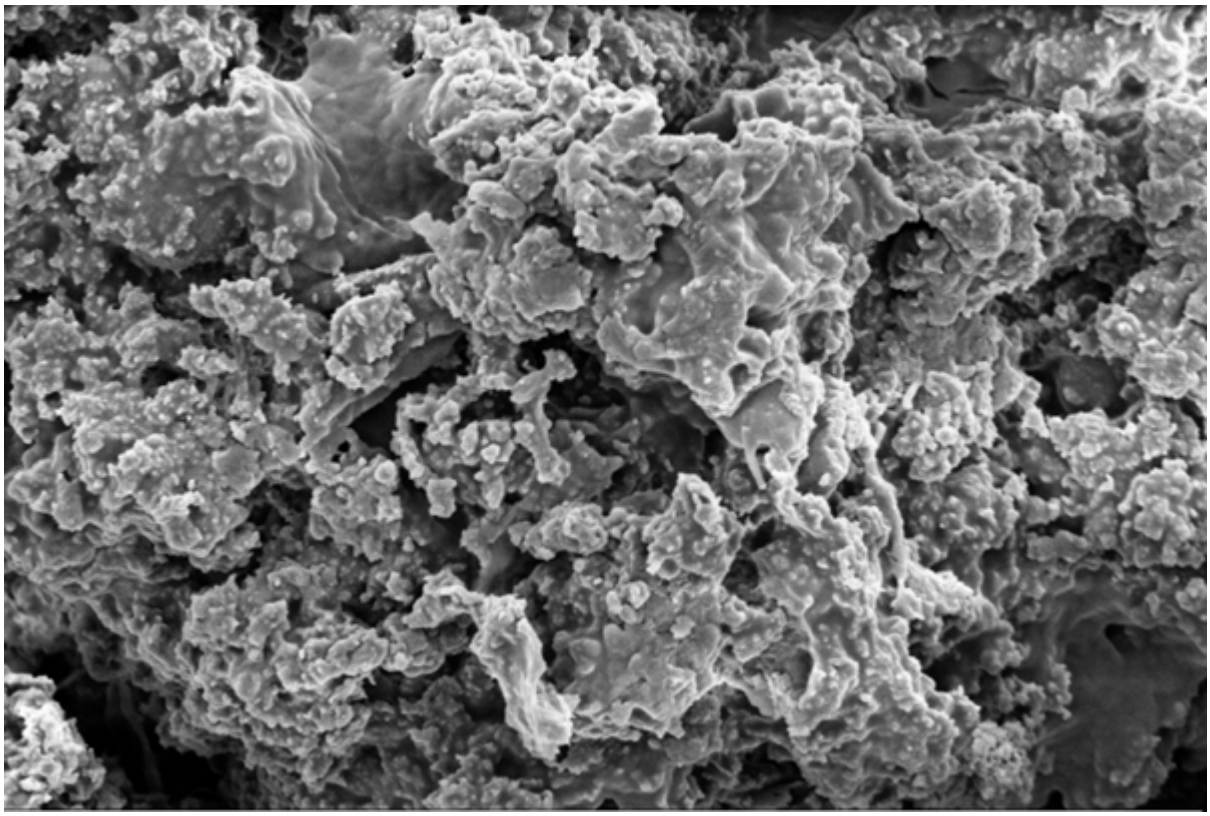

Fig. 5.8 SEM micrograph of HFS char

Fig. 5.9 SEM micrograph of unprocessed FSS

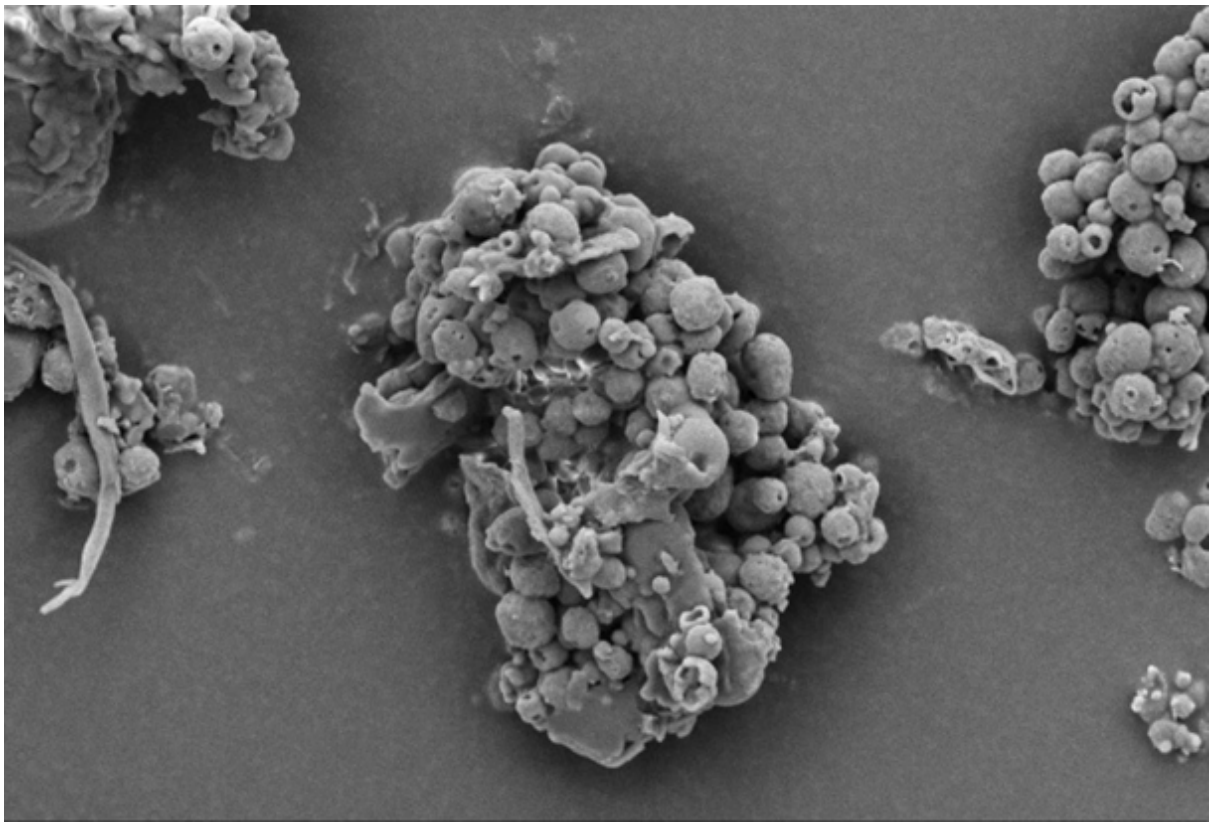

Fig.5.10 SEM micrograph of FSS char

The morphology of all the chars (Fig. 5.4 – HF char; Fig. 5.6 – SS char; Fig. 5.8 – HFS char; and Fig. 5.10 – FSS char) contains extensive hollow and porous structures, suggestive of devolatilization occurring during M-HTC (29; 30). The FSS char (Fig. 5.10) has agglomerations of well-defined spherical features, in contrast to the other chars' tampered structures intersected with tunnels. Devolatilization reactions, e.g. decarboxylation, dehydration, have been mentioned with the temperature ranges associated with HTC (31; 32). The hollow-like/porous features which characterize the chars' microstructures after M-HTC may be partly due to the selective heating of microwaves on water molecules and other polar substances within the unprocessed biowastes materials. This subsequently leads to thermal dissociation of bound water, and decomposition and dissolution of organics within the feedstock structure, leaving the tunnelling effects seen on the char structures (33). This would imply chars were formed by the direct conversion of solid biowastes due to these reactions. This conversion route for unprocessed HBW (except for the FSS samples) agrees with previous studies on char conversion from different feedstocks at about 180–230°C: sewage sludge at 200°C (2); lignocellulosic biomass e.g. corn digestate and rice straw at 230°C (34); and xylose, wood meal, lignin at 225°C (27). It is worth stating that most studies have maintained solid-to-solid char formation conversion route as the key or sole pathway of char formation (27; 34; 35).

5.2.2.2 Induced nucleation, polymerization of dissolved intermediates

The SEM micrograph of FSS chars looks entirely different from the others, as it reveals spherical, hollow-like features (see Fig. 5.10), as reported previously (29; 36; 37; 38). The formation of regularly shaped, hollow carbon microspheres from glucose and fructose solutions is well studied and known (39; 40). Such microspheres are formed from induced nucleation and polymerization of dissolved soluble intermediates (mainly furfural compounds including 5-hydroxymethylfurfural [5-HMF], furfural and 5-methylfurfural) when glucose, for example, is heated to temperatures similar to HTC conditions (28; 41). At 120°C to 140°C, fructose solution undergoes intermolecular dehydration to HMF (36). Another study which also reported the formation of carbon spheres from glucose under HTC conditions of 160°C to 180°C, further mentioned that after glucose hydrolysis, 5-HMF forms (37). These studies also concluded that the HMF intermediates were susceptible to subsequent polymerization/polycondensation reactions, leading to the formation of hollow carbon microspheres.

The formation of the FSS chars appears to follow this mechanism, as FSS is a cellulose-based recipe (see Table 3.1 in Chapter 3). The thermal hydrolysis of cellulose during M-HTC forms reducing sugar monomers, including glucose, which can exist in isomerism with fructose (2; 42). Intermolecular dehydration of these reducing sugars under HTC conditions leads to the formation of dissolved soluble intermediates, i.e. HMF, which subsequently undergo polymerization – characterized by further intermolecular water loss and forming spherical hollow char particles similar to those shown in Fig. 5.10.

In essence, both conversion pathways can be related to in the present study as modelled in Fig. 5.11. While the SEM micrographs of chars from SS, HFS and HF agree with the solid-to-solid conversion model (as no spherical particles were found on their structures), the FSS char micrographs agree with the secondary pathway. What is quite unknown is the extent to which the conversion pathways contribute to char formation, as the effect of the Maillard reactions (i.e. smell and colour changes due to reactions of reducing sugars monomers from the carbohydrate contents in HBW and cellulose in faecal simulant) are seen across all the feedstock used. One study used cellulose as a HTC substrate and argued that both pathways occurred during conversion to char; however, it maintained that at certain temperature ranges <200°C, the solid-solid conversion route predominates (26). Although the knowledge of char formation mechanisms from complex and heterogeneous substrates such as human faecal biowastes is still evolving, SEM studies conducted for the present study indicate the solid-to-solid conversion route to be the predominant pathway for HBW at the temperature used. Note also that conversion pathways during HTC may be sensitive to the nature/type of biomass substrate used, as the FSS chars support the second pathway (as evident in the proliferation of hollow microspheres, despite using the same process parameters for all the biowaste feedstocks). In summary, SEM studies of this work further confirm the evidence of thermochemical conversion of HBW during the M-HTC process and further support the hypothesis of char generation under M-HTC.

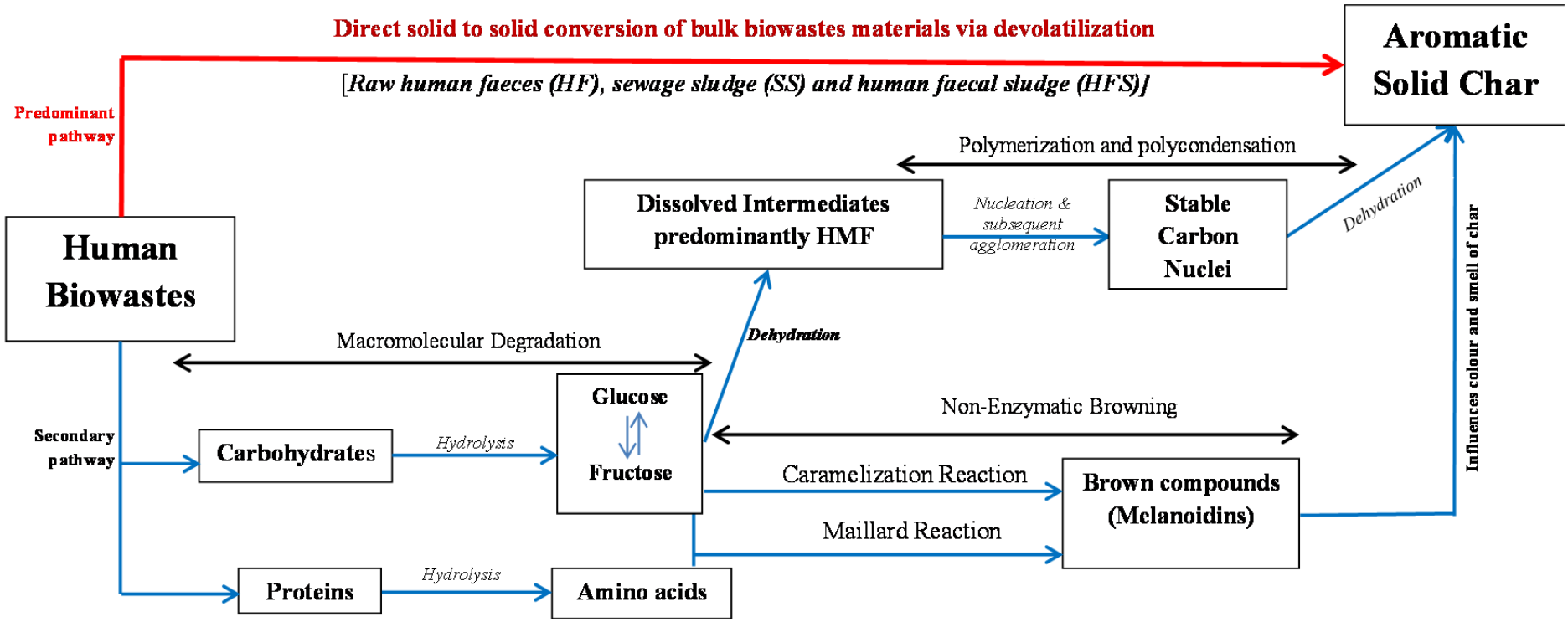

Fig.5.11 Schematic model of char formation from HBW

5.3 PATHOGEN DESTRUCTION IN CARBONIZED MATERIALS

Previous studies have indicated that the elevated temperature ranges, i.e. ≥140°C, can effectively kill bacterial pathogens (notably E. coli and helminthic eggs) (43). Further, high-temperature treatments can deactivate xenobiotic and endocrine-disrupting compounds in biowastes (10), producing end products free of biologically active organisms and bioactive exogenous compounds (44). Disinfection studies on sewage sludge (as the closest alternative to real human faecal sludge) at lower temperatures (70°C ≥ T ≤ 100°C), shorter residence times (≤ 30mins.) and different heat sources (i.e. conventional heating or microwave irradiation) have demonstrated efficacy (45; 46; 47; 48). Indeed complete destruction of pathogens in sewage sludge has been reported at 68°C under microwave irradiation (48).

No published research has reported M-HTC disinfection outcomes on human faeces. Hence the present study to establish the efficacy of M-HTC disinfection and to assess if the products of M-HTC are safe to handle and comply with relevant safety/health regulations and international guidelines, e.g. WHO (49). Comparative pathogen destruction tests were conducted on HFS, using both M-HTC and C-HTC processes and procedures as described in Section 4.4.19.

5.3.1 Effects of M-HTC on total coliforms (TC) and faecal coliforms (FC)

The figures below show the appearance of membranes used to test for faecal coliforms (FC) for unprocessed HFS (Fig. 5.12), and processed HFS under M-HTC (Fig. 5.13) and C-HTC (Fig. 5.14) respectively, after an incubation period of 18hrs.

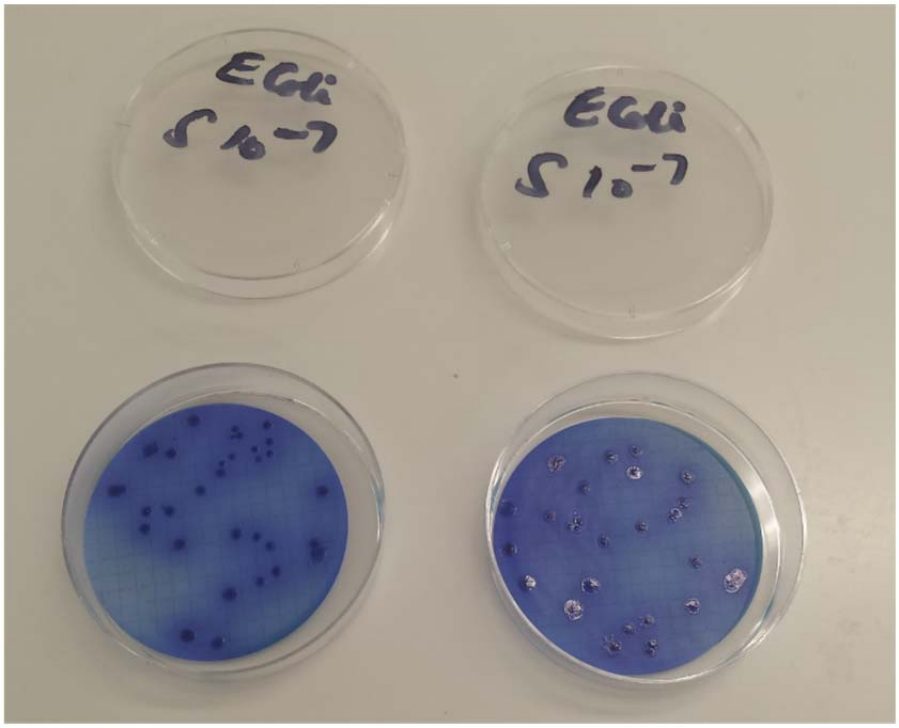

Fig. 5.12 Appearance of membrane of unprocessed HFS (diluted at 10^{-7}), showing the presence of blue FC colonies

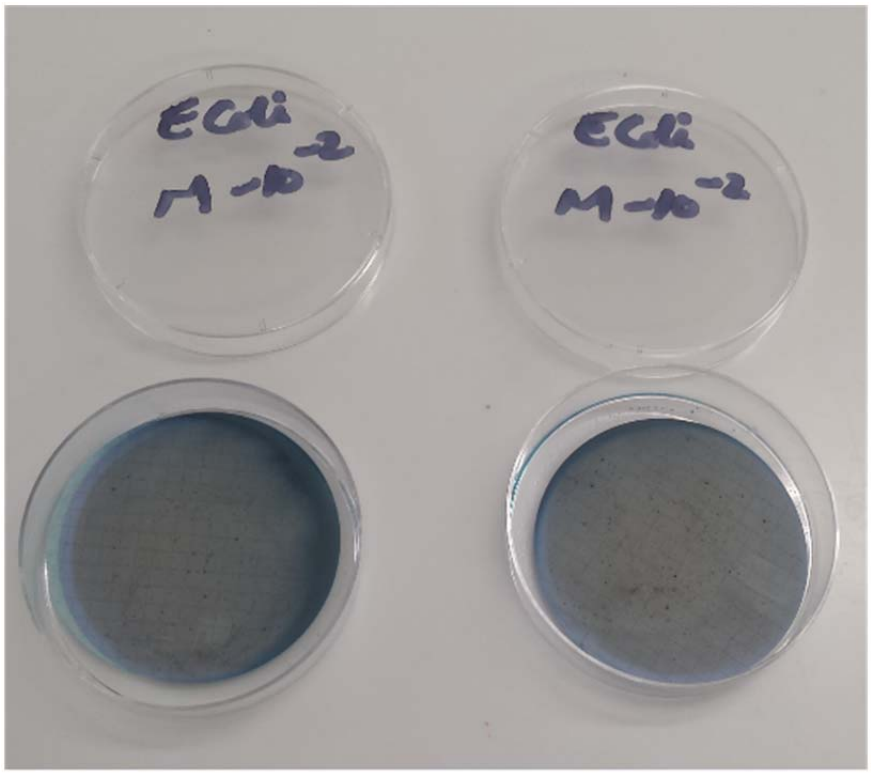

Fig. 5.13 Appearance of membrane of treated HFS using M-HTC (diluted to 10^{-2}). No blue FC colony was found after treatment

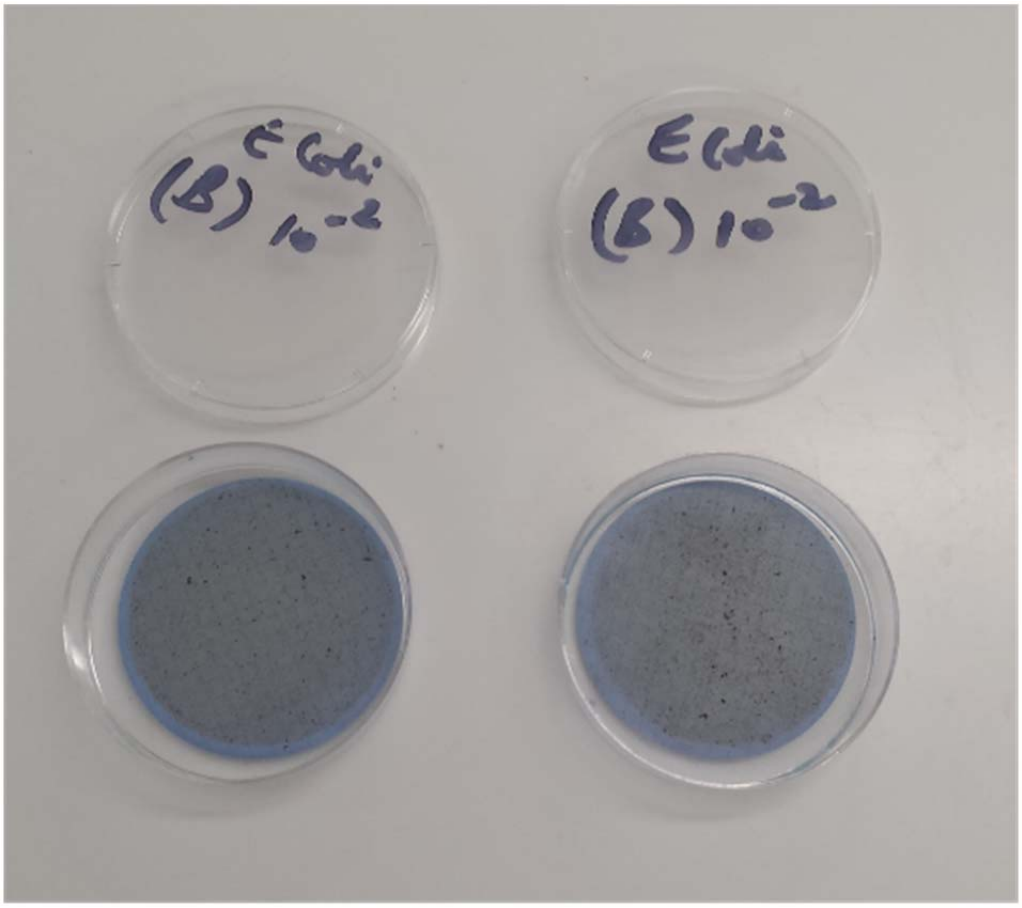

Fig. 5.14 Appearance of membrane of treated HFS using C-HTC (diluted to 10^{-2}). No blue FC colony was found after treatment

Faecal coliform-forming units (CFU) (denoted by blue colony coloration) were observed from unprocessed HFS samples (down to dilutions of 10^{-7}, see Fig. 5.8). No CFU were found on membranes from the carbonized liquors involving different heating sources at any dilution (Figs. 5.13 and 5.14).

These same results were obtained for total coliform units (denoted by pink coloration) – see Figs. 5.15 to 5.17.

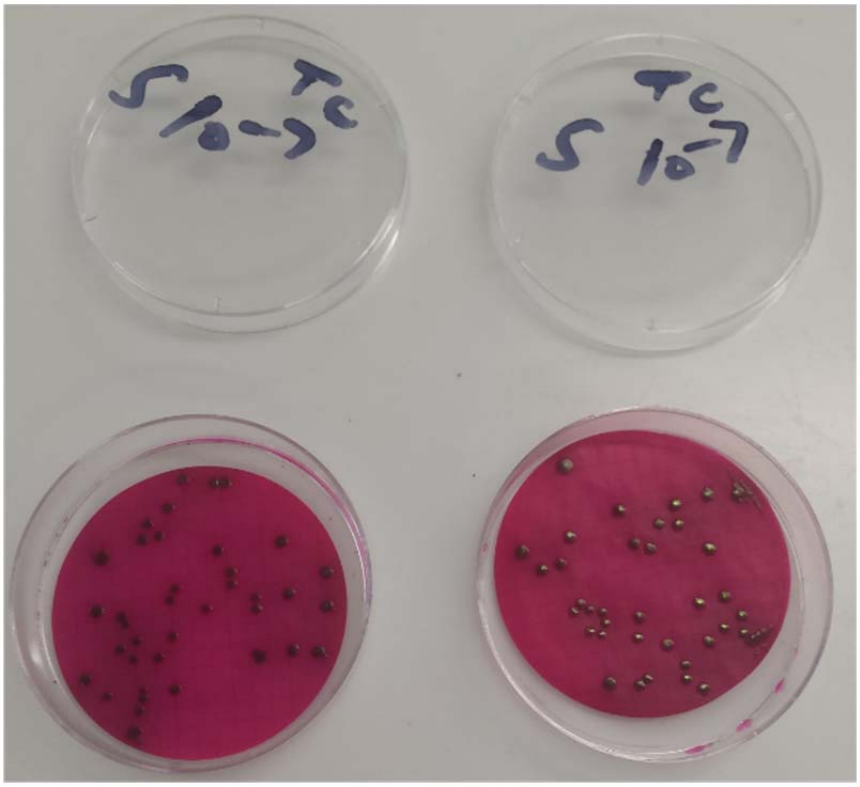

Fig.5.15 Appearance of membrane of unprocessed HFS (diluted at 10^{-7}) showing the presence of pink TC colonies

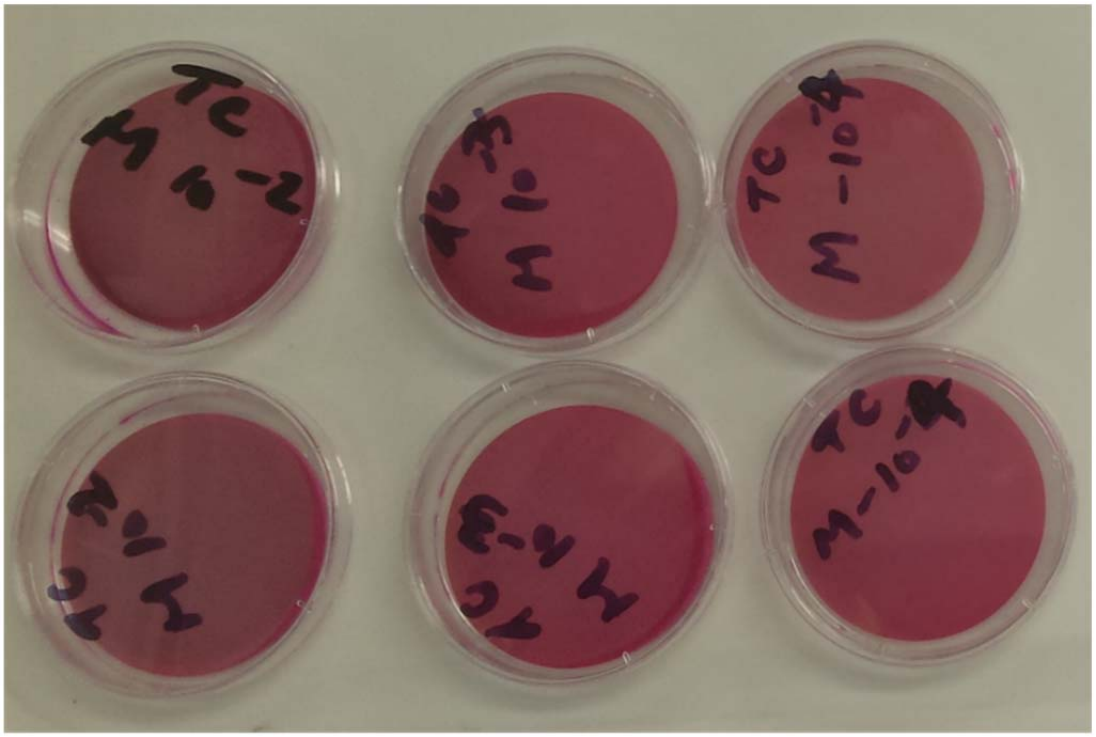

Fig. 5.16 Appearance of membrane of treated HFS using M-HTC (diluted to 10^{-2}, 10^{-3} and 10^{-4}). No pink TC colony was found after treatment

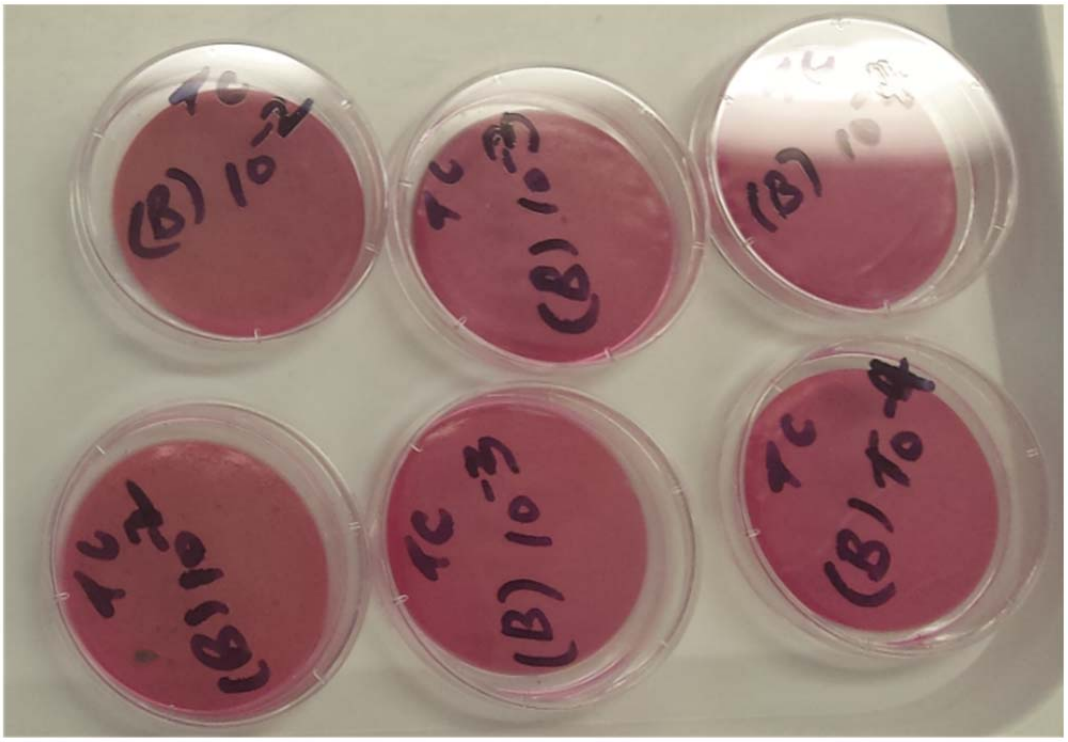

Fig. 5.17 Appearance of membrane of treated HFS using C-HTC (diluted to 10^{-2}, 10^{-3} and 10^{-4}). No pink TC colony was found after treatment

The amount of colony-forming units (CFU) per 100ml of the tested samples was quantitatively estimated (see Table 5.2).

Table 5.2 Coliform forming units (CFU) in tested samples after 18hrs of incubation

Sample	Sampling ID	TC counted (avg.)	FC counted (avg.)	Avg. TC (CFU/100ml)	Avg. FC (CFU/100ml)
Carbonized samples	C_HTC L 10^{-1}	0	0	< 1coliform/100ml (adopting standard nomenclature)	
	C_HTC L 10^{-2}	0	0		
	C_HTC L 10^{-3}	0	0		
	C_HTC L 10^{-4}	0	0		
	M_HTC L 10^{-1}	0	0		
	M_HTC L 10^{-2}	0	0		
	M_HTC L 10^{-3}	0	0		
	M_HTC L 10^{-4}	0	0		
Unprocessed	Unprocessed_ 10^{-4}	TNTC*	TNTC	Not estimated	
	Unprocessed _ 10^{-5}	TNTC	TNTC		
	Unprocessed _ 10^{-6}	TNTC	TNTC		
	Unprocessed _ 10^{-7}	37	30	740,000,000	600,000,000
	Unprocessed _ 10^{-8}	< 20 i.e. Counts below representative counts required		Not estimated	
	Unprocessed _ 10^{-9}				

*TNTC –Too numerous to count

Table 5.2 summarizes the levels of TC and FC in the unprocessed HFS to be 740M CFU/100ml and 600M CFU/100ml respectively; these are comparable to levels found in septic tanks and primary treatment tanks in conventional sewage treatment processes (50; 51; 52). No colony was detected in the treated HFS samples from both M-HTC and C-HTC. This finding is supported by other disinfection studies (45; 46; 53; 54) and indicates that HTC can be used to disinfect HBW, regardless of the heat source.

5.3.2 Health and regulatory implications

These results are significantly below the required limits and satisfy the WHO guideline values of <1000 colonies/100ml of faecal coliforms in processed faecal sludge, particularly for agricultural application purpose (49). These findings also suggest that M-HTC products would satisfy the Class A sludge classification of the United States Environmental Protection Agency (US EPA) (55). The products from M-HTC of HBW can be considered safe to handle, and fit for use or disposal purposes. Hence, M-HTC is a candidate for biowaste management technology that effectively disinfects HFS. In contrast, conventional sewage treatment plants and the other potential technologies described in Chapter 2 – for example, the freeze-thawing technology (56) – do not generate completely disinfected products and have yet to meet regulatory safety standards. In many cases, pathogenic load reduction did not meet Class B Biosolids (<2 $x10^6$ $MPN.g^{-1}$ of dry solids) (57) and cannot be considered completely safe for use/disposal without safety and precautionary measures, according to the WHO guidelines (49).

5.4 EVALUATION OF THE VALUE–ADDED PRODUCTS FROM M-HTC PROCESSED HBW

The exploration of the feasibility of generating intrinsically valuable material(s) from M-HTC processed HBW (char and liquid ammonia concentrates) focussed on the SS and HFS feed stocks in this section, due to their relevance beyond laboratory studies.

5.4.1 Char yield from HBW under M-HTC

Fig. 5.18 shows the solid char yield (dry basis) (%) recovered from both the HFS and SS feedstocks respectively at different reaction temperatures and residence times used during the M-HTC process.

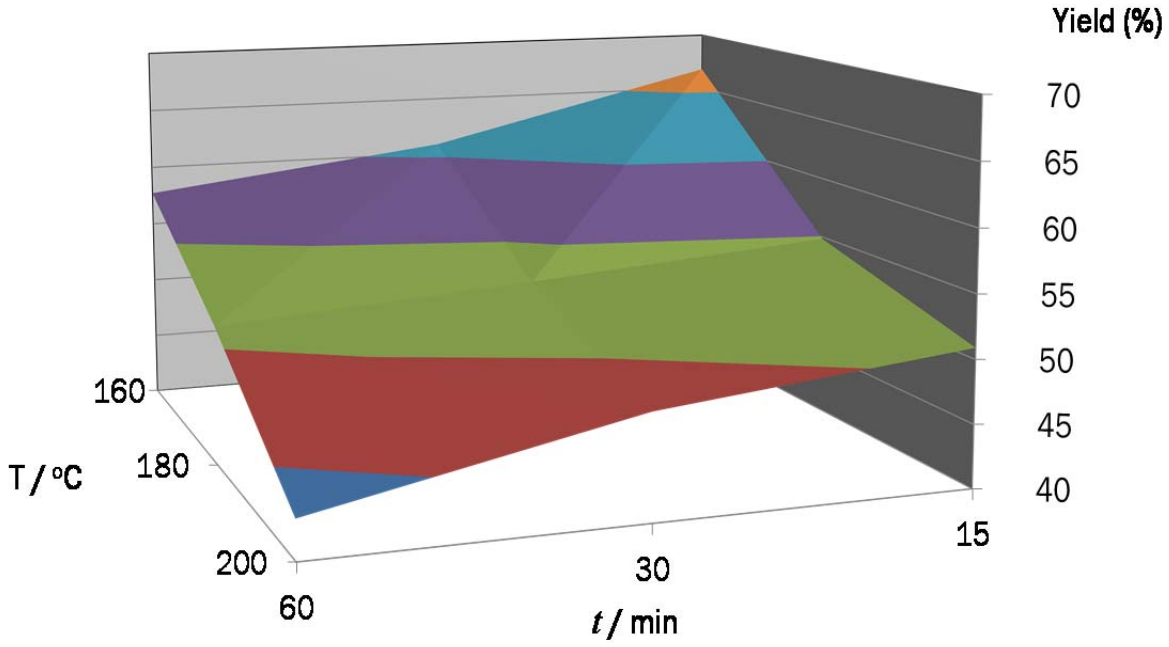

Fig.5.18 Summary of temperature and time study on char yield from SS and HFS (where possible, data has been averaged)

From Fig. 5.18, the highest char yields were recorded at the lowest temperature and shortest residence time used during the M-HTC process: up to 67% of char was recovered from both feedstocks at these conditions. Char yield, however, decreased gradually as the process parameters (i.e. temperature and residence times) increased, with both substrates behaving the same way. Over the temperature and residence times used, char recovered from both substrates decreased by up to 16%. Char yield from the HTC process is sensitive to the type, nature and compositional characteristics of feedstock, including initial solid loading/moisture content, among other factors (31). This may explain the yield observed from both substrates, although slight differences in solid loading must be noted (See Table 3.2).

The range of char (yield) recovered in the present study is similar to that reported in other studies (58; 59; 60), which all involved microwave as the heating source, although with different feedstocks and pre-treatments. More than 50% conversion efficiency of biowastes to solid char from the M-HTC process is feasible using 180 °C as a benchmark, as this temperature can both ensure pathogen kill (See Section 5.3) and carbonization of HBW.

5.4.1.1 *Influence of temperature and residence time during microwave heating*

As shown in Fig. 5.18, char yields from both substrates were influenced in a similar way under the same temperature and residence times. The influence of both parameters on char yield was investigated using SS as a representative substrate. The relative solid mass loss from starting SS material through solubilization during M-HTC (i.e. the percentage of solids transferred into liquor phase relative to starting material) at four temperature regimes and three residence times is shown in Fig. 5.19.

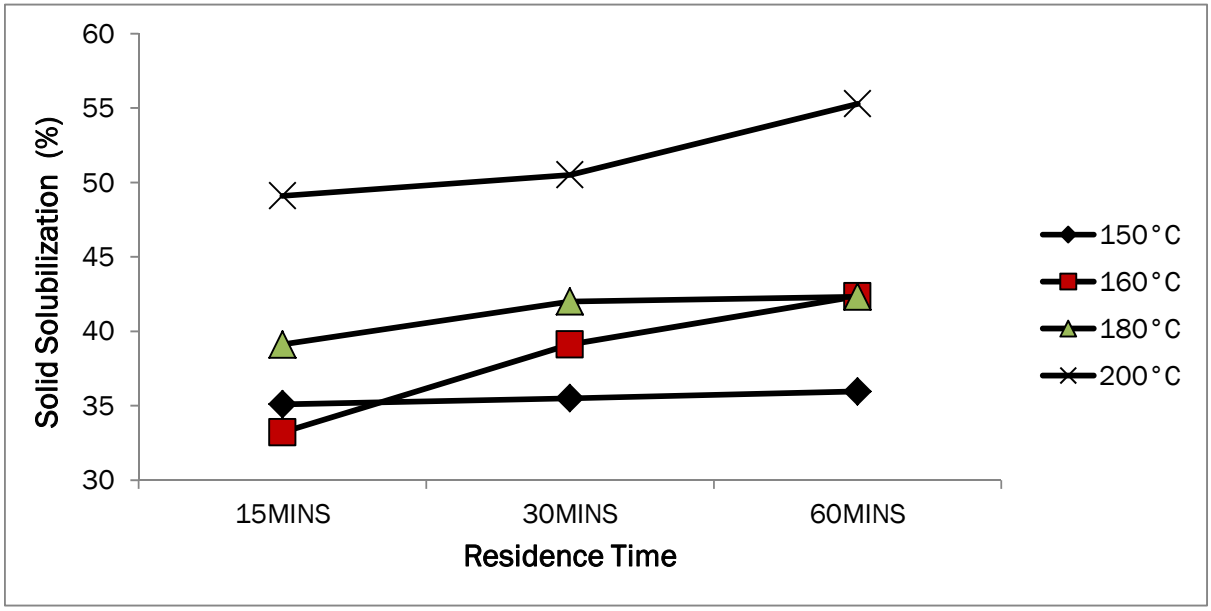

Fig. 5.19 Solubilization of SS as a function of temperature and residence time

From Fig. 5.19, increasing temperature can be seen to promote solids solubilization (and consequently decreasing yield of char) more significantly than increasing residence time. For example, at 60min. residence time increasing temperature from 150°C to 200°C resulted in a 20% increase in solids solubilization. This contrasts with the ca. 5% increase in solubilization observed when residence time was increased from 15min. to 60min. at 160°C, 180°C and 200°C respectively. Further it can be deduced from Fig. 5.19 that no significant solubilization occurred after 15mins. of residence time during the HTC process. The rate of mass loss ($g.s^{-1}$) at this residence time for all the temperature regimes is depicted in Fig. 5.20.

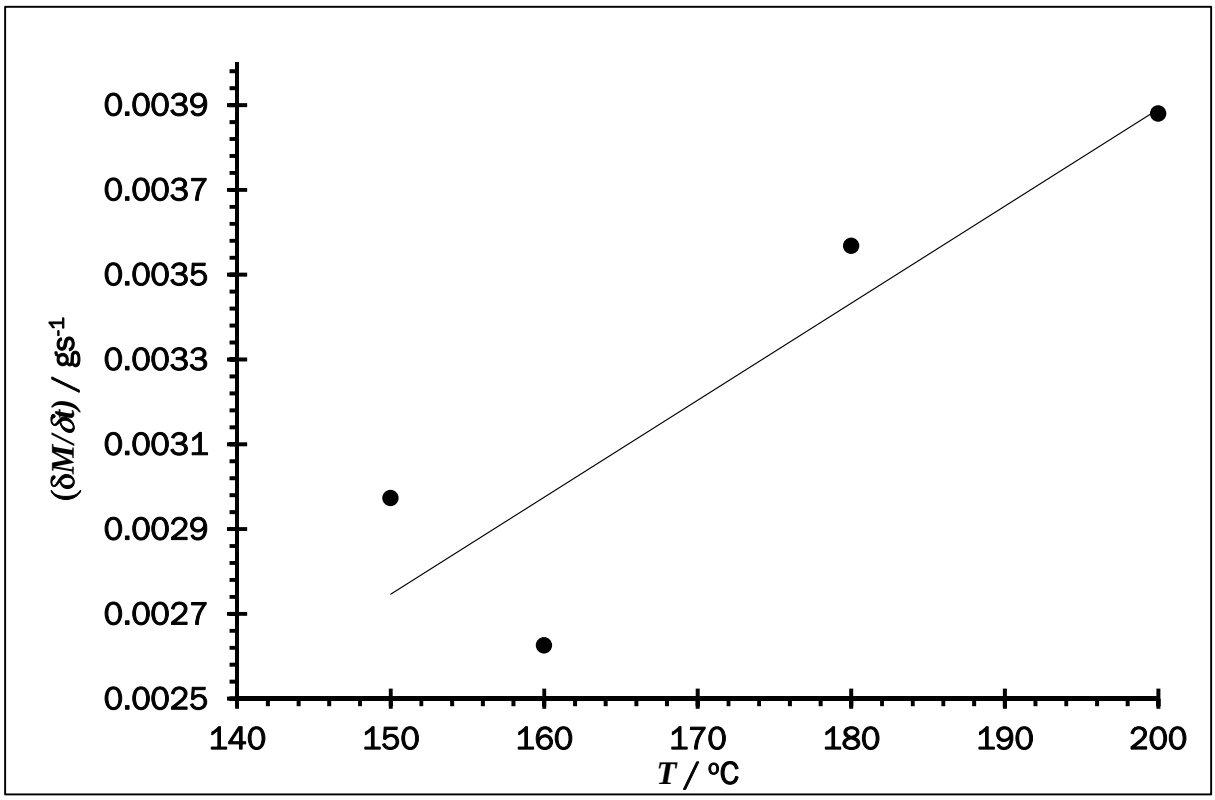

Fig.5. 20 Rate of mass loss of SS with increases in temperature for the shortest residence time (15mins.) (R^2 = 0.9)

Over the temperature range investigated in Fig. 5.20, the relative mass loss of starting SS increased from 150°C to 200°C at a corresponding rate of 0.0028g.s^{-1} to 0.0039g.s^{-1} respectively. In other words, char yield is occurring at a decreasing rate as temperature is increased (residence time, 15mins). Similar observations of a decrease in char yield with increasing temperature (this being the most influential parameter during the HTC process) have been reported with a range of heating methods and feedstocks (59; 61; 62; 63).

5.4.2 Recovery of ammonia concentrate liquor

Figs. 5.21 and 5.22 show the concentration of ammonia (mg.l^{-1}) in liquor recovered from carbonized HFS and SS respectively.

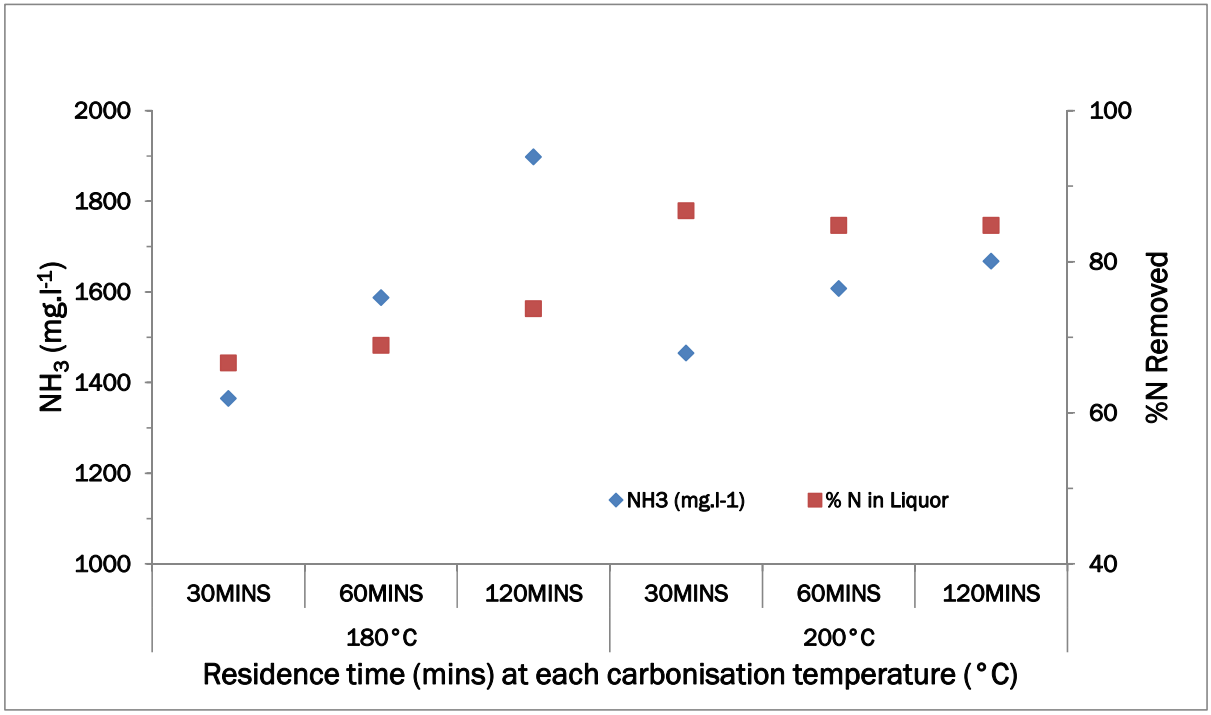

Fig. 5.21 Ammonia (mg.l^{-1}) in liquor recovered from HFS

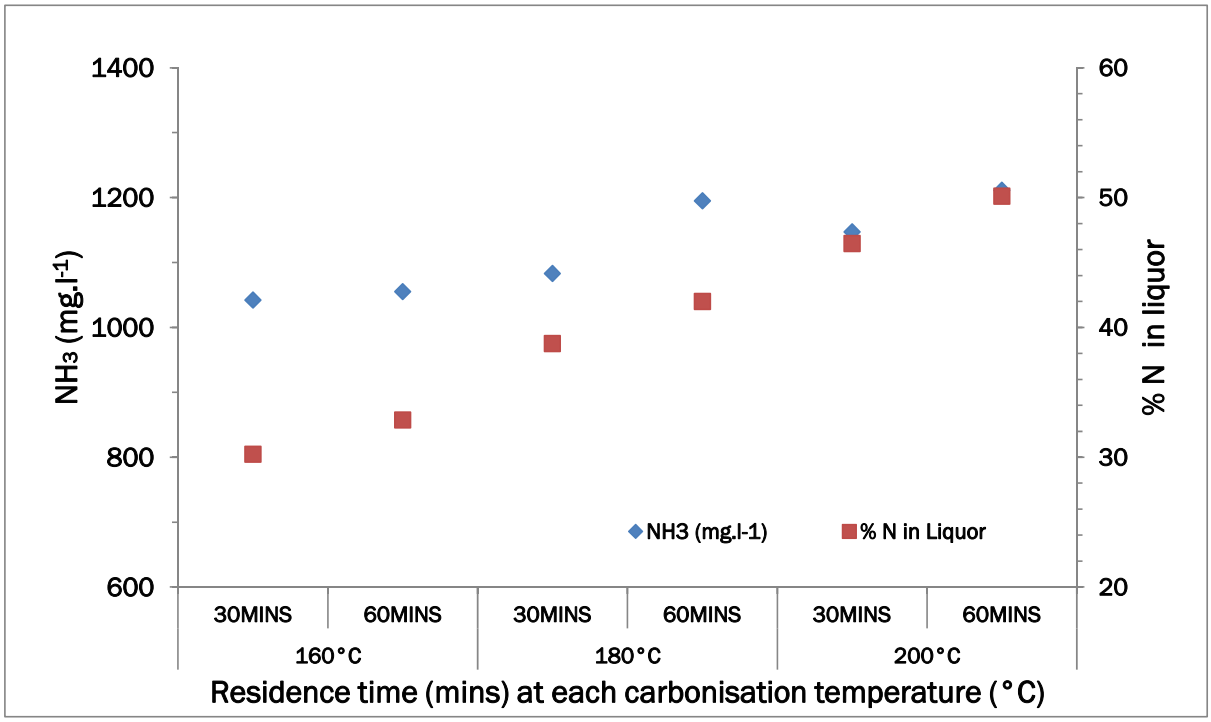

Fig. 5.22 Ammonia (mg.l^{-1}) in liquor recovered from SS

In most cases, more than 1g.l^{-1} of ammonia was recovered from both feedstocks, and the concentration of ammonia recovered was observed to depend on the feedstock, with more recovered from HFS than SS. For example, at 180°C and 60min., 1055mg.l^{-1} and

1588 mg.l^{-1} were recovered from SS and HFS respectively. This may be attributed to the presence of urine in the HFS feedstock. Similar recoveries were observed at 200°C at 30min. and 60min. residence times.

Ammonia recovery was observed to increase with temperature and residence time, and this is similar to previous studies (9; 10; 64) and consistent with nitrogen (N) depletion from unprocessed biowaste solids into the liquor phase (Fig. 5.21 and 5.22). Mass balance of nitrogen reveals up to 50% and 84% were depleted from unprocessed SS and HFS respectively into the liquor phase. Basically, protein and other nitrogenous compounds are the sources of N in the unprocessed biowastes. At temperatures greater than 160°C, these compounds are hydrolysed 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 (64), which further illustrates the increasing concentration of ammonia recovered from both SS and HFS as temperature increased to 200°C.

In essence, the M-HTC process flushes N-content in the solid phase of HBW into the liquor phase. A similar observation was recorded with the C-HTC process, as shown in Fig. 5.23. Comparatively, the conventional process recovered a slightly higher concentration of ammonia at 180°C and 200°C than M-HTC. This may be due to the longer residence of the conventional process.

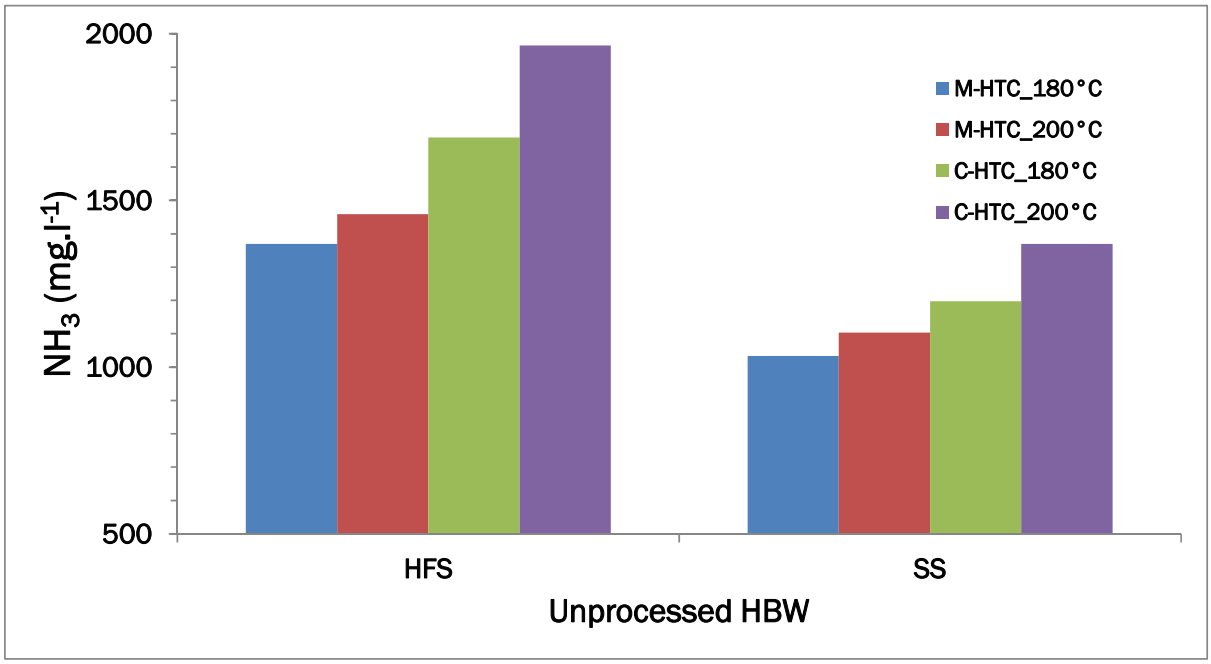

Fig. 5.23 Ammonia recovery under microwave and conventional heating

The level of ammonia in the liquor phase 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 M-HTC process.

5.4.3 Improved carbon solubilization

Chemical oxygen demand (COD) values indicate the fractions of carbon transferred into the liquid phase from hydrolysis and solubilization of organic and inorganic components during M-HTC. Apart from disposal processes, soluble COD is a helpful measure for assessing liquor use as a substrate for anaerobic digestion (AD) (65). Table 5.3 summarizes COD for HFS and SS liquors (21g.l^{-1} to 26g.l^{-}1). These values are comparable with other studies (10; 11), indicating utility for anaerobic digestion. Temperatures in the range 160°C to 180°C are considered to be optimal for generating AD feedstock from biowastes based on COD concentration (10, 66). Higher temperatures were reported to decrease the biodegradability of sludge (65; 67). This is because temperatures >200°C promote the production of highly soluble organics or toxic inhibitory intermediates detrimental to the methanogenesis phase of anaerobic digestion, and hence may affect methane yield (68; 69).

Table 5.3 COD and other properties of HTC liquor from HFS and SS

	HFS						SS					
	180°C			200°C			160°C		180°C		200°C	
t / min	30	60	120	30	60	120	30	60	30	60	30	60
pH	7.8–8.6						3.5 – 5.0					
VFA ($g.l^{-1}$)	6.7 ± 0.5	6.7 ± 0.1	6.5 ± 0.2	6.6 ± 0.2	6.5 ± 0.3	6.9 ± 0.3	5.2 ± 0.1	6.0 ±0.6	6.8 ± 1.0	5.8 ± 0.2	5.9 ± 0.1	7.2 ± 0.1
COD ($g.l^{-1}$)	21.3 ± 0.9	26.4 ± 0.6	25.7 ± 0.7	25.9 ± 0.2	26.4 ± 1.3	26.1 ± 0.6	21.2 ± 1.1	26.2 ± 0.9	21.4 ± 2.6	25.8 ± 0.2	23.6 ± 1.2	26.7 ± 0.2
TOC ($g.l^{-1}$)	7.8 ± 0.3	7.8 ± 0.1	7.2 ± 0.1	7.5 ± 0.3	7.7 ± 0.1	7.1 ± 0.1	8.9 ± 0.2	7.4 ± 0.2	9.3 ± 0.6	7.8 ± 0.1	8.5 ± 0.1	8.3 ± 0.2
TS ($g.l^{-1}$)	16.4 ± 0.1	17.1± 0.03	16.3 ± 0.1	16.3 ± 0.1	15.5 ± 0.3	15.1 ± 0.2	17.7± 0.3	17.0 ± 0.3	15.9± 0.03	15.0±0.1	13.2 ± 0.3	12.1 ± 0.2
VS ($g.l^{-1}$)	13.0 ± 0.3	13.5 ± 0.01	12.7 ± 0.1	12.7 ± 0.1	11.9 ± 0.2	11.5 ± 0.04	15.1 ± 0.3	14.5 ± 0.2	13.2±0.03	12.6 ± 0.1	10.7± 0.3	9.6 ± 0.1
FS ($g.l^{-1}$)	3.4 ± 0.3	3.6 ± 0.01	3.5 ± 0.1	3.6 ± 0.1	3.5 ± 0.2	3.7 ± 0.04	2.6 ± 0.3	2.6± 0.2	2.7± 0.03	2.5 ± 0.1	2.5 ± 0.3	2.5 ± 0.1
TSS ($g.l^{-1}$)	1.2 ± 0.4	1.6 ± 0.1	1.6 ± 0.3	1.6 ± 0.2	1.8 ± 0.4	1.8 ± 0.5	0.8 ± 0.2	0.9± 0.1	0.8± 0.2	0.7 ± 0.3	0.7 ± 0.2	1.0 ± 0.3
TDS ($g.l^{-1}$)	15.2± 0.4	15.5 ± 0.	14.7 ± 0.3	14.7 ± 0.2	13.7± 0.4	13.3 ± 0.5	16.9 ± 0.2	16.1± 0.1	15.1± 0.2	14.3± 0.3	12.5± 0.2	12.1± 0.3

Where: VFA – Volatile fatty acids

COD – Chemical oxygen demand

TOC – Total organic carbon

TS – Total solids in the HTC liquor

VS – Volatile solids in the HTC liquor

FS – Fixed solids in the HTC liquor

TSS – Total suspended solids

TDS – Total dissolved solids

5.5 COMPARATIVE PROCESS EFFICIENCY BETWEEN M-HTC AND C-HTC

The potential advantages of M-HTC over C-HTC in terms of biowaste process conversion efficiency, throughput and energy consumption were investigated. The four HBW substrates (ca. 160g for SS; 200g for FSS, HF and HFS respectively) were processed under both microwave and conventional heating at laboratory scale at 160°C, 180°C and 200°C. Char yield, average processing rate, i.e. average rate for processing each biowaste, and energy consumed were monitored.

5.5.1 Comparative char yield assessment

Table 5.4 shows the char yield recovered and the average processing time required to achieve carbonization. Here the conventional heating process tends to produce higher char yields with increasing temperature when compared with the microwave process across the HBW substrates, with the exception of SS.

Table 5.4 Comparative char yield (%) from microwave and conventional heating

Heating source	HBW substrates	Temperature range (°C)			Average processing time (hrs.)#
		160°C	180°C	200°C	
		Char yield (%)			
Microwave	SS	61.3	54.4	50.5	0.75
	FSS	51.2	32.5	27.2	
	HF	52.4	45.5	37.6	
	HFS	NF*	52.1	47.1	
Conventional (external hot plate heater)	SS	60.2	52.4	46.0	5
	FSS	51.0	40.4	37.5	
	HF	57.5	50.6	46.0	
	HFS	NF*	54.4	50.3	

* Preliminary experiments indicated that this temperature was *not feasible (NF)* for HFS

\# Average processing time includes the warming time to peak temperature and holding time at that temperature. When cooling time is included, M-HTC will take ≈20mins. to cool down to room temperature (due to the enhanced cooling provided for by the control features of the microwave system), while it will take 3-4 hours for the conventional process to cool down, depending on peak temperature used. Cooling time was not included.

Differences in char yield from microwave and conventional heating have also been mentioned with different feedstocks. One study (60) recovered 39.8% and 27.3% of char from treating willow chips under conventional and microwave heating processes respectively. However, differences in the heating rates, sample sizes and temperatures used in this work may have influenced the char yield: while char yield was measured at 170°C from the microwave process, 350°C was used for the conventional process.

Another study (70) also reported 33.7% and 49.9% char yield from straw pellets under microwave and conventional processes respectively, also at these temperature ranges. Generally, depending on type, characteristics (among other factors) of feedstock, an average 50–80% in char yield are typical of HTC processes within temperature ranges of 180–250°C, regardless of the heating source (31; 71; 72). Different yields are also characteristic of different feedstock properties, with moisture content and percentage solid loading being very crucial (73; 74).

5.5.2 Process time and throughput

When the overall process time required for processing unprocessed HBW is taken into account, the char recovery/processing rate from unprocessed HBW is significantly higher for microwave than for conventional processes, as shown in Table 5.5.

Table 5.5 HBW processing rate from both HTC methods

Heating source	Feedstock	Average wet sample mass of un-processed HBW processed /g	Total solids (TS) in unprocessed HBW (%)	Avg. unprocessed biowaste solids processing rate /g (TS) hr^{-1}
Microwave	SS	160	4.8	10.3
	FSS	200	3.7	9.8
	HF		2.9	7.8
	HFS		3.4	9.1
Conventional (external hot plate heater)	SS	160	4.8	1.5
	FSS	200	3.7	1.4
	HF		2.9	1.2
	HFS		3.4	1.4

The processing rate of M-HTC was greater than the conventional process in all cases by a factor of six. The difference in the HBW feedstock conversion/treatment rate is mainly due to differences in the heating mechanisms between the processes. For the conventional process, heat energy is transferred to material by convection and conduction from the heating source via thermal gradients to the core of the biowaste materials inside the reactor. By contrast, microwave heating – as explained in Chapter 2 – involves direct molecular vibrations, which cause dielectric heating. This leads to enhanced selective, homogenous and volumetric heating throughout the biowaste inside the microwave reactor. These attributes lead to a faster process via novel reaction pathways, potentially due to reduced activation energy (33; 75). The merit of the shorter residence time associated with microwave processing further implies higher throughputs potential, and this may represent a significant advantage over the conventional process

in terms of feedstock processing. Generally, conventional heating and other contemporary methods represent lower processing rates and potentially higher energy implications for processing biowaste. In fact, the process times used in the present study for C-HTC are relatively lower than those reported in literature, where longer processing/residence times (up to 72hrs.) have been used to convert different biomass wastes, including sewage sludge, into char products (2; 3; 1). When compared with other contemporary biowaste treatment methods, such as incineration, pyrolysis and biochemical processes, M-HTC is faster and involves significantly lower temperature regimes to process HBW (1; 2; 32; 72).

5.5.3 Energy consumption monitoring

Using a wattmeter to monitor energy consumed throughout the study, the energy expended per gram of unprocessed biowaste solid processed (Wh.g^{-1} TS) was estimated. Table 5.6 presents the energy expended during each process, i.e. M-HTC and C-HTC, comparatively with char yield recovered at each HTC temperature investigated.

Table 5.6 Comparative energy consumption and char yield

Feedstock	Temperature (°C)	Energy consumed (Wh.g^{-1}TS)		Char yield (%)	
		M-HTC	C-HTC	M-HTC	C-HTC
SS	160	103.6	194.9	61.3	60.2
	180	114.2	267.6	54.4	52.4
	200	123.3	279.3	50.5	46.0
HF	160	225.0	314.4	52.4	57.5
	180	249.1	381.0	45.5	50.6
	200	309.1	405.4	37.6	46.0
FSS	160	120.9	237.7	51.2	51.0
	180	137.2	244.5	32.5	40.4
	200	148.0	274.4	27.2	37.5
HFS	180	148.0	280.0	52.1	54.4
	200	159.8	318.1	47.1	50.3

In most cases, as shown in Table 5.6, energy required to process unprocessed biowaste solids using the conventional heating process at every other temperature considered almost doubles that required for M-HTC, despite the relatively small differences in the char recovered from both process. Additionally, as expected energy consumption increased with increasing temperature; however, the conventional 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 conventional process. This was also observed for the other biowastes processed. Basically, the higher energy consumption associated with the

conventional process as compared with M-HTC is due to the average processing time required for the process to achieve carbonization. Comparatively, M-HTC has higher process-conversion efficiency and consumes less energy when compared with the conventional process. This is similar to the conclusion of another study (60), which also identified the microwave process as being more efficient for converting willow chips into chars.

In summary, based on the small-scale laboratory experiments, the potential merits of M-HTC over the conventional heating process in terms of biowaste-processing efficiency include:

1. Faster processing times, due to rapid volumetric heating
2. Higher processing rates, due to the relatively lower residence time required
3. The lower energy requirement to convert biowaste into chars at all temperatures
4. Potential recovery of char yields close to the conventional process (less than 10% difference in many cases), despite higher energy consumption and processing time in the latter.

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CHAPTER 6 INFLUENCE OF M-HTC ON DEWATERABILITY OF SLUDGY BIOWASTE

6.1 INTRODUCTION

'Dewaterability' relates to the rate 'sludgy' materials release their water. It is an important parameter for assessing their 'filterability', which is the ease of separating the solid and liquid phases. Sludge dewatering reduces sludge volume and, most importantly, the costs of handling and transport for disposal. Dewatering is one of the crucial stages of biowaste management. The need to improve sludge dewaterability stems from its characteristic properties including rheology, high-moisture content and biological gel structure, which makes filtration or compression very difficult (1; 2). Mechanical dewatering, involving the use of vacuum separation, belt/filter presses, centrifuges and other related filter media (2; 3), is widely employed. This approach has a high-energy consumption and intensive capital expenditure. Alternative approaches to improving dewaterability include the use of sludge conditioning technologies such as:

- ultra-sonication (4);
- ozonation (5);
- addition of polyelectrolyte to sludge (6);
- addition of acids and surfactant (7); and
- a biological process involving fungal treatment (6).

Existing mechanical processes can potentially increase the energy requirement (and costs) of an off-grid self-sustainable toilet facility (8). Chemical conditioners also increase costs and can lead to secondary environmental pollution, while biological processes require a larger footprint (6). Such drawbacks require the characterization of the dewatering properties of HBW processing systems.

The nature of the end products generated by M-HTC suggests that this process may also be considered as a potential alternative for dewatering sludgy biowastes. The study objectives may be summarized as:

- testing the hypothesis that M-HTC is in and of itself a sludge dewatering technology;
- establishing optimal process temperature for enhanced dewatering properties of char products; and

- studying the underlying mechanisms behind observed changes in sludge dewaterability due to the M-HTC process.

These dewaterability studies were conducted with M-HTC and C-HTC (involving the use of an electrically heated plate). Section 6.2 discusses the approach to this study, while section 6.3 discusses the dewaterability rates of carbonized end products after M-HTC. The particle size distribution (PSD) of chars recovered from biowastes is a potentially useful measurement that is not widely reported in the literature (9; 10). PSD studies were conducted to further the understanding of the solid particle reaction during the HTC process and how it influences dewaterability (see Sections 6.4 and 6.5).

6.2 EXPERIMENTAL APPROACH

This study used primary sewage sludge (SS), which is – as has already been noted – a complex and highly variable heterogeneous biowaste, just like human faecal sludge (HFS) (see Chapter 3). The characteristics of SS used for this study are summarized in Table 6.1.

Table 6.1 Characteristics of SS used in the study

Parameter	Values
pH	5.5
Moisture content, MC (%)	95.2 ± 0.2
Total solids, TS (%)	4.8 ± 0.2
Capillary suction time, CST (S)	389.9 ± 28.9

Dewaterability rate was measured as capillary suction time (CST) according to Standard Method 2710G – Capillary suction time (CST) (11) with units of seconds. The method is widely used and indicated as the better method for measuring filterability of sludgy material over the specific resistance to filtration method (12; 13). Measurements were conducted using a CST apparatus (Triton–Type 165, Triton Electronic Ltd England). Details of the apparatus, principle of measurement and experimental procedure used are described in Chapter 4 (See Section 4.4.10). First, 160g of SS was processed under the M-HTC process at four peak temperatures of: 140°C, 160°C, 180°C and 200°C. The other process parameters were at fixed at 30mins. residence time and 900W microwave power. Microwave power was based on the microwave system power requirement (see Chapter 4), while the residence time was guided by a previous study that indicated under microwave irradiation, 30 to 60min. residence times have little effect on overall dewaterability (14). The same temperatures were used for conventional heating with a residence time of 3hrs. Measurements of MC and TS were conducted using standard methods (11). Measurements of PSD of char products were conducted using a laser

diffraction method (Standard Method ISO 13320: Particle Size Analysis – Laser diffraction methods (15); see Chapter 4, Section 4.4.11).

6.3 THE DEWATERABILITY OF CHARS FROM M-HTC OF SEWAGE SLUDGE

CST quantifies the time required for sludgy water content drawn by capillary forces to wet a piece of adsorbent chromatography filter paper positioned on three sensors. 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 (13). As shown in Fig. 6.1, dewaterability of carbonized SS material is feasible using the M-HTC process. For example, untreated SS had an average CST of 389.9±28.9s compared to 10.6±0.5s for char produced by M-HTC at 160°C; this was a significant improvement in dewaterability rate. Furthermore, dewaterability was even improved over the HTC carbonization temperature ranges used – the net effect being that the dewaterability rate of end products actually decreased with increasing temperature of carbonization. This is similar to some studies that reported about 40% improvement when pre-treated at 96°C, while at 175°C, a 75% improvement in dewaterability was reported (16–19). Another study also concluded that high-temperature ranges >150°C promoted pronounced dewaterability effects (20). In other words, the temperature ranges associated with M-HTC improved the dewaterability of sludge, with temperature identified as an important factor.

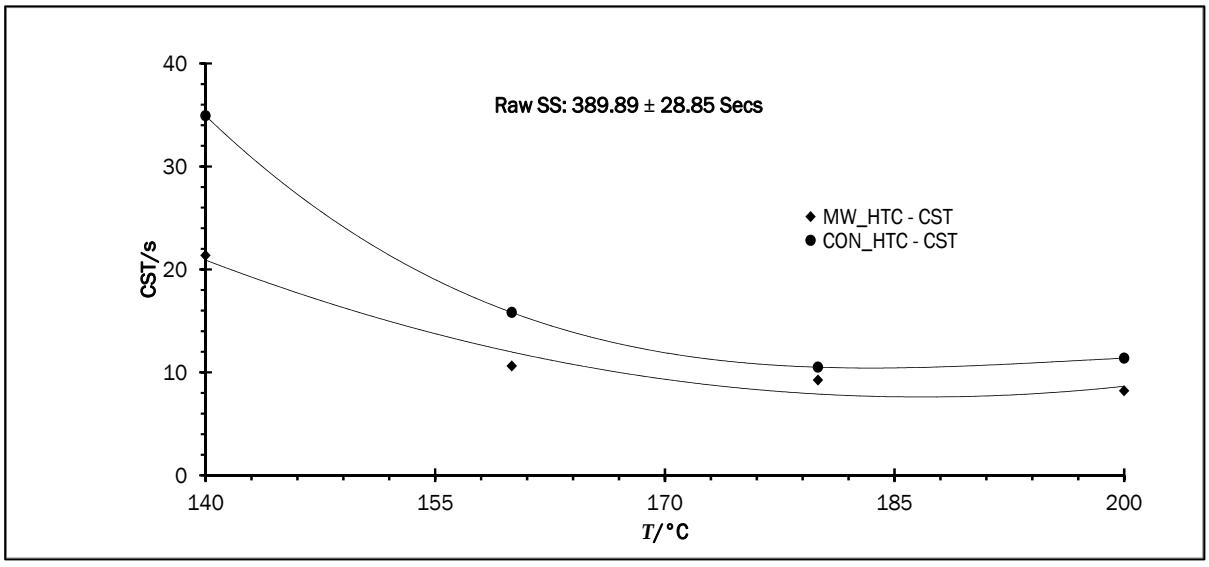

Fig.6.1 CST measurements of SS at different temperature ranges

When compared with C-HTC, which shows a similar trend in terms of CST behaviour with temperature changes, 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 140°C (by 38.8%) and 160°C (by 32.8%), but reduced towards 180°C (11.9%). These improvements are higher than those reported in another study: 13.8% and 17.8% improvement in dewatering rates of microwave pre-treated sewage sludge compared to those of conventionally heated sludge at 60°C and 65°C respectively (21). After 180°C, however, as seen in Fig. 6.1, no significant improvement in dewaterability was observed from both methods. This agrees with previous studies, which have suggested 175°C as the optimal temperature for dewaterability involving heat treatment (22; 23).

It is helpful to note that solid concentration/distribution also affects CST values (11), because larger solid particles tend to block movement of water, which is driven through capillary forces (21; 13). To factor this into consideration, the net effect of the M-HTC process on dewaterability was estimated using specific CST (S-CST) according to Equation 6.1:

$$Specific\ CST\ (\text{seconds/g}\ TS) = \frac{CST\ values\ (seconds)}{Total\ solids\ of\ sludgy\ material\ (dried\ weight,g)} \qquad 6.1$$

S-CST allows the dewaterability of samples having various solid concentrations to be compared (21). See Figure 6.2, which shows similar trends to Fig. 6.1 as ranges of TS of chars across both processes are similar (between 10 and 14%), apart from unprocessed SS, as shown in Table 6.1.

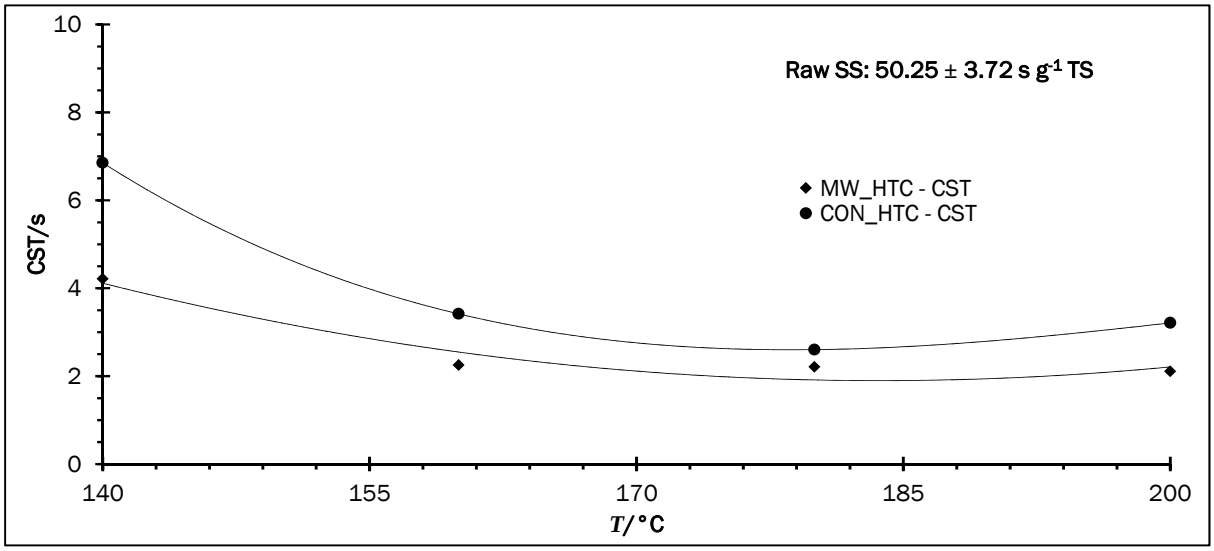

Fig. 6.2 S-CST measurements of SS at different temperatures

From Fig. 6.2, M-HTC yields char that dewaters at ≤ 2.5 s.g^{-1} TS at temperatures above ca. 150°C (c.f. untreated SS at 50.3 ± 3.72 s.g^{-1} TS). The S-CST data further indicated

that 180°C was the optimal temperature to attain enhanced dewaterability of char properties from the M-HTC of SS.

6.3.1 Mechanism behind improved dewaterability during M-HTC

Raising the temperature of sludgy materials decreases their viscosity and facilitates filterability. Heat transferred through conduction and convection during C-HTC disintegrates sludgy flocs (24). This also occurs during dielectric heating through microwave irradiation. Improvements in dewaterability and decreased heating time during M-HTC are due to the highly selective nature of the dielectric heating mechanism, causing rapid and volumetric heating effects. During M-HTC, microwaves selectively energize polar substances within biowastes and chemically bound water in the cells of SS. This subsequently leads to rupturing of the cell walls and membranes (23; 25), accompanied by chemical dissociation and release of bound water (23). In effect, the molecular heating effect of microwave irradiation facilitates the rapid disruption and disintegration of sludge flocs and bound water, and is responsible for improving dewaterability within a shorter heating time (26; 27).

Improved sludge dewaterability under M-HTC has been attributed to both the thermal and athermal effects of microwave heating (26; 28; 29). Thermal effects result from direct coupling of electromagnetic energy with water molecules and other polar organics in biowastes, causing rapid volumetric heating by the dielectric heating mechanism. Athermal effects are attributed to the vibrational effects of microwaves on hydrogen bonds in SS cell walls through the alternation of the electric field of water (polar substance), causing overall weakening. This may have facilitated the breaking of chemically bound water in sludgy biowastes (30;31) – i.e. the continuous aligning of polarised parts of biowaste macromolecules and water molecules with the poles of the electromagnetic field at a 2.45 GHz frequency, for example, initiates vibrational effects, which result in weakening and possible breakage of hydrogen bonds (32). Understanding of the contribution/extent to which both affect dewaterability is still developing, but may explain why M-HTC is slightly better than the conventional process used in this study.

6.4 EFFECT OF PARTICLE SIZE DISTRIBUTION ON SLUDGE DEWATERABILITY

6.4.1 Temperature rather than heating source crucial during HTC

The cumulative volume weighted distribution (%) profiles of particle sizes of both unprocessed and carbonized chars produced from M-HTC and C-HTC at the different carbonization temperatures used are presented in Figs. 6.3 and 6.4 respectively.

As shown in Fig. 6.3, particle sizes in unprocessed SS span a range up to 1700μm, whereas chars produced at the three carbonization temperatures 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. When comparing the profile of unprocessed SS to that of char obtained at 160°C, a striking difference characterised by a *swelling effect* can be seen. The effect is consistent with the disintegration/ fragmentation of solids, as observed in previous studies (33; 34). 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. These data further illustrate an increase in fragmentation of unprocessed SS solids with increasing temperature, supporting the increased solid particle solubilization discussed in Chapter 5 as being a function of reaction temperature. In summary, M-HTC initiated breakdown of solid aggregates and facilitated the removal of smaller particles of solids. Increasing the temperature further enhanced the fragmentation and solubilization of solid aggregates. Similar behaviour was obtained with C-HTC (see Fig. 6.4). However, for process temperatures below 200°C, average particle size distribution extended up to 1200μm. 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.

Hence, the particle size distribution profiles of chars from both HTC methods suggest fragmentation, and particle size reduction/re-distribution is determined by the process temperature rather than heating sources. This agrees with the findings of previous studies demonstrating that process temperature controls sludge disintegration and, by extension, particle size distribution and hence dewaterability (1; 35; 36).

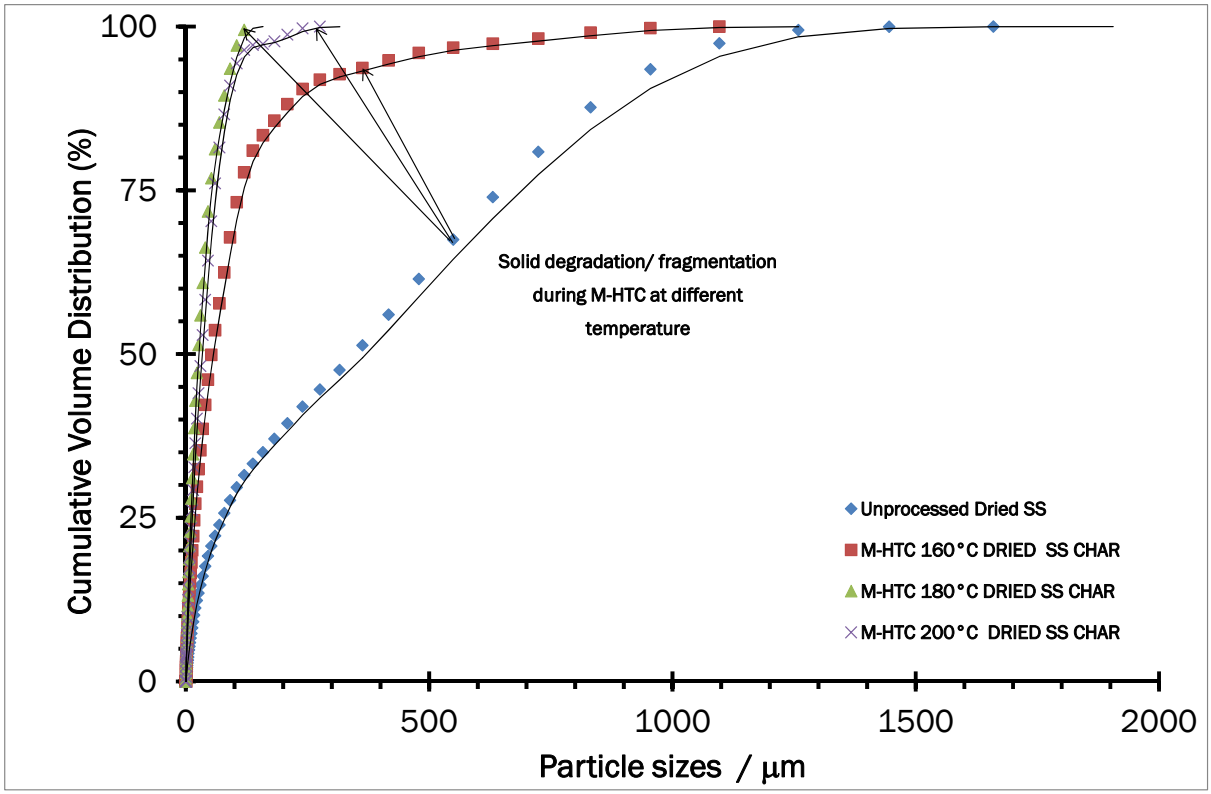

Fig. 6.3 Particle size distribution of unprocessed SS and chars from M-HTC

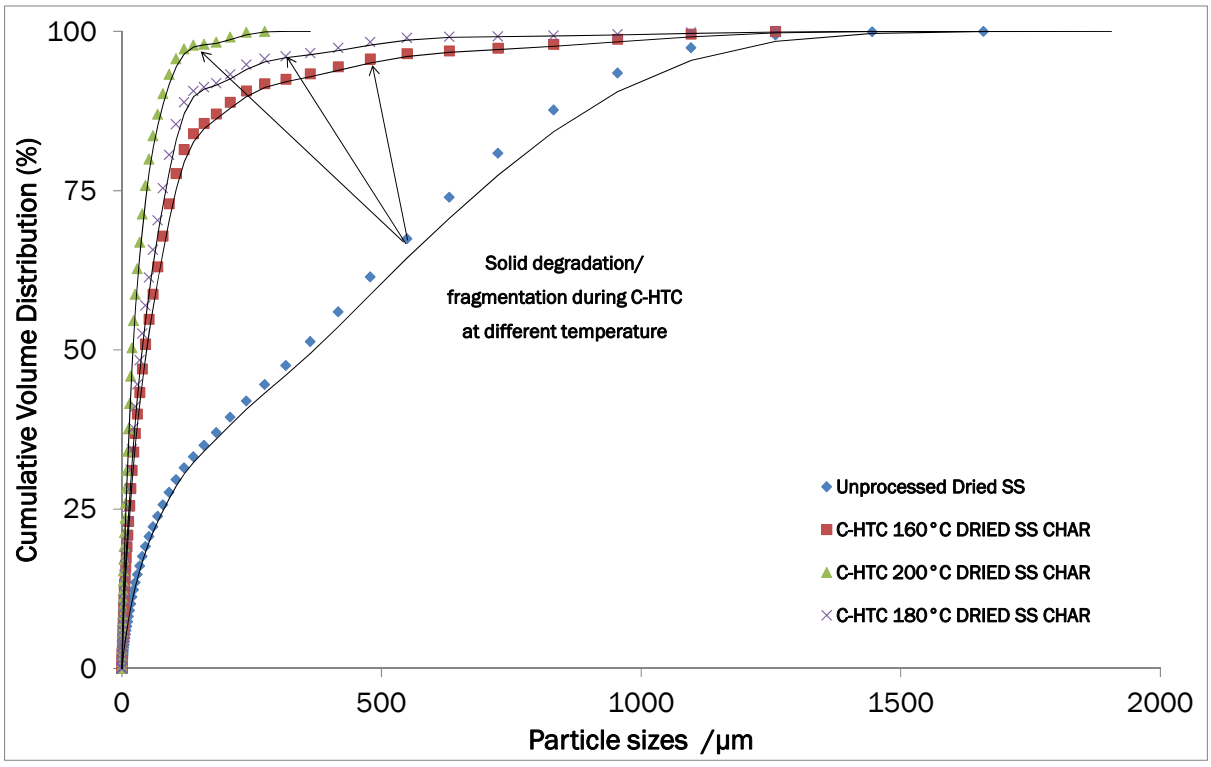

Fig.6.4 Particle size distribution of unprocessed SS and chars from C-HTC

6.4.2 Particle size redistribution and effect during dewaterability

The redistribution effect on chars' particle size and potentially their improved porosity (as discussed in Chapter 5) as a result of the HTC process may further explain the ease with which chars dewater compared to unprocessed SS. Table 6.2, presents the D10, D50 and D90 distribution of chars recovered at the three HTC temperature ranges compared to unprocessed SS, and shows a significant reduction in particle size. This further supports the proposition that fragmentation and solubilization increase with carbonization temperature, while char yield decreases. Using the cut-off diameter D90, unprocessed 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 unprocessed SS and CST values for chars obtained at 160°C. At 180°C and 200°C, D90 values decreased significantly to <90μm, in contrast to unprocessed SS and chars obtained at 160°C. This further illustrates why dewaterability was promoted by temperatures greater than 150°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 temperature used.

Table 6.2 D10, D50 and D90 distribution of unprocessed SS and carbonized chars from both HTC processes

		Diameter size (μm)		
		D10	D50	D90
	Unprocessed SS	17.1	347.4	875.8
M-HTC	M-HTC 160°C dried SS char	4.8	52.7	232.2
	M-HTC 180°C dried SS char	3.3	25.2	80.9
	M-HTC 200°C dried SS char	3.9	31.9	88.2
C-HTC	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	2.3	19.8	78.7

Where:

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

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

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

When compared with previous studies, the range of particle sizes reported in the present study are smaller, with ranges 120–140μm reported as optimum for improving dewaterability (1). Ranges 0–100μm are reported to worsen dewaterability (37; 38). However, this study has shown that both C-HTC and M-HTC produced lower particle size

distribution, 70–130μm (using D90 as the cut-off diameter), yet with improved CST values corresponding to improved sludge dewaterability.

6.5 OTHER EFFECTS OF MICROWAVE IRRADIATION ON PROCESSED SS

6.5.1. Improved sedimentation effect

M-HTC was also found to improve sedimentation and the settleability rates of char products. This can be attributed to the increased settling velocity of carbonized particulates/solids over unprocessed sludge. One review reported that due to microwave irradiation of sludge, the average settling velocity of irradiated sludge increased to 45mm.hr^{-1} compared to a peak value of 40mm.hr^{-1} for unprocessed sludge (39). The settleability/sedimentation effect was apparent when carbonized materials were allowed to settle by gravity, as shown in Fig. 6.5. In comparison with unprocessed SS, M-HTC processed solids settled quickly – showing a sharp interface between solid and liquid fractions of carbonized materials. This effect was also observed for all other HBW feedstock, including HFS processed for the present study. Hence this suggests that carbonized materials can be easily separated by decantation , without the need for complicated separation/filtration processes or related mechanical dewatering commonly associated with conventional sewage processes, all of which have additional energy requirements and cost implications (36).

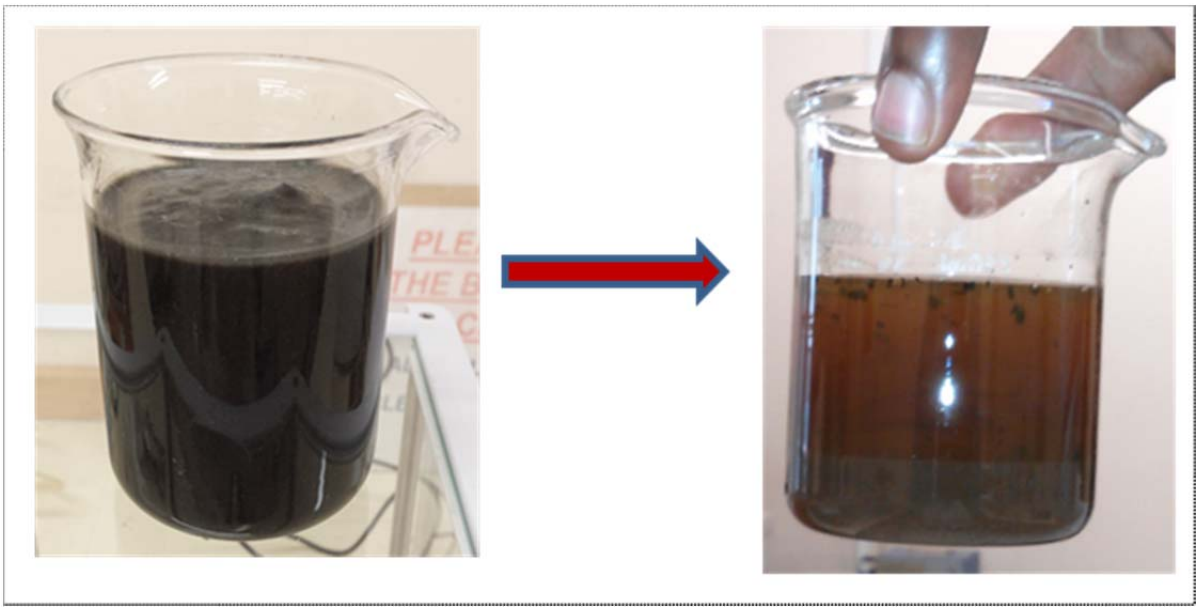

Fig. 6.5 SS feedstock before and after HTC treatment

6.5.2 Effects for drying

Studies of the SEM morphology of chars and dewaterability suggest there will be an improvement in the drying rates of chars, with an associated reduction in energy requirements. This was established in a previous study, which reported a reduction in thermal and electric energy requirements from 164kWh to 64.4kWh and 13kWh to 4.5kWh respectively for drying a ton of sewage sludge to 30% dry content by mechanical dewatering, as compared to when conventional HTC was incorporated (36).

Furthermore, wet chars can be easily dried at ambient conditions after decanting. Hence, successful dewatering and improved drying rates due to the HTC process could serve to be additional financial incentives for waste management in both developed and developing countries. Also, in countries like Switzerland where SS is not allowed on soils, but incineration is encouraged as an alternative disposal option (36), improved dewaterability and easy drying of M-HTC processed biowaste may represent a significant and valuable alternative process.

In summary, M-HTC can be adopted as a potential process to facilitate a faster drying of processed biowastes materials.

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CHAPTER 7 PROPERTIES OF CHARS RECOVERED FROM HUMAN BIOWASTES AND THEIR POTENTIALS USES

7.1 INTRODUCTION

Using the techniques/characterizations described in Chapter 4, the physicochemical properties of microwave hydrothermal carbonization (M-HTC) products were evaluated against the proposition that *M-HTC chars from HBW have comparable energy value, and carbon content, to those recovered from conventional methods.* As well as addressing the gaps in our knowledge relating to hydrothermal carbonization (HTC) chars from human faecal matter, the information will be helpful for the design and optimization of a self-sustainable sanitation facility. Importantly, such insights ultimately determine potential applications such as energy generation, carbon sequestration and use in agriculture.

The properties studied were:

- proximate and elemental analyses (Section 7.2);
- energy properties, i.e. calorific value and combustion behaviour of chars (Section 7.3);
- structural analysis, including surface functionalities, porosity and morphology (Section 7.4); and
- the distribution of metals (Section 7.5).

Where possible, the data have been compared to relevant literature values; however, it is helpful to note that there were differences in operating parameters (such as temperature, residence times, reactor pressure etc.), reactor design, solid concentrations and substrates used. In addition, literature data on HTC products from human faecal matter was not available.

7.2 PROXIMATE AND ELEMENTAL ANALYSIS OF M-HTC PROCESSED BIOWASTE

A proximate and elemental analysis of carbon, hydrogen, nitrogen and oxygen for unprocessed feedstock and chars recovered at each carbonization temperature is presented in Table 7.1.

Table 7.1 Proximate and elemental analysis of unprocessed and chars from all feedstocks at different carbonization temperatures

	FSS				SS				HF				HFS		
Parameters (units)	Unprocessed	160°C	180°C	200°C	Unprocessed	160°C	180°C	200°C	Unprocessed	160°C	180°C	200°C	Unprocessed	180°C	200°C
MC (%)	96.3	86.3	83.1	82.4	95.6	89.1	89.0	86.5	97.1	81.0	80.1	80.9	96.6	88.2	86.4
TS (%)	3.7	13.8	16.9	17.6	4.5	10.9	11.0	13.5	2.9	18.9	19.9	19.1	3.4	11.8	13.6
VS (%)	88.3	95.2	94.7	93.0	71.4	62.7	59.7	54.1	86.7	56.7	79.2	75.5	80.2	78.1	74.4
FS (%)	11.7	4.8	5.3	6.9	28.6	37.3	40.3	45.9	13.3	43.4	20.8	24.5	19.8	21.9	25.6
Volatile matter recovery (%)	-	42.4	34.2	28.6	-	50.6	48.2	33.8	-	34.3	41.5	32.7	-	45.0	38.5
Weighted VS/FS (recovery)	-	2.6	2.3	1.8	-	0.7	0.6	0.5	-	0.2	0.6	0.5	-	0.9	0.7
C (%)	39.1	52.5	55.6	59.6	36.9	36.9	36.8	37.5	47.8	38.3	53.9	56.1	41.3	44.4	48.9
H (%)	6.2	7.1	6.9	7.2	5.7	5.4	5.2	5.2	6.6	5.7	6.9	7.1	5.9	6.2	6.5
N (%)	2.6	1.6	1.7	1.9	4.9	3.3	2.9	2.5	5.9	2.4	2.6	2.6	5.9	1.8	0.9
O (%)*	52.2	38.9	35.8	31.2	51.5	53.8	54.5	54.3	39.7	54.0	36.5	34.3	46.9	47.6	43.8
Carbon densification factor [a]	-	1.34	1.42	1.52	-	1.00	1.01	1.02	-	0.80	1.13	1.17	-	1.07	1.18
Carbon efficiency (%)[b]	-	34.3	42.2	52.5	-	0.1	<1	1.5	-	<1	12.9	17.4	-	7.4	18.3
Carbon storage factor (CSF)[c]	-	0.21	0.18	0.16	-	0.21	0.21	0.17	-	0.20	0.25	0.21	-	0.21	0.20

* $Estimated\ by\ difference\ i.e\ O\ (\%) = 100 - \%[C + H + N]$

[a] $Carbon\ densification\ factor = \frac{\%\ carbon\ in\ dried\ chars\ solids}{\%\ carbon\ in\ dried\ raw\ biowastes\ solids}$

[b] $Carbon\ efficiency\ (\%) = \frac{\%C\ in\ Char - \%C\ in\ dred\ raw\ biowaste}{\%C\ dried\ raw\ biowaste}$

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

7.2.1 Proximate analysis

At the outset it is helpful to note that the nature and inherent variability of different biowaste results in ranges of the measured characteristics of chars.

Table 7.1 shows that at all temperatures, the total solids (TS) of chars are greater than of unprocessed biowastes (~5%), 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 (1). TS of chars were also observed to increase as carbonization temperature increased. (TS of chars recovered from primary sewage sludge [SS] increased from 10.9% at 160°C to 13.5% at 200°C, while those from faecal sludge simulant [FSS] increased from 13.8% to 17.6% over the same temperature range.) This supports the findings from Chapter 5, where carbonization temperature was identified as a factor in solid redistribution during HTC.

The mass balance was conducted on dry char, with 40% to 65% of solids recovered as char (as indicated by char yield) and up to 44% of solids transferred into the liquid phase (measured by TS in liquor). Mass losses recorded (<10% in most cases) were attributed to sample handling, transfer to and from reactor vessels, solid separation from carbonized slurry via sieves, and volatile loss during drying.

The volatile solids (VS) of chars and their percentage-weighted recovery from HTC processed biowaste ranged from 54% to 95% and 28% to 51% respectively. Both parameters decreased with increasing carbonization temperature. However, fixed solids (FS) ranged between 5% and 45%, and appeared to increase with increasing carbonization temperature. These observations were similar to those reported in a study on solids analysis of chars produced via HTC of lignin, cellulose and wood meal (2). In the study, volatile matter content reduced while FS increased as temperature was increased from 225 to 265°C (2). The standard method used for determining VS and FS content does not distinguish precisely between organic and inorganic matter of solids (3). This is because at 550°C, the temperature used in their determination, VS and FS are not restricted to the combustion of organic matter in solids only. Hence, decomposition of inorganic matter in solids may occur, increasing fixed solid deposits.

7.2.2 Elemental composition

HTC initiated changes in the elemental composition of chars recovered from unprocessed biowaste (Table 7.1). This is an important feature of HTC and applies to all feedstock and heat sources: microwave (4; 5) or conduction heating (2; 6; 7). Changes in elemental composition were observed to be dependent on carbonization temperature. An increase in the carbon content of chars and a corresponding decrease in the oxygen

content were observed for chars recovered at all carbonization temperatures. Human faeces (HF) chars at 160°C had a carbon content (38.3%) that was lower than the unprocessed HF feedstock (47.8%). Increasing the temperature resulted in higher carbon content, i.e. 53.9% and 56.1% at 180°C and 200°C respectively, indicating that 160°C was not effective for carbonizing HF. A previous study also recorded a decrease in carbon content of sewage sludge carbonized at 140°C when compared with unprocessed sewage sludge (8). Increasing carbonization temperature from 160 to 200°C, however, was observed to trigger a corresponding increase in char carbon content.

The increase in carbon content, as indicated by the carbon efficiency i.e. percentage carbon increment due to carbonization effects (see Table 7.1), appeared to be strongly dependent on the nature of the feedstock. SS yielded less than a 2% increase, while human faecal sludge (HFS), HF and FSS values increased by up to 18%, 17% and 52% respectively at 200°C. Hence 200°C would appear to be the most effective carbonization temperature for HBW in terms of carbon efficiency within the range studied.

The low carbon efficiency observed for SS may be attributed to partial/incomplete carbonization of thermally stable components such as fibrous strands commonly associated with sewage sludge, as depicted in the SEM images of SS chars (see Chapter 5). Similar studies on SS carbonization support this (8; 9). Other studies have recommended temperatures greater than 250°C, with acid pre-treatment and/or the addition of microwave adsorbent, to enhance the thermochemical decomposition of SS and hence improve the degree of carbonization (10; 11; 12). This was outside the scope of this work and was not investigated.

7.2.3 Carbon-related parameters of chars

The carbon densification factor indicates the ratio of carbon concentrated in chars (dry basis) compared with unprocessed biowaste. It was greater than 1 in all cases. Literature values for carbon densification range between 1 and 1.8 (13; 14; 15), and this was also observed in the present study. The carbon densification factor for FSS chars was observed to increase with carbonization temperature, due mainly to increasing carbon content during the HTC process up to a value of 1.52. This was consistent with other studies of conventional HTC (15; 14). M-HTC was found to increase the carbon content and carbon densities of chars. The energy-related implications of this observation (16; 17) are discussed in Section 7.3.

The carbon balance measurements were conducted on a dried basis of unprocessed materials, by quantifying the carbon content in liquid as total organic carbon (TOC) and solid phase as weighted carbon content in recovered char. Table 7.2 shows that

significant fractions of carbon in the feedstock biowaste material were retained in the recovered chars.

Table 7.2 Maximum weighted carbon (%) retained in chars at each carbonization temperature

Chars obtained from HBW	Carbonization temperatures		
	160°C	180°C	200°C
FSS	77.6	46.3	41.4
SS	67.9	60.6	51.6
HF	41.9	51.4	44.1
HFS	-	59.3	54.7

Between 42% and 78% of carbon from starting biowastes 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 (7; 18; 19). However, the percentage carbon retained in chars was sensitive to the nature of biowaste, with up to 51% for HF, 59% for HFS, 67% for SS and 77% for FSS. The amount of carbon retained in chars as a percentage of unprocessed feedstock decreased with increasing carbonization temperature, partly due to the increased solubilization effects at higher HTC conditions (see Table 7.2 and Appendices 3.1 and 3.2). Thus the level of carbon in the liquor phase ranged between 10% and 30%, depending on the biowaste material and carbonization temperature involved.

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 unprocessed feedstock after biological decompositions in a landfill (20). This factor provides a means for a relative comparison of sequestered carbon. Table 7.1 shows that CSF values ranged between 0.16 and 0.25. CSF was also observed to decrease slightly as the temperature increased from 160°C to 200°C (see Appendix 3.2 for more details). 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 (19). Another study also reported 0.22 for mixed MSW and 0.08 for food waste disposed in landfills (20). Comparatively, these ranges are very similar to those reported for the HBW feedstock used 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.

7.2.4 Molar ratio: H/C and O/C

Molar ratios of H/C and O/C were estimated from their elemental compositions and analysed with a Van Krevelen diagram to further understand the reaction pathways

involved during the M-HTC of each biowaste. Van Krevelen diagrams allow the delineation of reaction pathways: a straight line parallel to x-axis usually represents a decarboxylation pathway, while diagonally drawn lines usually denote a dehydration pathway (7), as shown in Fig. 7.1.

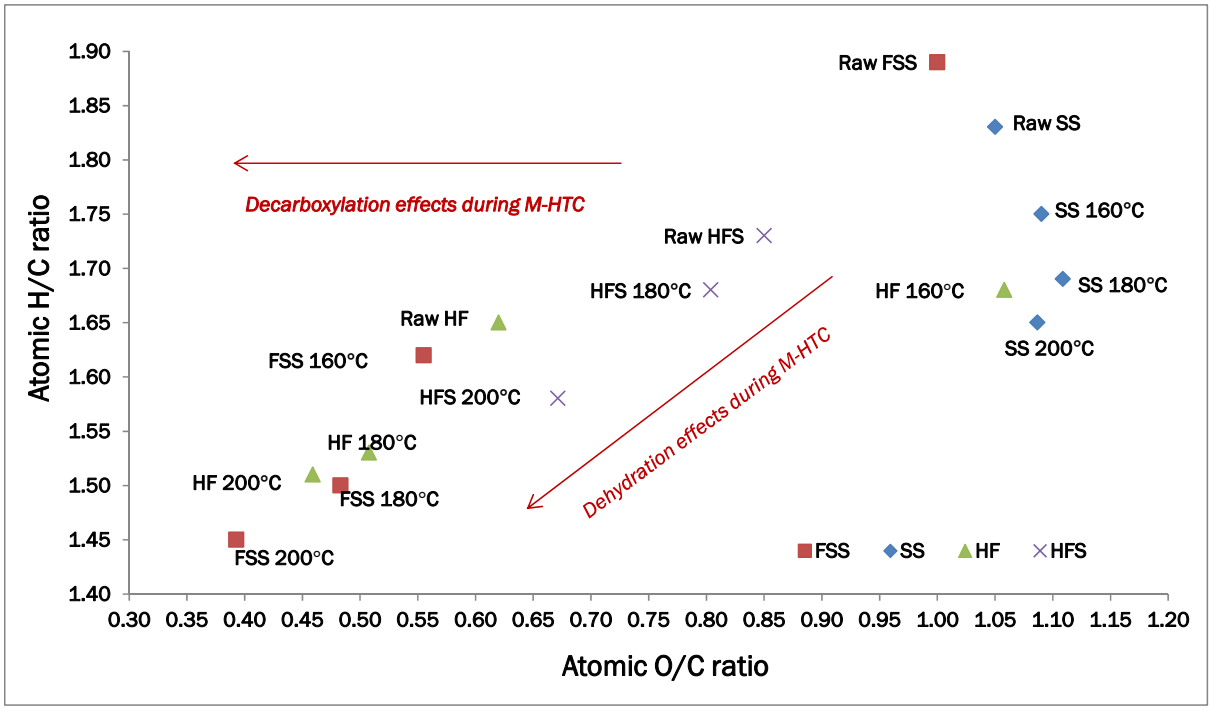

Fig.7.1 Molar ratio H/C against O/C of unprocessed biowastes and their chars at different carbonization temperatures

From Fig. 7.1, the microwave carbonization of unprocessed biowaste suggests they are predominantly governed by dehydration reactions. Note how the H/C ratio decreases with increasing HTC temperature; this is especially pronounced for chars recovered from HFS and FSS. This also supports the discussion in Section 5.2 on biowaste conversion mechanisms.

Decreasing O/C trends can also be seen in Fig. 7.1, indicative of decarboxylation occurring during carbonization, especially for chars recovered from FSS where O/C ratios decreased from 1.00 in unprocessed feedstock to 0.39 at 200°C. HF and HFS also shows slight changes in O/C ratios, reducing from 0.62 to 0.46 and from 0.85 to 0.67 respectively. These observations follow on from previous studies involving the carbonization of glucose, cellulose, starch, sucrose and sewage sludge under conventional processes (6; 14; 21; 22).

7.2.5 Molar ratio: C/N

The C/N ratios of unprocessed biowastes, and their chars, were also estimated (see Table 7.3). These have relevant implications in agriculture (23) and as a substrate/precursor for anaerobic digestion /H_2 production (24; 25).

Table 7.3 Maximum C/N ratios of unprocessed and recovered chars at different carbonization temperatures

Feedstocks	Unprocessed	M-HTC Temperature		
		160°C	180°C	200°C
FSS	17.9	39.6	38.2	35.2
SS	8.7	13.3	15.0	17.8
HF	9.5	19	24.2	25.8
HFS	8.2	-	28.3	63.7

The C/N ratio doubles in chars in most cases when compared to unprocessed biowastes. For example, unprocessed FSS increased from 17.9 to over 35 for all chars recovered at all carbonization temperatures. SS and HF C/N ratios were less than 10 before carbonization, and increased to approximately double their starting value following carbonization. HFS showed the greatest change and was the most sensitive to temperature, increasing from 8.2 to 63.7 at 200°C. M-HTC increased the C/N ratio in chars, compared to unprocessed feedstocks. This was due to the increased carbon content and dissolution of N-content into the liquor phase.

C/N tends to be feedstock-sensitive, and similar feedstock/temperature relationships showing feedstock relationships and temperature dependency have been reported previously (26). The study of the pyrolysis of: corn, hazelnut, dairy manure, paper waste, food waste and poultry waste at 300–600°C yielded C/N values which increased with temperatures from 51 to 70, 159 to 181, 234 to 250, and 676 to 900 for pyrolyzed corn, hazelnut, paper waste and pine respectively. Other biowaste (closer in nature to this work, i.e. dairy manure, food waste and poultry waste) also increased with temperature, but with C/N ratio values less than 30 – in common with those values obtained for SS, HF and HFS in the present study.

For the purpose of soil conditioning, or as a precursor for H_2 /biogas production, C/N ratios of 20 to 30 have been reported as optimum (27; 28; 24). Lower C/N values tend to be more favourable for plant growth. This is because higher C/N values favour N-immobilization and reduced nitrogen bioavailability to plants by competing soil microbes. A higher C/N supply provides soil microbes with excess C, useful for energy that

stimulates uptake of bioavailable N to balance their protein needs (23; 29), reducing the N-supply to plants. This was observed in field studies investigating the relationship between high C/N-containing chars and plant growth (26). Table 7.4 shows the similarity of the C/N values of chars recovered from HTC processes against commonly used organic-based substrates in agriculture.

Table 7.4 C/N of different organic-based materials (23; 27; 30; 31)

Material	Rotted barnyard manure	Corn stalk	Farm manure	Food scrap	Undisturbed top soil	Cattle manure	Leaves (varies)	Wheat straw	Coal and shale oil
C/N value	20	60	90	15	10	20	35 to 85	80	124

The need to further process chars recovered with high C/N ratios, i.e. those greater than 30, before applying to agriculture should be assessed (26). However, observations from this work indicate that while lower carbonization temperature, i.e. 160 to 180°C, will favour C/N ratios for soil-addition applications, higher carbonization temperature, greater than 180°C, tends to generate higher C/N ratio chars that are more suitable for combustion/energy-recovery purposes. Also lower N-content in chars recovered from temperature greater than 180°C will further reduce the amount of unwanted nitrogen oxides during combustion, reducing environmental impact.

7.3 HIGHER HEATING VALUE AND COMBUSTION BEHAVIOUR OF CHARS

The calorific value, also known as the higher heating value (HHV), is another important characteristic of chars. This enables the estimation/assessment of key energetic parameters such as energy densification: energy yield for comparative assessment with unprocessed biowaste and conventional fuels. Table 7.5, provides a comparison of the calorific values of chars recovered from each biowaste, and indicates how the calorific values of chars are sensitive to feedstock and carbonization temperature. While FSS and SS behave differently, the values obtained for HF and HFS at 180°C and 200°C are similar. Calorific values were observed to gradually increase with carbonization temperature, and for all the chars recovered the highest HHVs were obtained at 200°C.

The effect of M-HTC on biowaste was observed to generate significant calorific value improvement, up to 41.4% for FSS, 31.5% for HF and 26.4% for HFS. HF and HFS yielded the highest calorific values, averaged at 25MJ.kg^{-1}, which is greater than low rank fuels such as peat (13.8–20.5 MJ.kg^{-1}), lignite (16.3MJ.kg^{-1}) and some grades of bituminous coal (17–23.25MJ.kg^{-1}) (31; 32) (See Table 7.6). No significant calorific improvement

was observed for SS, and this was due to incomplete/partial carbonization, discussed previously (see Section 7.2.2).

The effect of residence time on the calorific value of chars recovered from HFS was studied further and was observed to also contribute to enhancement of calorific values. However, the effect was not as pronounced as changes in process temperature (see Appendix 3.3 for more details).

Similar observations have been reported in many studies, with many substrates and heating sources (5; 18; 33). The energy content of chars recovered from wastewater sludge ranges from 14.4 to 27.2MJ.kg^{-1} (7; 22; 34; 35). These are comparable to the HHVs obtained for all chars recovered in the present study, which contain the first reported observations for HFS (1).

7.3.1 Energetic parameters of HBW chars

During carbonization, the solid mass decreases due to solubilization and dehydration, indicated by their molar ratios, and these results in energy densification – as indicated by the energy enrichment factor (EEF). In Table 7.6, the EEF of all chars recovered from all unprocessed biowastes ranged from 0.98 to 1.41, and in most cases was greater than 1.

Similar energy densification ratios were reported for HTC chars produced from MSW (1.01 to 1.41 [34]) and wood-based substrates (1.11 to 1.43 [18]). This is evidence that M-HTC appears to promote energy densification in chars. Further, the process yields energy densification factors comparable to previous-reported HTC studies specifically run to enhance energy densification on a variety of feedstocks (36; 17). EEF was also observed to increase slightly with increasing temperature, with FSS recording the highest densification (1.41 at 200°C). This observation is similar to another study (18), which also reported the energy densification of chars produced from a wood mix increased from 1.1 at 215°C to 1.45 at 295°C.

Energy yield, also known as energetic retention efficiency, provides a means for assessing the energy recoverable from chars. Consistent with similar studies, energy yield decreases gradually with increasing carbonization temperature – primarily due to reducing char yield (6; 8; 33). Increasing temperature from 160 to 200°C resulted in a corresponding decrease in energy yield by ~30% for FSS, 9% for HF (ignoring the value at 160°C, as carbonization was not obvious at this temperature), and 13% for SS and HFS respectively.

With both parameters measured independently, a strong correlation between calorific values and carbon content was observed, as shown in Figs. 7.2 to 7.5. A correlation coefficient greater than 0.8 was obtained in all cases between energy values and carbon content of both the unprocessed biowastes and the chars recovered from them. This is comparable to a previous study (22), which reported a correlation coefficient of 0.9 for a variety of substrates, including sewage sludge, food waste and chipped wood. This implies the effect of HTC is to increase carbon content, producing higher char heating values.

Table 7.5 Maximum calorific properties of unprocessed and chars from all feedstocks at different carbonization temperatures

	FSS				SS				HF				HFS		
Temperature / °C	Unprocessed	160	180	200	Unprocessed	160°C	180°C	200°C	Unprocessed	160°C	180°C	200°C	Unprocessed	180°C	200°C
Calorific heating value / MJ.kg^{-1}	17.1	22.9	23.8	24.2	15.9	15.7	15.6	15.7	19.5	18.7	24.93	25.6	19.79	24.6	25.0
Energy enrichment factor, EEF[a]	-	1.34	1.39	1.41	-	0.99	0.98	0.99	-	0.96	1.28	1.31	-	1.24	1.26
Energy yield (%)[b]	-	68.4	45.2	38.4	-	57.2	56.6	44.3	-	50.1	58.1	49.4	-	61.1	47.9
Calorific improvement (%)[c]	-	33.6	39.0	41.4	-		< 1		-	<1	27.9	31.5	-	24.3	26.4

[a] $EEF = \frac{HHV\ of\ dried\ chars\ solids}{HHV\ of\ dried\ raw\ biowastes\ solids}$ [b] $Energy\ yield\ (\%) = EEF\ x\ char\ yield\ (\%)$

[c] $Calorific\ Improvement\ (\%) = \frac{(HHV\ of\ dried\ chars - HHV\ of\ dired\ raw\ biowaste)}{HHV\ of\ raw\ biowaste}\ x\ 100$

Table 7.6 Comparing heating values (32; 35; 37; 38)

Fuels	**Grades of coal**	**Corn stalk / Stover**	**Sugarcane bagasse**	**Softwood wood**	**Municipal solid waste**	**Refuse derived fuel**	**FSS**	**HF**	**HFS**	**SS**
HHV* / MJ.kg^{-1}	17 to 28	17.6 to 18.5	17.3 to 19.4	18.6 to 21.1	13.1 to 19.9	15.5 to 19.9	22.4 to 24.2	18.7 to 25.6	22.3 to 25.0	15.0 to 17.0

*Note:
1. Values vary, chiefly with moisture content
2. Char HHV depends on HTC process conditions, most importantly temperature used

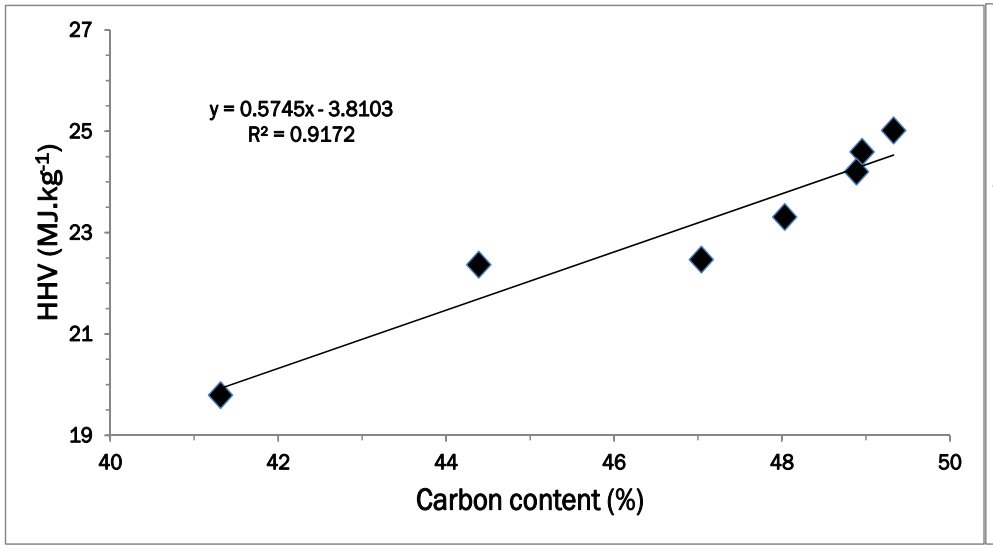

Fig. 7.2 HFS

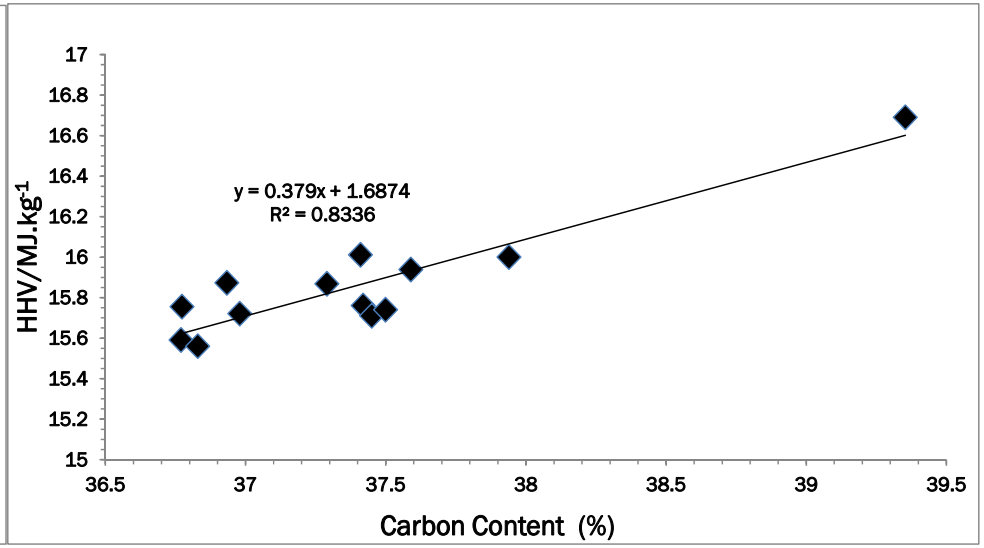

Fig. 7.3 SS

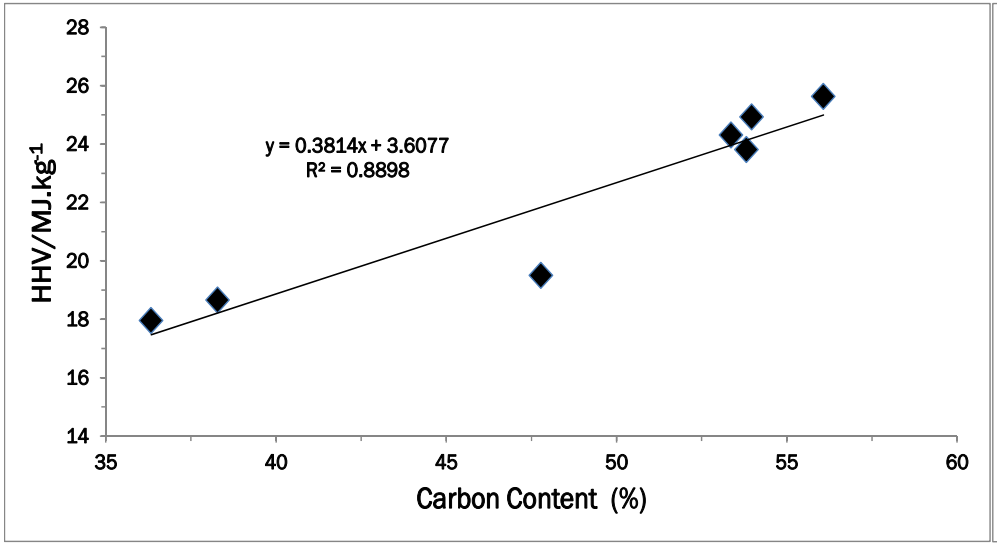

Fig. 7.4 HF

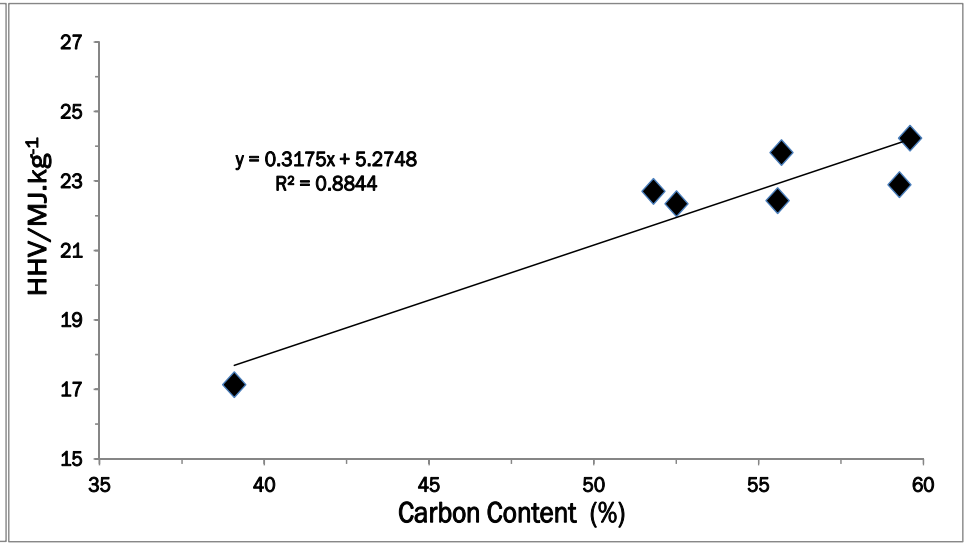

Fig.7.5 FSS

Figs. 7.2 to 7.5 Correlation of calorific values with carbon content for HFS, SS, HF and FSS respectively

7.3.2 Combustion behaviour of unprocessed biowastes and chars

Figs. 7.6 to 7.17 show the thermogravimetric (TG) and derivative TG profiles of unprocessed biowastes and their chars carbonized at 180°C and 200°C. Analyses were not conducted at 160°C, as degree of carbonization was assumed to be insignificant at this temperature. Table 7.7 summarizes key results of the thermogravimetric analyses (TGAs).

Table 7.7 Combustion parameters of unprocessed biowastes and chars

Sample descriptions		IT /°C	[a] PT /°C	[b] PT /°C	BT/°C	% BT
SS	Unprocessed	138.8	272.8	463.7	618.7	72.9
	Char at 180°C	127.0	219.5	278.2	525.6	67.2
	Char at 200°C	128.6	205.5	249.7	507.3	60.5
FSS	Unprocessed	131.8	281.8	446.7	543.9	88.9
	Char at 180°C	159.6	268.3	404.4	502.7	95.8
	Char at 200°C	156.0	263.6	372.4	477.8	95.9
HF	Unprocessed	151.1	269.8	489.1	567.2	87.2
	Char at 180°C	137.9	267.9	392.6	527.2	80.4
	Char at 200°C	148.3	255.6	375.2	524.4	83.8
HFS	Unprocessed	140.9	271.2	442.8	577.2	86.7
	Char at 180°C	146.0	281.9	383.0	522.4	82.6
	Char at 200°C	117.9	281.9	380.4	510.5	78.5

Where IT – Initial temperature where devolatilization starts

PT [a&b] – Peak temperature on the DG profile, corresponding to devolatilization and burning phases respectively

BT – Burnout temperature

% BT – Percentage weight of material combusted after BT

From Figs 7.6 to 7.17, the relatively slow heating (10°C.min^{-1}) of samples in air by TGA suggests three phases of combustion behaviour of unprocessed biowastes and chars: drying, decomposition/devolatilization and burning/ashing. The TG/DTG curves of the unprocessed biowastes, especially SS, were similar to a previous study of SS combustion in air (39). The temperature of the first stage ranged from ambient room temperature at the start of the analysis to about 150°C, corresponding to moisture loss via evaporation and/or dehydration. Some volatiles might also have been evaporated, contributing to the weight loss observed at this phase (40). After the drying phase, thermal decomposition resulted in devolatilization (i.e. weight loss via volatile release) of materials as temperature profile increased. This stage is generally associated with the decomposition of the organic content of material (41; 42). For unprocessed biowaste, this phase started

after drying at about 150°C and ended around 340°C for SS, between 350 and 360°C for both HF and HFS, while for FSS, the phase ended around 413°C. For chars, the temperature ranges associated with this phase were lower when compared with their unprocessed biowastes. This suggests chars were more easily degraded, as the phase ended at less than 300°C for most chars. Differences in peak temperatures, which corresponded to maximum weight loss at this phase, were analysed – as indicated as PT^a in Table 7.7.

The final stage, i.e. burning in air (O_2 atmosphere) and ashing, began after completion of the second stage. Once again this phase ended at lower temperatures (see BT column in Table 7.7) when the chars were compared with their unprocessed biowastes. During the decomposition stage, peak temperatures (PT^b in Table 7.8), corresponding to maximum weight loss at these phases, were lower for chars than for unprocessed biowastes. In Figs. 7.6 to 7.17, this phase had the lowest weight losses of all the stages for char samples. In essence, this suggests the HTC process reduced the ash content in the chars, as compared to the unprocessed biowastes.

The percentage BT reported in this work is comparable to those reported in previous studies involving the TG analysis of sewage sludge/blended with coal (43; 44). The peaks displayed from the DTG curve in Figs. 7.6 to 7.17 of both the unprocessed biowastes and chars can be related to the decomposition of organic-based components in HBW (45; 46; 47).

In summary, M-HTC results in marked differences in the combustion behaviour of unprocessed biowaste, as follows:

a. There was a distinctive DTG combustion profile and differences in amount of starting material combusted.
b. Increasing carbonization temperature influenced the combustion behaviour of chars, as it tends to make chars most reactive during the decomposition phases.
c. Chars exhibited a greater reactivity to combustion profile along the TG temperatures than unprocessed biowastes, as their peaks shifted toward lower values of TG temperature and they show lower burnout (BT) temperatures.
d. Maximum weight loss was recorded during the second phase for chars, while for unprocessed biowaste this occurs during the second and third phases. This suggests lower temperature regimes should be used to harvest energy from chars as compared with their materials. However, further investigation using the scanning calorimetry technique is imperative to quantify energy consumed at each phase.

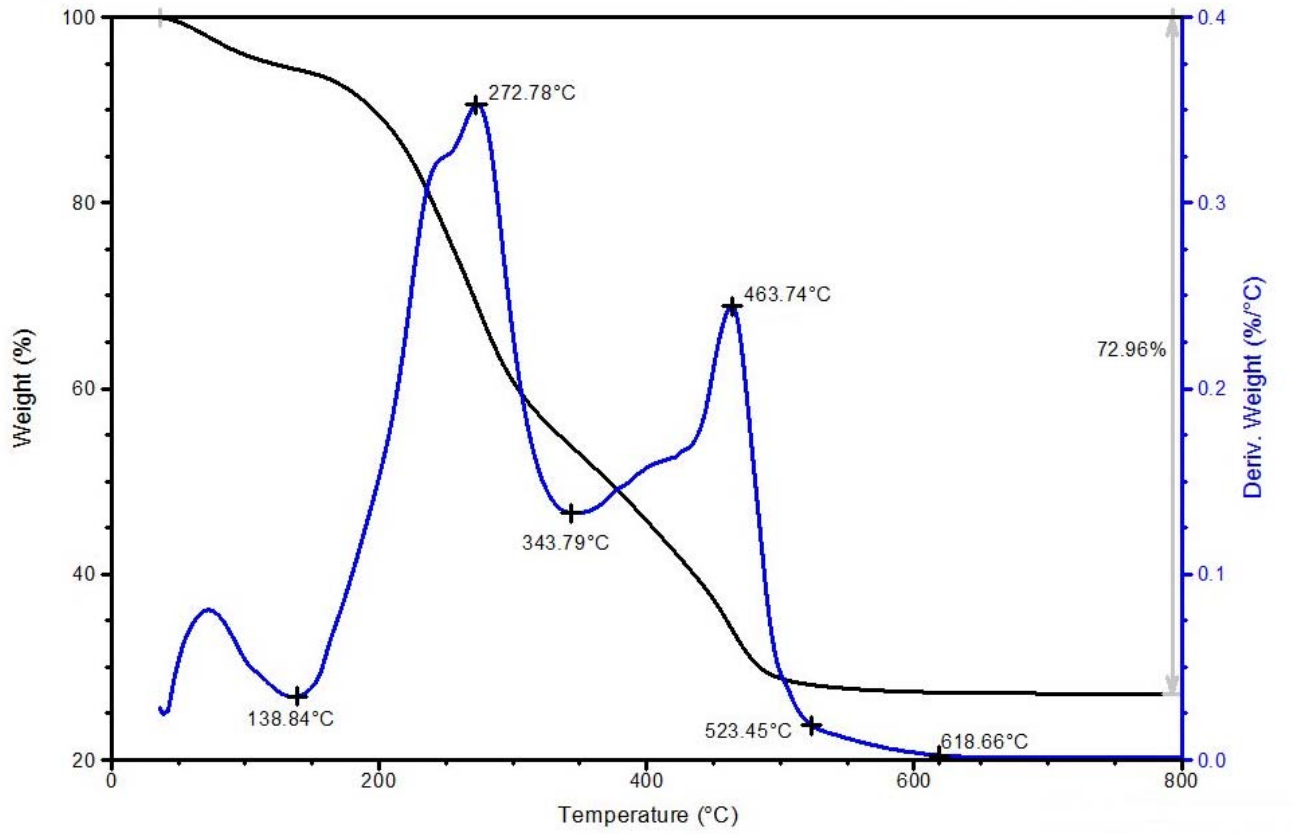

Fig.7.6 TG/DTG profile of unprocessed SS

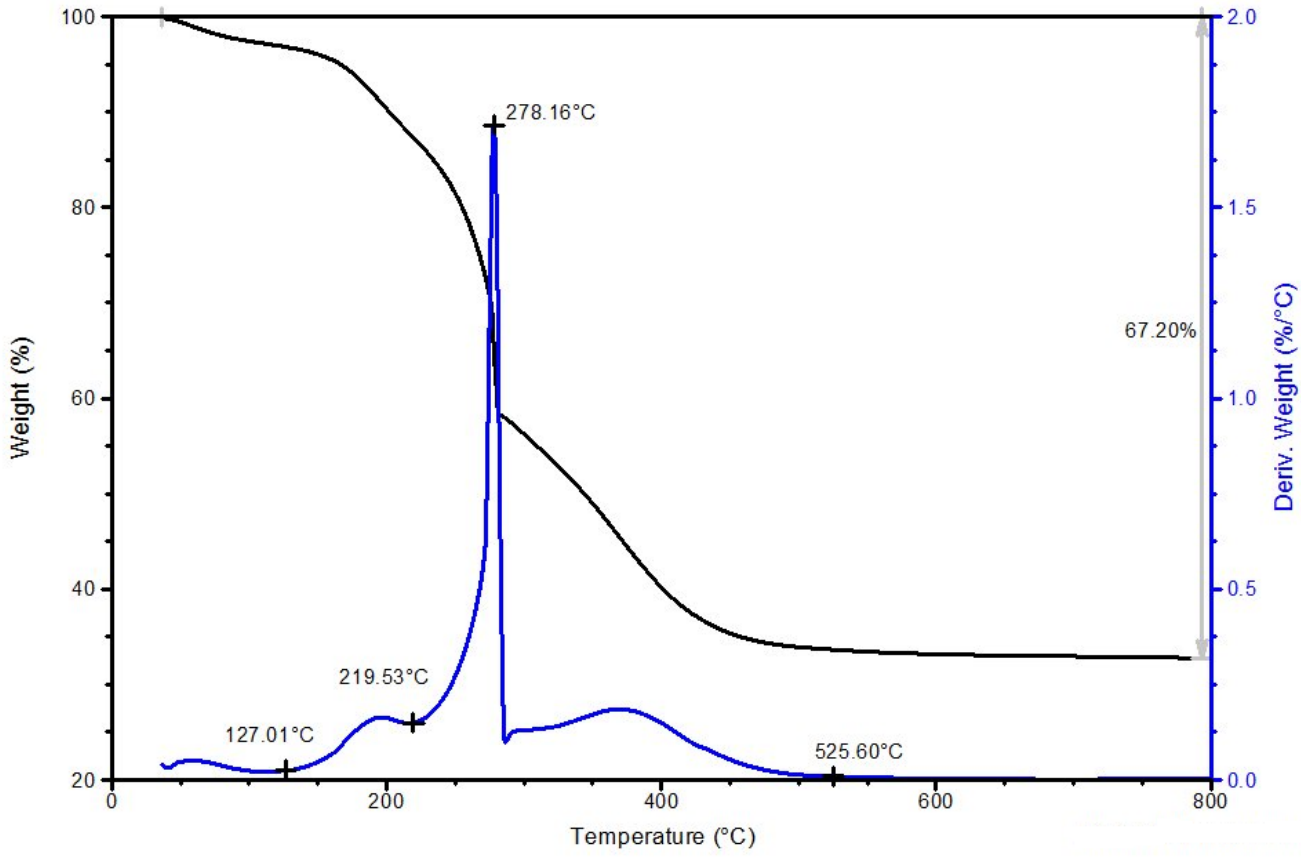

Fig. 7.7 TG/DTG profile of SS char at 180°C

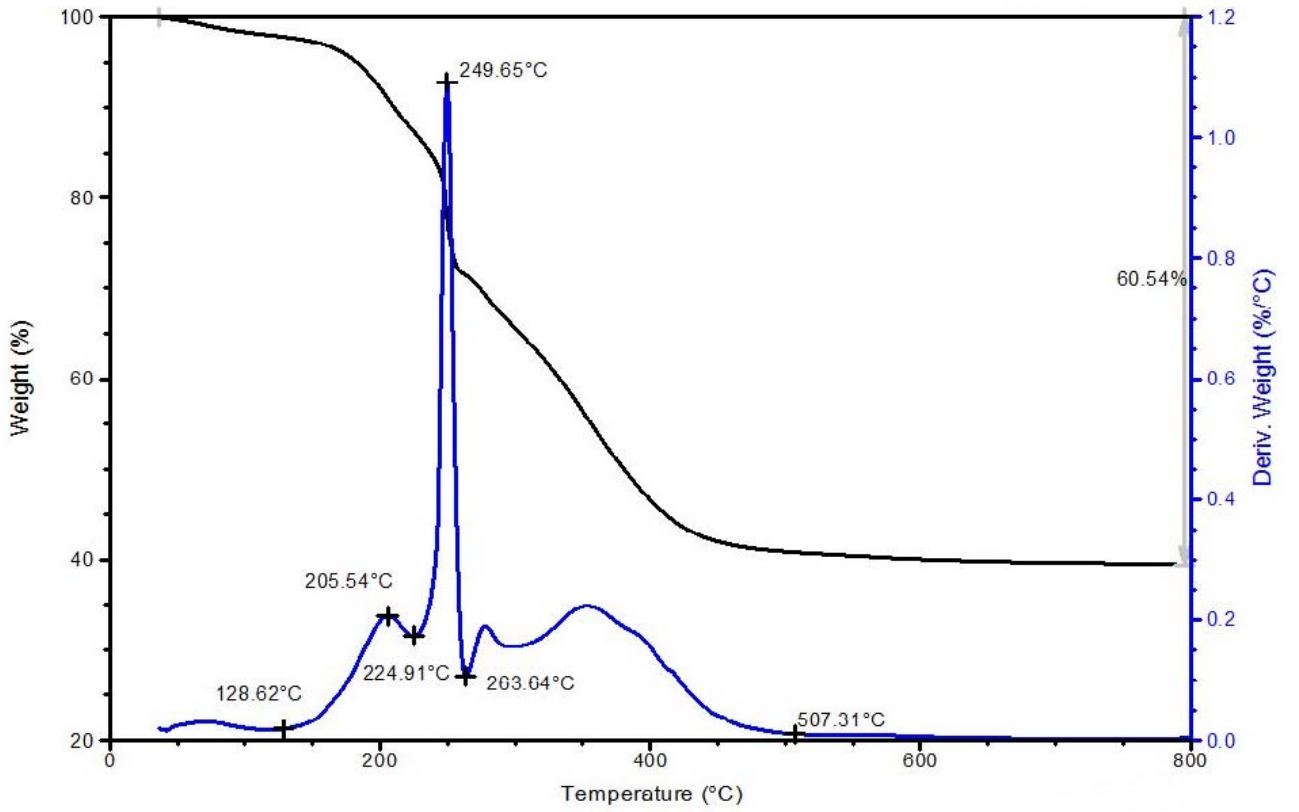

Fig. 7.8 TG/DTG profile of SS char at 200°C

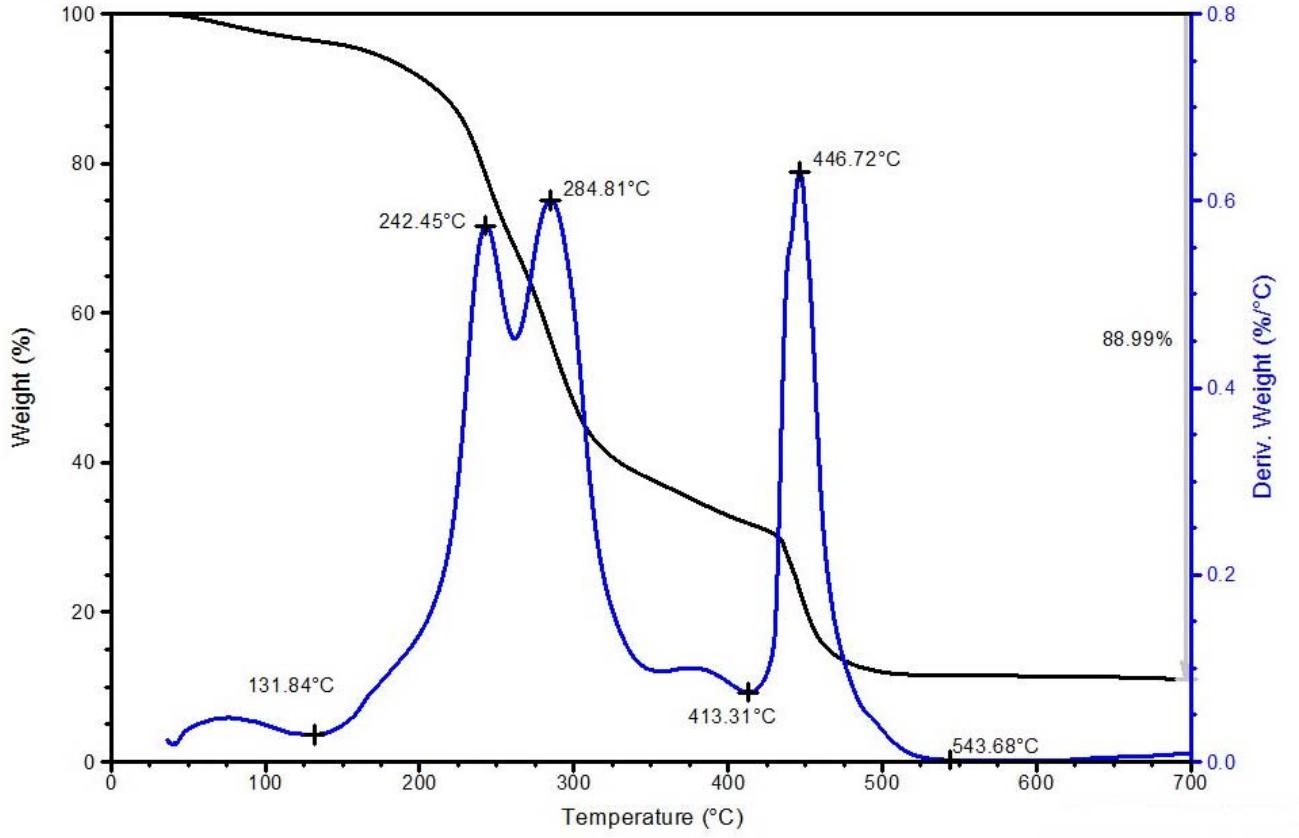

Fig.7.9 TG/DTG profile of unprocessed FSS

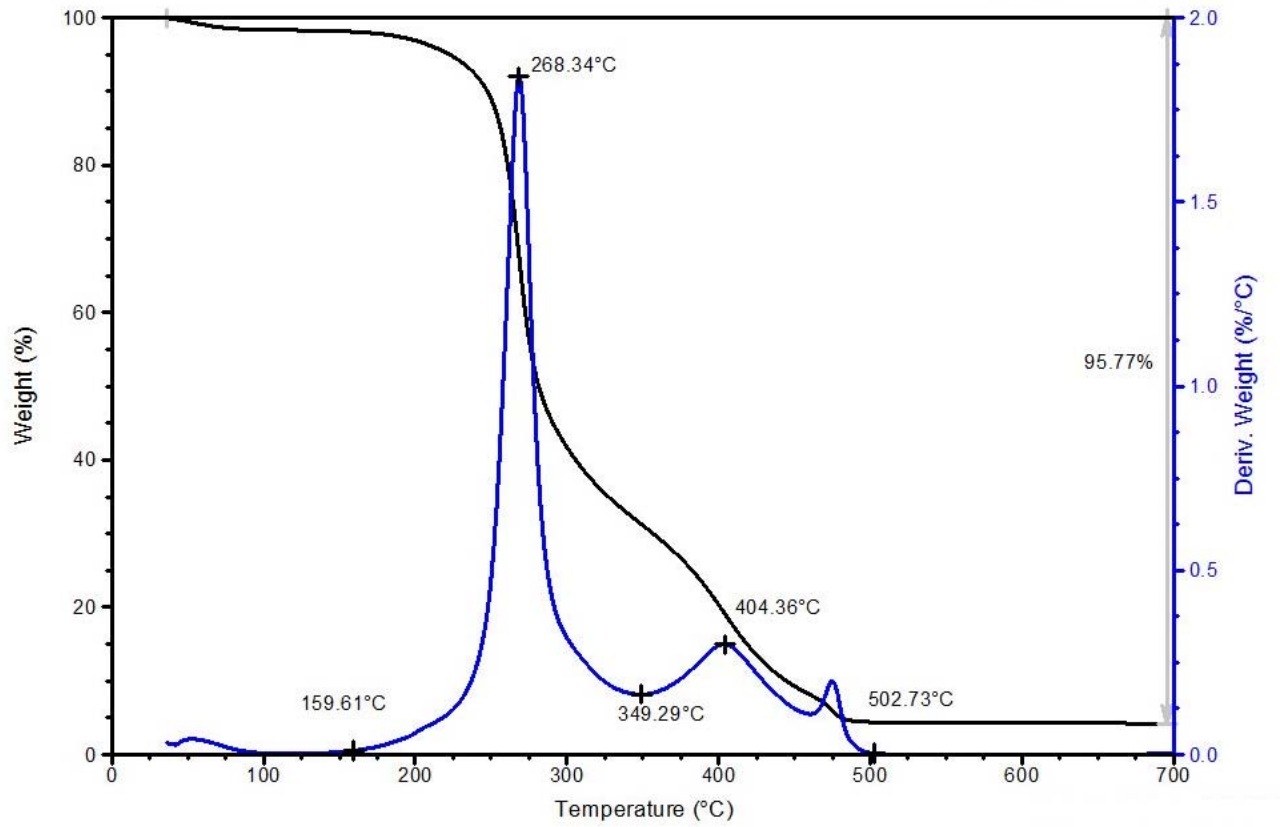

Fig. 7.10 TG/DTG profile of FSS char at 180°C

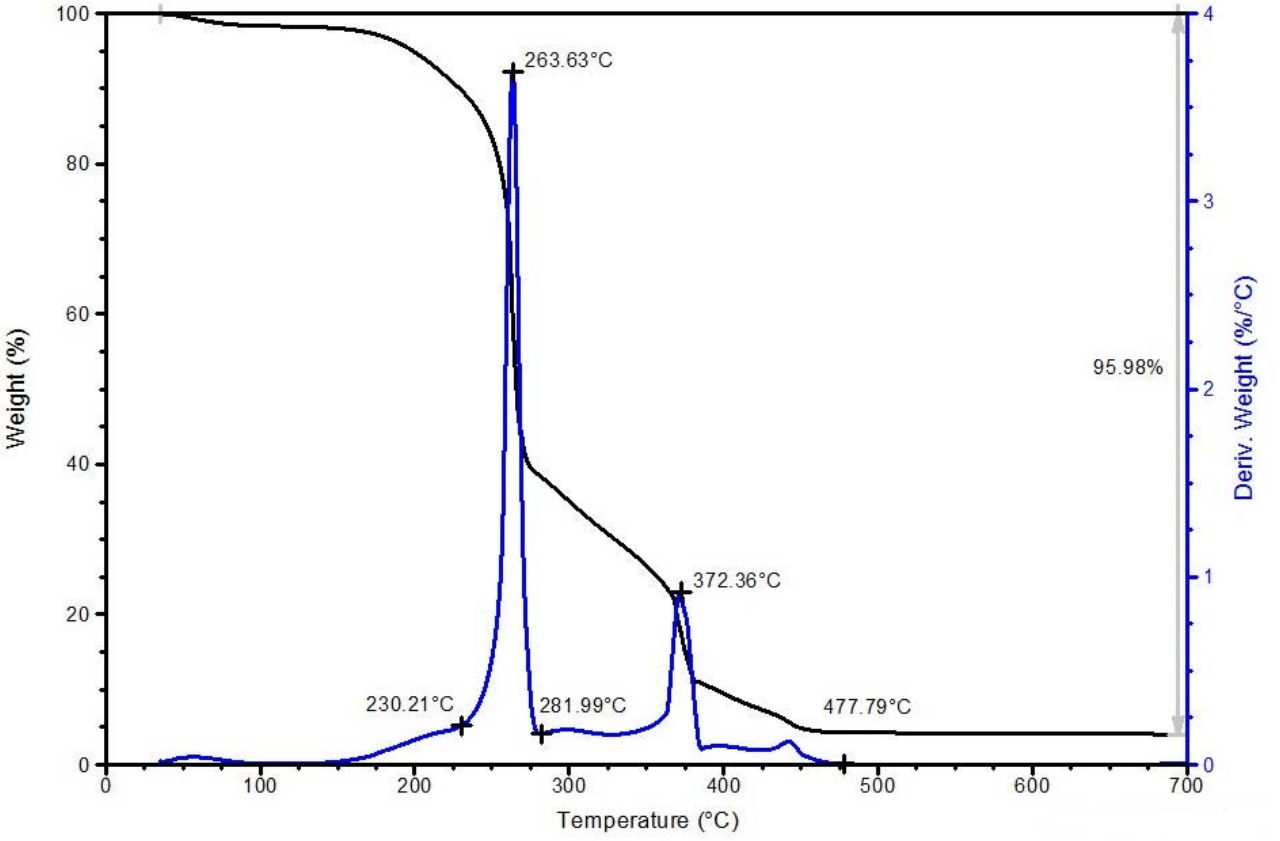

Fig. 7.11 TG/DTG profile of FSS char at 200°C

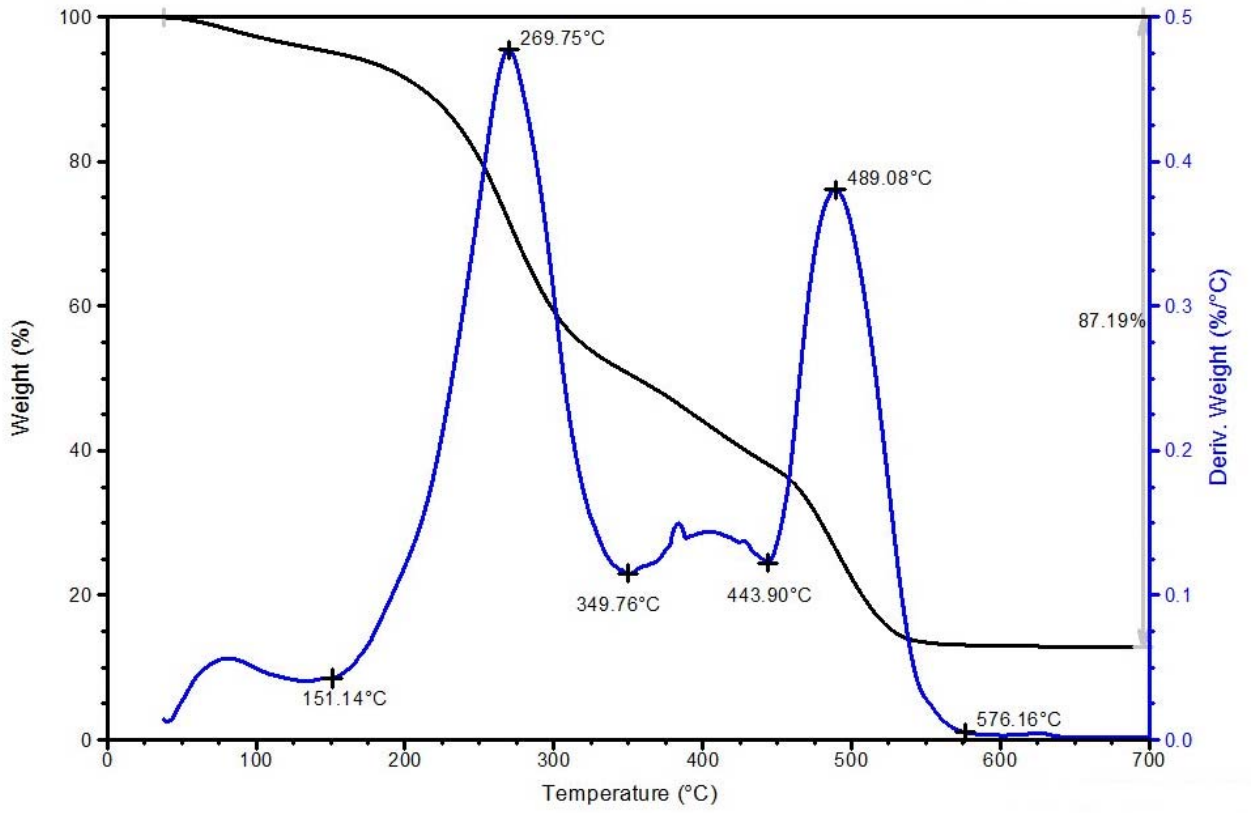

Fig.7.12 TG/DTG profile of unprocessed HF

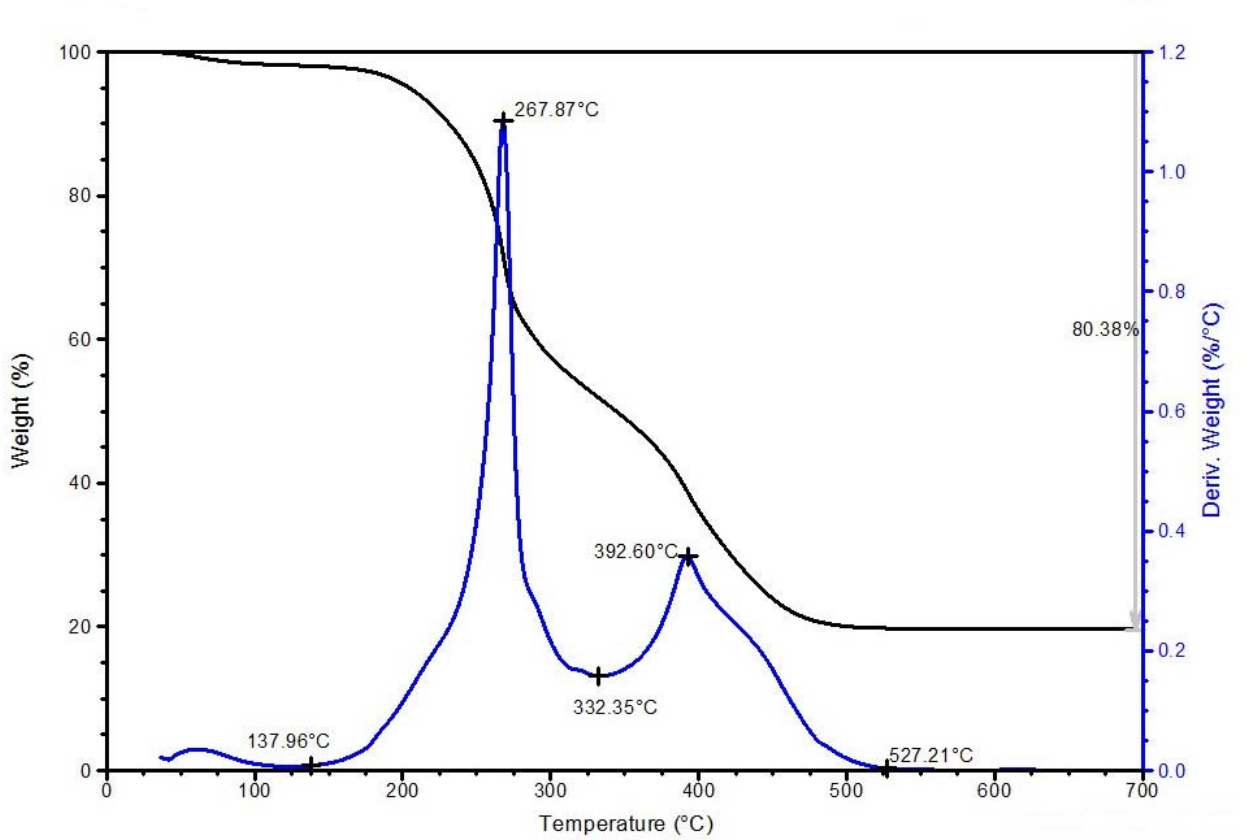

Fig. 7.13 TG/DTG profile of HF char at 180°C

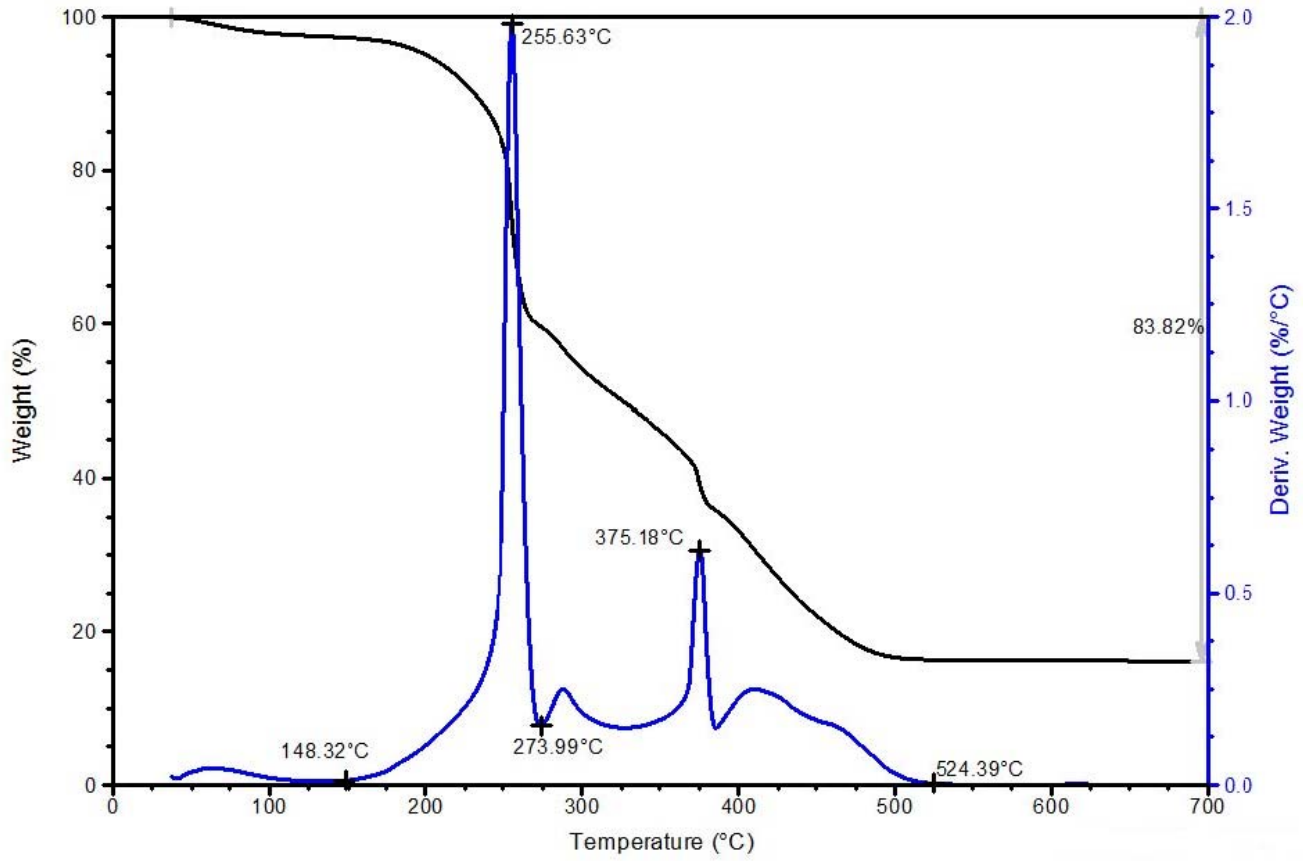

Fig. 7.14 TG/DTG profile of HF char at 200°C

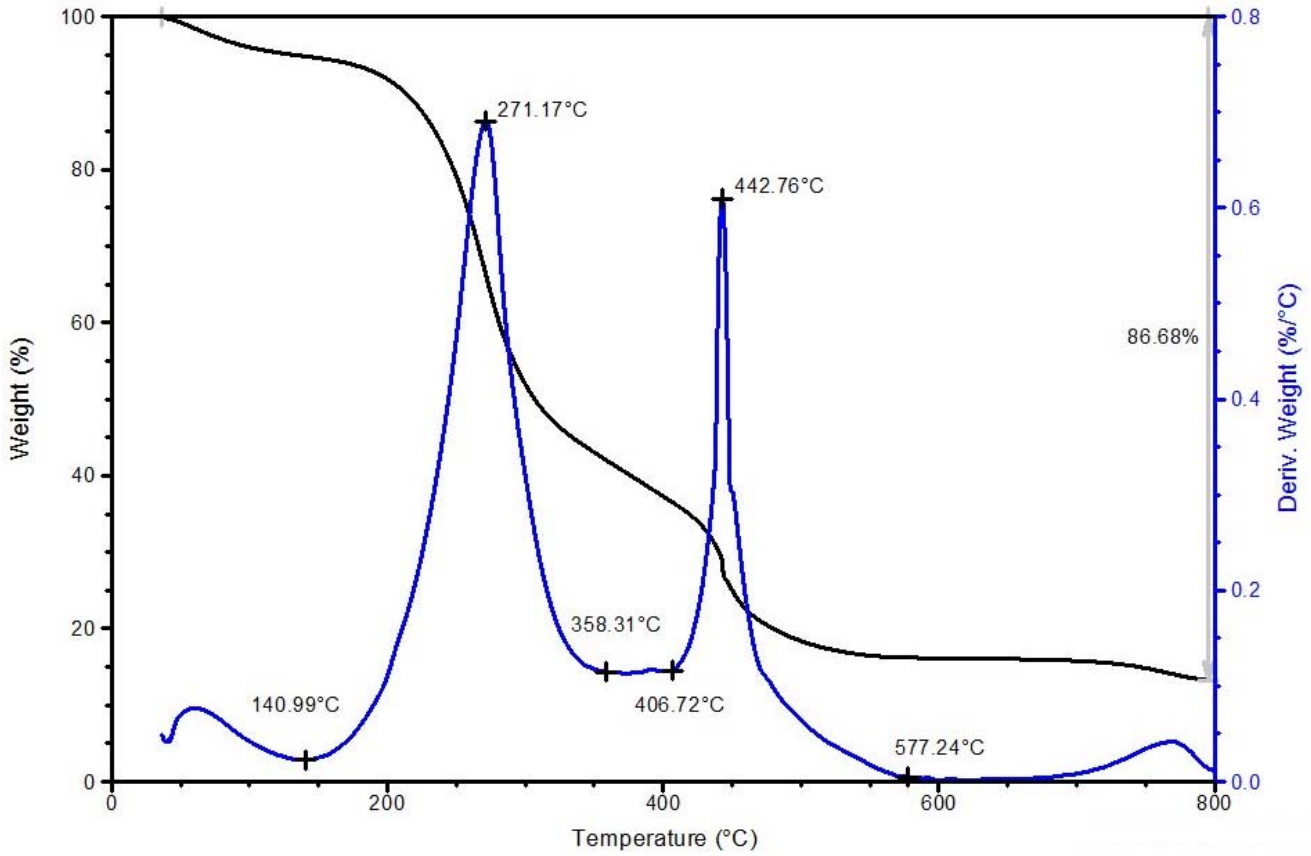

Fig.7.15 TG/DTG profile of unprocessed HFS

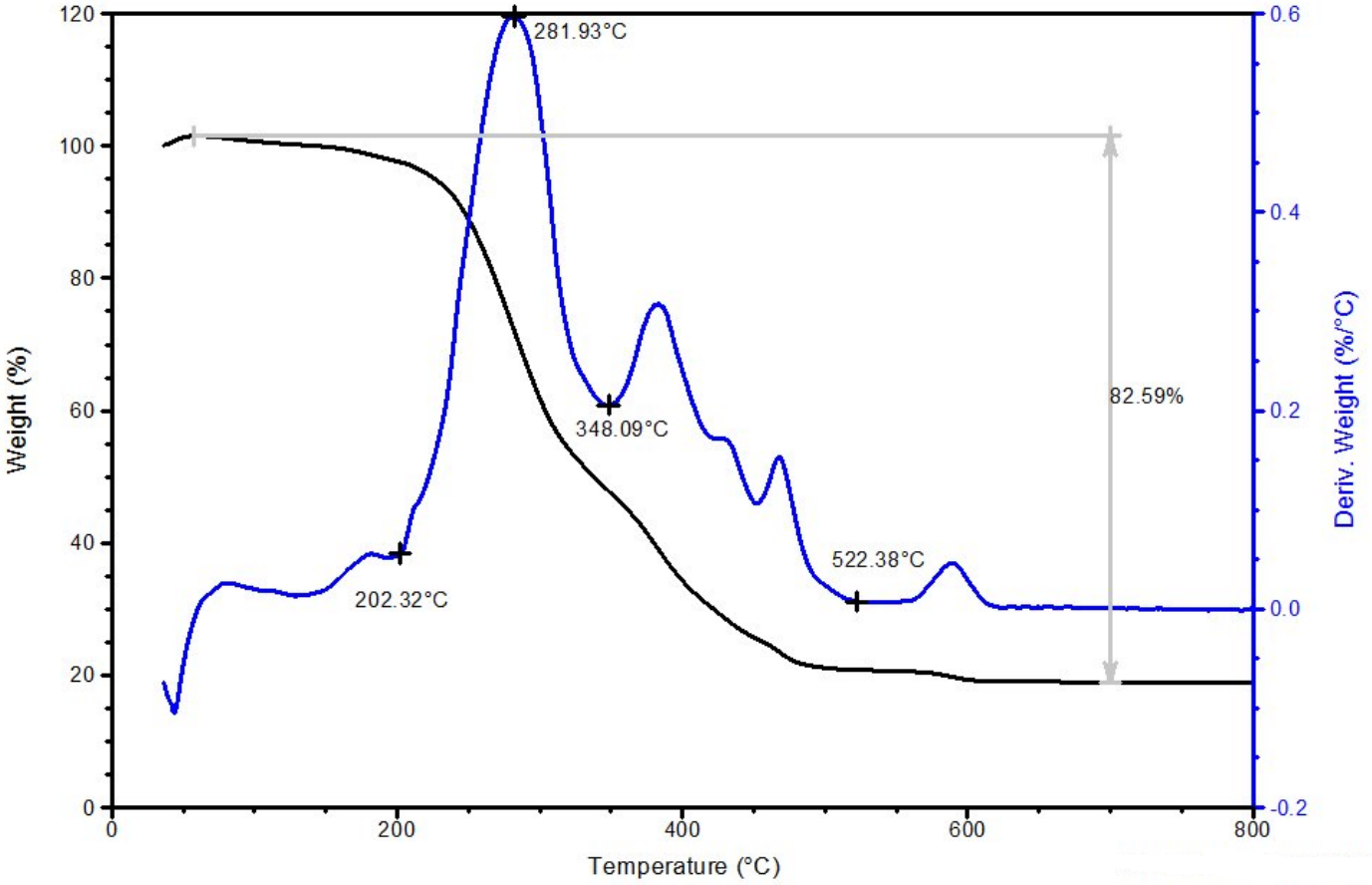

Fig. 7.16 TG/DTG profile of HFS char at 180°C

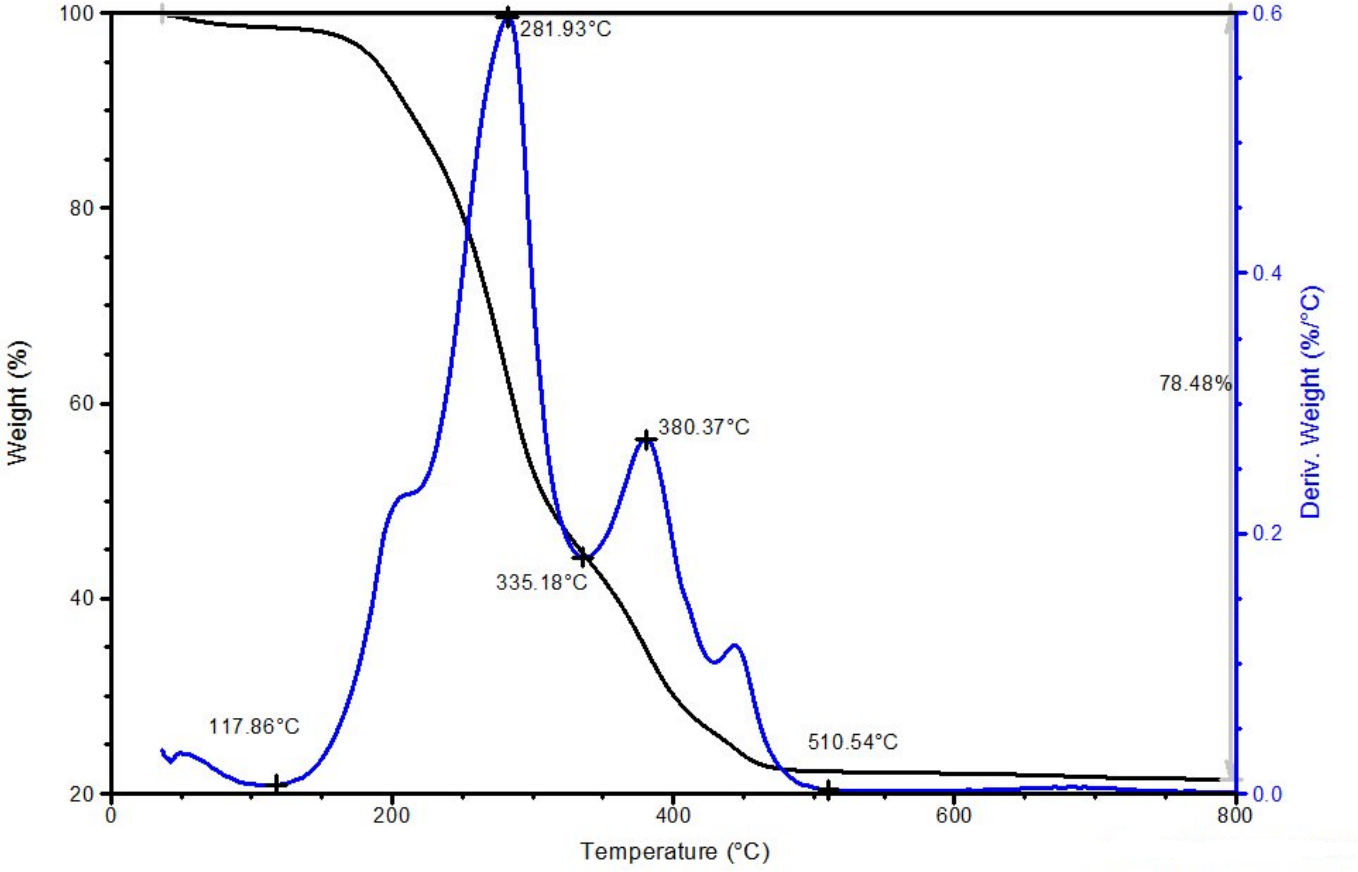

Fig. 7.17 TG/DTG profile of HFS char at 200°C

7.4 STRUCTURAL PROPERTIES

7.4.1. Porosity and surface area analysis

Char morphologies from the SEM images in Section 5.2.2, along with surface area ($m^2.g^{-1}$) and pore sizes obtained from M-HTC run at 180°C and 200°C are shown in Table 7.8.

Table 7.8 Surface area and pore sizes of unprocessed biowastes and their chars

Sample description		BET surface area/ $m^2.g^{-1}$	Pore size /nm	
			Adsorption	Desorption
HFS	Unprocessed	0.9	14.9	11.7
	Char at 180°C	1.7	19.1	16.4
	Char at 200°C	1.3	36.5	30.4
SS	Unprocessed	1.6	29.4	22.7
	Char at 180°C	4.2	25.6	21.8
	Char at 200°C	4.7	23.0	21.4
HF	Unprocessed	0.6	15.5	12.3
	Char at 180°C	1.8	10.0	8.8
	Char at 200°C	0.9	12.2	10.0
FSS	Unprocessed	0.5	14.6	11.6
	Char at 180°C	1.0	9.6	8.2
	Char at 200°C	0.9	12.1	9.9

The pore sizes, ranging from 9.6nm to 36nm, may be classified according to the IUPAC classification as Type 2 pore sizes, *mesopores* 2nm to 50nm (48), and are similar to the pore sizes of HTC chars of sunflower and walnut (36). The char pore sizes were consistent with their surface areas ranging between $0.9m^2.g^{-1}$ to $5m^2.g^{-1}$, similar to values reported for chars recovered from microwave dry pyrolysis of straw pellets and willow chips characterized under BET and mercury porosimetry (49). Literature values for BET surface areas of most HTC chars (derived from conventional heating) for feedstocks such as apricot, sugar bagasse, willow, algal and sewage sludge range between $0.67m^2.g^{-1}$ and $14.68m^2.g^{-1}$ (50; 35; 51; 52; 53); these are comparable to the values observed in the present study.

The surface area of the chars was generally greater, by more than 50% in most cases, than that of the feedstock. This can be attributed to *tunnelling effects* caused by heating and the mass transfer processes during the M-HTC process, as described in Chapter 5. This corroborates the SEM studies, which revealed enhanced porous features in chars.

This in part could explain why higher porosity is associated with chars produced from microwave heating over conventional heating, as observed in other studies (49; 54). For HFS, HF and FSS, increasing the temperature from 180°C to 200°C was associated with a decrease in surface area with increasing temperature. The SS char showed an increase by 0.4$m^2.g^{-1}$ in surface area with increasing temperature. A previous study indicated that increasing temperature reduced char porosity under conventional heating, from 1.14$m^2.g^{-1}$ at 200°C to 0.17$m^2.g^{-1}$ at 350°C (49). HTC of cellulose has also been reported to produce mesoporous chars of low surface area at process temperatures of 180°C to 200°C (14). When compared with average surface areas of commercially activated carbon, about 1500$m^2.g^{-1}$ (55), an activation step will be required if HTC chars are intended for sorption studies.

7.4.2. Functional surface analysis of unprocessed biowastes and their chars

Fourier Transform Infrared (FTIR) studies were conducted to further investigate the microchemistry of HBW and their chars, and Figs. 7.18 to 7.21 show the FTIR spectra of feedstocks and chars recovered at 180°C and 200°C. Tables 7.9 to 7.12 summarize the spectral analysis. The interpretations of the FTIR spectra and band assignments were informed by published studies of HTC char produced from sewage sludge, food materials and cellulose (56; 57; 58; 59; 60) under comparable thermochemical conditions.

Figs. 7.18 to 7.21 appear to show that the spectra of chars are a 'superposition' of components in unprocessed biowaste. Although some differences in FTIR spectra patterns are discernible from unprocessed biowaste, the main difference is seen in the difference in absorbance band intensities. In most cases, spectra from both unprocessed biowastes and their chars contain several similarities in band peaks, with the intense and broad absorptions in the region 1006cm^{-1} to 1058cm^{-1}, assigned to the C-O stretching typical of carbohydrates or polysaccharide-like substances that are expected to be present in HBW (60; 61). Two sharp absorption bands, typically at 2920cm^{-1} and 2850cm^{-1}, assigned to C-H stretching due to the aliphatic methylene groups (62; 59) were also present. Other bands at 720cm^{-1}, commonly observed in HBW e.g. sewage sludge, may be associated with long-chain aliphatic compounds with conjugated characteristics bands (56). Another prominent band was observed at 3271cm^{-1} to 3280cm^{-1}, due to of O-H hydroxyl vibrations. Bands at 1620cm^{-1} to 1629cm^{-1}, and conjugated bands at 880cm^{-1} to 700cm^{-1}, due to C=C vibrations and aromatic C-H bends respectively, were attributed to the presence of aromatic structures that were indicative of aromatization as a potential reaction pathway (61; 35; 63).

O-H and N-H stretching at 3330cm^{-1} to 3336cm^{-1}, assigned to H-bonded hydroxyl and amino groups, were seen in the chars from SS, HFS and FSS, but not in their feedstocks. A feature at 1535cm^{-1} due to N-H in plane and 1408cm^{-1} N-O band stretching was not seen in the chars, while being present in the feedstocks; this is signified in Tables 7.9 to 7.12 as 'D' for 'disappeared'. Such bands are typically bands of protein (secondary amides) present in unprocessed HBW, which are not present in chars due HTC solubilization effects. This phenomenon has been described before in studies on sewage sludge composting (60; 62; 64), a further evidence of the transfer of nitrogen from unprocessed feedstocks into the liquor phase during the M-HTC process.

There were changes in the aliphatic and polysaccharide band intensities of unprocessed biowastes and their chars, which provide further evidence of organic decompositions during the HTC process. For example, a decrease in band absorbance intensity at 1000cm^{-1} to 1100cm^{-1} (carbohydrates bands) and 2850cm^{-1} to 2920cm^{-1} (aliphatic) can be seen from Figs 7.18 to 7.21. This may be attributed to the effect of dehydration during the HTC process, already noted above in the H/C –O/C Van Krevelen diagram in Section 7.2.4. These observations are in line with the conclusions of a previous study (65), which noted that that the FTIR spectra of organic matter are usually qualitatively similar but differ in the relative intensity of absorbance band and specific bands.

Table 7.9 Assignment of the principal IR absorption bands in the spectra of unprocessed SS and their chars

Location of wave numbers (cm^{-1})		Vibrations	Band assignment of functional group/component
Unprocessed SS	SS chars		
	3335	N-H stretch & O-H stretch	Aliphatic secondary amines stretch and hydroxy group
3275	3273	O-H stretch	Hydroxy group
2955		C-H stretch	Aliphatic methylene group
2920	2920		
2850	2850		
	1649	C=O	Primary amide, carboxylates (H-bonded C=O carbonyl stretch)
1626	1629	C=O stretch C=C stretch	Carboxylate and conjugated aromatic ring mode
1620			
1535	D	N-H in plane	Secondary amides
	1452	C-O stretch	Carbonate ion
1408	D	N-O stretch	A source of nitrate in unprocessed biowaste
1381	1377	Methyl C-H bend N-O stretch	Provides indication of long-chain aliphatic compounds Nitrate in solid wastes
1232	1259	C-O stretch C-N stretch	Carboxylic acids or Tertiary amide
	1024	C-O stretch	Characteristic polysaccharide bands for C-O stretching of polysaccharides or polysaccharide-like substances
1010	1006		
796	798	NH_2 out of plane	Primary amine groups
	719	Methylene C-H rocking	Provide indication of long-chain aliphatic compounds
	657-692	O-H or C-H out of plane bend S-O bend	Skeletal vibrations of hydroxy out of plane bend or C-H bending vibration as corroborated with bands at 1200-1000, 1600-1300 (56) inorganic sulphates

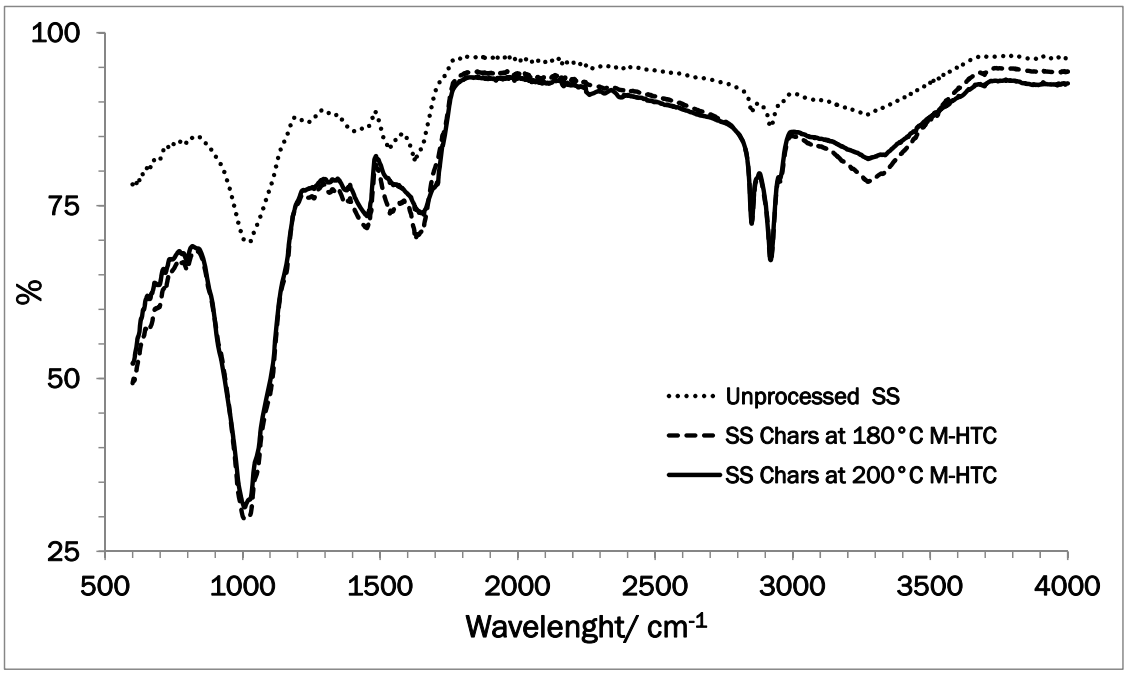

Fig. 7.18 FTIR spectra of unprocessed SS and carbonized chars at 180°C and 200°C

Table 7.10 Assignment of the principal IR absorption bands in the spectra of unprocessed FSS and their chars

Location of wave numbers (cm^{-1})		Vibrations	Band assignment of functional group/component
Unprocessed FSS	FSS Chars		
3331	3336	O-H stretch	Hydroxy and carbonyl groups characteristic of cellulose-based substrate
3292	3286		
3005	3005	C-H stretch	Aliphatic methylene group
2922	2922		
2852	2852		
1743	1743	C=O stretch	Vibrations of carbonyl, esters or carboxyl
1626	1651	C=C C=O	Presence of aromatic rings, ketones/quinones
1535	D	N-H in plane	Secondary amides
1454	1452	C-H bend	Aliphatic methylene group
	1367	O-H bend	Aromatic bend
1359			
1315	1315		
	1278	O-H bend	Primary or secondary OH in- plane bend
1244	1242	N-H bend Stretches of C-O H-O	Secondary amide Hydroxyl, ester or ether vibrations
1203	1199		
1159	1159		
1059	1103		
1051	1055	C-O stretch	Polysaccharide bands
1031	1030		
893	896	Bends due to N-H C-O	Skeletal vibrations due to secondary amine, carbonate, inorganic sulphates
804			
	696		
659	663		

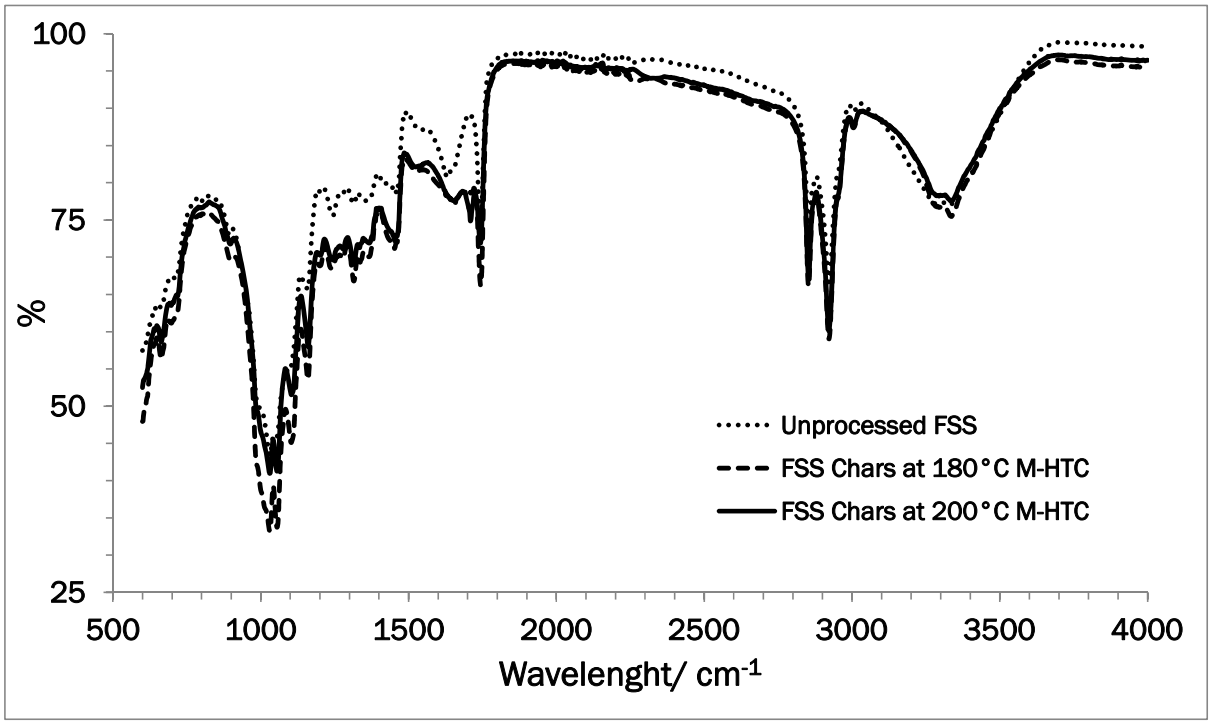

Fig. 7. 19 FTIR spectra of unprocessed FSS and carbonized chars at 180°C and 200°C

Table 7.11 Assignment of the principal IR absorption bands in the spectra of unprocessed HF and their chars

Location of wave numbers (cm^{-1})		Vibration	Band assignment of functional group/component
Unprocessed HF	HF Chars		
3271	3271	O-H stretch	Hydroxy group
2920	2920		
2850	2850	C-H stretch	Aliphatic methylene group
1626	1626	C=O and C=C stretch	Carboxylate e.g. quinone and aromatic rings
1535	D	N-H in plane	Secondary amides
1442	1452	C-O stretch	Carbonate ion
1408	D	N-O stretch	A source of nitrate in unprocessed biowaste
	1379		A band typically observed for composted i.e. decomposed organic Very reproducible
1317	D		Aromatic primary and secondary amides
1236	D	C-N stretch	
1033	1058		Typical carbohydrate or polysaccharide bands
	1014	C-O stretch	
	881		
	779		C-H bending vibrations indicating the presence of adjacent aromatic hydrogen in biochar samples and potentially N-H wag
	721	C-H bend N-H bend	
696	700		
667	665-9	S-O bends	Inorganic sulphates

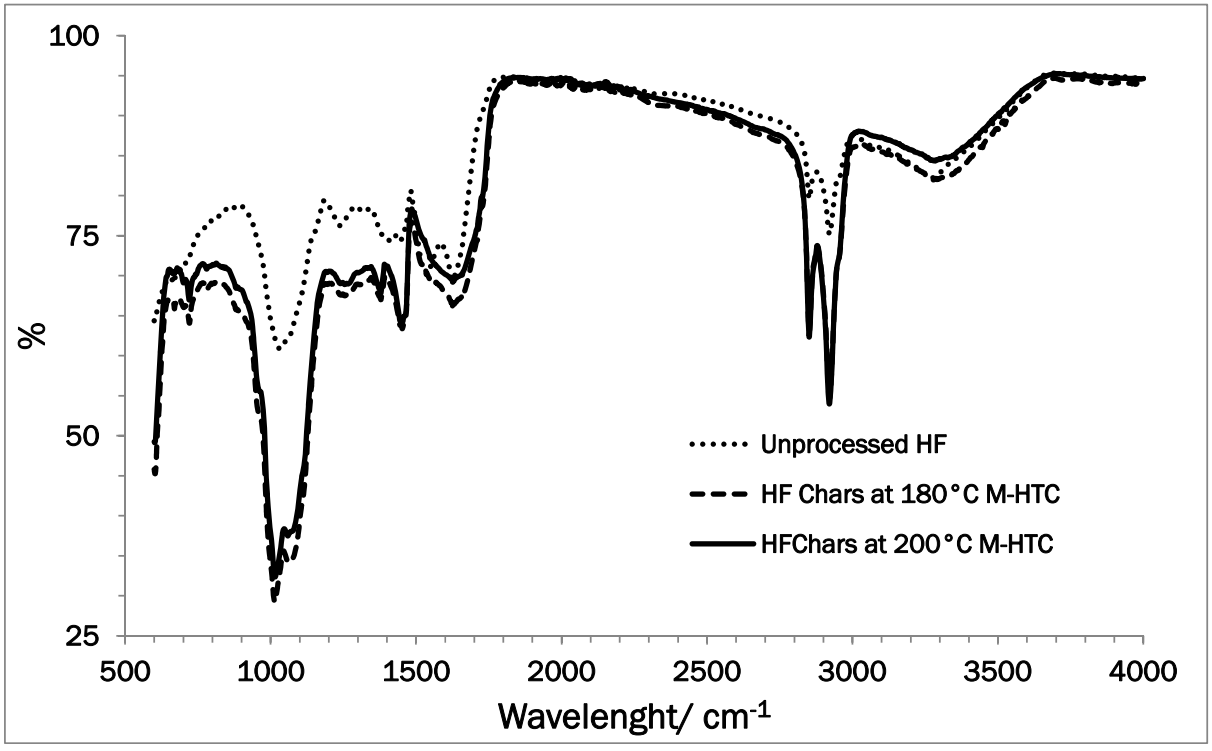

Fig.7.20 FTIR spectra of unprocessed HF and carbonized chars at 180°C and 200°C

Table7.12 Assignment of the principal IR absorption bands in the spectra of unprocessed HFS and their chars

Location of wave numbers (cm^{-1})		Vibrations	Band assignment of functional group/component
Unprocessed HFS	HFS Chars		
	3335-6	N-H stretch & O-H stretch	Aliphatic secondary amines stretch and hydroxy group
3273	3276-81	O-H stretch	Hydroxy group
2918	2918	C-H stretch	Aliphatic methylene group
2850	2850		
	1741	C=O stretch	Esters and carboxylic acids
	1658	N-H bend C=O stretch	Amide
1626			Carboxylate
	1579-85	N-H bend N-O	Secondary amide or nitro-compounds
1548			
1444	1452	C-O stretch	Carbonate ion
1408	D	N-O stretch	A source of nitrate in unprocessed biowaste
	1367-9	N-O stretch	Nitrate source
1315	1315	C-O	Carboxylic acids
	1274	C-N stretch	Secondary amines
1244	D	N-H bend C-O stretch	Secondary amides Alcohols
	1201-3		
	1099		
	1053	C-O stretch	Very consistent carbohydrate or polysaccharide-like bands
1049			
1030	1028		
896	896	C-H bend	C-H bending vibrations, indicating the presence of adjacent aromatic hydrogen in biochar samples and potentially N-H wag
	717	N-H bend	
	702		
657	661-3	S-O bends	Inorganic sulphates

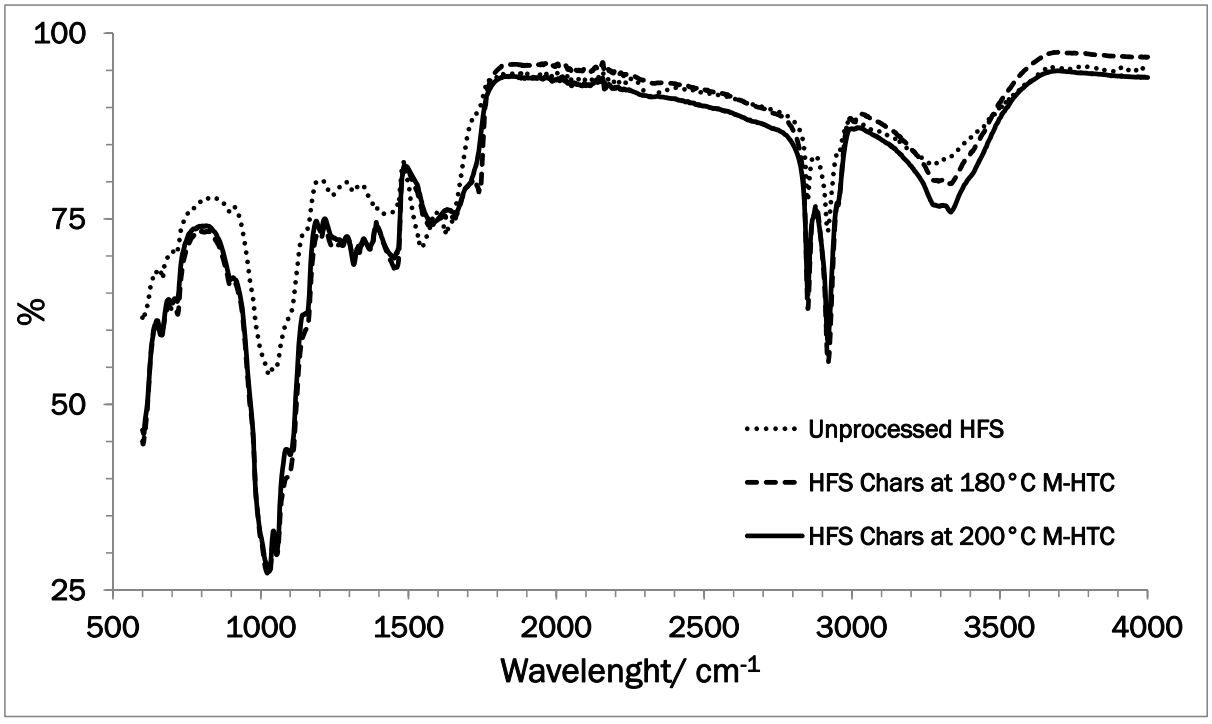

Fig. 7. 21 FTIR spectra of unprocessed HFS and carbonized chars at 180°C and 200°C

7.5 NUTRIENT AND METALS ANALYSIS

Nutrients (P, K) and metals analysis in solid chars recovered after the M- HTC process is important because:

- The fates of solid chars and recovered liquor are expected to be different, hence the distribution/partitioning factors can serve as a guide to potential recovery of specific nutrients or metals.
- Their concentration in chars will determine potential applications. For example, if chars are to be used as soil ameliorants, elemental quantification of P, K and Na is crucial: P and K are associated with plant growth, while Na and Cu reduces growth (29; 26).

Elemental metal component concentrations and their distribution coefficients were analysed according to method outlined in Section 4.4.9 for samples obtained from SS (as a representative HBW material) and chars obtained from M-HTC run at 150, 160°, 180° and 200°C for 15min., 30min. and 60min. respectively (see Table 7.13 and Appendices 3.4 and 3.5). (SS was used in order to manage the unquantified risk associated with using HFS and HF on the ICP-OES analytical equipment).

Differences in metals' concentrations in SS and associated M-HTC chars were expected to be unlike those from other substrates, partly due to differences in concentrations of elements, organic components and the complex heterogeneous nature of different HBW materials. However, partitioning behaviour into the solid/liquor phases of carbonized materials during M-HTC was not expected to be significantly different. An extended percentage weight distribution/partitioning fraction of each metal analysed into solid and liquid fractions of carbonized materials is summarized in Fig.7.22.

Table 7.13 Averaged elemental concentrations ($g.kg^{-1.}$) in chars produced by the M-HTC of SS over the residence times investigated

	T / °C				
Metals	Unprocessed	150°C	160°C	180°C	200°C
B	1.4	0.5	0.5	0.5	0.5
Cd	0.9	0.5	0.4	0.5	0.5
Co	0.4	0.2	0.2	0.2	0.2
Cr	1.4	0.8	0.8	0.8	0.9
Cu	8.4	5.3	5.2	5.7	5.5
K	338.7	81.1	75.9	78.9	76.6
Mo	0.6	0.3	0.3	0.4	0.4
Na	49.8	12.4	11.9	12.1	11.6
Ni	0.7	0.4	0.4	0.4	0.4
P	329.8	165.7	161.9	178.9	187.9
Se	3.4	1.8	1.7	1.8	1.9
Zn	14.6	8.8	8.6	9.2	9.3

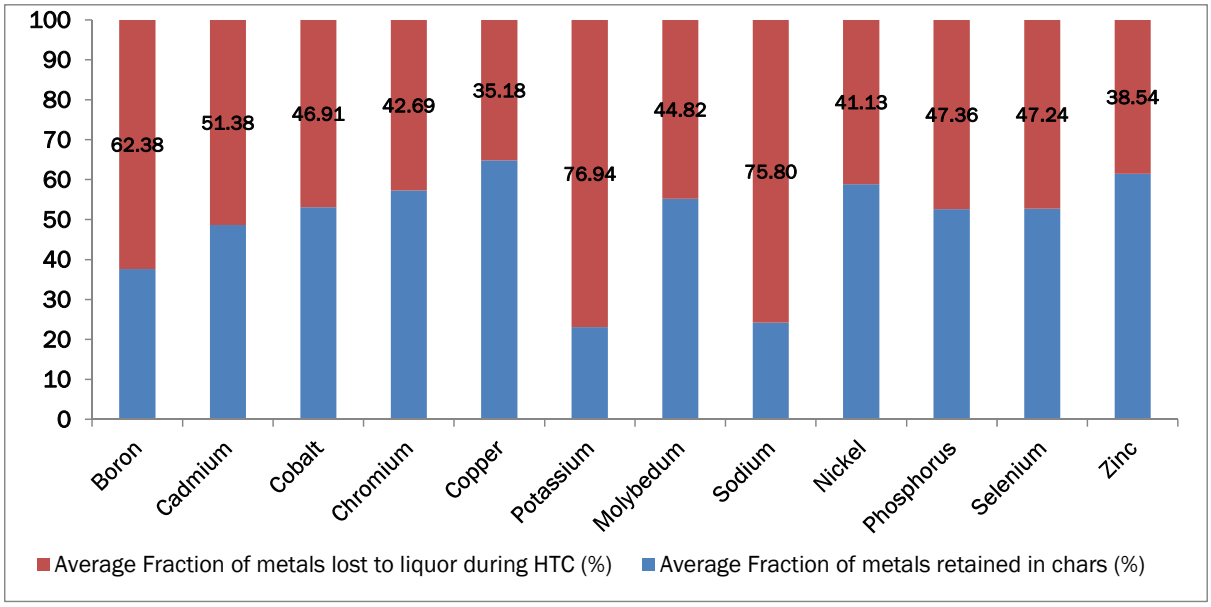

Fig.7. 22 Percentage weighted distribution of elements between solid chars and those lost into the liquor phase after M-HTC process of SS

M-HTC processing changed the elemental distribution of the SS between the solid and liquor phases (Table 7.11 and Fig. 7.22), with a significant reduction in solid phase concentrations (greater than 50% in all cases). Fig. 7.22 reflects the affinity of individual elements for the liquid phase, notably sodium and potassium (76%), compared to copper, zinc, nickel and other metals, which were more strongly are retained in the chars. This is similar to previous studies (66; 67), which concluded that K, Na and N were preferentially partitioned into the HTC liquor phase, with high fractions of copper and zinc in the solid phase. This raises questions about the bioavailability of these elements if chars were to be used as soil conditioners. In contrast, the high affinity and retention of P (>50%) in chars may be seen as an advantage, for P is nutrient for crop growth. If used as solid fuel, phosphorus can be recovered in the ash content of combusted chars (66). Combining these results with the ammonia recovery observations, it can be inferred that M-HTC promotes on nutrient distribution (notably N and P) into the liquor phase.

7.6 RELEVANCE OF MICROWAVE PROCESSING OF HBW

Fig. 7.23 summarizes the potential M-HTC workflow for HBW for potential applications from chars as solid fuel and soil ameliorant, as well liquor recovery (for ammonia recovery, energy recovery via anaerobic digestion or recycling).

7.6.1 Relevance of carbonized materials

The principle issues and concerns that inform HBW sludge management are:

- Insect nuisance and vector management (68).
- Pathogenic content and associated health risks. (Note that conventionally treated sewage sludge can rarely be classified as Class A Biosolids (69). Direct exposure

constitutes a health risk, while windborne transmission of aerosolized sewage sludge may take place – especially during field application (70)).

- Potential contamination of surface/groundwater and crops (71).
- Leachate contamination or releases of dioxins/greenhouse gases.
- Foul odour and environmental impact.

The present research has presented the concept that M-HTC may be used in the management of HBW, either as a stand-alone onsite sanitation facility or integrated into existing centralised HBW sludge treatment infrastructure. Further, the studies described have presented evidence that shows how M-HTC can mitigate, if not eradicate, these concerns because:

- The process can produce sterile end products, which can be classified as Class A Biosolids – as demonstrated with the pathogenic destruction of faecal and total coliforms in Chapter 5.
- The challenges associated with material handling, storage, transportation and/or re-use are reduced, with mitigation of threats to crops, surface/groundwater or disposal via landfill.
- Challenges associated with poor dewaterability are also eradicated, as the process can ensure carbonized materials are easily separated into solids and liquid phases in less than 10 seconds (based on CST experiments), or liquid content can be decanted if allowed to settle by sedimentation. This, as discussed in Chapter 6, has energy-saving advantages (66).
- The process can completely eradicate the odour challenges of faecal biowaste, as demonstrated in the present study. This can be very significant for public acceptability, as carbonized materials produced from microwave HTC have a better odour than the foul odour of unprocessed biowastes.

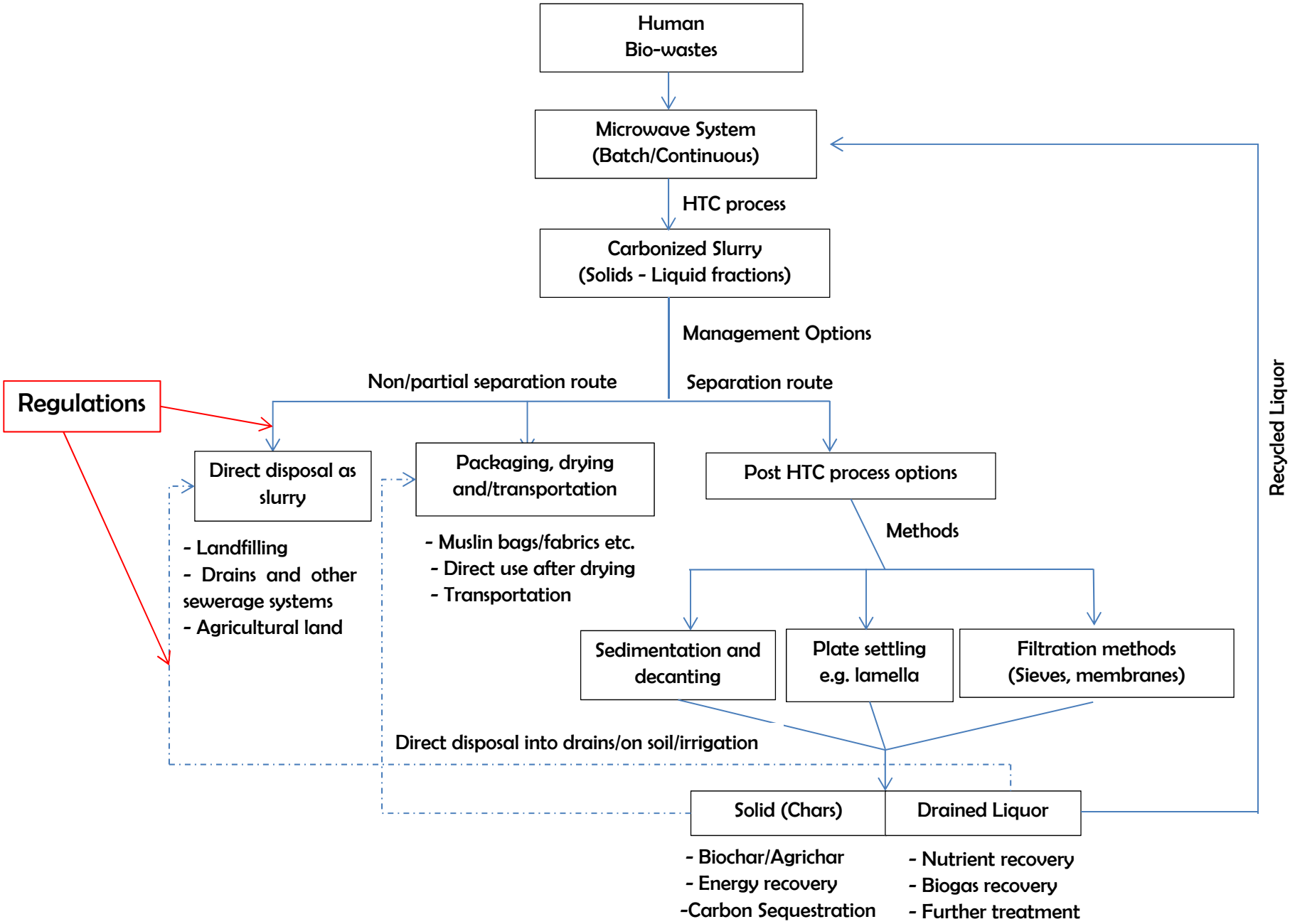

Fig 7. 23 Schematic outline of HBW processing and management options, adopting the M-HTC process

7.6.2 Relevance of recovered solid chars/liquor

M-HTC of HBW does more than manage a problem; it has the potential to yield useful products.

- It may be used to generate energy in a sustainable manner, for chars are a potential clean energy resource.
    - ❖ The handling characteristics of the chars obtained in the present study from HBW were suitable for compaction into briquettes, which can be combusted as solid fuel (34; 9).
    - ❖ CHN studies indicated the reduction of N-content in solid chars. Further, the discussion of the mechanism underpinning odour eradication (Section 5.2.1.3) indicates that that the removal of sulphur-containing compounds by M-HTC may be predicted. The removal of N, and potentially S, enhances the suitability of chars for combustion (37).
    - ❖ SEM and BET studies indicate that M-HTC enhances char porosity by over 75%, improving the combustion reactivity of char – because higher porosity causes more active air distribution. This observation is supported by the observed elevated reactivity of chars during the TGA analysis, such as the decrease in combustion burnout temperatures.
    - ❖ HHV results for the M-HTC generated chars from HBW are comparable to conventional fuels, which opens up the potential for co-combustion. Studies have shown that co-blending chars with coal improves the combustibility index and reduces ignition temperature (43; 72). For example, blending chars from bagasse with coal has been found to reduce the ignition temperature of blends from 427°C of coal to 275°C of blends (72). More work in this area will include the co-blending of chars from HBW with conventional fuels, and assessing their solid fuel reactivity profile.
- The chars generated in this work where characterised with respect to C/N ratio, porosity, pH, ammonia content and nutrient content, and were found to be comparable to chars produced by conventional HTC and a range of less noxious substrates. The benefits of char in agriculture are well reported (73; 74); M-HTC chars derived from HBW may applied to soil to:
    - ❖ replenish plant nutrients,
    - ❖ improve water-holding capacities,
    - ❖ sequester carbon,
    - ❖ reduce GHG emissions.

Some qualification is needed, for further investigations on the bioavailability of nutrients and other elements should be run to evaluate the safety/suitability of these materials for crops and for soil nourishment.

- Finally, the liquor recovered from M-HTC has value. It contains recoverable leachates that may be:
    - ❖ recycled into the HBW management system,
    - ❖ used as a substrate for biogas recovery, or
    - ❖ used as liquid fertilizer, due to its ammonia content.

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CHAPTER 8 CONCLUSION, CONTRIBUTION TO KNOWLEDGE AND FUTURE WORK

8.1 CONCLUSION

Microwave hydrothermal carbonization (M-HTC) was investigated in this doctoral research as an alternative and efficient technology capable of addressing the challenges of poor sanitation, which still claims the lives of many in middle- and low-income territories. The background theories behind the exploration of M-HTC to process human biowastes (HBWs) were based on premises that:

- HBWs are not only bio-hazardous, but rich in organic resources that can be beneficially exploited; and
- water, which constitutes up to 95% w/w in HBW, can interact with microwaves, with this electromagnetic interaction causing dielectric heating.

The overall research focus were to demonstrate that the dielectric heating generated during the M-HTC process could both treat and transform HBWs into a safe form and also realize intrinsic value from them.

In Chapter 5, a comparative sensory assessment and SEM studies of HBW before and after the M-HTC treatment provided evidence that indicates M-HTC reliably overcomes the heterogeneous nature of HBW, converting it into new end products that are distinctive in odour (M-HTC completely eradicated the foul odour associated with unprocessed HBW), appearance (colour change and texture) and microstructures. This in essence, addressed the first objective of the research (See Table 1.4). The complete transformation of the foul odour associated with HBW could improve public acceptance, and hence promote M-HTC's potential use as a mobile processor, representing a safer alternative to the current faecal emptying approach in developing economies. Thermal hydrolysis of macromolecular components in HBW and subsequent chain reactions during the M-HTC process were responsible for the colouration and smells produced from the carbonized biowaste. The conversion model of HBW into carbonaceous solid chars was observed to include a combination of solid-to-solid conversion and induced nucleation pathways. The solid-to-solid conversion pathway was observed to be the predominant pathway for all substrates studied, except the synthetic faecal simulant. Furthermore, aside from generating stabilized and consistent end products, the M-HTC process ensured complete pathogen destruction: <1CFU/100mL using *E. coli* as the

pathogenic indicator. This addressed the second objective of the research. Thus, M-HTC technology reliably satisfied the fundamental biowaste Class A pathogen treatment requirement, as the end products generated were below the WHO's and EPA's regulatory limits for Class A Biosolids classification.

Chapter 6 also addressed in more detail the second and part of the third objectives of this research. The chapter evaluated the potential of the M-HTC process as a stand-alone sludge dewatering process, and was found to be better than conventional approach – most significantly at 140°C (by 38.8%) and 160°C (by 32.8%). Both HTC processes indicated that an increase in carbonization temperature from 140°C resulted in a corresponding decrease in dewatering time. At 180°C, for example, the rate of sludge release decreased from 389.9 ± 28.9s in unprocessed sludgy HBW to 9.3 ± 0.6s (M-HTC) and 10.5 ± 0.5s (C-HTC) in processed HBW. Further increases in carbonization temperature after 180°C, however, showed no significant improvement in dewatering. The particle size distribution of processed HBW indicated gradual shifts to the proliferation of smaller particles during the carbonization process as carbonization temperature was increased from 160°C to 200°C. Similar observations were recorded during the dewaterability studies involving the C-HTC process; these suggest that carbonization temperature, rather than the heating source used to achieve carbonization, influences dewaterability. Successful dewatering could improve the financial incentives for waste management in both developed and developing countries, if the contingent sustainability value of such management is assessed.

Chapter 7 provided more details on how the third and fifth objectives were addressed. Value-added-products recovered from the HBW – in the form of carbonaceous solid chars and ammonium liquid concentrates – were evaluated; these have relevance in energy generation and use as fertilizers in agriculture, as outlined in Chapter 7. In terms of yield, more than 50% of solid chars (dry basis) and 1g.L^{-1} of ammonia can be recovered by processing HBW using 180°C as a benchmark for the M-HTC process. Additionally, carbonized solid chars demonstrated enhanced carbon and energy properties following the M-HTC process. When compared with unprocessed HBW, the carbon content in the solid chars increased by up to 52%; the carbon densification factor was greater than 1 in all recovered chars. The calorific values of the solid chars increased by up to 41%, yielding heating values that averaged 25MJ.kg^{-1}, which are greater than low-rank coals. This suggests their use either as a stand-alone solid fuel or one that can be co-combusted with other fuels of similar heating value. However, co-combustion of HBW chars with other fuels requires further assessment to establish compatibility of

combustion parameters, such as ignition points and combustion reactivity. TGA studies revealed that the solid chars exhibited greater reactivity when compared with unprocessed HBW. This buttressed the findings from the BET (and SEM studies), which indicated improved porosity in solid chars by more than 50% in most cases. Improved porosity enhances air distribution during combustion and hence explains the faster reactivity of chars during their thermal decomposition in air, as observed from the TGA studies.

The C/N ratios, P, K quantification in chars and the amount of ammonia recovered from the HBW supported their use in agriculture. CHN analyses of the solid chars revealed that nitrogen is depleted from HBW into the liquor phase of end products during the M-HTC process. This was further buttressed by FTIR studies, which showed the disappearance of specific peaks at 1408cm^{-1} (due to N-O band stretching) and 1535cm^{-1} (due to N-H in plane), associated with protein components found in unprocessed waste but not in the chars.

Carbonization temperature was observed to be the most influential parameter during the M-HTC process. This affected yield, dewaterability, particle size distribution and other physic-chemical properties evaluated. As carbonization temperatures were increased over the range investigated for the present study, ammonia recovery in the liquor phase increased but char yield decreased due to increased solubilization (as deliberated in Chapter 5). However, increasing carbonization temperature favoured higher carbon content and higher calorific values of solid chars.

Finally, benchmarking M-HTC against existing conventional HTC technologies, M-HTC was found to yield fewer value-added products than C-HTC. Comparative operational figures that relate to energy use, process time and throughput capacity (fourth objective of the research) were discussed in Section 5.5. No significant differences were observed in the compared physic-chemical properties of end products from both processes. However, the M-HTC process was more efficient in processing time (30mins./6hours) and showed a significant reduction (by up to 50%) in energy consumption.

8.2 CONTRIBUTION TO KNWOLEDGE

The science and proof of concept of a novel and efficient sanitation technology, M-HTC for HBW management, demonstrated in this doctoral research have never been reported before. The key contributions to knowledge from this research are summarized as follow:

- Instead of close alternatives, this study used real human faecal sludge and further reported its disinfection outcomes – establishing the efficacy of M-HTC disinfection of faecal sludge at higher temperatures. This has never been reported before, as only sewage sludge is used in most cases as a surrogate to establish disinfection.
- The physic-chemical properties of the treated faecal material, such as the energy content and other characterizations reported in this work, further address gaps in the literature.
- Using wet biomass in HBW for HTC overcame the challenges associated with drying (i.e. the energy and costs associated with drying) feedstock before being burnt (incineration) or subjected to further treatment. This essentially opens up the technological transfer opportunities of the process for other wet biomass, such as livestock wastes, swine manure etc.
- This work also provided insights into the operational parameters, technical specifications, reaction pathways and conversion models required for value recovery from HBW. Further, the work provided evidence supporting the operational and energy efficiency of dielectric heating compared to the conventional conduction heating process.
- Scaling and process optimization at bench and pilot scales (details not included in this work) suggest the potential readiness of this sanitation technology for adoption on a commercial scale. This would provide opportunities for integration with existing sanitation systems, either as a stand-alone unit or a mobile processing unit.
- The work further confirms a changing perspective of human biowaste – i.e. as a resource and not a waste – and hence encourages a renewed interest in HBW management.

8.3 PROSPECTS FOR FUTURE WORK

Energetics of HBW during the M-HTC process were not investigated for the present study. In addition to recovering heat loss during the HTC process, potential energy recoverable from the liquor, if used as a substrate for anaerobic digestion, for example, coupled with information on the heating values of the chars, could provide a holistic assessment of the self-sustainability of this sanitation technology.

The potential for the co-combustion of chars recovered from HBW with low rank fuels as a complementary energy resource needs further assessment. The direct use of chars and recovered liquor in agriculture also require additional assessment of heavy metals and

other contaminants. Other factors such as endocrine-disrupting and exogenous compounds which may be present in recovered liquor, ought to be considered. Furthermore, high concentrations of ammonia are environmentally damaging for rivers and watercourses, and use and dispersal of such concentrates require management and planning. Extended studies of their application in agriculture and their effects on greenhouse gas mitigation, growth and soil fertility improvement are much needed to further demonstrate their potential as soil ameliorants.

Finally, the feasibility and suitability of the M-HTC technology either as a stand-alone sanitation system or as a complementary system that can be integrated with existing sanitation (centralised/decentralised) systems particularly in places where sanitation are still lacking should constitute areas for future research.

APPENDIX 1 GLOSSARY OF TECHNICAL TERMS

Anaerobic digestion	A series of biological processes that decomposes organic materials in the absence of oxygen.
Biomass	In the context of renewable energy, organic materials produced by biological processes.
Biosolids	Organic materials produced from sewerage treatment, used mostly in agriculture.
Calorific value	Heat of combustion of a sample – defined as amount of heat liberated by a unit mass of a sample when burned in pure oxygen in an enclosure of constant volume. When the latent heat of vaporization of water (as a combustion by-product) is factored into determination of calorific value, it is called higher heating value (HHV) and, if not, it is called lower heating value (LHV).
Carbon efficiency	Percentage increase in carbon content in char due to the carbonization process.
Carbonization	Thermochemical decomposition of organic materials to form solid residues characterized by high-carbon content.
Char	Organic solid product of carbonization process.
Class A Biosolids	US EPA classification of treated biosolids with reduced pathogens less than 1000MPN.g^{-1} total solids (dry-weight basis). This is also equivalent to less than 1000CFU.100mL^{-1} (WHO Standard).
Class B Biosolids	US EPA classification of treated biosolids with reduced pathogens less than 2 x10^6 MPN.g^{-1} total solids (dry-weight basis).
Combustion	Thermal decomposition of organic material in the presence of air (oxygen).
Dewaterability	Rate at which sludgy materials release their water.
E. Coli	Bacteria from intestinal track of mammals used as indicator of faecal contamination.
Enteric viruses	Viral entities contained in faecal material.
Fixed solids	Residue left in a dish after dried TS is ignited to 550^{0}C for at least 1 hour. Usually expressed in mg.l^{-1} fixed solids for liquid or % fixed solids for solid or semisolid samples.
Helminth eggs	Ova of parasitic worms.
Moisture content	Water content in a material, expressed in % wt. of the material.
Nutrients	Elements needed for biological growth; i.e., nitrogen and phosphorus.

Pathogen	Infectious agent including virus, bacteria or parasite that causes disease in host.
PEEK & PTFE	Polytetrafluoroethylene (PTFE) and Polyetheretherketone (PEEK) are synthetic polymers of high temperature and pressure rating used in high-thermal processes.
Pt/Co Scale	Used to measure the colour intensity in natural & treatment water.
Pyrolysis	Decomposition of organics at elevated temperature in the absence of oxygen.
Sanitation	Adequate facilities and services for the safe disposal of human urine and faeces.
Solid solubilization	Thermal disintegration and fragmentation into smaller fragments during HTC process.
Total dissolved solids	Portion of TS that passes through a 1.2µm glass-fibre filter paper.
Total solids	Residue left in evaporating dish after evaporation of liquid content from a sample and subsequent drying in an oven at specified duration (usually 12–24 hours for solids and 1 hour for liquid samples) and temperature (103–105˚C). Expressed in % total solids for semisolids or solids samples or $mg.l^{-1}$ total solids for liquid samples.
Total suspended solids	ortion of TS retained by a 1.2µm glass-fibre filter paper after filtration. Expressed in $mg.l^{-1}$ total suspended solids as it relates to liquid samples only.
Valorization	Processing activities used to reuse and recycle useful products from wastes.
Vectors	Rodents and insects that can spread disease by transferring pathogens.
Volatile solids	Weight loss after sample is ignited to 550˚C. VS are usually expressed in $mg.l^{-1}$ volatile solids for liquid or % volatile solids for solid or semisolid samples. Note FS and VS determination does not precisely distinguish between organic and inorganic content in samples. Although the former is more favoured as they are more combustible at the ignition temperature, weight loss is not confined to organic content only – as it may include decomposition or volatilization of minerals salts at ignition temperature.
Wastewater	Contaminated water discharged from domestic, municipal or industrial operations.

APPENDIX 2 STABILITY OF TEMPERATURE AND PRESSURE DURING THE M-HTC PROCESSING

Figs. A to D show the variations of temperature and pressure over all the carbonization residence times used during the M-HTC processing of all feedstocks at 180˚C and 30mins. This stability of temperature and pressure monitoring were crucial to ensure the reproducibility of M-HTC processing.

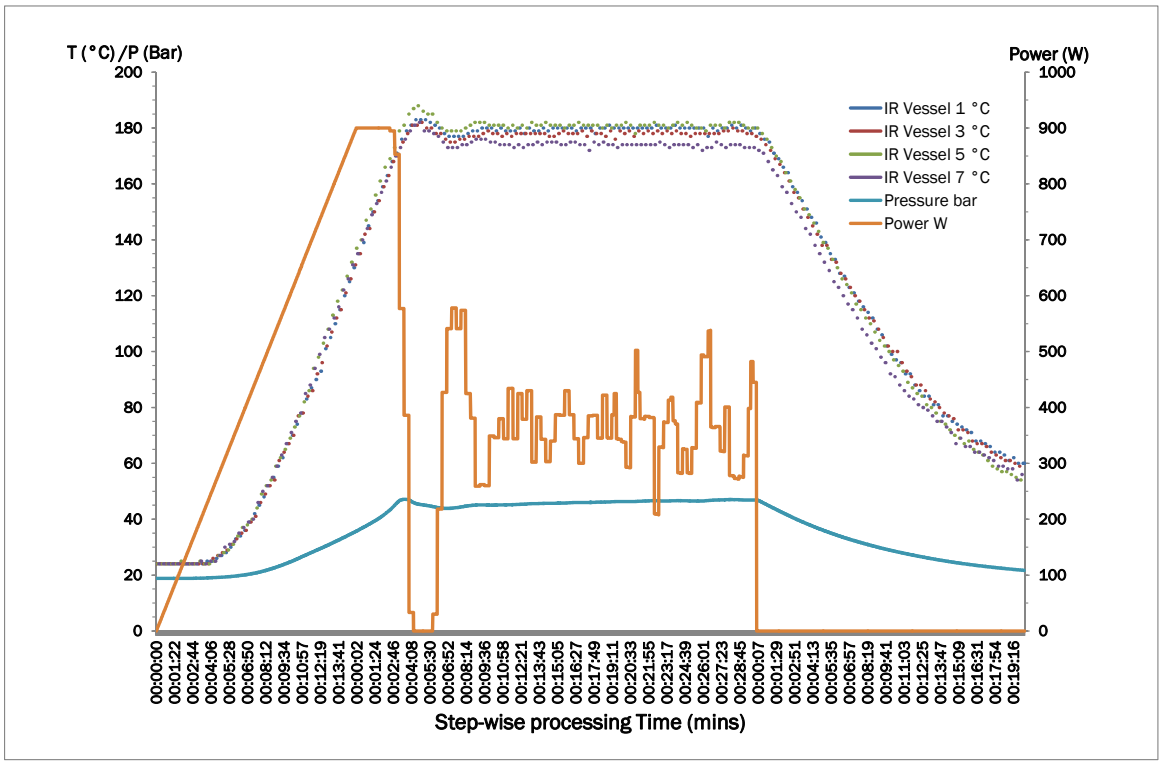


Fig. A P/T stability during M-HTC processing of SS

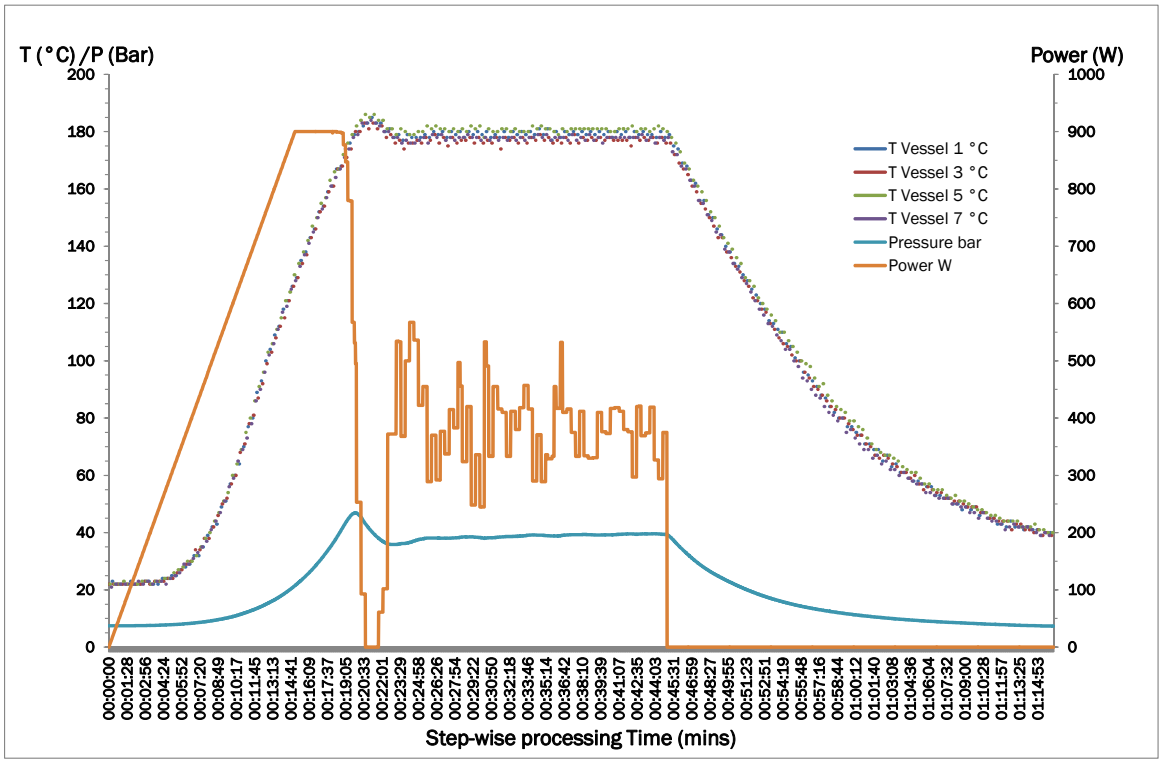


Fig. B P/T stability during M-HTC processing of FSS

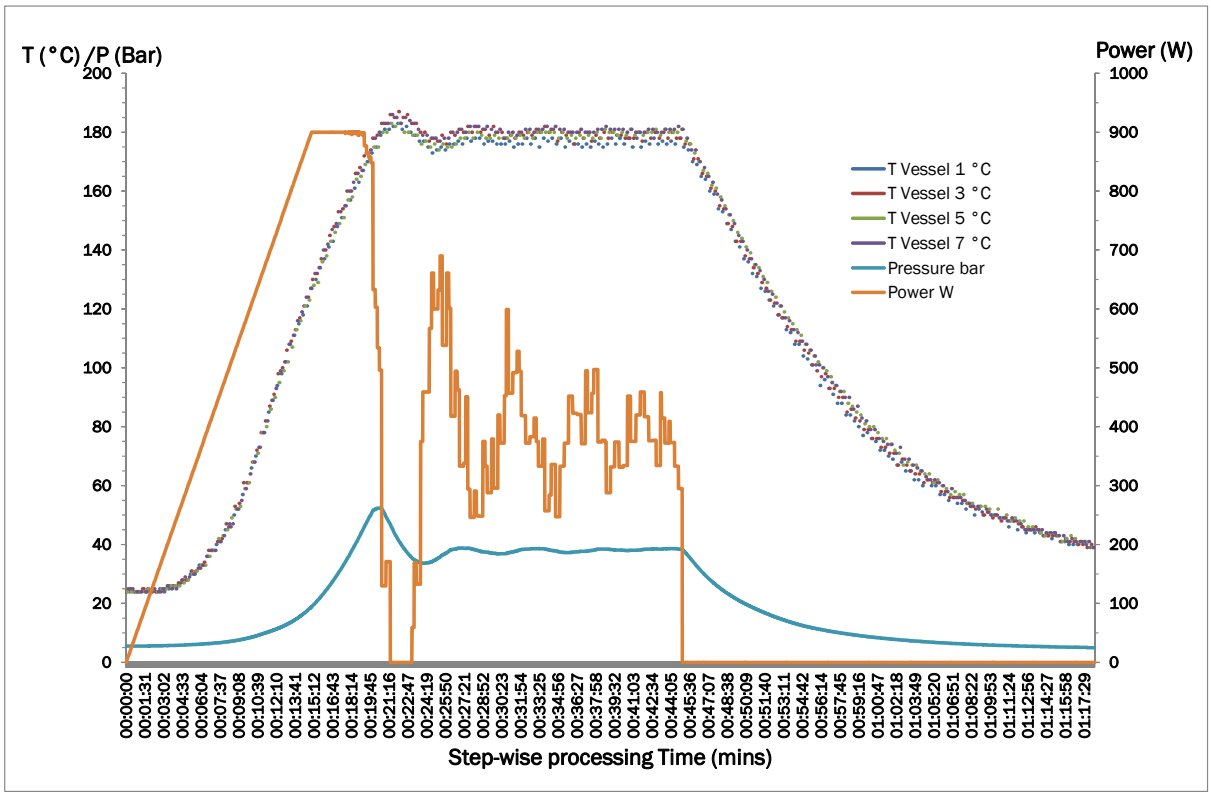


Fig. C P/T stability during M-HTC processing of HF

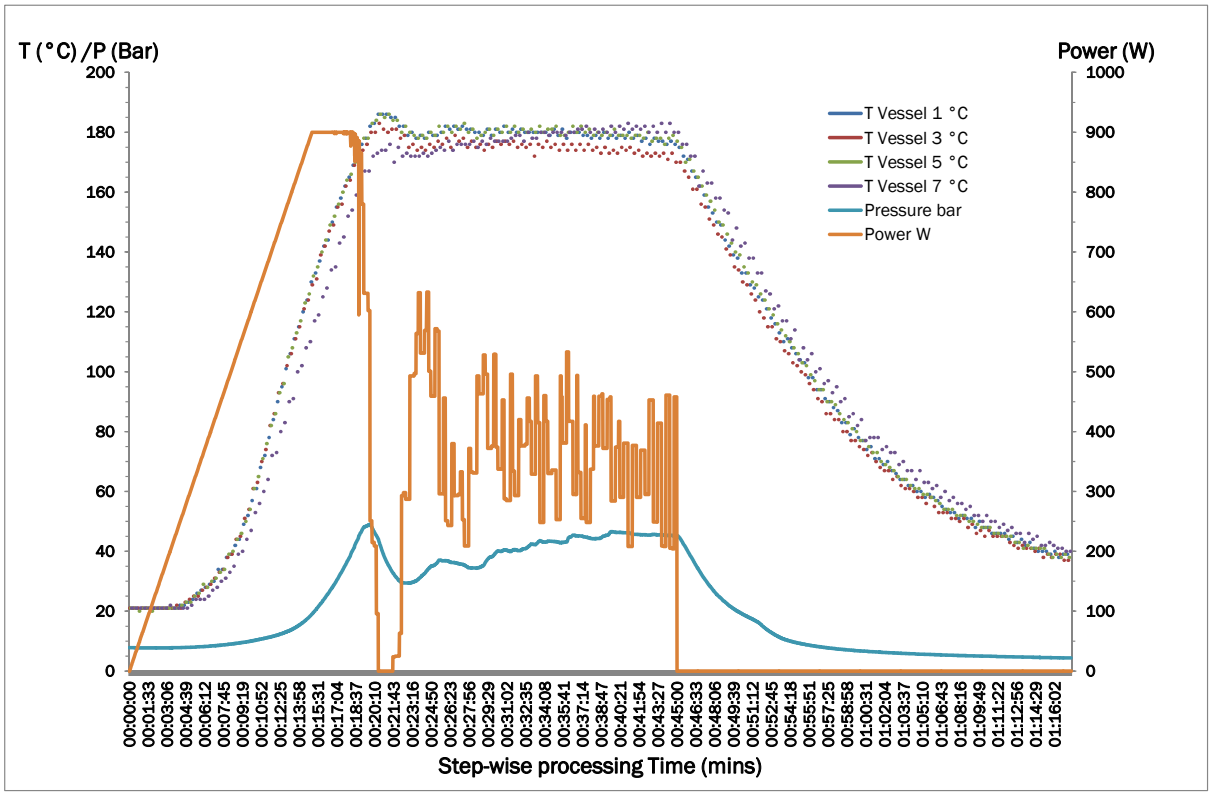
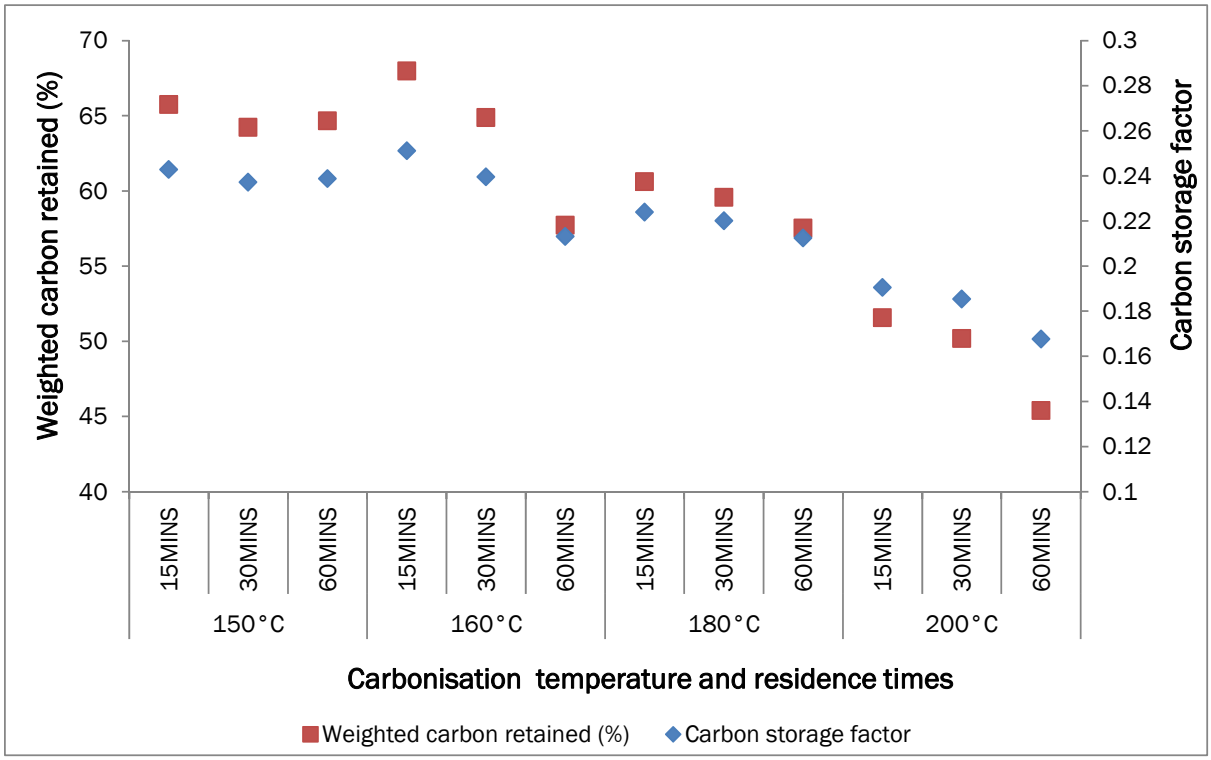


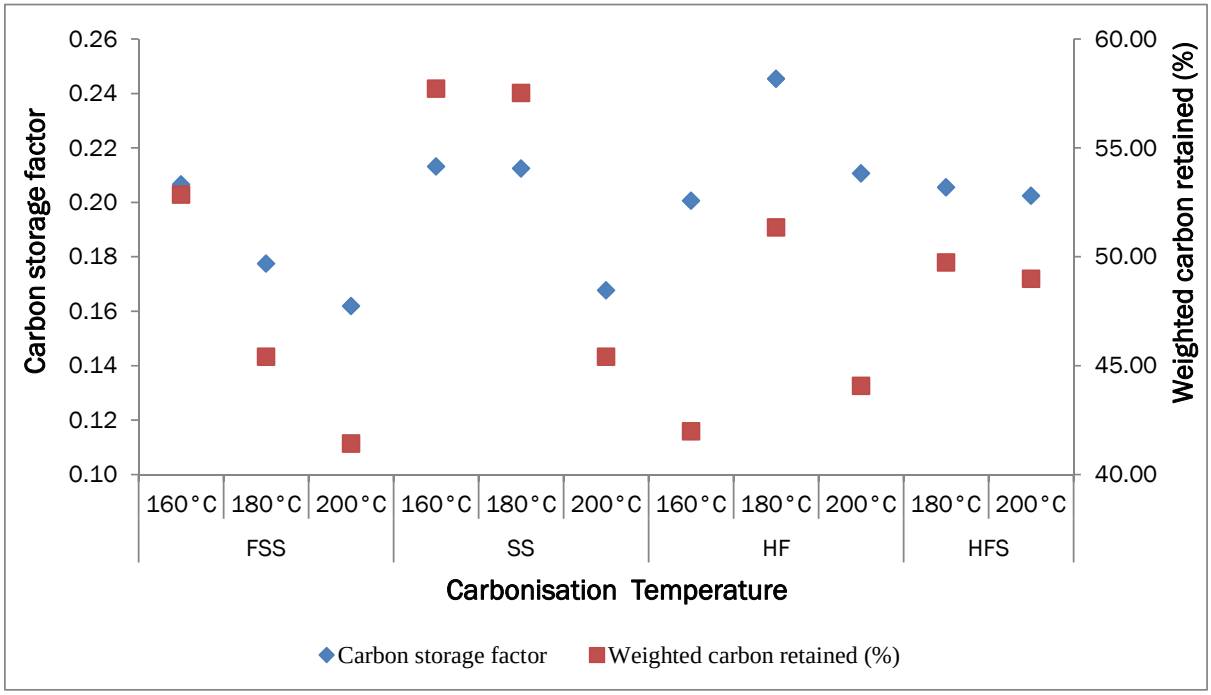
Fig. D P/T stability during M-HTC processing of HFS

APPENDIX 3

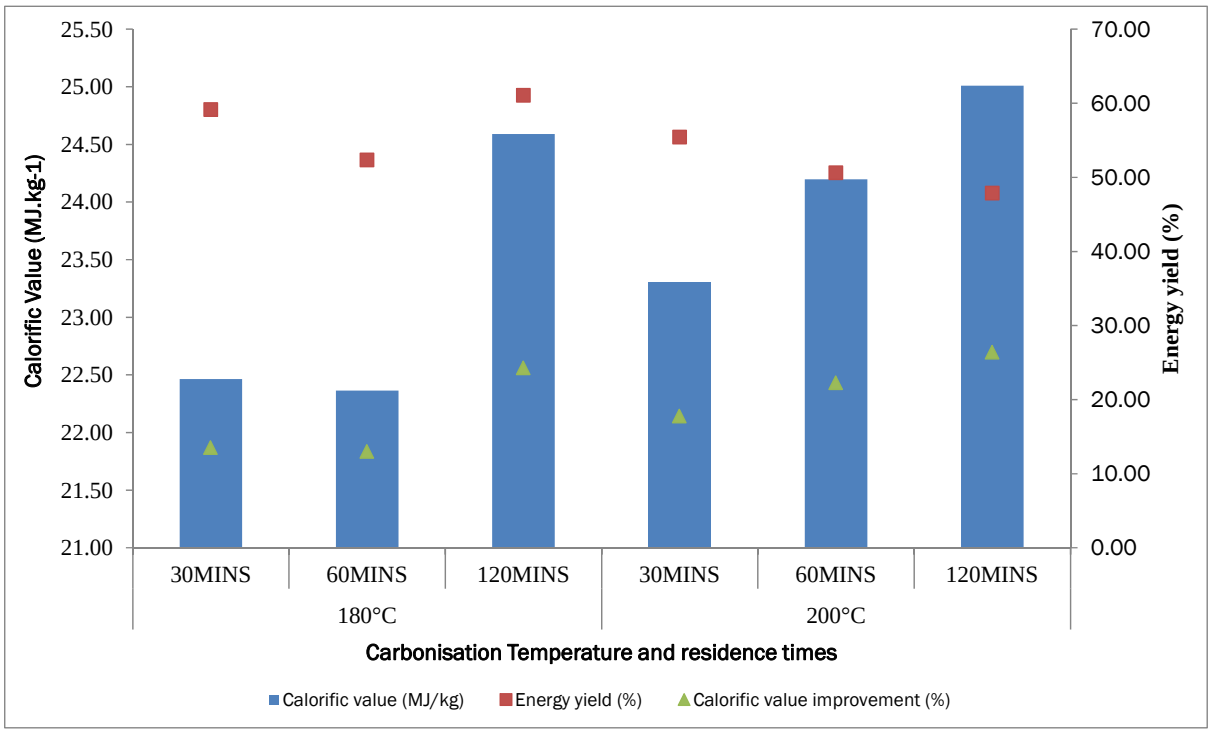
Appendix 3.1 Variation of CSF and weighted carbon retained in Chars with temperature and residence time using SS as representative biowaste



Appendix 3.2 CSF vs. Retained carbon in chars from all feedstock at different carbonization temperatures as a function of residence time



Appendix 3.3 Variation of carbonization temperature and residence times on HHV of chars recovered from HFS



Appendix 3.4 Nutrient and metals in unprocessed SS and chars at 150 to 200°C for 15, 30 and 60mins.

Nutrient and heavy metals measured in chars ($g.kg^{-1}$)													
Temp(°C)	Time(min)	B	Cd	Co	Cr	Cu	K	Mo	Na	Ni	P	Se	Zn
150	15	0.5	0.5	0.2	0.8	5.3	77.9	0.3	12.2	0.4	159.3	1.8	8.7
150	30	0.6	0.5	0.2	0.8	5.5	86.7	0.4	13.5	0.4	173.1	1.9	9.2
150	60	0.5	0.4	0.2	0.8	5.2	78.6	0.4	11.6	0.4	164.6	1.8	8.7
160	15	0.5	0.4	0.2	0.7	4.6	69.9	0.3	11.7	0.4	150.9	1.7	8.0
160	30	0.5	0.4	0.2	0.8	5.1	80.5	0.3	12.2	0.4	162.5	1.7	8.6
160	60	0.5	0.5	0.2	0.8	5.7	77.2	0.3	12.1	0.4	172.6	1.8	9.3
180	15	0.5	0.5	0.2	0.9	6.1	72.5	0.4	10.9	0.4	175.2	1.8	9.1
180	30	0.5	0.5	0.2	0.9	5.8	89.3	0.4	13.1	0.4	186.1	1.9	9.7
180	60	0.5	0.5	0.2	0.8	5.2	75.1	0.3	12.4	0.4	175.3	1.8	8.9
200	15	0.6	0.5	0.2	0.9	5.9	83.9	0.4	12.5	0.4	195.4	1.9	9.6
200	30	0.6	0.5	0.2	0.9	5.9	84.2	0.4	12.7	0.4	202.2	1.9	9.9
200	60	0.5	0.4	0.2	0.8	4.9	61.7	0.3	9.7	0.4	165.9	1.7	8.3
Unprocessed		1.38	0.9	0.4	1.4	8.4	338.7	0.6	49.8	0.7	329.8	3.41	14.6

Appendix 3.5 Partitioning/distribution in chars (%) as a function of carbonization temperature and residence times

Fraction of Nutrient and heavy metals retained in chars (%)													
Temp (°C)	Time (min)	B	Cd	Co	Cr	Cu	K	Mo	Na	Ni	P	Se	Zn
150	15	38.6	47.9	51.6	57.4	63.7	23.0	53.8	24.4	58.5	48.3	51.7	59.5
150	30	40.1	49.9	54.6	58.9	65.2	25.6	56.3	27.1	61.9	52.5	54.5	62.7
150	60	36.7	46.6	51.1	55.3	61.9	23.2	53.4	23.3	57.6	49.9	51.1	59.2
160	15	34.5	44.7	48.5	50.8	55.4	20.6	50.0	23.6	52.9	45.8	48.3	54.9
160	30	36.3	45.8	50.4	54.5	61.3	23.8	52.4	24.4	54.5	49.3	49.9	58.5
160	60	37.6	48.5	51.3	56.0	68.1	22.8	53.7	24.3	56.1	52.3	52.2	63.3
180	15	35.7	49.3	53.8	60.4	73.2	21.4	56.3	21.9	59.4	53.1	53.2	62.4
180	30	38.9	52.2	56.0	61.5	68.7	26.4	59.1	26.4	63.2	56.4	55.9	66.5
180	60	37.6	49.0	52.9	54.2	61.8	22.2	55.1	24.8	55.9	53.2	52.8	60.9
200	15	40.3	52.2	58.0	62.7	69.9	24.8	60.1	25.2	64.1	59.3	57.0	65.9
200	30	39.9	52.6	59.2	62.6	70.3	24.9	60.9	25.6	63.5	61.3	57.8	67.4
200	60	35.3	44.8	49.6	53.3	58.4	18.2	51.1	19.4	58.9	50.3	48.7	56.5

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SUSTAINABLE WATER AND SANITATION SERVICES
FOR ALL IN A FAST CHANGING WORLD

Hydrothermal treatment of human biowastes as an alternative sanitation strategy

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REFEREED PAPER

One of the evolving approaches to mitigating the challenges of poor sanitation involves the exploration of new, sustainable and affordable technologies. These need to be capable of effectively treating faecal and other related wastes without any health, or environmental damage and competitive with existing strategies. This paper presents results from hydrothermal carbonization (HTC) of human biowastes; treated at >130^{0}C under pressure. Analysis shows the process is autothermic and could generate valuable end-products. These were, a carbonaceous solid material i.e. char with a high calorific value which can be used as fuel or soil conditioner, and liquid ammonia concentrate for fertilizer. The results of this study provide useful information essential for the design and operation of an HTC system (for faecal sludge treatment) which will be integrated into a self-sustainable sanitation facility planned for prototype development.

Background

The challenges of poor sanitation in the developing and remote regions of developed countries are well documented. There are long standing international programmes and strategies aimed at ameliorating poor sanitation but there is a need for novel, cost-effective, sustainable and efficient technologies for faecal waste management. These also need to be able to meet the needs of increasing population and rapid urbanization. This was the basis of the 'Reinvent the Toilet Challenge' (RTTC); an initiative funded by the Bill and Melinda Gates Foundation. The project is "*about prototyping, conceptualising, and designing of highly innovative ways and means of disposing human waste (which will primarily ensure safe disposal and protect the environment) drawing on the high-value engineered circumstances demanded by potential widespread, near-term adoption in developing world*" [Gates, 2011]. Objectively, we seek to develop a safe, affordable, self-sustainable (in terms of energy requirements) and eco-friendly toilet facility targeted at decentralised households or small collections of networked households. Effectively, the toilet needs to collect human biowastes including faecal sludge, treat and convert them into safe and usable products. This is required without additional financial burden or need for piped water or sewerage systems with a budget of less than $0.05 per cap per day.

Hydrothermal carbonisation (HTC), a novel thermochemical process; is currently being researched to treat and convert human biowastes biomass into useful end-products. The process uses water at *subcritical conditions* (<300^{0}C) to transform biowastes (contained in a closed pressure vessel) into a coal-like material, herein referred to as char by supersolvation. The technological suitability of the HTC process for faecal sludge treatment was based on the following considerations:

- HTC can utilize raw wet biomass characterized by high moisture content precluding pre-drying and its associated costs [Libra et al, 2011]. This makes it suitable for human excreta with moisture content range of 65 - 85% [Wignarajah et al, 2006].
- Lower energy consumption when compared with other thermal/thermochemical processes such as incineration, dry pyrolysis, gasification, or supercritical reactions.
- Production of sterilised end-products. The process involves high temperature (180 – 200^{0}C) which will effectively kill pathogens in human faecal biowastes.

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ORIGINAL PAPER

Microwave Hydrothermal Carbonization of Human Biowastes

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Abstract The challenges of poor sanitation due to poor faecal sludge management, particularly in the developing and other remote regions of developed countries, are well documented. As a potential technological and complementary approach to managing human biowastes, microwave hydrothermal carbonization (M-HTC), a thermochemical process, was used in this study to convert human biowastes into a safe material without any foul odour. The process also recovered value-added products i.e. solid chars and liquid ammonia concentrate. Primary sewage and raw human faecal sludges were subjected to microwave heating at 160, 180 and 200 °C, at different residence times: 30, 60 and 120 min under autogenous pressure. As a result, up to 60 % energy densified chars were recovered from the raw biowastes. The calorific (higher heating) values of chars recovered after the process, particularly those from human faecal sludge, increased from 19.79 up to 25.01 MJ/kg. Also, up to 80 % ammonia was recovered in the liquid fraction of carbonized human biowastes. Solid char yield and other estimated physicochemical properties were observed to be dependent on both the reaction temperatures and residence times of the process. The results of this study show M-HTC is a potential value-added recovery process for managing human biowastes and further provides essential information useful for the design and optimization of a self-sustainable sanitation facility.

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Keywords Human biowastes · Microwave heating · Carbonization · Solid chars · Ammonia recovery

Introduction

Poor sanitation is one of the greatest global challenges of the twenty-first century. Currently, 1 billion people still practice open defecation while another 2.5 billion people do not use improved sanitation facilities [1]. The combined effects of open defecation, unimproved sanitation facilities and faecal contamination of drinking-water resources are largely responsible for the high prevalence of diseases such as diarrhoea, which kills around 700,000 children every year [2]. Due to the severe public health and environmental consequences associated with poor human biowastes management, the need to develop efficient sanitation technologies to complement long-standing international programmes and strategies aimed at ameliorating poor sanitation, particularly in developing economies, is imperative. Although human biowastes are bio-hazardous in nature, their chemical composition suggests they can also be viewed as a *renewable* biomass resource that can be maximized for different purposes. For example, human excreta contain 65–85 % moisture content (MC): valuable elements such as nitrogen, phosphorus and potassium (essential components of fertilizers) and organic macromolecules including carbohydrates (10–30 %), fat (5–25 %) and undigested protein (10–15 %) [3]. *Terra preta do Indio*, also called Amazonian dark earth, which are highly fertile and productive black soils found in the Amazon basin region, was reported to have evolved from the prolonged use of soil ameliorants derived from human biowastes [4]. With an estimated average generation rate of 120–400 g/cap/day of wet human faeces and 0.6–1.2 L/