An Integrated Waste Management Process: Integrating Hydrothermal Carbonisation with Anaerobic Digestion for Opportunities to Valorise Digestate and Waste Biomass

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"Use it up, wear it out, make it do, or do without."

- New England proverb

This thesis uses Cambria font for the main body of text. The font was chosen based on results from a legibility study[1], which showed text legibility was highest for Cambria against traditional fonts.

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[1] Chaparro, B.S., Shaikh, A.D. and Chaparro, A. 2006. The Legibility of Cleartype Fonts. Proceedings of the Human Factors and Ergonomics Society Annual Meeting. 50(17), pp.1829–1832.

DECLARATION OF AUTHORSHIP

The candidate confirms that the work submitted is his own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

The following jointly authored publications are part of the thesis:

1. Parmar, K.R. and Ross, A.B. 2019. "Integration of Hydrothermal Carbonisation with Anaerobic Digestion; Opportunities for Valorisation of Digestate." *Energies* 12(9): 1586. doi:10.3390/en12091586. https://www.mdpi.com/1996-1073/12/9/1586

Details of contributions from the candidate and co-authors are listed below:

1. The candidate performed all of the experimental work, and majority of the analysis and write-up. His supervisor Dr. Ross contributed with comments, guidance and proof reading.

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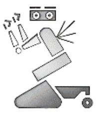

ABSTRACT

In the last decade, significant growth exhibited by the organic waste management industry in the UK has begun to decline due to removal of incentives, reduced material availability due to competition and implementation of quality standards for environmental regulation. Therefore, the purpose of this thesis is to provide a proof of concept for a novel approach to integrating biomass conversion technologies for improved organic waste management, maximising energy recovery and accelerating the process of composting. Specifically, the research aim is to identify the potential opportunities for the integration of hydrothermal carbonisation (HTC) with anaerobic digestion (AD) to treat and valorise digestate and green waste materials.

AD operators competing for feedstock often accept contaminated wastes which produce digestate that does not meet the quality specification for application as a fertiliser. As a result, operational expenses increase due to storage, transport and gate fees required for the disposal of digestate. Digestate, when applied to land also gives rise to concerns about eutrophication and fugitive greenhouse gas emissions. Additionally, the emissions generated from the composting of green wastes are not captured. Furthermore, if these biomass materials are not utilised as an agricultural product the nutrients they hold are lost, unless they are recycled. Literature has highlighted several key development areas within the AD industry aimed at decreasing the operating costs of digestion facilities. Digestate enhancement technologies, such as HTC and pyrolysis thermochemical processing, have been recognised for treating and increasing the value of digestate to secure use and create new markets. However, a significant gap in the literature, which this thesis intends to fill, lies in comparing thermochemical technologies, experimentation on a range of digestate materials and assessment of the application of products generated. Synthesis of this study's findings show that the aim and objectives of the study have been met. Opportunities for valorisation lie in enhanced biogas generation from the recirculation of HTC process waters into AD and the use of hydrochar as a soil amender. Furthermore, the integration approach also introduces alternative recalcitrant AD feedstock via HTC pre-treatment which allows for acceleration of solubilisation and the humification process, whilst mitigating greenhouse gas emissions.

Chapter-specific results show that composition analysis of the feedstock materials demonstrate digestate and green waste have considerable energy recovery potential, due to high fractions of protein and lignocellulose respectively. The application of HTC process waters via AD generates bio-methane owing to the high concentrations of soluble organic compounds, particularly from high biodegradable process waters from the HTC of sewage sludge digestate and grass clippings at 200 °C. Hydrochar, when applied in agriculture as a soil amender has the potential as a slow release fertiliser due to improvements in fresh plant mass yields owing to being humic like and exhibiting good macro and micro nutrient content, especially from sewage sludge digestate. Furthermore, hydrochar and pyrochar converted from digestate materials are not suitable as a solid fuel due to high inorganic content and low energy density, resulting in very likely slagging and fouling propensity. However, high temperature 250 °C HTC co-processing by blending with green wastes, particularly woodchip, increases calorific values (up to 20 MJ per kg), energy density (up to a factor of 1.2) and reduces inorganic concentrations (by up to 50 percent), improving solid fuel properties.

It was also found that the enhancement of digestate via pyrolysis is not favourable due to requirements of dewatering digestate, low liquid yields and high slagging and fouling potential of pyrochar as a solid fuel. HTC is more suitable for waste biomass treatment as it promotes demineralisation and solubilises organic compounds.

The significance of this study will benefit the circular economy and aids in reaching climate change targets from the generation of renewable energy and production of hydrochar that locks in carbon and provides benefits to agriculture. This is especially important in terms of reducing fossil fuel use and its impacts on soil erosion and fertility. The contributions of this thesis will be of interest to researchers in the fields of microbiology and chemical processing for the production of bio-hydrogen, bio-alcohols and fine chemicals from the fermentation of HTC process water. Soil scientists will also be interested in the potential of hydrochar applied in agriculture for remediation and soil amelioration. Moreover, researchers in the field of energy and storage will be interested in the combustion and electrical storage potential of hydrochar.

TABLE OF CONTENTS

CHAPTER VII

CHAPTER VIII

CHAPTER IX

LIST OF PUBLICATIONS & PRESENTATIONS

Journal Papers

- Parmar, K.R. and Ross, A.B. 2019. Integration of Hydrothermal Carbonisation with Anaerobic Digestion; Opportunities for Valorisation of Digestate. *Energies*. 12(9), p.1586. doi:10.1016/j.biortech.2016.04.057

- Takaya, C., Parmar, K., Fletcher, L. and Ross, A. 2019. Biomass-Derived Carbonaceous Adsorbents for Trapping Ammonia. *Agriculture*. doi:10.3390/agriculture9010016

- Phillips, D., Mitchell, E.J.S., Lea-Langton, A.R., Parmar, K.R., Jones, J.M. and Williams, A. 2016. The use of conservation biomass feedstocks as potential bioenergy resources in the United Kingdom. *Bioresource Technology*. 212, pp.271–279. doi:10.1016/j.biortech.2016.04.057

Conference Presentations, Posters and Prizes

- 2018: EPSRC UKERC Energy CDTs Masterclass, Sheffield, GB
  Poster: A new waste management system; integration of HTC with AD to valorise waste biomass

- 2017: 1st International Symposium on Hydrothermal Carbonization, London, GB
  Poster: Predicting yields, properties of products and application from the HTC of digestate
  Prize: Winning poster awarded from The Royal Society of Chemistry - Journal of Materials

- 2017: Supergen Bioenergy Hub Assembly and Leaders Consultation Event, Belfast, GB
  Oral: Waste pre-treatment; accelerated hydrothermal composting

- 2017: International Bioenergy Conference, Supergen Bioenergy Hub, Manchester, GB
  Oral: AD management; mass and energy balance of a novel digestate enhancement technology

- 2016: Resource Recovery from Waste (RRfW) Conference, Leeds, GB
  Poster: Integration of HTC with AD; an advanced waste management technique

- 2016: European Biogas Association Conference, Ghent, BE
  Poster: Integration of HTC with AD; approaches and digestate characterisation

- 2016: 24th European Biomass Conference and Exhibition (EUBCE), Amsterdam, NL
  Poster: Integration of HTC with AD; industrial issue and solution concept

- 2016: The AD Network: Early Career Researcher Event, Birmingham, GB
  Oral and Poster: Concept for the integration of thermochemical processes with AD

- 2015: 1st International Biomass Emissions Conference, Leeds, GB
  Poster: The characterisation of bark and heartwood from waste conservation biomass feedstocks.

LIST OF TABLES

LIST OF FIGURES

ACRONYMS & ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
AD	Anaerobic Digestion
ADF	Acid Detergent Fibre
ADQP	Anaerobic Digestate Quality Protocol
AGR	Agricultural Residue Digestate
AI	Alkali Index
Al	Aluminium
ar	As Received
BAI	Bed Agglomeration Index
BAS	Biosolids Assurance Scheme
BC	Before Christ
BCS	Biofertiliser Certification Scheme
BEIS	Department for Business, Energy and Industrial Strategy
BMP, ex, theo	Biochemical Methane Potential, Experimental, Theoretical
BMW	Biodegradable Municipal Waste
BSI	British Standards Institution
C	Carbon
Ca	Calcium
CAPEX	Capital Expenses
CEC	Cation-Exchange-Capacities
CH_4	Methane
CHP	Combined Heat and Power
CNG	Compressed Natural Gas
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
Cr	Chromium
Cu	Copper
CV	Calorific Value
db	Dry Basis
daf	Dry Ash Free Basis
DECC	Department Of Energy and Climate Change
DEFRA	Department for Environment and Rural Affairs
DM	Dry Matter
DTG	Differential Thermogravimetric
EBC	European Biochar Certificate
EfW	Energy-From-Waste
EU	European Union
Fe	Iron
FC	Fixed Carbon
FI	Foiling Index
FID	Flame Ionisation Detector
FiT	Feed-In Tariff
g	Grams
GC-MS	Gas Chromatography - Mass Spectrometry
GHG	Greenhouse Gas

GVA	Gross Value Added
H, H_2	Hydrogen
H_2O	Water / Vapour
H_2S	Hydrogen sulphide
HACCP	Hazard Analysis and Critical Control Points
HGV	Heavy Goods Vehicles
HHV	Higher Heating Value
HMF	5-hydroxymethylfufural
HPL	High-Pressure Liquid Chromatography
HTC	Hydrothermal Carbonisation
IBI	International Biochar Initiative
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ISR	Inoculum to Substrate Ratio
K	Potassium
Kg	Kilogram
Kj	Kilo Joule
LNG	Liquid Natural Fuel
MBT	Mechanical Biological Treatment
Mg	Magnesium
Mj	Mega Joule
Mn	Manganese
Mo	Molybdenum
MtCO2e	Mega Tonnes Carbon Dioxide Equivalent
MSW	Residual Organic Fraction of Municipal Waste Digestate
MWe	Megawatt Electric
N, N_2	Nitrogen
Na	Sodium
NH_3	Ammonia
NH_4^+	Ammonium
Ni	Nickel
O, O_2	Oxygen
OFMSW	Organic Fraction of Municipal Solid Waste
OLR	Organic Loading Rate
OPEX	Operational Expenses
OWS	Organic Waste Systems
P	Phosphorous
Pb	Lead
pH	Potential of Hydrogen
PAH	Polycyclic Aromatic Hydrocarbons
PAS	Publicly Available Specification
PFI	Private Finance Initiative
POPs	Persistent Organic Pollutants
R b/a	Acid to Base Ratio
RHI	Renewable Heat Incentive
RPM	Rotations per Minute

RTFO	Renewable Transport Fuel Obligation
S	Sulphur
Si	Silica
SI	Slagging Index
SS	Sewage Sludge Digestate
SVI	Slag viscosity Index
TAN	Total Ammonium Nitrogen
TCD	Thermal Conductivity Detector
TCI	Total Capital Investment
TGA	Thermogravimetric Analysis
TN	Total Nitrogen
TOC	Total Organic Carbon
TRL	Technology Readiness Level
TS	Total Solids
UASB	Up-Flow Anaerobic Sludge Blanket
UK	United Kingdom
USA	United States of America
VFA	Volatile Fatty Acids
VGF	Vegetable Garden and Fruit Digestate
VM	Volatile Matter
VOC	Volatile Organic Compounds
VS	Volatile Solids
WEOC	Water Extractable Organic Carbon
WfH	Waste from Households
WHC	Water Holding Capacities
WRAP	Waste & Resources Action Programme
Wt%	Weight / Mass percentage
XRF	X-Ray Fluorescence
Zn	Zinc

CHAPTER I

Introduction

This thesis provides a solution concept to a problem arising from the organic waste management industry, particularly from anaerobic digestion (AD) biogas generation facilities. It does this by addressing gaps in the knowledge of integrating thermochemical biomass conversion technologies with AD to enhance the functionality of digestate. This chapter introduces the current waste management landscape to identify the root cause of issues, highlights the benefits for an integrated waste management technique to provide an opportunity to valorise and functionalise digestate and other green wastes, before providing the aim and objectives, and thesis structure.

1.1. Background: organic waste management in the United Kingdom

The following sections provide an overview of the organic waste generation, management and technologies employed in the United Kingdom (UK). The development of UK waste strategies influenced by the actions of the European Union (EU), including the adoption of sustainable development are presented. The various drivers for waste management, including legislation and policy measures are discussed. Lastly, an overview of the technologies applied in waste management is presented.

1.1.1. Waste definition and hierarchy

Providing a definition of waste is important; it provides clear classifications that help develop waste management policies and application of regulatory controls to protect both the environment and human health. However, describing solid waste can be very subjective. Solid waste can be described as a left over, redundant product or material of no or marginal value for the owner and which the owner wants to discard [1]. Of course solid waste can also be seen as materials in the wrong place if its properties are valuable somewhere else. Therefore, this notion varies with regards to scarcity, location, matter state, owner income level and societal values. Generally, solid waste has low value due to key aspects of heterogeneity and its hazardous nature. Legally defining waste is important to effectively manage hazardous waste by regulation and enforcement. The EU definition is derived from the Waste Framework Directive 2008 as ‘any substance or object which the holder discards or intends or is required to discard’ [2].

The Waste Framework Directive also provides the development of a waste management strategy through a hierarchy of treatment options. The hierarchy, illustrated in Figure 1, encourages waste reduction, re-use and recovery with disposal as the least desirable option. When applying the waste hierarchy, it is encouraged to take measures that deliver the best overall environment outcome. This may deviate from the waste strategy, and is justified by life-cycle thinking, taking into consideration the overall impacts of the generation and management of such waste [3]. The options are as follows:

1. ***Waste prevention and reduction.*** In the highest ranking option and in the topmost section of the waste hierarchy is the strategy that the production of waste should be prevented or reduced. Prevention and reduction of waste at source can be achieved by applying lean manufacturing approaches, applying alternative processes and developing clean technologies that don’t require the same quantity of material in the end products, therefore producing less waste in their creation. Applying this strategy can make significant savings in raw materials, energy use and a reduction in emissions, including production and waste disposal costs.

2. ***Re-use.*** The next preferred option in the hierarchy is the collection and re-use of segregated materials, for example the glass bottle. The re-use strategy may also include new applications once they have served their original purpose. This option can be commercially attractive. However, in some circumstances re-use may not be desirable due to the economic and environmental costs involved in the cleaning, recovery, transportation and energy usage in the entire process – i.e. life-cycle, which can outweigh any benefits achieved.

3. ***Recycling and composting.***
    a. ***Materials recycling.*** The recovery and recycling of materials from waste are re-processed to produce a marketable product, for example the re-melting of glass and aluminium cans. The potential for recycling from waste is high, but may not be appropriate in some cases. For example, a market need is a necessity for economic gain, otherwise the process results in large supplies of unwanted materials. Energy and costs expended in their preparation to this stage is wasted.

   b. ***Composting.*** This is the biodegradation of the organic fraction of waste for stabilisation and application as a soil conditioner and plant-growing medium. On a domestic scale, the composting of garden and food waste has been encouraged as a direct way of recycling. For the larger scale, compositing has been extended to stabilise green waste from parks and gardens, including municipal solid waste and sewage sludge. Quality is an important factor in the sale of compost, since contamination is a prominent issue compared with non-waste sources.

4. ***Energy recovery.*** Energy can be recovered from waste incineration and gasification, including gas produced from landfill and anaerobic digestion. Many waste streams, including municipal solid waste, sewage sludge and scrap tyres contain an organic fraction which can be combusted. The decomposition of the biodegradable fractions of the waste in landfill and anaerobic digestion produce a gas that consists mainly of methane. This methane is collected in a controlled way and burnt to provide power and heat or transport fuel.

5. ***Disposal in landfill.*** Disposal within the hierarchy is the least desirable option. Where disposal to landfill occurs, the process is controlled and managed in a way that reduces hazards to the environment, including human health. Any biodegradable waste, over a period of time will degrade, neutralise and become stable, essentially turning into an inert material.

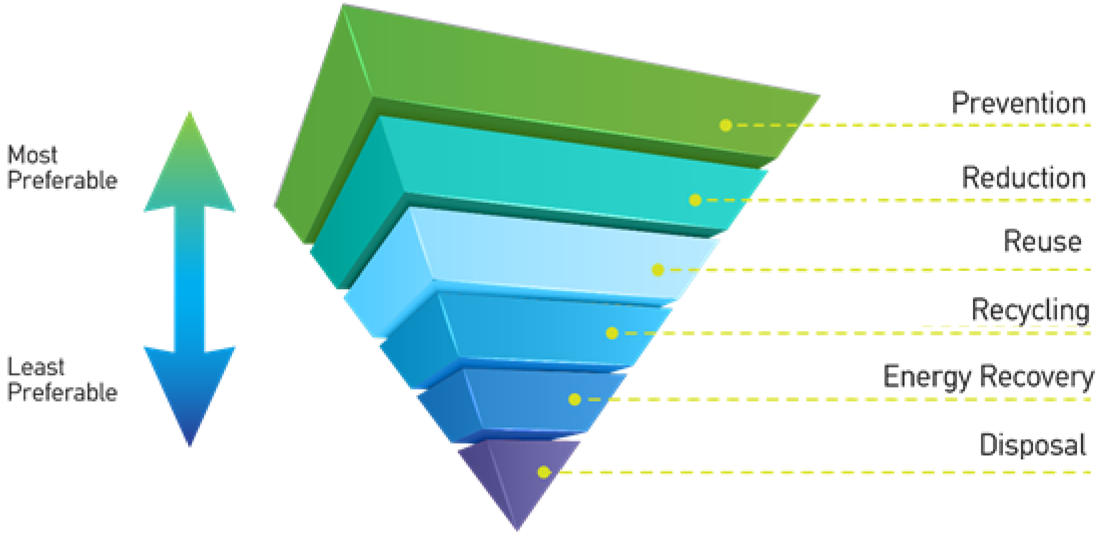

Figure 1. The Waste Framework Directive waste hierarchy.

New thinking has emerged to further promote sustainability within the waste hierarchy. With the pyramid now in its current orientation, the base appears at the top signifying the most preferable option; the new concept is to replace the linear into a circular economic model. The circular economy is a strategy that is restorative or regenerative by intended design. The linear ‘take, make, and dispose’ economic model is now considered an outdated way of disposing of waste and is reaching its physical environmental limitations.

The new circular concept shifts towards the use of renewable energy, eliminating the use of toxic chemicals and materials which impairs the re-use and recycling options. It also aims for the elimination of waste through superior design of materials, products and systems and strives for more sustainable business models. Action is now being taken in Scotland to switch from the linear to a circular economy. Scotland has placed a ban on municipal biodegradable waste to landfill, as part of their Zero Waste Regulations Initiative. As the first ban of its kind, England and Northern Ireland could follow suit in the near future.

To enable a zero waste to landfill system and a circular economy, it is evident that more energy and resources need to be captured. For this to occur there is a need for improved waste management at both strategy and processing stages. The greatest avoidable and recyclable fraction of waste is organic material. Organic waste is an ideal material that can be imposed onto the circular economy and zero waste philosophy. Organic waste is biogenic materials derived from humans, animals and plants, which may include: organic fraction of municipal solid waste, wastewater sludge or biosolids, manure and animal residues and crop residues, industrial waste and sludge and green and garden waste.

1.1.2. Current waste generation and management

The UK generates a significant amount of waste, most of which is sourced from the domestic setting and is not segregated. Segregation, an act of setting materials apart from others can help towards a circular economy and enable clean growth. On the other hand, some provisions have been put in place to remove the linear disposal model by the introduction of recycling targets and landfill reduction targets. As a result, the total UK waste generation is declining. In 2004, total waste arisings, including industrial sectors, was at 325 million tonnes and has been reducing on average at around 14 percent, to a total of 203 million tonnes generated in 2010 [4]. In 2012 and 2014, the UK experienced an increase of the total amount of waste generated by 7.6 percent, totalling 222 million tonnes [5]. This has been attributed to the increase in construction, demolition and excavation as a result of the growth of our infrastructure.

Nearly 28 million tonnes of total waste generated in 2010 was identified as Waste from Households (WfH). Approximately 44.6 percent of this proportion was recycled and a total of 7.7 million tonnes of biodegradable municipal waste (BMW) was sent to landfill in 2016, a value that is 22 percent of the 1995 baseline value. BMW is the fraction of municipal waste such as food waste, green waste, cardboard and paper that will degrade when landfilled. DEFRA states that the UK is still on track to meet the EU target to recycle 50 percent of household waste and restrict BMW landfilled to 35 percent of the 1995 baseline by 2020 [5]. It should be noted current and future levels of BMW represent a significant resource potential for material recycling and energy recovery. In the light of these reduction statistics, avoiding landfill is advantageous for reducing environmental impacts. However, the figures for materials recycled are not increasing at the same rate as expected. Local authorities recorded a sharp decline in 2016/17, where approximately 4 million tonnes of WfH was sent to landfill; a staggering reduction of 19.4 percent from the year previous. In the same year, around 11 million tonnes of waste material was recycled or composted. Nevertheless, materials sent to incineration in the same year increased by 11.5 percent, the majority with no energy recovery [5].

Interestingly, when extrapolating the rate of increase, data suggests incineration will overtake recycling and composting rates from 2017/18 and beyond. Tolvik, a waste and bioenergy consultancy, noted that there were 40 Energy-from-Waste (EfW) facilities in the UK in 2017, up from 26 in 2014, having a combined operational capacity of handling 12 million tonnes of waste per year. Currently, with 16 EfW sites under construction and a further 13 in active development, handling capability is expected to rise to nearly 16 million tonnes by 2022 [6]. This suggests an incineration market is being driven and will increase the demand for waste material to be combusted. Evidently, there is need for development for the preferred options of recovering and recycling within the waste hierarchy strategy.

1.1.3. Recovering value from biodegradable waste

To execute the waste hierarchy, align with zero waste targets and achieve a circular economy there needs to be a radical change in the management of waste. Creating value from wastes can reduce the pressure on natural assets and can accomplish a paradigm shift in the recovery of resources from biodegradable wastes. Currently, there are three dimensions of material value from waste materials; technical engineered materials, bio-based substances and energy production. The latter two will be the main focus in this thesis due to their biological nature.

1.1.3.1. Bio-based substances and products

Bio-based food and feed ingredients. Biodegradable waste that arrives from homogenous waste streams, for example the food and drink industry, can be recovered wholly and repurposed as food and feed for agricultural livestock. Effluent derived from the dairy industry in the process of cheese production can provide protein feed for cattle in raw form. Further separation of the whey protein from similar streams through the use of membrane technology can bring additional value from the waste stream for the food industry.

Bio-chemicals and building blocks. The biochemical industry has the largest market penetration potential compared to other bio-based sectors. Currently, only 5 percent of chemicals are derived from renewable resources [7]. Bio-plastics represents approximately 1 percent of the 300 million tonnes of plastic produced annually, however the production capacity is expected to reach 6.1 million tonnes in 2021, forecasting notable growth in the market [8]. A vast array of bioplastic products can be derived from bio-chemicals using conventional plastic processing technologies, with multiple applications thereafter. Lignocellulosic polymers cellulose, hemicellulose and lignin also have potential in high-value applications, such as clothing fibres, films and filters.

Bio-surfactants. Bio-surfactants can be found as components of various products within industry and household applications. For example detergents, cleaners, personal hygiene, food processes, agricultural chemicals and oleo field chemicals. Household detergent is the largest application, accounting for over 40 percent of the bio-surfactant market in 2013, which is expected to grow annually at a rate at 4.3 percent to 2020 [9].

Humic substances. Composting produces humic material through microbial aerobic transformation and stabilisation of organic matter. This process also occurs naturally with plant litter, animal residue and manure decomposition. The procedure of composting must ensure that the material is fully stable and has undergone the process of humification, to produce a substance called humus. Humus denominates the fraction of soil organic matter that is amorphous and without the cellular characteristic structure of plants, micro-organisms or animals [10]. The first stage of the composting process humifies the easily degradable organic material and can degrade recalcitrant lignocellulosic woody materials however this can take several weeks. The characteristics of humic substances include the ability to retain moisture and nutrients which are essential for plant life. Nitrogen, potassium and phosphorus can therefore be recycled from biological waste and be valuable commodity for the soil industry.

1.1.3.2. Bioenergy

Solid, liquid and gaseous forms of fuel can be obtained from bioenergy processes. Today bioenergy is exploited to meet 10 percent of total global energy demand from the heat, power and transportation sectors [11]. It is valued over fossil fuels due to its abundance and it can theoretically help to meet renewable energy targets in a low carbon society. Bioenergy is derived from a wide variety of biological matter (biomass) sources. Waste materials from a biogenic source that is produced or brought about by living organisms, such as forest, agricultural, livestock and municipal derived wastes form a massive underutilised biomass resource.

In order to understand the availability of waste biomass its definition is an important factor. Waste biomass is classified into three potential bioenergy feedstock residues. These are primary, which include agricultural and forestry residues; secondary, which include sawmill co-products and arboricultural arisings and lastly tertiary, which include contaminated and clean waste wood, municipal organic wastes, sewage sludge and animal manures [12]. However, it should be noted that classification methodologies differ and there is no single classification scheme. End-of-life materials, that is when a product is at the end of its useful life from the vendor’s point of view, can be an optimum and sustainable use of biomass when compared to biomass obtained directly from food crops or virgin wood sources. However, its carbon content and other elements must be extracted first and can be consistent with the waste hierarchy of re-use and recycle. There is potential for significant growth in the use of biofuels, in road, freight and aviation if advanced technologies to process wastes and woody feedstock are developed and commercialised.

Recent technical advances and increasing biomass resources in the bioenergy sector has been largely shaped by economical and societal developments. However, creating a sustainable and continuous supply chain of biomass feedstock is still a key issue for the development of bioenergy and its security. Current bioenergy generation challenges include environmental impacts and sustainability of resources in terms of supply chain capability. A viable option, it seems, is to find a feedstock that mitigates the direct need for land use and which has high resource availability. Future bioenergy production will more than likely be dominated by the technology employed in first generation biofuels, as they are well matured. Additionally, the integration of first generation biofuel plants into second or third generation plants could lower productions costs and provide resource needs where material is in demand. Co-processing waste biomass materials with recalcitrant lignocellulosic feedstocks can provide extra leverage in terms of meeting resource needs. However, due to the heterogeneous nature of waste biomass further development is required in procuring and processing to make it suitable. Recent policy announcements may drive sustainable biofuel production forward.

1.1.4. Drivers for waste management and bioenergy

The current UK strategic policy framework and its development will govern future waste management and bioenergy policies. Bioenergy is the only renewable source that can provide gaseous, liquid and solid forms of energy that can directly replace fossil fuels. Therefore, in the context of energy recovery within the waste hierarchy bioenergy is deemed an important component of the renewable energy mix in the UK. Especially, in the UK’s bid to meet its climate change obligations and renewable fuel targets.

1.1.4.1. Climate change obligations

The obligations in the Climate Change Act commits the UK government to reducing greenhouse gas (GHG) emissions by at least 80 percent of 1990 levels by 2050 [13]. However, in May 2019 the UK government adopted the Climate Change Committee’s recommendation to reach net zero emissions by 2050 [14]. Strategic policy making has identified bioenergy to have the potential to further decarbonise heat, power and transport sectors. The two main UK government departments responsible for collating this input are the Department for Business, Energy and Industrial Strategy (BEIS), formally known as DECC, which leads policy for reducing and mitigating emissions and the Department for Environment and Rural Affairs (DEFRA) which leads on domestic adaptation policy.

In 2017, UK emissions were 43 percent below 1990 levels. Therefore, the UKs has met its first carbon budget (2008-12) and is outperforming the second (2013-17) and third (2018-22) carbon budgets. However, it is estimated that the UK will not to be on track to meet the fourth carbon budget, which covers the period 2023-27 [15]. The energy supply sector that experienced the least reduction of carbon dioxide (CO_2) emissions is transport, experiencing a lowly 1 percent reduction from 1990 levels.

1.1.4.2. Policies supporting bioenergy

A number of policy drivers and financial incentives have been put in place to increase UK production and demand for biomass and biofuels. As a result, the bioenergy market has seen growth and is expected to further contribute to UK energy demands. In 2012, DECC's UK Bioenergy Strategy paper evaluated that sustainability-sourced bioenergy could contribute 8 to 11 percent by 2020 and by 8 to 21 percent by 2050 of the UK's total primary energy demand [16]. A number of support schemes currently back bioenergy production, which, however piecemeal, do offer the opportunity for more efficient technologies to develop and become commercially viable. The Feed-in Tariff (FiT) scheme, Renewable Heat Incentive (RHI) and Renewable Transport Fuel Obligation (RTFO) are the principal government levies and policies designed to meet the 2020 renewable targets in electricity, heat and transport sectors.

Announced in 2008, the FiT scheme are payments made to ordinary energy users for the renewable electricity they generate. Biomass combustion, EfW and combined heat and power (CHP) from biogas technologies currently benefit from this levy, however the scheme closed in April 2019. The RHI scheme introduced in 2009 promotes the use of heat generated from renewable sources. Technologies such as biomass boilers, air and ground source heat pumps and solar thermal are supported in both non-domestic and domestic schemes. In addition, the non-domestic scheme includes biogas, bio-methane, water-source heat pumps and geothermal. RHI tariff rates for biomass boilers have seen rates reduce more rapidly since 2013, falling from 8.8p to 2.71p on 1st July 2017. This is primarily due to spending caps; more focus on heat pumps and less on biomass; the requirement for larger biomass installations and more support for bio-methane in the non-domestic sector [17]. This RHI scheme is due to close by 2021.

The RTFO was announced in 2005 in response to the EU Biofuels Directive in 2003, which requires fuel providers to meet targets for transport biofuels sales or buy certificates to make up the shortfall. Recent changes to the RTFO in 2018 see increasing the biofuels volume target from the current 4.75 percent to 9.75 percent in 2020, and 12.4 percent in 2032. Biofuels include; bioethanol and biodiesel blended to 5 percent for conventional vehicles running on petrol and diesel, compressed natural gas (CNG) bio-methane for large vehicles mainly busses and trucks and lastly bio-butanol for aviation. Bio-butanol has been touted as an advanced drop-in biofuel for aviation, where full compatibility is maintained with internal combustion engines without corroding pipelines and it is more energy dense than bioethanol.

1.1.4.3. Policy strategy for emerging transport fuels

Importantly, an additional target has also been set for advanced waste-based renewable transport fuels for the emergence of 4th generation transport fuels, starting at a target of 0.1 percent in 2019 with the aim to rise to 2.8 percent in 2032. The introduction of these new targets will help reduce locking in first generation biofuels and promote the development of more advanced second, third and fourth generation biofuels for the transport sector. More is also being done to aid research and development for capturing energy from waste biomass. In addition to the new targets, £22 million of government funding is available to industry to develop cutting edge technologies for the production of waste-based advanced low carbon fuels in the UK for both aviation and freight. The current issues and challenges with the production of waste-based fuels will be identified and discussed in the following sections.

1.1.5. Waste treatment and energy recovery technology overview

Currently, a number of waste based fuels are created from differing waste management and treatment techniques. These techniques involve thermochemical and biochemical processes which substantially reduce the volume of waste, destroy pollutants and offer the opportunity to recover materials and chemical products [18].

Thermochemical treatment methods include incineration and gasification. Biochemical treatment methods include mechanical biological treatment (MBT) and composting, landfilling, fermentation and anaerobic digestion. Biochemical conversion technologies involve the use of natural biodegradation entities like microorganisms (i.e., bacteria, fungi, protozoa, etc.) with the capacity to synthesise intra- and extra-cellular enzymes to catabolise and breakdown biomass into gaseous or liquid fuels, such as bioethanol, bio-butanol and bio-methane. These techniques will be discussed in the next sections to provide an overview of their advantages and disadvantages.

1.1.5.1. Incineration and gasification

Incineration and gasification technologies are thermochemical methods which are employed in EfW practices. Incineration is a method that combusts waste material in an oxygen rich environment at temperatures above 800 °C [19]. Advantages of this process include treating both organic and inorganic waste, without the need for separation, for up to a reduction in volume by 80 percent. It can also treat hazardous materials, whilst recovering energy and other useful materials before treatment. The process itself is not complex. However, high initial capital costs for incinerator installation and sophisticated emissions control measures are required. Emission reduction controls are placed to clean-up the flue gas to maintain pollution levels compliant with environmental regulations. However, not all of these emissions are captured. Emissions from incinerators include heavy metals, dioxins and furans which are highly toxic pollutants to living organisms. Incineration sites must conform to emissions limits and dispose of fly ash produced in the process at hazardous waste landfills, or operators face penalties.

Gasification is a method that converts carbon in waste materials into synthetic gas (syngas). Syngas is a mixture of methane, hydrogen and other hydrocarbons which is produced in an oxygen-deficient environment, whilst using a gasifying agent such as air, hydrogen, vapour and their mixes [20]. Gasification is faster and more efficient that the direct combustion of the waste materials process found in incinerators. This is due to achieving higher temperatures during engine combustion of the syngas for the production of electricity, creating higher efficiencies and yields. Gasification efficiency is dependent on the homogeneity of its feedstock. Therefore, the waste material requires pre-possessing to remove inorganic materials as well as recyclables. Furthermore, lower levels of dioxins and acid gases are produced during the processes compared to that of incineration. Disadvantages include low net energy recovery if the waste material is wet or high in moisture and the complexity of the technology can induce higher capital costs. In both incineration and gasification methods, elements such as nitrogen, potassium and finite phosphorous which are key plant nutrients, are lost in the process.

1.1.5.2. Landfill, mechanical biological treatment and composting

Techniques that employ the presence of oxygen are called aerobic treatment. These include conventional waste management activities at landfill sites (however organic waste is stabilised without the presence of oxygen in a landfill cell), mechanical biological treatment (MBT) for separating recyclables and treatment of biological materials, and lastly a technique called composting to stabilise organic waste and then applied to remediate soils [21].

The landfilling process is relatively safer than some thermochemical management techniques. Compared to that of incineration and gasification, landfill creates far lower amounts of hazardous by-products. When landfills are properly managed and come to their end of its useful life, sites can be turned into parkland turning them into assets. During the landfill process, sites generate odour, leachate, CO_2 and CH_4 throughout the degradation periods. Leachate must be treated by law, since the potentially toxic liquid reside from the site can enter local water courses. Moreover, landfill gases produced at the very least must be flared to burn the methane, if they are not already generating onsite energy by combusting the gas in combined heat and power (CHP) units.

MBT is a two stage process. The first is the mechanical stage, where residual waste undergoes preparation and separation of bags and large bulky items. Further materials are then separated for recycling. The second is the biological stage, where the biodegradable fractions are biologically treated by either aerobic digestion (composting) or anaerobic digestion. MBT generally reduces waste volumes and the biodegradable content that would be normally sent to landfill. Greater amounts of recyclable materials are captured and this therefore helps to increase the rate of re-processing. However, the MBT process can reduce the quality of recyclable materials compared to having separate collection schemes. Additionally, long term contracts for the procurement of waste can undermine recycling and waste minimisation options.

Composting is a natural biological process, where micro-organisms including bacteria and fungi break down and reduce the volume of organic matter into decomposed fractions called compost. Compost has its advantages for its application as a soil amender and fertiliser supplement. When added to poor soils, compost can improve the water-holding capacity and structure. It can also promote the growth of other microbes, fungi and plants through bioavailable nutrients. Compared to landfilling, compost avoids excessive methane and leachate production. Disadvantages to the composting process include no energy capture, odour, pests and storage. With regards to the application of compost, accumulation of inhibitory compounds, such as salts, nutrients and heavy metals can upset ecosystems in the long term.

1.1.5.3. Fermentation and anaerobic digestion

Techniques that employ biological processing in the absence of oxygen, i.e. anaerobic conditions, include landfill cells, fermentation processes that apply enzymes for the production of bioethanol (alcohol fermentation) and methanogens for the production of bio-methane (anaerobic digestion) [21].

The fermentation process utilises the enzymatic process on any feedstock that contains sugar and starch as a substrate. An ideal feedstock is corn, but waste biomass that is not fit for human consumption can also be utilised. These include corn stover, switchgrass, paper pump, sawdust and organic fractions of municipal solid waste (OFMSW). The costs associated in receiving waste biomass is low and sometimes none i.e. free. The production process is well established and technology used is mature, furthermore the infrastructure required can be deployed rapidly. Bioethanol is it biodegradable and can be blended with petrol, thus associated carbon emissions of petrol saved is reduced. Bioethanol is also less toxic and polluting than petrol. The disadvantages of producing bioethanol through fermentation is that it requires mass quantities of feedstock. Therefore, if feedstock resource is inadequate, the cultivation of energy crops to fulfil capacity requires a lot of land. For the latter, the food versus fuel dilemma is prominent. Producing fuel creates the risk of diverting farmland or corps for biofuel production to the detriment of food supply for a growing population. Additionally, the enzymes used are expensive and contracts are usually incentive driven as government funding provides key capital.

Anaerobic digestion (AD) is another fermentation process but uses metabolic pathways of mesophilic and thermophilic bacteria to utilise a greater variety of organic waste streams. An AD plant produces two outputs: biogas (main) and digestate (by-product). Biogas mainly constitutes of methane and can be used to produce electricity and heat when combusted in a CHP, or it can be further processed and compressed to be utilised as a transport fuel for vehicles or injected into the gas grid. Digestate is the material that remains undigested (whole digestate) after the processing and can be further separated by dewatering to products called liquor (liquid digestate) and fibre (solid digestate). Solid digestate can be processed into a compost-like material due to its bulky quality and can be used as a soil conditioner or fertiliser due to its high levels of plant nutrients. A higher proportion of the plant nutrients remain in the liquid digestate which can be used as a liquid fertiliser.

The digestion process requires an initial loading of water for dilution purposes then regular loadings of organic matter, including monitoring to mitigate the shutdown of the biological processing. If shutdown occurs the reactor contents requires removal and re-starting of the process, which can take a number of days. Digestate markets exist, however the value of digestate is low. Generally, digestate is sold inexpensively, if not given away for free. If digestate quality standards cannot be met and the digestate produced is contaminated then disposal costs are high. The storage of digestate can also increase operational costs and can cause environmental pollution via leaching and fugitive methane emissions. Also, the spreading of digestate has to be carefully managed to avoid overloading the land with nutrients to reduce and mitigate eutrophication in local bodies of water.

1.2. Identification of problem: digestate quality

Organic waste being treated by anaerobic digestion has sharply increased, with a triple increase of digestion plants constructed and operating in the UK over the last decade. The increase is largely due to policy changes to encourage renewable heat, electricity and transport fuel generation. This has been achieved through a number of governmental financial incentives. Also, minimum quality standards for the sale of digestate have been set by legislative and non-legislative controls. The Biosolids Assurance Scheme (BAS) regulates digestate produced from sewage sludge (biosolids) for its use as a fertiliser. For digestate produced from other sources i.e. source-segregated biodegradable materials, the Biofertiliser Certification Scheme (BCS) implements the Anaerobic Digestate Quality Protocol (ADQP) for its use as a fertiliser [22]. The quality protocol sets out the end-of-waste criteria and the British Standards Institution publically available specification (BSI PAS 110) for minimum quality standards for certification [23]. The introduction of these assurance and certification schemes provides stronger environmental protections and operators can set a higher value on the sale of good quality digestate.

However, with more AD facilities currently operating there is increased competition for resource demand. Operators are now facing feedstock availability issues and having to accept lower quality feedstock to keep producing biogas. Accepting lower quality feedstock ultimately effects digestate quality. If minimum quality standards are not met, this causes issues in its handling and management when disposing to land thereafter. Maintaining digestate quality is a major challenge faced by most operators. To guarantee the quality and certification of the digestate for sale as a fertiliser product, limits and controls must be placed on the incoming feedstock. Many sites now implement a hazard analysis and critical control points (HACCP) planning procedure to manage the quality of digestate. This influences plant layout, design and equipment selection and the acceptance of incoming feedstock into the plant to increase the probability of meeting digestate assurance schemes. The market value of digestate can range anywhere from -£13 to £3 per tonne dependant on quality and demand. In 2014, 19 AD sites were PAS110 accredited under the BCS scheme with 1 million tonnes of digestate meeting minimum quality criteria [24]. In other words, 3.5 million tonnes of digestate did not meet specification. As a result, an increase of operational expenses (OPEX) can occur from the storage, transportation and disposal of digestate with little to no market value. If digestate is not traded, the costs to landfill or incinerate can be up to -£70 per tonne.

1.2.1. Digestate application and enhancement

Assurance and certification schemes have helped expand the digestate market for its recycling to land. However, further impacts of recycling digestate to land have now become apparent. Fugitive ammonia (NH_3) and GHG emissions have been recorded over a larger time frame. Additionally, if the agricultural land is close to a ground water source, the nutrients have the potential to run off during periods of heavy rain and cause eutrophication, which affects aquatic ecosystems negatively. Another emerging challenge to the recycling of digestate to land is of one of societal perception. Farmer assurance schemes now take note on meeting supply chain expectations. For example, the supply chain can consist of the malting or animal product industries, which have their own quality assurance bodies, including supermarkets and consumers of products. Negative perceptions of the application of digestate are increasing and unwelcomed, especially in relation to physical contaminant levels and human waste being a part of the food chain. As a result, some agricultural markets are abstaining from certain digestates and could potentially become more risk-averse, further reducing access to markets for digestates in the future.

Pathogens are bacteria, virus or other microorganisms that can cause disease, can occur within the digester and remain in the digestate. The digestate is classified as contaminated and cannot be sold due to hazards to health. The pathogens Salmonella and E. coli often occur in the digestate produced at AD facilities treating biosolids without pre-treatment steps. Thermal hydrolysis is a pre-treatment process, which is commonly used for biosolids digestion to create pathogen-free digestate and increase biodegradability to improve methane yields. Many digesters operate at mesophilic conditions; therefore, if pathogens are not removed they remain in the digestate. Given the right conditions, pathogen levels in digestate can increase or be contaminated externally, consequently it must be stored on site for a long enough period until concentrations are at safe levels before the digestate can go to market. This presents a waste management storage issue, especially if space is limited. Storing digestate on site can present further issues from odour, continued toxic gas generation and further residual GHG emissions, including additional contamination from its storage environment.

Interest is now growing in exploring alternatives to land recycling, including transforming and valorising digestate which could also add value to the whole digestion process. In 2012 WRAP [25] released a study to identify and raise awareness of the opportunities and challenges of a number of digestate enhancement technologies [25]. Enhancing digestate can provide additional value chains and income for operators of AD, as well as minimising environmental impacts. In summary, finding an outlet for uncertified digestate and increasing resource availability through utilising more complex wastes are currently the most prominent issues for the AD industry. This thesis addresses these issues through a novel process integration approach.

1.3. Purpose: integration of conversion processes

A number of barriers are emerging with the expansion of anaerobic digestion operations. They include shrinking gate fees for raw materials, increased measures and costs for digestate disposal and uncertainty about the long-term sustainability of recycling digestate to land. Innovation, analogous to the bio-refinery concept, is now required to provide the AD industry with longevity. Bio-refineries are key to realising the full potential of biomass resource by the integration of different processes, maximising outputs to create sustainable production of bioenergy and bio-based products. The bio-refinery concept integrates two or more processing technologies to increase systems efficiency and provide greater number of products and their yields, including providing multiple energy vectors.

The purpose of this thesis is to explore the potential opportunities for the integration of biological and thermochemical conversion processes; namely, biological mesophilic anaerobic digestion and hydrothermal carbonisation (HTC), which is a relatively newly researched thermochemical conversion method. This thesis will also compare another thermochemical method called pyrolysis to understand how these technologies compare. Developing integration strategies will provide operators with economic benefits through gross value added (GVA), additional income and savings from digestate management. Refining biomass and focusing on extracting fine chemicals, including nutrients, energy and functional materials will provide operators with multiple value added chains. Furthermore, increasing commodities and generating higher value products from waste biomass has the potential for exposure to the chemical, pharmaceutical and cosmetic markets.

Potentially the benefits are three-fold: the production of renewable biological resources will enable growth in the bio-economy; material and energy loops will close and narrow for a regenerative circular economy and bioenergy will move away from the challenges associated with first and second generation practises.

1.3.1. Benefits of integration

In businesses that employ systems engineering, integration allows existing technologies and systems to focus on delivering increased value to the customer by improving product quality and performance, at the same time providing value to the company by reducing operational costs and improving response time. In much the same way, the integration of conversion processes, as outlined in this thesis, can provide synergetic benefits with respect to chemical reactions, material management and energy savings. Synergy is a concept that the value and performance of two processes combined will be greater than the sum of separate individual processes.

A number of research papers have been published since WRAP's report on their study of identifying digestate enhancement technologies. For example Grycova et al., 2011, Mumme et al., 2011 and Monlau et al., 2015, which look at pyrolysis, gasification and hydrothermal technologies to convert digestate [26–28]. Pyrolysis and HTC are the two main thermochemical technologies under investigation to transform digestate into a carbonations solid and liquid fractions. Whilst the majority of published papers have focused on pyrolysis technologies there still remain a number of barriers for the industrial uptake of a pyrolysis and AD integration strategies. Barriers include; high parasitic energy demand as energy is consumed in the drying of feedstock to achieve below 10 percent moisture content; high operating temperatures; controlling emissions from kilns; and utilisation and treatment of co-products such as pyrolysis solids (pyrochar) and pyrolysis oils. Viewing pyrolysis as a synergistic technology for AD is becoming less apparent.

Hydrothermal carbonisation is an alternative approach for converting both dry and wet biomass into a coal like solid material called 'hydrochar', auspiciously for the production of bio-coal. Its relatively recent interest has been explored to treat high moisture content feedstocks and as an alternative approach to dewatering for biosolids. HTC typically results in energy densification of biomass due to the deoxygenation of the material, resulting in a higher caloric value than that of the starting material. The coal-like product has also recently been reported to have the potential as a slow release fertiliser. The liquid co-product (process waters) contains solubilised organic compounds, which also creates an opportunity for recycling the process waters back into the anaerobic digester, thereby reducing the demand for water required for dilution. There is also potential for HTC co-processing by blending digestate with more recalcitrant biomass, such as woody waste, to be further treated by AD.

HTC is therefore a potential route for processing digestate and biomass blends into a functional material, increasing biogas yields and further reducing volumes of digestate, including recalcitrant biomass sent to incineration or landfill. Also, HTC process waters have the opportunity to aid in facilitating the extraction of nutrients and chemicals for additional revenue streams. Due to HTC only recently being applied to process digestate there are a number of knowledge gaps for its viability for integration, predominantly in reaction theory and product application.

1.3.2. Valorisation of digestate and waste biomass

Integration strategies to further refine waste biomass provide opportunities for the current AD sector by their ability to accept a wider range of biomass wastes and by generating further revenue streams from value added products. However, increasing the capacity for processing when integrating more technologies also increases the demand and price of available waste biomass, which the AD industry is already facing. Therefore, the availability of waste biomass must be understood. An under-represented source of waste biomass is woody waste generated through land management at conservation sites. Low grade biomass is currently underutilised and it is estimated that about 500,000 tonnes of biomass is generated per year as a result of land conservation techniques in the UK [30]. Utilising this source of waste biomass, including other wastes generated by land management in AD operations has the potential to alleviate competition for the availability of feedstock.

Integrating processes with AD can be seen as an opportunity for emergent biotechnology. Introducing processing options for a greater variety of biomass also increases the opportunities for the production of fine chemicals used in bio-based products, which are higher value-added products. Maximising the recovery of waste biomass by adopting the biorefinery concept can help the AD sector through the slowing of development seen in recent years. Adopting such a strategy will align with the renewed RTFO and also align with the recent governmental report called ‘From Waste to Resource Productivity’ which aims to exploit the potential of unlocking valuable resources from waste [31].

1.4. Aim and objectives

A number of technology options have been identified for the enhancement of digestate to reduce volumes, and add value to the digestate and digestion process. However, current heat and pressure based technology options, such as pyrolysis require feedstock pre-processing and have a number of barriers associated with industrial uptake. Moreover, subsequent pyrolysis products require post-processing to improve their properties for application. On the other hand, hydrothermal carbonisation has been highlighted as a potential treatment and enhancement route. Therefore, the research aim is to identify the opportunities for the integration of hydrothermal carbonisation with anaerobic digestion to treat and valorise digestate and green waste materials.

The aim will be accomplished by fulfilling the following research objectives:

1. **Understand the effect of feedstock composition on product composition and yields.**
   - Solid digestate from the AD of four different waste streams and three types of green waste will be characterised initially and then used as a feedstock for treatment by HTC and pyrolysis (solid digestate only). Composition of the products will be analysed thereafter.
   - Results from this objective will provide an understanding of how the biochemical structure of the waste materials affects the yield and composition of the products formed under thermal degradation mechanisms of biomass.

2. **Understand the effect of process and conditions on product composition and yields.**
   - The digestate and green wastes will also be thermally treated via HTC and pyrolysis (digestate only) with varying process conditions. HTC will be performed using three loading rates and three temperatures. Pyrolysis will be performed using three temperatures. Both thermochemical processes will use a fixed retention time of 1 hour. Yields and composition of the product will be analysed thereafter.
   - Results from this objective will provide an understanding of how the change in process conditions affects the yield and composition of the products and provide an insight to the reaction mechanisms of HTC and pyrolysis.

3. **Understand the effect of blending digestate with three types of recalcitrant lignocellulosic biomass on the product yield and composition.**
    - The blending of digestate with three green waste high in lignocellulosic material, specifically garden hedge (privet), grass clippings and woodchip will be investigated by HTC to reduce the need for digestate dewatering in industrial practice.
    - Experiments will be conducted using 50 percent blends in HTC at one solid loading ratio, three temperatures and 1 hour retention time. Yields and composition of the product will be analysed thereafter.
    - Results from this experiment will allow for an understanding of the influence of biomass biochemical components on the composition of resulting solids and characters on the process waters.

4. **Understand potential routes of application of hydrochar and pyrochar.**
    - Hydrochar and pyrochar created will be further analysed for its potential for a solid fuel material through the understanding of its combustion behaviour.
    - Hydrochars will be analysed and tested for its agronomic properties by phytotoxicity to germination and plant growth tests.
    - Results from these experiments will uncover potential application routes for the solid fraction after thermochemical conversion and further understanding of the feedstock properties required for quality specification.

5. **Understand potential applications for process waters.**
    - Process waters created after HTC experiments will be characterised and then recycled using small scale batch anaerobic digestion using mesophilic conditions.
    - Results from this experiments, specifically bio-methane generation will produce an insight into inhibitory mechanisms present derived from toxic compounds in the process waters.

1.5. Organisation of chapters

Chapter 1. Introduction - establishes the background, purpose and importance of this study and provides an outline of the thesis structure.

Chapter 2. Literature Review - provides a summary of the previous research on anaerobic digestion, pyrolysis and hydrothermal carbonisation. With focus on digestate and an overview of the main findings of integration methods proposed. Issues around sustainable deployment, including barriers and challenges are discussed, plus areas for further investigation.

Chapter 3. Methodology - describes the sources of materials used for thermochemical processing and outlines the main methods used for the analysis and application of hydrochar, pyrochar and HTC process waters. Methods include elemental and biochemical analysis and estimation techniques for calorific value, combustion behaviour and bio-methane generation potential. Methods for agronomic properties such phytotoxicity and plant growth via soil germination tests are also given.

Chapter 4. Characterisation of Digestate and Green Waste Feedstock - assesses and compares the chemical composition of the digestate and green waste, including identifying a digestate to be blended with green waste for HTC co-processing. This evaluation provides an aid to the optimisation of conversion processes, including the basis for engineering product properties.

Chapter 5. Integration Concepts and Effects of HTC Processing Compared to Pyrolysis - explores thermochemical conversion integration strategies with anaerobic digestion and with this, compares the influence of feedstock composition from Chapter 4 and process variables of HTC and pyrolysis on the product yields. The influence of HTC co-processing on material balance is also evaluated.

Chapter 6. Characterisation of Products: Hydrochar, Pyrochar and HTC Process Water Composition - evaluates the HTC and pyrolysis product compositions generated from digestate materials, and the products from the blending of digestate and green waste in HTC co-processing using a number of char and process water characterisation techniques. Hydrochar and pyrochar properties are examined and compared for likely application outcomes. HTC process water properties are also examined to give an indication of bio-methane generation performance.

Chapter 7. Application of Hydrochar and Pyrochar - assesses the behaviour upon combustion of the hydrochar and pyrochar generated from the HTC and pyrolysis of digestate, green waste and blends for its application as a solid fuel. Slagging and fouling indices are used and serve as key indicators for combustion behaviour. This chapter also assesses the hydrochars agronomic properties as a growing media, specifically phytotoxicity and plant growth from the germination of tomato seeds. This analysis provides insights to meeting quality criteria for hydrochar to be used as a soil amender product.

Chapter 8. Anaerobic Digestion: Treatment and Application of HTC Process Water - assesses the treatment of HTC process waters by laboratory scale anaerobic digestion tests. Mesophilic conditions are used for the generation of biogas and observations for inhibition. Process water composition is evaluated to gain further insight on biogas performance and any inhibition mechanisms.

Chapter 9. Conclusions, Research Limitations, Recommendations and Direction - synthesises the results of the previous chapters on how the objectives were met; provides a summary conclusion; discusses the limitations of the research presented and provides recommendations for further work. The results in this study are used to highlight potential benefits and challenges in the integration options for sustainable waste management techniques and bioenergy generation. The future direction of research activities are also proposed and references are provided at the end of the thesis.

CHAPTER II

Literature Review

This chapter provides the context of this thesis by reviewing the development, current knowledge and latest findings of anaerobic digestion, pyrolysis, hydrothermal carbonisation and their deployment, including theoretical and methodological contributions to the integration of AD with pyrolysis and HTC. This will underpin the argument for the development of the integration of AD and HTC approach and highlight the knowledge gaps and the need for further validation through experimental investigations to satisfy the aim and objectives of this study.

2.1. Anaerobic digestion

Anaerobic digestion is a collection of processes by which microorganisms metabolise substrates, the nourishment in the organic material, in the absence of oxygen. This occurs strictly under anaerobic conditions. The AD process produces a biogas containing methane, which can be used as a fuel, and a by-product named digestate which can be used as fertiliser as it contains a source of plant nutrients.

Biogas from the decomposition of organic material was first recorded being utilised for heating bath water in Assyria in 900 BC, with further scientific understanding being developed in the 1700's. The first anaerobic digester was built in India in 1859, and by 1895 AD was being used in England to recover biogas from the stabilisation and waste management of sewage, municipal and agricultural wastes, and food production residues [32].

Within the UK, the AD process has been successfully utilised for the treatment of several waste streams and for the production of renewable energy. The AD process requires pre and post-treatment steps in order to utilise waste streams and microbial digestion requires operating temperatures suitable for naturally occurring mesophilic or thermophilic anaerobic and facultative bacteria species. Figure 2 illustrates a schematic diagram showing the inputs and outputs of an AD facility.

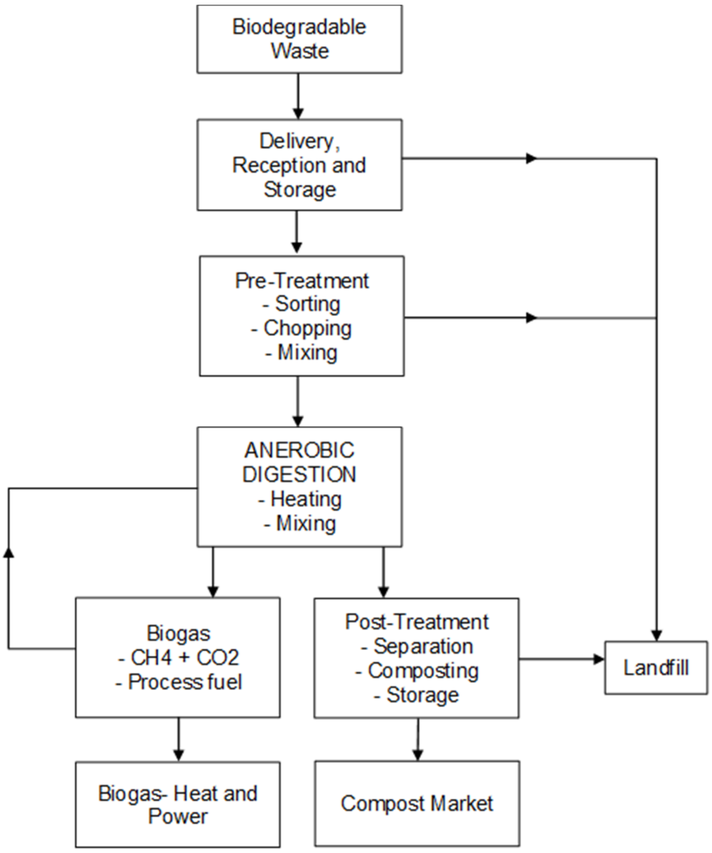

Figure 2. Schematic diagram of anaerobic digestion processes (sourced from [33]).

Digestion is a multi-step process involving a number of reactions taking place through microbial activity from different groups of anaerobic bacteria. These bacteria metabolise numerous organic and inorganic compounds and each of these compounds is degraded by different bacteria species. Each species produces a by-product, which is the food for another species. The species of microbes utilised within the AD plants determines the operating temperature of the digester. Currently, mesophilic conditions (30 ˚C to 38 ˚C) are used for mesophilic bacteria (mesophiles) for the production of methane. Thermophilic anaerobic digestion requires operating temperatures of 40˚C and above for thermophilic bacteria (thermophiles) stability.

Efficient metabolism of substrate is only achieved through a synergistic relationship between the different groups of bacteria. Anaerobic metabolism in mesophilic conditions can be presented as a four-step process involving four major groups of bacteria to produce biogas containing methane. The major groups of bacteria involved are: 1) hydrolytic bacteria, 2) fermentative acidogenic bacteria, 3) acetogenic bacteria and 4) methanogens. The four-step process is illustrated in Figure 3, which also shows the substrate breakdown amongst each step.

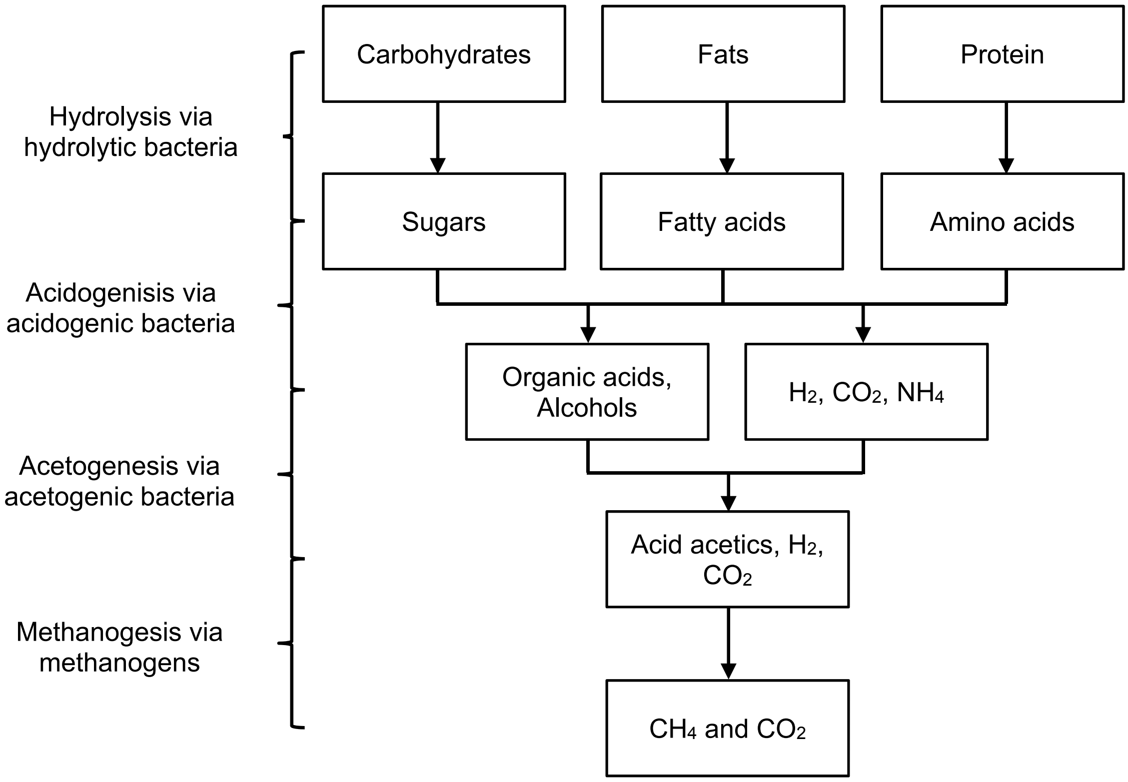

Figure 3. The four steps of methanogenic biomass degradation.

During hydrolysis, carbohydrates, fats (lipids) and proteins are broken down into soluble monomer molecules such as sugars, fatty and amino acids. At the acidogenesis stage, soluble monomer molecules are broken down into organic acids, alcohols, ketones, acetate, carbon dioxide and hydrogen. These compounds are then further broken down into acetate and carbon dioxide during the acetogenesis stage. Finally, at methanogenesis, acetate is consumed to produce to methane and additional carbon dioxide. Alternatively, methane is also produced via the reduction of carbon dioxide by hydrogen. The resultant mixture of gases is termed biogas and can be further upgraded to create a methane-rich gas termed biomethane.

2.1.1. Feedstock and biogas composition

Significant quantities of organic material are available for utilisation as a feedstock for anaerobic digestion, including, for example, energy crops, industrial by-products and waste fractions. Purpose-grown crops include maize, switch grass and beets. In industrial processes, large quantities of organic by-products are accumulated. These include sewage sludge from wastewater treatment plants, agro-industrial by-products (e.g. manure, agricultural residues etc.) and food processing by-products (e.g., slaughterhouse wastes, whey, brewers' spent grain, distillery slops, fruit and vegetable wastes). Finally, waste fractions for anaerobic digestion include the organic fraction of municipal solid waste, source-separated organic wastes, food, feed leftovers and kitchen waste.

Not all waste products and crops are equally suitable for biogas production. Therefore, to assess the suitability and profitability of AD feedstocks the characterisation of the input material is necessary. Analysis on total solids (TS), volatile solids (VS), nitrogen content, chemical oxygen demand (COD) and availability of macro and micronutrients should be carried out on the feedstock in question. Furthermore, the accumulation of inhibitory substances should be evaluated, including antibiotics, heavy metals, disinfectants, ammonia and hydrogen sulphide [34]. Initially, anaerobic digestion has been widely practiced to treat and stabilise sewage sludge from municipal wastewater treatment plants since the early 1900's and is still the most widely used sludge treatment method today. It was not until the 1970's that organic wastes from municipal and industrial sectors were introduced as AD feedstocks.

Table 1 lists the most materials currently used as AD feedstocks. The previously mentioned sectors, wastes, residues and by-products are the most sustainable resources amenable for biogas production. Along with the materials produced by different sectors of society, there is growing interest in the utilisation of aquatic biomass from marine and fresh waters, specifically species of microalgae and microalgae (seaweed) [35,36]. This also extends to woody biomass (high fractions of lignocellulosic compounds), normally recalcitrant to the digestion process.

Table 1. Compositions of some anaerobic digestion feedstocks (modified from [34]).

Type of feedstock	Organic content	C:N Ratio	DM[a] (%)	VS[b] % of DM	VS (%)	Methane yield (m^3 CH_4/ kg VS)	Methane production (m^3 CH_4/m^3)
Maize silage	Carbohydrates	17.0	15-40	90.0	-	<0.45	-
Switch grass	-	-	-	-	-	-	-
Waste water sludge	-	-	5.0	75.0	3.8	0.4	15.0
Straw	Carbohydrates, lipids	90.0	70-90	80-90	-	0.15-0.35	-
Pig slurry	Carbohydrates, proteins, lipids	7.0	5.0	80.0	4.0	0.3	12.0
Whey	75-80% lactose, 20-25% protein	-	5.0	90.0	4.5	0.3	15.0
Brewers spent grain	-	-	20.0	90.0	18.0	0.3	59.4
Fruit and vegetable wastes	Carbohydrates, lipids	35.0	15-20	75.0	-	0.25-0.50	-
Source separated organic wastes	-	-	10.0	80.0	-	0.5-0.60	-
Grass cuttings	Carbohydrates, lipids	18.0	20-25	90.0	-	0.30-55	-

[a] ,dry matter, [b] ,volatile solids

Biogas is mainly comprised of methane, carbon dioxide and other traces of gas such as hydrogen sulphide (H_2S), ammonia (NH_3), hydrogen (H_2), nitrogen (N_2), oxygen (O_2) and vapour water (H_2O). This mixture of gasses is the result of by-products of the groups of bacteria that work in synergy during the anaerobic digestion process. Table 2 shows the typical chemical composition of biogas from AD [37].

Table 2. Typical chemical composition of biogas (sourced from [37]).

Biogas composite	Percentage
CH_4	55-70 (vol. %)
CO_2	30-45 (vol. %)
H_2S	500-4000 (ppm)
NH_3	100-800 (ppm)
H_2S	<1 (vol. %)
N_2	<1 (vol. %)
O_2	<1 (vol. %)
H_2O	<1 (vol. %)

The resulting methane concentration in biogas can be estimated using predictive calculations, including the Buswell formula, or small scale tests via biochemical methane potential (BMP) tests. The relationship between the two gas products, CO_2 and CH_4, depends on the mean oxidation state of carbon in the feedstock. Figure 4 shows an overview of the mean oxidation state of different substrates and the corresponding CO_2 and CH_4 concentrations [34,38]. On average the ratio of carbon dioxide to methane in biogas stands at 40 percent and 60 percent respectively. This is due to feedstocks containing a mixture of carbohydrates, proteins and fats which give concentrations of CH_4 of about 50 , 55 to 70 and 70 to 75 percent respectively [34]. It should be noted that predictive calculations are always an overestimate of methane production. This is due to non-degradable organic components found in biomass feedstocks causing negative deviation from the theoretical oxidation states.

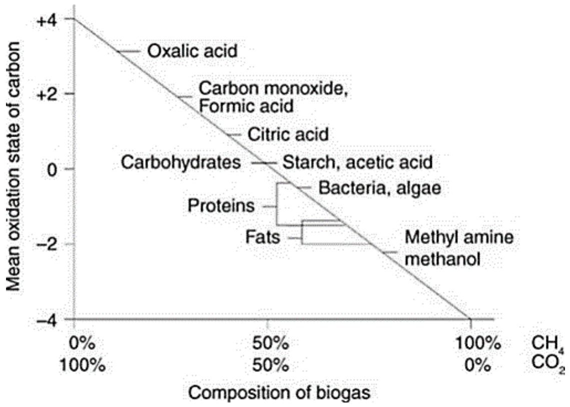

Figure 4. Influence of oxidation state on gas composition (sourced from [38]).

2.1.2. UK and EU uptake

Anaerobic digestion has been widely applied in the UK for the treatment of sewage sludge. And only recently has AD been recognised to play an integral role on wider sustainable resource management systems and has been used for treating other waste or with purpose-grown crops. Interest generated in the application of anaerobic digestion in the EU and UK has developed in particular in relation to five key areas: food security, air quality, energy security, economic growth and incentives linked to climate change. Compliance with EU directives and policies has also pushed AD into the market for the treatment of organic wastes.

The AD sector in the UK is growing rapidly and between 2013 and 2015 the number of AD units saw a 57 percent increase resulting in 254 plants operating in 2016 and at the time of writing (in August 2019) 639 AD sites are operational in the UK; an increase of 251 percent in three years [24,39–42]. Media reported slow development in 2017 to 2018, suggesting that the UK AD industry output has fallen since the announcement of subsidy reductions from FiT and RHI. Figure 5 illustrates where these AD plants are located in the UK, including the type of waste accepted [42]. AD units are often found with the MBT process, onsite farms and waste water treatment plants.

The figure shows that the majority of the plants treat agricultural and farm waste, plus sewage sludge in Northern Ireland and in the Midlands and Southern England. In 2014, 259 AD facilities processed 5.26 million tonnes of feedstock and provided 238 Megawatt electric (MWe) of generating capacity. The majority of the feedstock processed was food waste (35 percent), crops (26 percent), other industrial wastes (21 percent), manure/slurry (14 percent) and crop waste (4 percent) and a total estimate of 4.5 million tonnes of digestate was produced [24]. With the increase of operational sites, the figure of installed capacity now stands at 305 MWe at the 1st quarter of 2018 [43], enough to power 50,000 homes, a 28 percent increase compared to that of 2014 levels. The latest figures of the amount of digestate produced remains unreported, but is likely to be at least approximately 6 million tonnes in line with increases in operational sites and generating capacity.

Food security and air quality are both affected significantly by the farming sector. Approximately 27 $MtCO_2e$ of total greenhouse gas emissions arise from English agriculture, where 55 percent is derived from nitrous oxide, 36 percent from methane and 9 percent from carbon dioxide released from farming activities, especially associated with the use of synthetic fertiliser [44]. Defra states that 5 tonnes of carbon dioxide equivalent could be saved for every one tonne of nitrogen derived from the production of synthetic fertiliser by the use of digestate [45].

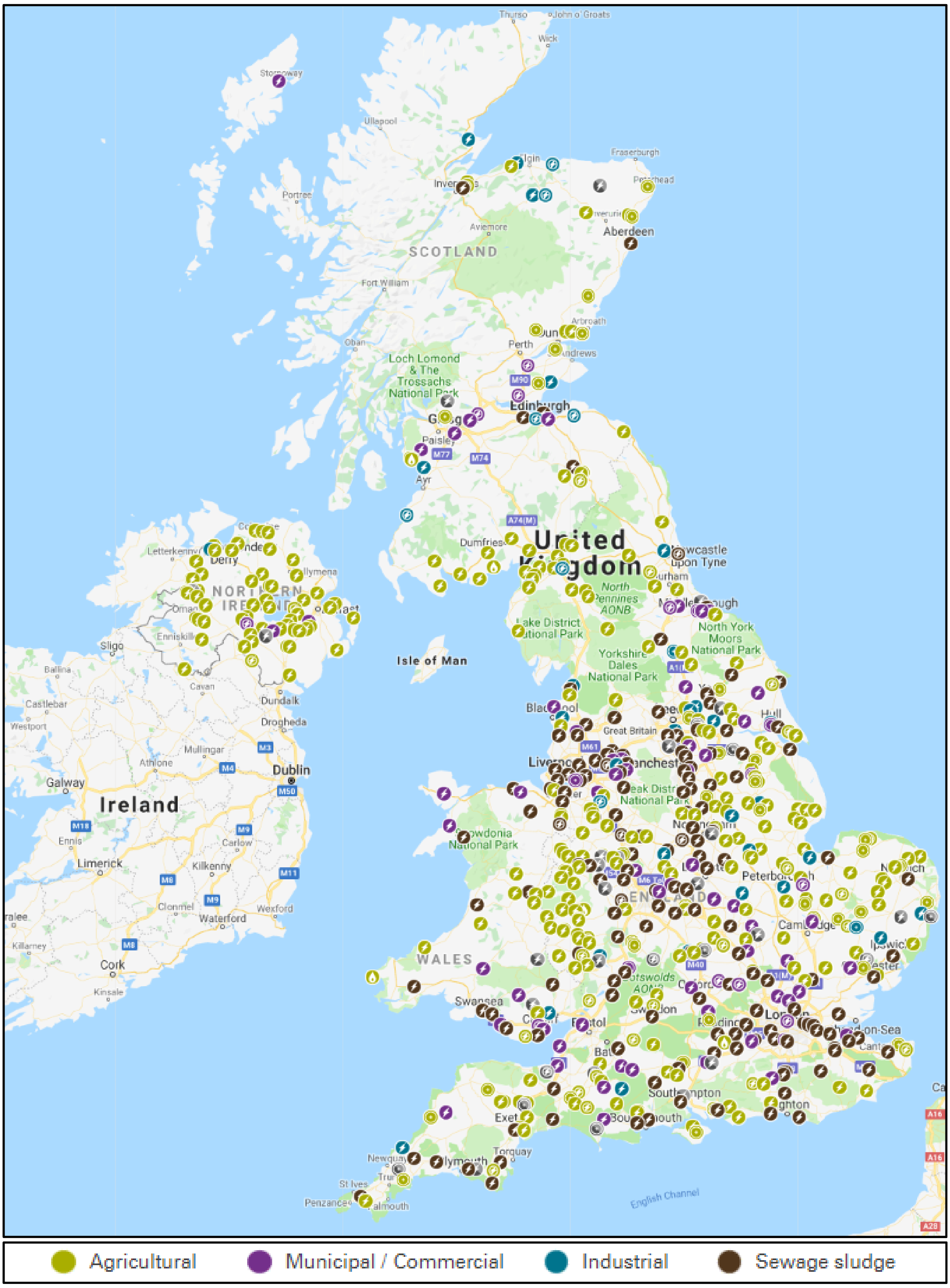

Figure 5. Map of 639 active AD sites producing biogas in the UK in 2019 (sourced from [42]).

AD can also be beneficial for energy security and the flexibility it provides in terms of the fuel produced. Biogas can be generated constantly, given that it has constant supply of feedstock and can be stored directly in the national grid in the form of gas. Biogas can also be upgraded to biomethane, which can compressed to produce liquid natural fuel (LNG) for application as a renewable transport fuel suitable for heavy goods vehicles (HGV's). AD also offers a move towards a low carbon and resource–efficient economy presenting opportunities for the growth of new industries and services. Benefits to economic growth can be found within the operation of plants and also from the manufacture, construction and delivery of AD equipment. Approximately 35,000 new jobs may be generated from the use of AD technologies and with continued success it may be possible to export products and services from the UK [45].

2.1.3. Operational challenges

The AD industry has been developing over the last 30 years and has faced a number of technical and economic challenges. These challenges predominantly arise around issues of operating costs and product markets.   The capital and operational expenses, CAPEX and OPEX, for an anaerobic digestion site compared to that of other waste management processes is relatively inexpensive to construct and operate. AD is also a flexible technology and can be built on many different scales, from large facilities treating sewage sludge or municipal waste, to smaller plants handling materials from a farm or small community. However, challenges to the industry have appeared as a result of environmental legislation and standards. This will be discussed in further detail to provide context for the problem statement in Chapter 1.

On a commercial scale, the capital investment to construct and implement a digestion facility can be high due to the purchasing of a range of equipment. The equipment required is; lift station pumps; large tanks; mixers; heating systems; covers; storage vessels; piping for gas and hot water; gas pumps; flow meters; safety features; generators; electrical wiring and controls as well as power transmission lines; design engineering and onsite buildings for the housing of generators, maintenance and contractor operations [34]. The payback period of this capital investment is reported to be between 3 to 7 years, but only with the addition of financial support from grants, savings and subsidies [46–48]. AD operator gate fees, a charge that is levied upon a given quantity of waste received at a processing facility, have been steadily declining. In 2015, the median gate fee was £40 per tonne, it was reduced to £26 per tonne in 2016 for England [49] and according to WRAP the range has widened with lowest gate fees dropping below £0 per tonne if not held by a private finance initiative (PFI) contract. The steady decline over the past three years has been attributed to overcapacity.

The market for biomethane has opened up with respect to the option for injecting into the grid. Currently, there exists no specific standard for biomethane injection into the grid in the UK but quality protocols for end-of-waste and EU standards do exist and operators do need to be aware of them since standards are being developed [34,50,51] . This can cause some operators to over-specify their biomethane quality to manage risks from grid acceptance. The process of upgrading biogas reduces carbon savings made from the digestion process, so it is important that the processing facilities are well operated. Maintaining the operational stability of an AD plant is challenging, especially to maintain quality standards of products generated.

Initial operation of AD tanks requires seeding, therefore a long start up time is expected due to low growth yields of anaerobic bacteria families. Once up and running, tanks need to be maintained and fed regularly which is a 24 hour operation. Preparation of the biomass is also required and in some cases watering down is required. The issue derives from the waste material creators who compress the AD feedstock for better handling and transportation, which reduces its water content. Dilution is therefore required before digestion, which demands a high water load. The digestion process is also sensitive to its environment. Key process variables such as pH, temperature and alkalinity need to be monitored to prevent severe inhibition and shut down of the facility [34]. Digestion of slurries, mixtures that contain fine particles, are also a risk to the operation of a plant. Sand and other heavy particles can sediment at the bottom of the digestion tank, causing issues with mixing and will eventually need to be removed and cleaned, causing the need to stop and restart the digestion process.

A number of anaerobic technology configurations have been researched to alleviate issues of operation and some have been put into commercial application. In some cases newer systems have not yet achieved commercial success and others have been replaced by more advanced technologies. The two main technology advancements can be categorised by two criteria: biomass contact with the bacteria and the organic loading rate (OLR), the flow rate of feedstock into the digester. When biomass is given as a food source for bacteria, the term substrate is used.

Substrate can either be fixed to a surface (attached growth) or can mix freely with the reactor contents (suspended growth). Improving substrate contact with the bacteria typically involves more mixing to allow suspended growth for increased biogas production. Systems configured in this way use granular inoculum, which is a small clumped amount of bacteria used to start a new culture. An Up-Flow Anaerobic Sludge Blanket (UASB) is commonly used in the waste water treatment industry to treat biosolids and apply relatively higher organic loading rates to keep microbial communities balanced for increased degradation of the biomass substrate [52]. Anaerobic digesters that accept non-biosolids can experience increased inhibition by the substrate used. Feedstocks that contain high amounts of fats can cause inhibition due to the over-production of volatile fatty acids (VFA) which will cause microbial communities to be unbalanced and create system instability. Other issues that can upset the community and slow digestion are fluctuation in temperature and the amount of non- or slowly degradable (recalcitrant) materials such as seeds or wood.

Contamination can influence unfavourable operations and increase risks to health and safety, including the management and sale of digestate. Contamination can cause toxic effects on the digestion process. Toxic compounds like persistent organic pollutants (POPs) and heavy metals, namely copper; zinc; chromium; cadmium; lead; nickel; mercury, including an overload of nitrogen can decrease and stop the metabolic rate of certain microbial families, which can reduce the metabolism rate of other microbes within the digester [53]. When the digestion process is inhibited, the rate of odours produced is increased. Odour comes from the build-up of gaseous nitrogen, ammonia, which is itself inhibitory to the digestion process and hazardous to humans due to asphyxiation. In addition to ammonia, H_2S is also produced in anaerobic conditions. H_2S is also a toxic gas, which is foul smelling, inhibits the digestion process, contributes to sulphur dioxide when combusts and creates a corrosive environment when present with moisture. Before biogas is utilised, H_2S requires removal or it can cause fouling of the combustion equipment.

2.1.4. Technology maturation

Even with these issues, the AD industry has flourished. Currently there exist two types of AD processing conditions; namely mesophilic and thermophilic digestion. The two types are determined by the temperature used by the digester. Mesophilic digestion operates between 35 °C to 38 °C and is the most common system found, having a more stable operation but generating a lower biogas production rate and not greatly reducing pathogen concentrations. Thermophilic digestion operates at higher temperatures between 50 °C to 65 °C; at these temperatures pathogen concentrations are reduced and the process therefore provides a more rapid reaction though it requires higher energy for heating and is more sensitive to environmental changes.

There are a number of advantages of using AD over other waste management techniques for biodegradable materials. AD is a mature and proven technology which has economic advantages as it develops rural economic growth but there is room to improve its efficiency. Local tax revenue is increased by creating jobs through contracting, site work, permit and engineering design, including hiring skilled labour to keep the digester running at optimum levels. Businesses can be built around the nutrient and energy markets to provide additional incomes. Energy independence can also be gained. The AD process is a net energy producing process, therefore on-farm energy needs can be met and can be operated off-grid. Biogas can be used to generate electricity for lighting barns or houses including heat for onsite greenhouses. Energy can also be provided to the local grid with locally sourced renewable energy. Environmental advantages include reducing greenhouse gas emissions by capturing the methane that may otherwise been lost to the atmosphere or flared during composting and landfilling activities respectively. Material sent to landfill is also reduced and this helps to mitigate the associated environmental impacts as discussed above. Anaerobic digesters also have the ability to handle soluble waste from industrial practises, thus avoiding costly waste water treatment and discharge options. Advantages to the agronomic sector include creating sustainable agricultural practices.

Digestate can be used as a liquid and fibrous fertiliser to conserve and improve soil health on land used for food and agriculture, displacing the use of synthetic chemical and pesticides. Digestate can also improve soil water retention ability. Benefits also accrue to society. Community relationships are improved by reducing the odours associated with manure spreading directly on land by spreading less odorous digested materials. An AD facility can also provide an educational focal point, where operators can allow a learning environment by connecting with schools and adults by providing tours and facilitating discussion about sustainability. AD technology has shown it can provide many benefits, though advancement is required for it to achieve more.

Recent advances alleviating some issues in the AD industry include pre-digestion processes, biogas upgrading and end-use certification schemes for digestate application. Pre-digestion technologies include thermal hydrolysis and ultrasound technologies to further improve energy performance by increasing material solubilisation and biogas yields. Technologies for upgrading biogas to bio-methane for grid injection and transport fuels have also been developed. These include scrubbing and precipitation technologies to remove hydrogen sulphide (H_2S) plus physical, chemical adsorption and membrane technologies for the removal of carbon dioxide (CO_2) to purify the biogas to 95-99+ percent bio-methane. Certification schemes for quality digestate have been introduced to give confidence to consumers that digestates are safe, consistent and fit for purpose.

2.1.5. Digestate markets and challenges

Once biogas generation has been completed, the remaining digested effluent, digestate, consists of the feedstock materials after bacterial metabolism of the substrate during anaerobic digestion. Therefore, the composition and quality of the digestate is highly dependent on the composition and quality of the feedstock used.

Until recently, literature has focused on assessing the nutrient and heavy metal content of digestate for the route of fertiliser application. Digestate contains easily assessable macro- and micronutrients and because of this, it is deemed a valuable crop fertiliser. Recycling digestate to land is highly preferred as it is considered the most sustainable utilisation of digestate. Digestate used as a bio-fertiliser reaps many benefits for society and the environment, as well as preserving fossil reserves of mineral phosphorous. Digestate, for the use as a bio-fertiliser needs to be of a high quality and free of contaminants, including pathogens, chemical and physical impurities and pollutants [34].

Regulatory frameworks and quality protocols and standards are therefore implemented in countries with developing biogas sectors. Current regulatory frameworks in the UK include End-of-Waste (EoW) criteria and Publicly Available Specification (PAS 110) for digestate, which includes updated knowledge of the impacts and restrictive levels of contaminants allowed in the fertiliser product.

Article 6 of the Waste Framework Directive details conditions to be satisfied for specified wastes to cease to be classified as a waste. These are called the End-of Waste criteria, which are dependent on whether:

- the substance or object is commonly used for specific purposes;
- a market or demand exists for such a substance or object;
- the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products;

- the use of the substance or object will not lead to overall adverse environmental or human health impacts [54].

A quality protocol document created by the Environment Agency and WRAP sets out the specific end of waste criteria applicable for the production of quality digestate. If these criteria are met, quality outputs from anaerobic digestion will normally be regarded as having been fully recovered and to have ceased to be waste which can be used in specific markets, without the need for waste management controls [55].

The PAS 110 certification system aims to implement quality assurance to unify the approach and develop a healthy market for digestate to be traded as a 'bio-fertiliser' [56]. Wellinger et al., (2013) [34] summarises the definition of quality protocols for digestate that is suitable for fertilisation purposes. The protocols are related to its properties, such as nutrient content, pH value, dry matter and organic dry matter content and homogeneity. Features related to health and safety also include that the fertiliser is:

- free of physical impurities (plastic stones, glass, non-digestible matter);
- free of any pathogenic and other undesired biological content;
- safe for living organisms and for the environment.

The only feasible way to ensure the production of high-quality digestate suitable as a fertiliser, from both a technical and economic point of view, is to use high-quality feedstock as substrate for AD. However, due to resource availability and variation of feedstock this is not always possible. Therefore, digestate that does not meet quality protocols or waste regulation may require further processing for treatment or valorisation to reduce storage, transportation and handling costs of the waste material. Digestate that is difficult to dispose, thus poses challenges to waste management operations.

2.1.6. Digestate enhancement technologies

Interest has grown in enhancement technologies to treat and valorise digestate that do not meet quality protocols in effort to create value added products from waste digestate. A joint report by WRAP and Zero Waste Scotland identified second-generation enhancement technologies that have potential to valorise digestate. Four themes were identified in their methodology process to create boundaries around research investigations. These were: 1) Heat and Pressure Based Technologies, 2) Novel Product Synthesis, 3) Nutrient Recovery and 4) Waste Bio-refinery Platform [57].

Wrap (2015) [57] details each of these themes as follows:

1. Heat and pressure based technologies
   High temperatures and pressures in systems operating both at and below the critical point of water. Applied to organic material to recover energy as solid carbonaceous matter, syngas or organic rich liquid fraction. Pre-treatment can also be applied to enhance subsequent thermal hydrolysis.
2. Novel product synthesis
   Production of a range of products from fermentation reactions during digestion often combined under the broad heading of the carboxylate platform.
3. Nutrient recovery
   Technologies utilised for the recovery of nutrients, nitrogen, phosphorous and potassium using chemical precipitation and membrane processes.
4. Waste bio-refinery platform
   Technology system integration as a bio-refinery optimised depending on the input material chosen. Incorporating both biological and thermal degradation routes, which may also involve nutrient recovery streams.

A number of potential technologies were identified, with six technologies highlighted for further study. Table 3 lists these six technologies and their potential application to optimise the digestion system and or the value of digestate. It is worth noting that whilst pyrolysis was in the original long list of 18 process technologies, it was not selected as part of the six technologies for further study within the WRAP report.

Table 3. Identified digestate enhancement options and their potential applications (modified from [57]).

Process options	Potential applications		
	Adding value to the feedstock	Reducing digestate volume	Adding value to the digestate
Hydrothermal carbonisation	X	X	X
Extractive phosphorous recovery			X
NEO energy		X	X
Waste bio-refinery platform	X	X	X
Carboxylate platform	X		
Bioplastic synthesis	X		X

Most research conducted on the resource recovery of waste is focussed on second-generation crops that do not compete directly with food, including crop residues. Heat and pressure-based technologies, also called thermochemical conversion processes, are also applied to crop residues to release the potential of recalcitrant lignocellulose either through conversion to energy or hydrolysis to simple sugars. Such processes are pyrolysis, gasification or the use of hydrothermal technologies [58].

From a technical point of view, digestate material is not an ideal candidate for conversion. Thermochemical conversion into energy products typically require moisture content of feedstock at 30 percent or less. Such is the case for pyrolysis technology. However, hydrothermal technology can accept both dry and wet organic matter and is not troubled by the presence of high ash, nitrogen or other containments [57]. Typically, pyrolysis and hydrothermal carbonisation (HTC) is applied for the conversion of organic matter to a solid carbonaceous material with similar properties to that of fossil coal and soil amendment products.

Therefore, the next sections will further discuss pyrolysis and HTC for the aim of integrating thermochemical techniques with AD to treat and valorise digestate, including lignocellulosic materials as a way of introducing alternative AD feedstock.

2.2. Thermochemical conversion processes

In this section, two thermochemical processes namely pyrolysis and hydrothermal carbonisation will be reviewed due to the roles they can play in enhancing digestate. Their operation, reactions, product streams and current technology status will be discussed.

2.2.1. Pyrolysis

The pyrolysis process converts organic matter into carbonaceous solid and volatile products via thermochemical decomposition in a dry inert atmosphere. Pyrolysis requires dry organic matter (below 10 percent mass fraction) in the absence of oxygen at moderate temperatures (250 ˚C to 750 ˚C) at atmospheric pressures [59]. In general, high temperature pyrolysis has three zones of thermochemical decomposition. The first occurs with temperatures below 130 ˚C and 165 ˚C where water and light volatile compounds are lost. The second appears between 140 ˚C and 540 ˚C where devolatilisation occurs. At this stage, most of the organic material is decomposed here, namely polysaccharides, proteins and lipids, in that succession. The third zone takes above 540 ˚C where carbonaceous matter is created from the decomposition of residual compounds [60]. Each of the three product streams from pyrolysis, namely solid, liquid and gas, have properties that provide value from the process.

The product yields obtained from the pyrolysis process are largely dictated by the biochemical composition of the biomass feedstock material. The primary products of cellulose and hemicellulose decomposition are liquid phases via condensable vapours and gas phase. Lignin decomposes to liquid, gas and solid char products. Soluble non-structural materials in biomass, called extractives contribute to liquid and gas products through volatilisation or decomposition [58,61]. Generally, minerals and other inorganic materials remain in the pyrochar and are collectively termed ash. The pyrolysis product distribution of components from the biochemical composition of biomass is shown in Figure 6.

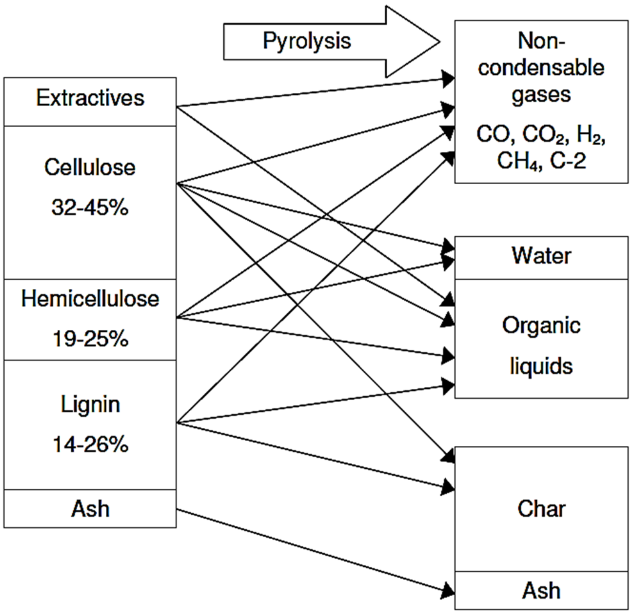

Figure 6. Schematic representation of biomass pyrolysis (sourced from [61]).

2.2.1.1. Pyrolysis products and composition

The process conditions applied also affect yields and composition of the products from pyrolysis. There are two main types for the pyrolysis of biomass, namely fast and slow pyrolysis with intermediates. Each process is characterised with varying severities of heating rates and vapour residence times, which influence the pyrochar, liquid and gas yields and composition. A summary of the process conditions and yields ranges are shown in Table 4.

Fast pyrolysis is characterised by high heating rates, using temperatures typically between 450 ˚C to 550 ˚C and short vapour residence times, typically from 1 to 5 seconds. In this configuration, the feedstock is required to be prepared as small particle sizes and a design that extracts the vapours quickly. Such designs exist in fluidised bed, stirred or moving bed, and vacuum pyrolysis systems. Fast pyrolysis favours the production of liquids, giving high yields of bio-oil. Slow pyrolysis is characterised by slower heating rates, using temperatures between 350 ˚C to 400 ˚C and comparatively longer solid and vapour residence times, typically from 2 to 30 minutes. In such a configuration, horizontal tubular kilns are used for the targeted production of pyrochar with high yields [61].

Table 4. Pyrolysis process scope and product yield ranges (modified from [61]).

Pyrolysis type	Process conditions					Yields (wt%, db)					
	Temperature (˚C)		Residence time (ms - days)		Heating rate (˚C/s)	Char		Liquid		Gas	
	Range	Typical	Range	Typical	Range	Range	Typical	Range	Typical	Range	Typical
Slow	250 - 750	350 - 400	min - days	2 - 30 mins	< 1	2 - 60	25 - 35	0 - 60	20 - 50	0 - 60	20 - 50
Intermediate	320 - 500	350 - 450	1 - 15 mins	4 mins	10 - 300	19 - 73	30 - 40	18 - 60	35 - 45	9 - 32	20 - 30
Fast	400 - 750	450 - 550	ms - s	1 - 5 s	> 550	0 - 50	10 - 25	10 - 80	50 - 70	5 - 60	10 - 30

To allow comparison of the products from pyrolysis, data from studies in literature have been evaluated. Muley et al., (2016) carried out pyrolysis of cellulose and lignin model compounds at five different temperatures (500, 550, 600, 650 and 700 ˚C) with retention times of 10 minutes [62]. Feedstocks and subsequent solid and liquid products were analysed for their elemental compositions, shown in Appendix Tables 1 and 2 respectively. To the author's knowledge, a hemicellulose model compound was not included within the study and has not been found in literature with the same process conditions applied with elemental analysis of subsequent pyrolysis products. The data shows that high process temperatures, to some extent, increase the carbon and nitrogen content and decrease the hydrogen and oxygen content of the biochar. Such evaluation cannot be proposed for the bio-oil composition, which suggests greater complication in pyrolysis reaction theory. However, it can be noted that the bio-oil products from pyrolysis show high levels of oxygen. It was also reported that GC-MS analysis revealed that the majority of the bio-oil consisted of phenolic and hydrocarbon compounds.

2.2.1.2. Pyrolysis technology status

The main barriers for industrial uptake of pyrolysis include the requirement for biomass feedstocks to have low moisture content (10 percent or less) to reduce negative effects of stability, viscosity, pH, and corrosiveness of the pyrolysis liquids [63]. Therefore, feedstock high in moisture requires further dewatering or drying prior to conversion.

The energy balance for the pyrolysis process is unfavourable due to parasitic energy loads. High operational expenses are exhibited due to the energy consumption for feedstock preparation and drying, including high operating temperatures, in addition to heat loss and maintenance [64,65]. Controlling the emissions from pyrolysis processes also requires additional equipment and energy requirements [66]. Additional challenges also lie in the of treatment, upgrading and utilisation of pyrolysis liquids due to their relatively high oxygen content, which are not considered a hydrocarbon [67,68]. The high oxygen content causes issues during utilisation due to non-volatility, corrosiveness, immiscibility with fossil fuels, thermal instability and a polymerisation when exposed to air [69]. However, most of these issues arise from the source of feedstock used for processing [70].

2.2.2. Hydrothermal carbonisation

Hydrothermal processes are defined as chemical and physical transformation of materials at high temperatures (100 °C to 600 °C), high pressure (50 to 400 bar) in sub and supercritical water conditions. This reforming biomass technology has the potential for energetic advantages. The advantage lies in the avoidance of large enthalpic energy penalties due to the phase change to steam when water is heated at high pressures [71].

In the hydrothermal process, the solid organic material is submerged in water and is kept in a liquid state by allowing pressure to rise along with the steam pressure within the reactor. Therefore, hydrothermal reactions allow the processing of biomass feedstock with high moisture content, removing the need for dewatering and drying. Within this process, there are three main regions of water that can be exploited and are identified as carbonisation, liquefaction and gasification as shown in Figure 7.

Firstly, hydrothermal conversion via “carbonisation” occurs in sub-critical conditions, between 100 °C and 350 °C and sufficient pressure to maintain a liquid state. This region is exploited for greater transformation of biomass into solid products. The second region is between temperatures of 350 °C and up to 400 °C, with pressures lower than that of the critical point of water. This region is called “liquefaction” and is where more liquid carbons are formed and more gas is produced. Lastly, the third region is defined by temperatures and pressures above the critical point of water (374 °C and 221 bar). Supercritical reactions occur in this region which is labelled as ‘gasification’, here the primary product is a gas phase [71]. The focus of this thesis is to produce greater yields of hydrochar from the waste biomass using the least parasitic energy. Therefore, this study will focus on investigating the region of hydrothermal carbonisation.

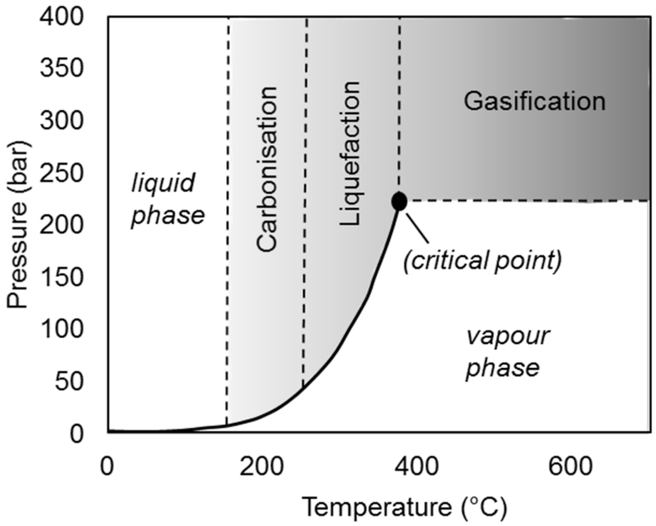

Figure 7. Hydrothermal processing regions referenced to the pressure-temperature phase diagram of water (modified from [71]).

2.2.2.1. HTC products and composition

The intended application of hydrothermal process can vary depending on its operating conditions. Varying temperature and retention time will affect the pressure at which the hydrothermal process converts organic material. Therefore, the product yield and composition are dependent upon the process severity. The hydrothermal carbonisation (HTC) process is rather complex. Six reactions stages have been identified 1) hydrolysis; 2) dehydration; 3) decarboxylation; 4) condensation; 5) polymerisation and 6) aromatisation. Each stage does not occur linearly but rather simultaneously, as shown in Figure 8, and reaction rates vary depending on process conditions and the feedstock used.

Studies have been conducted to understand the reaction chemistry under various process severities in order to determine the yield, composition and application of the product streams [71–75]. Table 5 shows hydrothermal process conditions and typical product yields. To the author's knowledge, typical ranges for liquefaction and gasification have not been found in literature. A study by Peterson et al., (2008) has recognised the effects of solid loading, that a dry mass fraction of more than 15 percent in the reaction mixture is favourable in order to run hydrothermal processes economically [71]. However, most hydrothermal experiments conducted report a solid loading of 10 percent or lower [76,77]. Considering this further, research is required to investigate whether higher carbon recovery in the hydrochar can be achieved with greater solid loads to optimise efficiency.

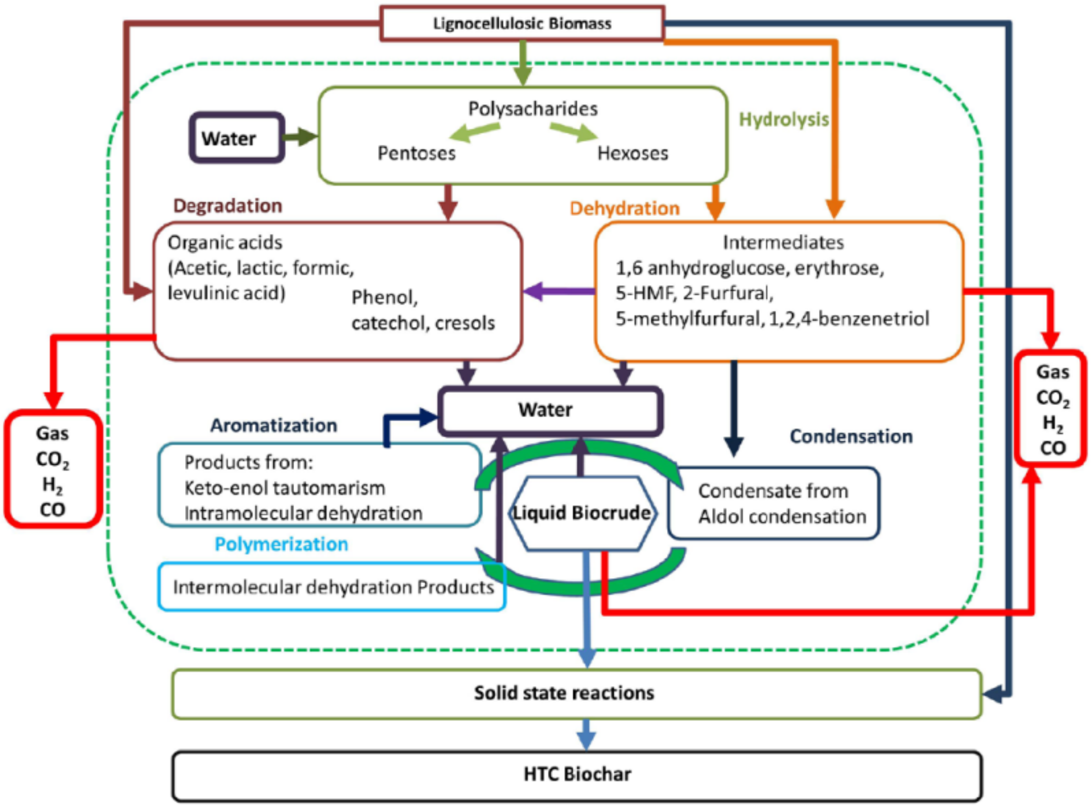

Figure 8. Hydrothermal carbonisation reaction pathways for lignocellulosic biomass (sourced from [78]).

Discussion of further breakdown of temperatures within the carbonisation stage (100 °C to 350 °C) and resulting product yields was also not found in the literature. An article by Reza et al., (2014) [79] reports the effects of retention times. The article reports hydrochar mass yields from retention times over 6 hours are comparably similar to mass yields to just after a minute. This is due to lignin degradation and hydrochar formation rates being analogues after 1 min for HTC at 260 °C. However, this is not to say that the characteristics of the hydrochar will remain stable.

Table 5. Hydrothermal process scope and product yield ranges (sourced from [73]).

Hydrothermal stage	Process conditions					Yields (wt%, db)		
	Temperature (˚C)	Heating rate	Residence time	Pressure	Cooling rate	Char	Liquid	Gas
Carbonisation	180 - 350	Moderate	Mins to hours	High autogenous	Slow	50 - 80	5 - 20	2 - 5

A study by Kang, Li, Fan, & Chang, (2012) [80] allows comparisons to be made of wood meal and model compounds: lignin, cellulose and hemicellulose alternative D-xylose including their hydrochar following hydrothermal carbonisation. The study carried out carbonisation of these materials at 33 percent solid loading in three different temperatures (225 °C, 245 °C and 265 ˚C) with a retention time of 20 hours. Feedstocks and subsequent solid products have been analysed for their proximate and elemental compositions, shown in Appendix Table 3. It was reported that the carbon content in all of hydrochar is between 63 and 75 percent, with increasing process temperatures positively affecting the carbon content. The report evaluates that carbon recovery is much higher within hydrochar than it is with pyrochar produced via pyrolysis at 620 ˚C. It was also reported from the proximate analysis that volatile matter was between 35 to 55 percent which decrease at higher temperatures. However, discussion of any trends regarding the content and fate of ash was absent. It can be noted, where ash measurements were taken, that the ash content increased with higher temperatures. Therefore, further investigation to compare and validate reporting the differences of hydrochar and pyrochar from the same material is required.

The composition and structure of the HTC solid product, hydrochar differs from the pyrolysis solid product, pyrochar. The chemical structure and elemental composition of hydrochar more closely resembles natural coal than pyrochar, owing to having higher H:C and O:C ratios [73]. This improvement has been attributed to deoxygenating reactions and that both dehydration and decarboxylation mechanisms occurred repeatedly during hydrothermal carbonisation [80]. However, these experiments were performed using homogenous model compounds, and would be likely to produce different results if using high ash materials like digestate. Therefore further atomic ratio analysis and heating analysis is required to validate this statement.

2.2.2.2. HTC technology status

The main barriers of the industrial uptake of HTC is due to its relatively lower technology readiness level (TRL), compared to that of other thermochemical techniques, owed to operational requirements of high temperatures coupled with extreme pressures. Currently, there is a lack of fundamental thermodynamic data at these extreme conditions, and a limited understanding of reaction kinetics and mass transfer effects on the process [81]. Therefore, a major challenge of this technology is economies of scale and safety considerations. Nevertheless, HTC facilities have been emerging from 2010 (as discussed in 2.4 Sustainable Deployment), however data on process and outputs are not available nor published online to confirm the veracity of successful operations.

2.3. Integration of AD and thermochemical processing

The integration of different energy processes is key to realising the potential of renewable technologies. A hybrid energy system, consisting of two or more renewable energy sources used together has the potential to provide increased system efficiency, including a greater balance in energy supply. A synergetic effect is created. Such integrations can further allow better waste management, such as the case for digestate from anaerobic digestion, allowing to create value added products via thermochemical methods.

Integration of these technologies will also act as an advantage in boosting the "circular economy" by reducing cradle to grave products. A boost to the "bio-economy" can also be achieved by improving resource use efficiency, in terms of the production of bio-based products. The transition to a bio-based industry is emerging. New strategic approaches are required for this realisation and new productive concepts are gaining momentum. Monlau et al., (2016) [82] summarises these approaches and concepts as:

1. Progressive integration/ industrial symbiosis, of different conversion technologies with functional connections and links across different process creating a "system".
2. Development of new value-chains, which implement a "cascading" biomass utilisation scheme. A scheme where the output of one process becomes the input of the following with biomass flowing through a number of processes and conversions. This also targets the "zero-waste" goal.
3. Processing biomass according to a "closed-loop" philosophy. In a closed loop, plant nutrients are returned to the soil, creating more ecologically sustainable farming and preserving soil quality, fertility and organic matter, without the use of synthetic fertiliser. This approach can also be viewed as a carbon capture, or carbon stocking.

Newly designed bioenergy systems or bio-refineries, encapsulating this multi-functional, cascading and closed loop arrangement offer significant efficiency gains. It also maximises the value extracted from a given amount of biomass by fulfilling both material and energy needs from the same feedstock, whilst reducing disposal to landfill [83]. However, material and energy balances must be investigated to realise any economic potential of such integrations before taking a systems engineering approach to develop integration approaches. Therefore, this thesis will consider options for integration approaches and discuss benefits and challenges for each.

2.3.1. Integration potential and life cycle analysis

The main findings from the studies that have focused on the integration of AD with pyrolysis and with HTC will be discussed here to understand the key gaps of integration knowledge.

A study by Hübner & Mumme, (2015) [84] investigated the integration of pyrolysis after anaerobic digestion, focusing on the use of pyrolysis liquid products (liquors) for biogas production. Three pyrolysis liquors produced at 330 ˚C, 430 ˚C and 530 ˚C, and four COD-based concentrations of 3, 6, 12 and 30 g per L were investigated. It was reported that the three lower concentrations of COD showed considerable biogas production, whereas the highest COD dosage caused process inhibition. The highest methane yield was observed for the 330 ˚C pyrolysis liquor, followed by the 430 ˚C sample then 530 ˚C. Therefore, it was concluded that pyrolysis temperature has strong impact on degradability of pyrolysis liquor and up to 63.4 percent of the COD and volatile organic compounds (VOC's) was removed by the methanogen microflora. Thus indicating high adaptation of the pyrolysis liquors by the microbes and energy recovery by the anaerobic digestion process. However, the report did not mention any requirements for digestate de-watering, nor any potential routes for the liquid fraction of the digestate.

Another study by Monlau et al., (2016) [82] investigated a functional integration of pyrolysis after anaerobic digestion for sustainable resource management, focusing on the comparison between solid-digestate and its derived pyrochar for soil amendment. In this approach, digestate would be de-watered prior to pyrolysis and the resulting pyrochar would be used as a soil amender, with any syngas and bio-oil produced applied towards energy recovery. It was reported that P and K are enriched within the pyrochar and total N showed no differences. Greater heavy metal concentrations were found within the pyrochar and it exhibited higher surface areas, a greater water holding capacity and a more recalcitrant carbon structure. In conclusion, it was found that both solid fraction digestate and digestate pyrochar have good and complementary properties as soil amenders.

A life cycle study was performed by Righi et al., (2016) [85] assessing anaerobic digestion placed after high ligno-cellulosic waste biomass pyrolysis, removing digestate altogether and the need for its de-watering. The study pyrolised corn stover to obtain syngas, bio-oil and biochar. The bio-oil and gas outputs were then anaerobically digested and biogas production measured. Two different utilisation pathways for the biochar was analysed: a) burning in hard coal power plant (combustion scenarios) and b) addition to soil amendment (amendment scenarios). For each of the utilisation pathways, three sub-scenarios had been evaluated, which differ in the technical performance of five key parameters: (1) electricity consumption of the pyrolyser; (2) biogas yield from anaerobic digestion; (3) percentage of methane in the biogas; (4) electrical efficiency of the CHP unit and (5) thermal efficiency of the CHP unit. The values of each parameter had been classified according to three levels of performance – worst, average and best. The performances of each of these scenarios can be seen in Appendix Table 4 with "best scenarios" system boundaries for the two pathways shown in Appendix Figure 1.

The performance results from this study were then rated against impact categories. It was concluded that both approaches enables relevant primary energy savings of non-renewable sources without worsening abiotic (non-living chemical and physical parts of the environment that affect living organisms and the functioning of ecosystems) resource depletion. Furthermore, the study showed a strong reduction of GHG's emissions, eutrophication and acidification in all scenarios when biochar is used for soil amendment instead of corn stover as mulch. However, without real world data i.e. application of the solid products, the veracity of the claims remains diluted. Therefore, the chars in this thesis will be assessed for their combustion behaviour.

2.3.1.1. AD with HTC

A study by Funke et al. (2013) [86] investigated the cascaded production of biogas and hydrochar from wheat straw (a lignocellulosic waste material) by hypothetically placing HTC after anaerobic digestion. Their focus was on the energetic potential and recovery of carbon and plant nutrients. The study reports hydrochar from wheat straw digestate with a higher heating value (HHV) of 31.5 MJ/ kg (dry basis). It also evaluates that around 60 percent of the original energy in the input material is found within the digestate and that half of this energy can be recovered in the hydrochar.

Therefore, it was assessed that a system integration of AD and then HTC subsequently doubled the recovery of the energetic content of the straw as biogas and hydrochar (to 65 percent) which is reduced to 54 percent when considering the auxiliary energy required running the cascaded process. The energetic potential of the combined fermentation and carbonisation can be seen in Appendix Figure 2. It was deemed that the liquid and gas products were considered losses; however, the energetic potential can be potentially increased if the HTC process water is recycled back into AD. Nevertheless, the inhibitory compounds present in HTC process waters generated from digestate and lignocellulosic wastes requires further investigation.

Furthermore, the study analysed the distribution and fate of elemental carbon, nitrogen and phosphorus in the solid and liquid products at four temperatures (190 °C, 210 °C, 230 °C, and 250 ˚C) with retention times of 6 hours. It was reported that the recovery of carbon was highest for straw digestate hydrochar and decreased with increasing temperature (ranging from 56 to 76 percent of the original input) and the majority of nitrogen (60 to 65 percent) and phosphorous (77 to 80 percent) were also recovered in the hydrochar produced. To validate this, further investigation of the fate of elements, nutrients including ash (inorganic compounds) is required.

Another study evaluating the integration of AD with HTC placed at the back end using lignocellulosic waste was conducted by Reza, Werner, Pohl, & Mumme, (2014) [87]. Mass and energy balances where taken from the production of biogas followed by carbonisation of wheat straw. The wheat straw was processed using a novel up flow anaerobic solid state reactor (UASS) in both mesophilic and thermophilic conditions and then hydrothermally carbonised at 230 ˚C for 6 hours with a ratio of digestate to water at 1:4 (25 percent solid loading). Elemental analysis, HHV, mass yield and biochemical analysis (with the exception of digestate hydrochar) was determined. It was reported that the combination of AD and HTC yielded 13.2 MJ of energy per 1 kg of dry wheat straw, resulting in a 20 percent increase than HTC alone and a 60.2 percent than AD alone. In order to validate these findings, a number of digestate materials should be investigated further to understand the effect of the biochemical composition on energy recovery.

Moreover, HTC process waters and hydrochar should also be utilised in either biological or combustion processes to ascertain their applications for energy recovery. Recycling of the HTC process water could make industrial application more feasible by increasing outputs of value added products, such as mineral fertiliser, or using anaerobic digestion to create further biogas or chemicals from the carboxylate platform. These approaches could be potentially used for an industrial scale HTC plant leading to an economic advantage.

2.4. Sustainable deployment

The UK is increasingly becoming more reliant on imported energy and it will become more exposed to change in international fuel prices. In 2012, Russian coal mined in the Siberian coalfield accounted for approximately one third of the UK's total coal consumption and has imported coal from other countries including the USA, South Africa and Australia [88]. The IMF Commodities Team, (2013) reported coal delivered from Australia to Europe to be priced at 2.29 Euro per GJ in 2013 [89]. A proportion of electricity is still supplied from coal-fired power stations, in the UK, with some converting to biomass firing; however, sustainable supply of biomass and biomass-derived fuels is still an issue.

Material resource is an important factor in the development of a facility for the production of energy. Dedicated energy crops like poplar wood chips from short rotation forestry can command prices of nearly 80 Euros per ton dry matter, and therefore can account for up to two thirds of the final product price in large scale facilities [78]. If using waste biomass, which is very likely to contain metal and plastic residues, an initial pre-treatment screening is required to remove these materials, screening will also increase costs before biological and thermochemical processes can occur. However, waste biomass including agricultural residues, residual municipal solid waste and sewage sludge can generate extra income if the plant operator is paid for the disposal and treatment of the waste material, which will significantly reduce the cost of the products after conversion. Currently, the price of pyrochar or hydrochar cannot compete with bituminous coal and that largely depends on the source of the material. However, pyrochar and hydrochar could be more competitive with industrial wood pellets for co-firing, with the pellets priced at 8 Euro per GJ [90].

High total capital investment (TCI) and material flow management represents another challenge to industrial scale thermochemical plants. Studies by Erlach, Wirth, & Tsatsaronis, (2011) and Stemann, Erlach, & Ziegler, (2013) consider the economics of a whole HTC plant and realise that such a reactor will represent the investment of between 8.5 to 21.3 percent of the TCI, which is also dependent on the capacity and feedstock used [91,92]. TCI is also increased because of wastewater treatment due to the greater moisture contents of the biomass or from increased water loading to solid biomass ratios. Higher water content in the feedstock will also increase the fuel consumed in a thermochemical system, as the whole biomass needs to be heated up prior to processing, especially in a continuous design. Therefore, high solid loadings of up to 30 percent will be investigated further in this study.

Many economical evaluations in literature are based on lab-scale experiments and then scaled up using modelling software with many assumptions [78]. Therefore, there lies a margin of uncertainty in results published without real world data. Currently, there are five operational HTC plants, these are summarised in Table 6. It is worth noting that most of the plants are continuous in design and have degrees of process water recirculation. Notably, the AVA-CO2 plant is a hybrid HTC and solar plant successfully processing waste biomass feedstocks.

Table 6. HTC plant operators, reactor characteristics and costs (sourced from [93]).

HTC plant operators	Year operations began	Reactor Type	Biomass capacity (per year)	Heating medium	Process conditions	Cost
AVA-CO2	2010	Batch	50,000 tons	Steam	220 - 230 °C; 2.2 - 2.6 Mpa; 5 - 10 hours	€ 6-10 million
TerraNova	2010	Continuous	8,000 tons	Oil	200 °C; 2 - 3.5 MPa; 4 hours	€ 5-6 million
Ingelia S.L	2010	Continuous	6,000 tons	Steam	180 - 220 °C; 1.7 - 2.4 MPa; 4 - 8 hours	Unknown
SunCoal	2012	Continuous	50,000 tons	Steam	200 °C; 2 MPa; 6 - 12 hours	€ 3 million
TFC	2012	Continuous	10,000 tons	Oil	200 - 230 °C; 2 - 2.5 MPa; 3 - 4 hours	€ 2.9 million

Biological conversion of the residual process water from HTC to yield methane via anaerobic digestion can make HTC more economically feasible. Depending on the feedstock and degree of process water recirculation around 1.5 to 5.2 m^3 of waste water per ton of hydrochar is produced [94,95]. Stemann et al., (2013) reports findings of an increase in energy yield of around 9 percent when the HTC process water was anaerobically digested. Therefore, the recycling of HTC process waters via AD will be further investigated in this study to generate additional biogas.

2.5. Synopsis of the areas for further investigation

The literature has provided some insight to the integration of HTC and pyrolysis with HTC, however beneficial results have been reported using single feedstocks. Therefore, it is difficult to understand the full range of behaviour and scenarios on the efficacy of the integrated process. In order to realise such integration strategies further studies are required at material and energy flow levels.

Therefore, this study seeks to address the following areas for further investigation:

A range of digestate should be thermochemically converted with the same operational conditions to understand how the variance of material composition affects the reactions of HTC and pyrolysis and product properties. Additionally, experiments on varying process conditions such as temperature and material loading should also be conducted to understand how the process reactions affect the final product composition. Furthermore, green wastes should also be hydrothermally carbonised for solubilisation as a way of introducing alternative recalcitrant AD feedstock.

Finally, experiments to assess the behaviour of the solid and liquid products should be investigated to understand how (i) the material compositions and (ii) process conditions affect the quality of the solids products as a solid fuel and soil amender, including HTC process water digestibility for methane generation. Predictive theoretical calculations and small-scale application tests such as slagging and fouling indices (combustion behaviour), plant response tests (phytotoxicity to plant growth) and biochemical methane potential tests (biogas generation) should be employed to understand opportunities for valorisation and product engineering.

To aid in understanding the underlying fundamental chemistry during conversion and application behaviour a full suite of chemical composition analysis should be undertaken. This includes analysis of the chemical composition for the solid materials before and after conversion, including a suite of liquid analysis after HTC conversion. Understanding the presence of inhibitory compounds is required to avoid inhibition of the digestion process, which would negatively affect biogas yields and composition and ultimately technology synergy for integration.

The methods employed for these investigations are fully explained in Chapter 3. Subsequent results Chapters (4 to 8) also provide a further more detailed relevant literature review prior to the discussion of findings. Further work and research interests are discussed in Chapter 9 for the continued development of this integrated system.

CHAPTER III

Methodology

The materials and experimental techniques employed in this study to characterise materials, and to convert and transform digestate and green waste feedstock will be discussed in this chapter. Information with regard to the source of the feedstock materials is given before preparatory techniques for the conversion process, and analytical techniques for solid and liquid composition analysis are described.

3.1. Materials and preparation

Information on the source and generation of digestate and green waste materials used in this study will be provided in the following sections. The site locations, operational conditions and any preparation of the digestate and green wastes will be described. Lastly, the method for sample preparation prior to the application of experimental techniques is explained.

3.1.1. Source of digestate

Supply of dewatered digestate samples were received from Organic Waste Systems (OWS), Belgium and Yorkshire Water, UK. These samples were collected following anaerobic digestion of four different waste streams: (i) agricultural residue (AGR) comprised of mainly maize (>80 percent) with fractions of whole plant and grass silage together with manure, (ii) residual organic fraction of municipal solid waste (MSW) after mechanical separation, (iii) sewage sludge (SS) comprised of pre-treated primary and secondary biosolids and lastly, (iv) source separated organic household waste comprised of vegetable, garden and fruit (VGF) material.

The AGR, MSW, and VGF digestates were produced using thermophilic conditions in a test digestion facility simulating a full-scale dry anaerobic composting (DRANCO) processing plant, with a loading rate of 15, 8, and 7 kg of volatile solids (VS) per m^3 per day and a residence time of 30, 45, and 25 days, respectively. The SS digestate was collected from a waste water treatment plant with a commercial scale AD facility (Dewsbury, UK); pre-treatment was applied via thermal hydrolysis operating at 160 °C and 6 bar. The AGR and MSW digestate were air dried at 52 °C without fractionation. VGF digestate was dewatered in a screw press to increase the total solid (TS) concentration to 40 percent. The SS digestate was dewatered to increase the TS concentration to 15 to 20 percent, thereafter the material was partially oven dried at 60 °C prior to transportation.

3.1.2. Source of green waste

Grass clippings were received from University of Leeds Estate Services and kept frozen at minus 18 °C to reduce the rate of decomposition. Garden hedge pruning was obtained from Burley Model Allotments, Leeds and then air dried. Supply of woodchip, with specification G30 and G50, was purchased from a local market (Garforth Log Supplies, Peckfield House Farm, Garforth, Leeds, UK) which use premium grade Larch and Spruce softwoods.

3.1.3. Sample work-up

In industrial practice, digestate comes in the form of a slurry, however samples were received pre-dried or dewatered to reduce transportation costs. The SS digestate was received with approximately 72 percent moisture and was oven dried for 48 hours to reduce the moisture content and allow for size reduction. Prior to any size reduction exercise, all feedstock samples were scrutinised and sieved to remove large contaminants. However, due to the heterogeneous nature of digestate it cannot be said with high confidence that all contaminants were removed prior to experimentation.

Additionally, due to seasonal changes and transport logistics the input materials for anaerobic digestion exhibited variation; in addition, the operating conditions for each AD site will fluctuate. To mitigate sources of error for this study, laboratory standard measures were taken to ensure homogeneity for conversion and chemical analysis. Prior to conversion and chemical analysis, size reduction was performed to create particle sizes of less than 2 cm in diameter using a laboratory grade grinder (Jaw Crusher BB 200, Retsch, Haan, Germany). The grinder was cleaned thoroughly to ensure that no cross contamination of the samples occurred.

3.2. Experimental design

A schematic diagram of the entire experimental design is provided in Figure 9. The diagram shows routes for pyrolysis and hydrothermal carbonisation of the feedstock with varying process conditions. It also shows the analytical techniques of both feedstock and products after conversion, including further experiments to understand the behaviour of the products during application. This thesis will mainly focus on hydrothermal conversion. However, the feedstock has been processed by two thermochemical methods; hydrothermal carbonisation and pyrolysis to aid in the comparison of the solid products. Detailed description of the experiments are given in the following sections.

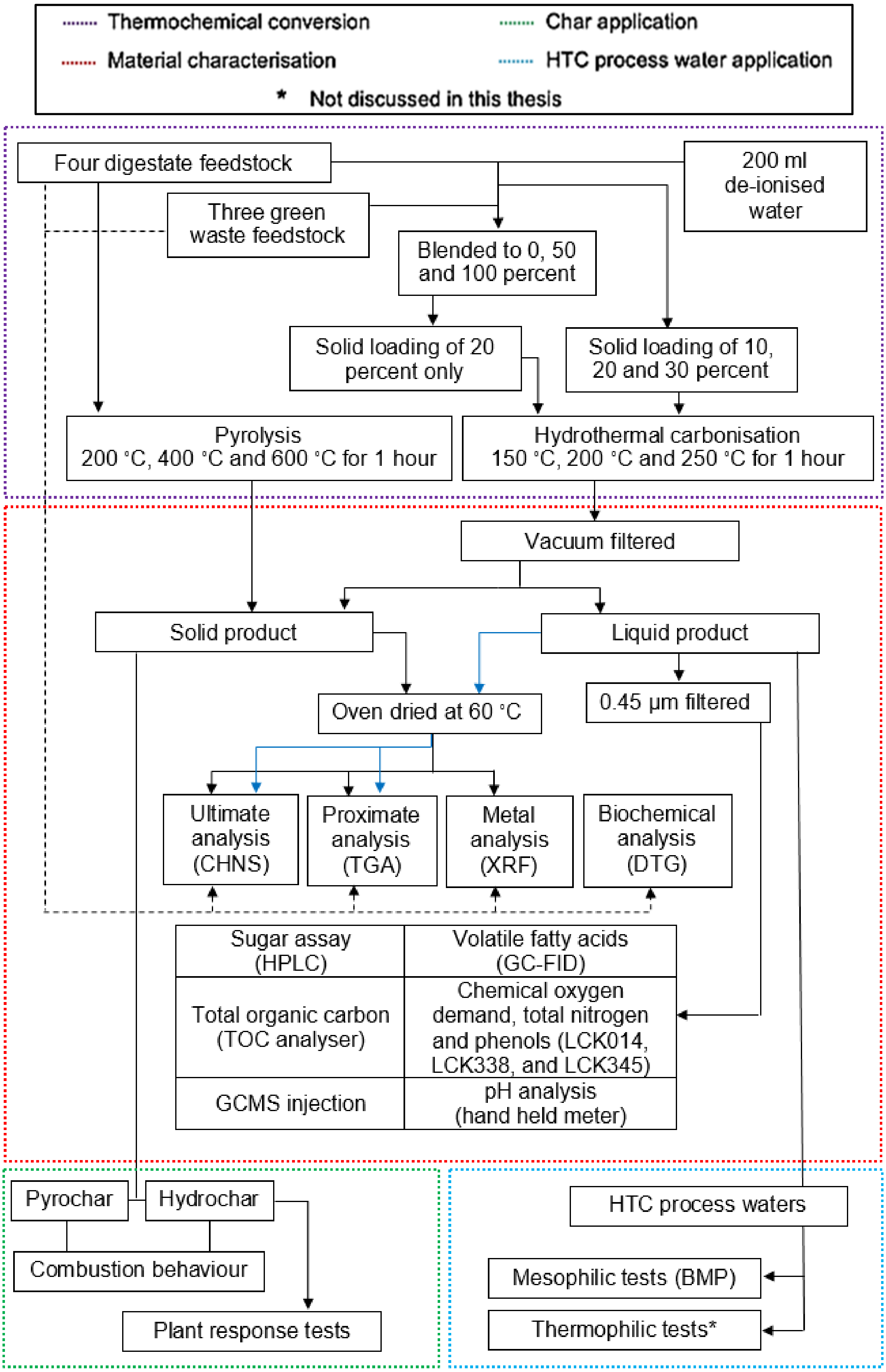

Figure 9. Schematic diagram of the experimental techniques employed in this study.

3.3. Hydrothermal carbonisation

Hydrothermal carbonisation reactions were performed in a 600 mL stainless steel Parr 4836 bench-top reactor (Parr, Moline, IL, USA) at holding temperatures of 150 ˚C, 200 ˚C, and 250 ˚C, illustrated in Figure 10. Three masses; 20, 40 and 60 g of feedstock was added to a constant capacity of 200 mL of deionised water, to achieve 10, 20, and 30 percent water loading, referred to as solid loadings herein. The act of loading with these ratios mimics the industrial process of managing whole (slurry) digestate. Feedstock for co-processing was blended at 0, 50 and 100 percent and loaded at 20 percent into the reactor.

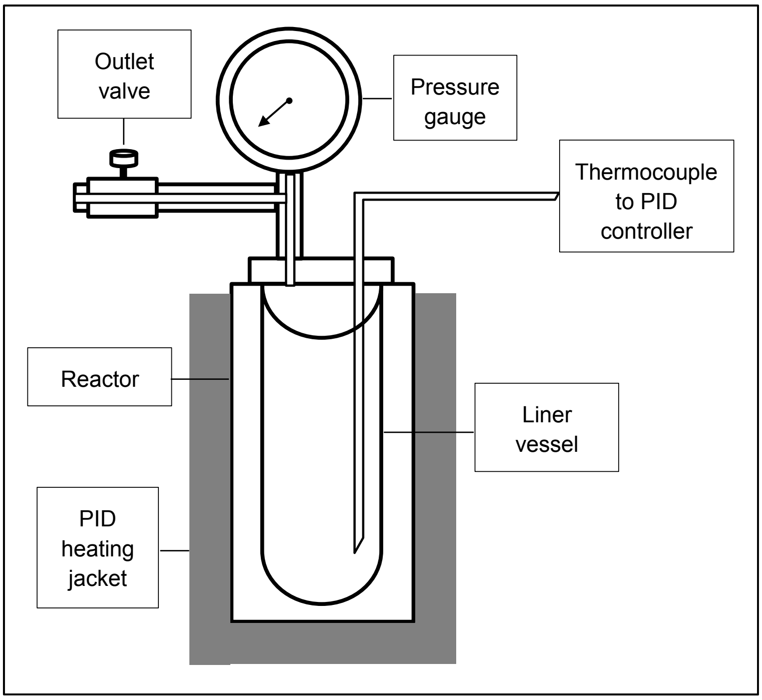

Figure 10. HTC reactor experimental set-up schematic diagram.

Reactions were performed in quartz silica internal vessels, allowing accurate material balance measurements. Temperatures were ramped using a proportional–integral–derivative (PID) controller, at approximately 8 ˚C per minute. Holding temperatures were set with assistance from an auto-tuning feature within the PID. The final hold temperature was retained for 1 hour; thereafter the reactor was removed from the heater and allowed to air cool within a vented fume cupboard. Once the reactor reached ambient air temperature, gasses were released to the atmosphere. Liquid and solids products were fractionated using a vacuum filter with 150 mm Grade 1 qualitative circle inserts (1001–150, Whatman, Cambridge, UK). The generated hydrochar were then oven dried at 60 ˚C for a minimum of 48 hours. The mass balances of containers and materials were taken to allow accurate measurements of product yields and to reduce uncertainties. The yield data assumes 100 percent hydrochar dewatering capability and the yields of gas are assumed by difference of the total input and output masses.

3.4. Pyrolysis

Pyrolysis reactions were performed in an upright 850 mm reactor, at 200 ˚C, 400 ˚C and 600 ˚C in an inert atmosphere. Figure 11 illustrates the experimental set up of the pyrolysis reactor used. The pyrolysis reactor consists of a horizontally aligned tube furnace containing a sealable steel cylinder. The feedstock is inserted into a basket then into the tube furnace, along with a k-type thermocouple to monitor temperatures. Nitrogen is fed through an inlet at the top of the reactor at a rate of approximately 300 ml per minute initially to remove oxygen, and to flush the gaseous products made during conversion.

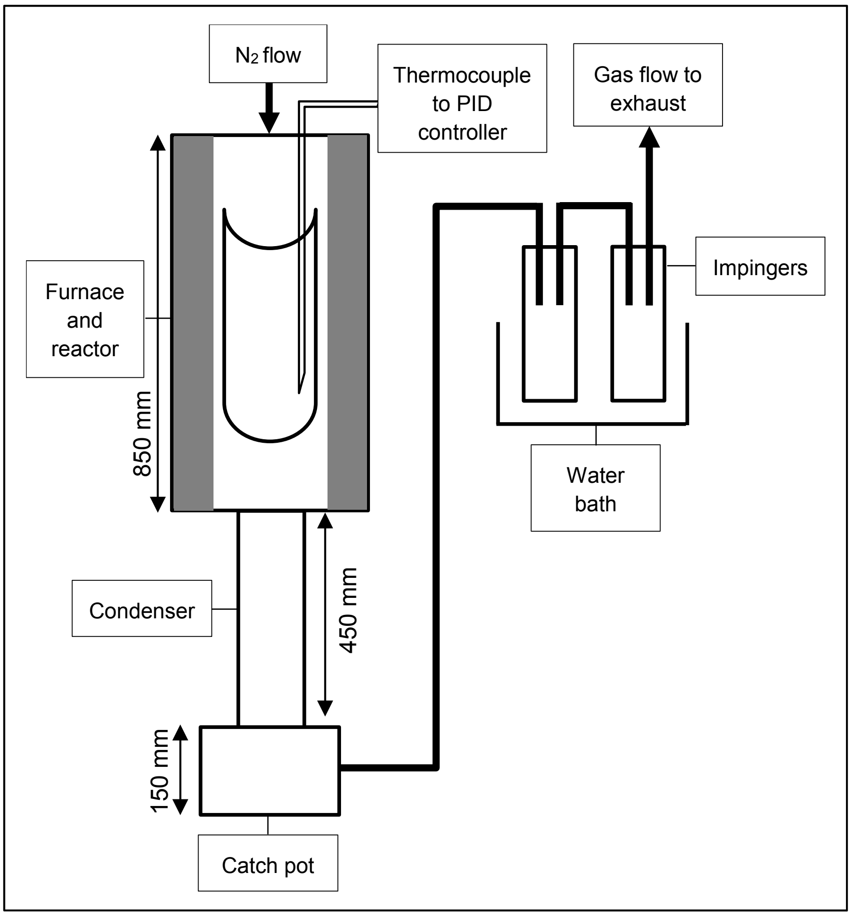

Figure 11. Pyrolysis reactor experimental set-up schematic diagram.

Flushed gases then flow into a condenser which is maintained at 5 ˚C using a water chiller. The temperature difference allows removal of the majority of the condensable gases from the gas stream and as a result condensates are deposited in the catch pot placed underneath. The gas stream then enters a set of impinges which further remove particulates and condensable compounds. The impinges are filled with quartz wool, water and sodium hydroxide to enhance the capture of volatiles. The remainder of the gas stream leaves through an exhaust.

Approximately 100 g of the feedstock is weighed and added into the pyrolysis rig. The reactor is then heated up to the desired retention temperature, with a heating rate of 4.5 ˚C to 7.2 ˚C per minute. Once retention temperature is reached, the furnace is kept at this temperature for an hour then is turned off to cool down, with a cooling rate of 0.4 ˚C to 1.4 ˚C per minute. When temperatures drop below 100 ˚C the basket is removed, allowed to cool further, then mass balances are taken to calculate yields of solids and liquids. The mass of gas produced is assumed by difference.

3.5. Chemical analysis of feedstock and product streams

Solid materials for chemical analysis were air dried and homogenised in a Retsch grinder, and subsequently sieved to achieve particles sizes of less than 100 μm. The equipment was thoroughly cleaned and dried between each use to avoid contamination.

3.5.1. Proximate and ultimate analysis and heating value

The proximate analysis of the solid materials was determined using a thermo-gravimetric analyser (TGA/DSC 1, Mettler Toledo GmbH, Greifensee, Switzerland). The TGA provided the percentages of moisture, volatile matter and fixed carbon content of the samples, determined by the difference in mass loss at the relevant stages of heating. These percentages were then used to calculate the proximate amount of ash within each sample. The proximate ash content may be a slight underestimate due to some ash volatisation at high temperatures. All measurements were performed in duplicate and the mean values are reported. The TGA used a heating profile as illustrated in Figure 12.

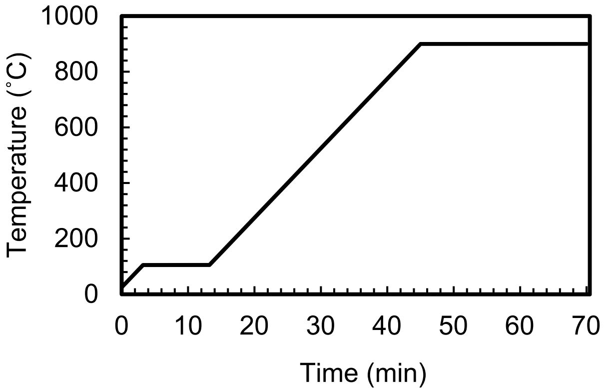

Figure 12. Thermo-gravimetric analyser heating profile.

The analyser was set from 25 ˚C to 900 ˚C with a heating rate of 25 K per min. This heating rate was programmed to hold a temperature of 105 ˚C for 10 minutes, which allowed the moisture content to be driven from the sample. Heating from 105 ˚C to 900 ˚C and being held for 10 minutes allowed volatile matter to be released. The sample was subjected to a constant flow of nitrogen (N_2) at 50 ml per min until 900 ˚C. After 10 minutes at 900 ˚C, the flow of nitrogen was switched to air and held for 15 minutes, allowing complete combustion of the fixed carbon to produce a residue of the sample comprising of ash (inorganics).

The contents of elemental carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) were analysed using an Elemental Analyser (Flash 2000, Thermo Scientific, Waltham, USA). The instrument was calibrated and checked using calibration standards and certified biomass reference materials (Elemental Microanalysis, Devon, UK) as shown in Table 7.

Table 7. Standards used in the elemental analyser.

Standards	Ultimate analysis (wt%, db)				
	C	H	N	S	O
B2044 BBOT	72.52	6.09	6.51	7.44	7.43
B2276 Oat meal	47.76	5.72	2.09	0.16	-
B2306 Coal	-	-	-	2.03	-

Standards and samples were accurately weighed out between 2.0 to 3.5 mg within tin capsules and then crimped to remove any air to avoid effects of parasitic atmospheric nitrogen. The samples were then combusted in a 1000 ˚C furnace in a helium atmosphere, along with a known amount of oxygen. The analyser automatically calculates the conversion of carbon dioxide (CO_2) to carbon, nitrogen oxides (NOx) to nitrogen, sulphur dioxide (SO_2) to sulphur and water vapour to hydrogen. The gases pass through a gas chromatography column onto a thermal conductivity detector (TCD) which identifies the composition based on the response and retention time of the individual gases. Elemental analysers only measure organic CHNS, and not elemental compounds from inorganic materials. Therefore, elemental analysis of high ash solid substrates might not reveal the actual CHNS and O concentrations. Sample preparation prior to elemental analysis is vital as samples need to be wrapped precisely, otherwise there will be inconsistencies in subsequent analysis. All measurements were repeated in duplicates and mean values are reported.

Predictive HHVs (kJ/kg) were calculated with ultimate analysis using Equation 1. The equation is given according to an approximation given by Friedl et al. [96] for biomass fuels with an estimated standard error of ± 337 kJ/kg. Values are presented as dry basis (db) with hydrogen corrected for moisture content.

$$\mathrm{HHV} = 3.55\mathrm{C}^2 - 232\mathrm{C} - 2230\mathrm{H} + 51.2\mathrm{C} \times \mathrm{H} + 131\mathrm{N} + 20{,}600 \tag{1}$$

3.5.2. Biochemical analysis

Protein content was calculated by utilising the total nitrogen value derived from elemental analysis using Equation 2. A conversion factor of 6.25 (equivalent to 0.16 g nitrogen per gram of protein) is used for the composition of amino-acids. This method is deemed more accurate than acid extraction techniques such as the Kjeldahl method [97].

$$\%\ \mathrm{Protein} = 6.25\ \times \%\ \mathrm{Nitrogen} \tag{2}$$

For the qualitative determination of feedstock lignocellulosic composition, the mass loss rates from the thermogravimetric analyser were used. Differential thermogravimetric (DTG) curves, obtained from the TGA data, illustrate the thermal decomposition of lignin under pyrolysis conditions occurs between 200 °C to 500 °C, cellulose between 250 °C to 400 °C and hemi-cellulose between 200 °C to 275 °C. A wet chemical method should be employed for a quantitative measurement of the lignocellulosic composition, discussed further in the methodology limitation section.

3.5.3. Inorganic analysis

Metals and inorganic analysis by X-ray fluorescence (XRF) spectroscopy was performed on solid materials, which were ashed and then formed into fused glass discs before analysis. Ashing was performed in an electric furnace at a temperature of 550 °C for 2 h, then removed and mixed to allow homogeneity. The samples were then further heated to 850 °C and sustained for a further 2 h to reduce potassium devolatilisation, as described in [98]. The resulting ashes were placed into a desiccator, ground by pestle and mortar, and subsequently sieved using a 106 μm aperture.

The fused glass discs consisted of 0.7 g of ash sample and 6.3 g of flux, which were mixed and fused at a temperature of 1100 °C using an electric fluxer (Katana K1 Prime, Quebec, Canada). The samples were then analysed using an X-ray florescence spectrometer (ARL PERFORM’X, Thermo Scientific, Waltham, USA).

3.5.4. Predictive slagging and fouling indices

To predict the likelihood of fouling during combustion of solid materials, various slagging and fouling indices have been derived based on fuel chemical composition. The equations for alkali index (AI), bed agglomeration index (BAI), acid base ratio (R b/a), slagging (Babcock) index (SI), fouling index (FI), and slag viscosity index (SVI) are given in Table 8.

For AI a value of < 0.17 represents safe combustion, an AI of 0.17 to 0.34 predicts probable slagging and fouling and an AI > 0.34 predicts almost certain slagging and fouling. For BAI, a value of BAI < 0.15 predicts that bed agglomeration is likely to occur. For R b/a a value of < 0.5 indicates a low risk of slagging and R b/a > 1.0 predicts a high to severe risk of slagging. For SI a value of < 0.6 predict a low slagging inclination, SI of 0.6 to 2.0 predicts a medium slagging inclination and SI > 2.0 predicts a high slagging inclination. For FI values < 0.6 indicate a low fouling inclination, an FI of 0.6 to 40.0 predicts a medium fouling inclination and a FI > 40.0 indicates a high fouling inclination to occur. For SVI a value > 72 indicates a low slagging indication, SVI of 65 to 72 suggests a medium indication and SVI of < 65 indicates a high slagging inclination during biomass combustion.

Table 8. Predictive slagging and fouling indices [99].

Slagging and fouling indices	Equation	Interpretation
Alkali index	$\mathrm{AI} = \frac{\mathrm{Kg}(\mathrm{K_2O} + \mathrm{Na_2O})}{\mathrm{Gj}}$	AI <0.17 safe combustion AI >0.17< 0.34 likely slagging and fouling AI >0.34 almost certain slagging and fouling
Bed agglomeration index	$\mathrm{BAI} = \frac{\%(\mathrm{Fe_2O_3})}{\%(\mathrm{K_2O} + \mathrm{Na_2O})}$	BAI <0.15 bed agglomeration likely
Acid base ratio	$\mathrm{R}\frac{\mathrm{b}}{\mathrm{a}} = \frac{\%(\mathrm{Fe_2O_3} + \mathrm{CaO} + \mathrm{MgO} + \mathrm{K_2O} + \mathrm{Na_2O})}{\%(\mathrm{SiO_2} + \mathrm{TiO_2} + \mathrm{Al_2O_3})}$	$\mathrm{R}\frac{\mathrm{b}}{\mathrm{a}}$ <0.5 low slagging risk
Slagging index	$\mathrm{SI} = \left(\frac{\%(\mathrm{Fe_2O_3} + \mathrm{CaO} + \mathrm{MgO} + \mathrm{K_2O} + \mathrm{Na_2O})}{\%(\mathrm{SiO_2} + \mathrm{TiO_2} + \mathrm{Al_2O_3})}\right) * \%\mathrm{S}\ (\text{dry basis})$	SI <0.6 low slagging inclination SI >0.6 <2.0 medium slagging inclination SI >2.0 high slagging inclination
Fouling index	$\mathrm{FI} = \left(\frac{\%(\mathrm{Fe_2O_3} + \mathrm{CaO} + \mathrm{MgO} + \mathrm{K_2O} + \mathrm{Na_2O})}{\%(\mathrm{SiO_2} + \mathrm{TiO_2} + \mathrm{Al_2O_3})}\right) * \%(\mathrm{K_2O} + \mathrm{Na_2O})$	FI <0.6 low fouling FI >0.6< 40.0 medium fouling FI >40.0 indicate high fouling
Slag viscosity index	$\mathrm{SVI} = \frac{(\%\mathrm{SiO_2} * 100)}{\%(\mathrm{SiO_2} + \mathrm{MgO} + \mathrm{CaO} + \mathrm{Fe_2O_3})}$	SVI >72 low slagging inclination SVI >63< 72 medium slagging inclination SVI <65 high slagging inclination

3.5.5. Process water analysis

The process waters generated from the HTC of digestate and green waste materials have been analysed for their chemical properties. Properties include pH, total organic carbon (TOC), chemical oxygen demand (COD), solubilised phenols, total nitrogen (TN), volatile fatty acids (VFA), other volatiles and total sugars.

3.5.5.1. pH measurement

Measurements of pH were taken by a dedicated pH meter (HQ11D, Hach Lange GmbH, Düsseldorf, Germany). The meter was calibrated using 4, 7 and 10 pH buffer solutions. Measurements were taken in triplicate, with average values reported.

3.5.5.2. Total carbon

The carbon content of the process water was analysed using a total organic carbon (TOC) analyser (IL 550, Hach Lange GmbH, Düsseldorf, Germany). The TOC analyser operates by injecting a water sample into a furnace at high temperatures to convert any carbon present into carbon dioxide. The resultant gas is then reduced and separated when passed through an internal gas chromatography (GC) column then onto a thermal conductivity detector (TCD). The amount of carbon dioxide evolved from the sample is then calculated based on the retention time within the GC column. The final value is then proportional to the amount of carbon in the sample.

For the comparison between organic and inorganic carbon, a sample of the original sample is injected into the instrument initially to allow quantification of total carbon (organic plus inorganic carbon). Acid is added to the next sample, which allows reaction with the inorganic carbon removing it as carbon dioxide. This sample is then injected into the furnace, which allows carbon dioxide to be detected purely from the organic carbon fraction of the process water. The inorganic carbon content is then quantified by subtraction of organic carbon from the content of total carbon.

3.5.5.3. Chemical oxygen demand, phenols and total nitrogen

Chemical oxygen demand (COD), phenols, and total nitrogen (TN) were determined by cuvette test kits (LCK014, LCK338, and LCK345), in combination with a visible spectrophotometer that averages 10-fold absorbance readings (DR3900, Hach Lange GmbH, Düsseldorf, Germany).

3.5.5.4. Volatile fatty acids

Total volatile fatty acids (VFA) were determined in the process water directly after filtration using a 0.2 µm syringe filter by a gas chromatograph (GC) (5890 Series II, Hewlett Packard, CA, USA) fitted with a flame ionisation detector (FID) and a wall coated open tubular capillary fused silica column (25 m × 0.32 mm × 0.44 mm; Nordion, Helsinki, FL). Helium was used as a carrier gas, with a flow of 60 mL/min.

3.5.5.5. GCMS liquid injection

The HTC process waters were injected into a GC-MS (Shimadzu 2010) for the determination of unknown volatile compounds. The column oven was held at 50 °C, with an injection temperature of 250 °C and a split ratio of 10:1, which was sufficient for the sample type, and was held at a time of 35 min. Helium was used as a carrier gas, at a flow of 20 ml per min and pressure pf 73 kPa. Oxygenated compounds were separated on an Rtx 1701 60 m capillary column, 0.32 mm internal diameter and 0.25 µm film thickness. The temperature program started at 50 °C, and ramped up to 240 °C and held for 20 min. Compounds were then identified using the NIST mass spectral database. Results are given as spectral graphs and compound identification tables for the products detected up to 12 minutes. This was done to focus on the low weight molecular fraction of the volatile compounds present in the HTC process waters.

3.5.5.6. Total sugars via HPLC

To identify the sugars within the process waters, a sugar column (SupelcloGEl Pb with distilled water eluent) was coupled with a size exclusion guard (SEC, Dionex) to remove any salts and inorganics before separation. These were then used within a high-pressure liquid chromatography (HPLC) instrument (Dionex ultimate-3000 system, Thermo Scientific, Waltham, USA). This process works by injecting the process water onto the column which is carried through by an eluent which separates ions by charge and size. A conductivity detector present at the end of the column gives a reading in milli-seconds, the response is proportional to the concentrations of ions present which is based on the retention time and previously calibrated standards. The size exclusion guard works by separating compounds based on molecular size, with the smaller molecules retained for longer as they interact with the gel within the guard, larger molecules are unaffected. A refractive index detector was used which detects compounds based on the magnitude of refraction delivered when the analyte passes through the column relative to the solvent. Identification of known compounds was carried out using a range of calibration standards (Sigma-Aldrich, USA).

3.5.5.7. Elemental, total and fixed solids

The carbon, hydrogen, nitrogen and sulphur content of the process water was calculated by drying a known volume of process water at 60 °C over a period of 48 h to reduce the loss of volatile organic compounds. Dried samples were then analysed using a Flash 2000 CHNS analyser (CE Instruments, USA). Total solids and fixed solids within the process water was calculated by heating to 550 °C in a muffle furnace in air. Oxygen was calculated by difference.

3.6. Agronomic analysis

To understand the agronomic behaviour of hydrochar, the phytotoxicity to plant germination and growth was assessed using plant response tests. Additionally, data for nutrient and heavy metals concentrations were utilised from the elemental and inorganic analysis as previously described.

3.6.1. Plant response tests

Tomato plant response and contamination by weed seeds and other propagules, including germination, seedling growth and abnormities in a blended sphagnum peat with hydrochar growing medium (PBGM) was assessed using method code OFW004-006, with slight modification, in accordance to the BSI PAS100 compost specification. The plant response test set up can be seen in Figure 13.

Irish sphagnum moss peat was sieved through a 10 mm aperture sieve then sealed in a container to prevent loss of moisture. Moisture analysis was then performed on the peat to calculate mixtures of 20 g of char with 80 g of peat to create a 25 percent mass fraction (w/w, dry basis) compost samples for the plant response tests. The addition of fertiliser was not used in this experiment. Growth kits were then filled and moistened accordingly to the method code using Tomato cultivar Shirley F1 Hybrid seeds. Three seeds were used for each compost sample (triplicate) including a peat-only control. A lighting pattern of 16 hours on and 8 hours off was used. Exactly a single 5 ml of distillation water, with conductivity under <100 mS/m, was used to periodically water the seedlings. After 10 days, the total number of germinated tomato seedlings was recorded. After 14 days the measurement was repeated, including any observations of weed growth. After 28 days of growth, the plants were cut off at the surface of the growing media and then weighed to record fresh mass (±0.01 g).

Figure 13. Plant response equipment set up (top) and PBGM sample test pots (bottom).

For the calculation and expression of tomato plant germination indices, the following equation was used for 10 (G10) and 14 (G14) days:

$$\text{Total number of germination in test samples as a percetange of total number of germination in PBGM} = \frac{\text{mean number germinated in test samples}}{\text{mean number germinated in control samples}} \times 100 \qquad (3)$$

For the calculation and express of tomato plant mass the following equation was used:

$$\text{Mean top growth mass per tomator plant in control samples at 28 days} = \frac{\text{total top growth mass of tomato plants in control samples at 28 days}}{\text{number of germinated tomatoe plants in control sample at 14 days}} \qquad (4)$$

$$\text{Mean top growth mass per tomator plant in test samples at 28 days} = \frac{\text{total top growth mass of tomato plants in test samples at 28 days}}{\text{number of germinated tomatoe plants in test samples at 14 days}} \qquad (5)$$

Then using Equations 5 and 6 for the calculation of:

Mean top growth per tomato plant for test samples as a percentage of the mean top growth per tomatoe plants for control samples at 28 days =

$$\frac{\text{Mean top growth mass per tomatoe plant in control sample}}{\text{Mean top growth mass per tomatoe plant in test samples}} \times 100 \tag{6}$$

3.7. Bio-methane production and biodegradability

Biochemical methane potential (BMP) tests were carried out to assess cumulative methane production, the degree of biodegradability and any effects of inhibition from the chemical properties of HTC process waters during anaerobic digestion.

3.7.1. Theoretical biochemical methane potential (BMPth)

The theoretical biochemical methane potential (BMP_{th}) of the process waters during methanogenesis have been calculated based on Boyle's equation (see Equation 7) with a, b, c, d and x, y, z being molar fractions. This equation is a stoichiometric calculation for maximum biogas potential using elemental composition and includes the presence of proteins which takes into account any ammonia and hydrogen sulphide produced in the reaction.

It is assumed that: constant temperature and perfect mixing is maintained; microbial conditions are ideal to allow full digestion; input materials consists of only C, H, N, S and O; electrons are exclusively used for microbial metabolic energy; products of reaction only include CH_4, CO_2 and NH_3 and there is no accumulation of inorganic compounds.

$$\mathrm{C_aH_bO_cN_d} + \left(\frac{4a-b-2c+3d}{4}\right)\mathrm{H_2O} \rightarrow \left(\frac{4a+b-2c-3d}{8}\right)\mathrm{CO_2} + \left(\frac{4ab+2c+3d}{8}\right)\mathrm{CH_4} + \mathrm{dNH_3} \tag{7}$$

3.7.2. Experimental biochemical methane potential (BMPexp)

Experimental BMP (BMP_{exp}) tests were conducted using a multichannel analyser comprised of reactors, flow cells and a data acquisition system (AMPTS II, Bioprocess Control, Lund, Sweden) as shown in Figure 14. This system consists of 15 glass bottles with stirrers, a carbon dioxide (CO_2) capturing unit with pH indicator (3 M sodium hydroxide solution and 0.4 percent thymolphthalein) and a gas flow meter which automatically converts to standard temperature and pressure (0 °C and 100 kPa).

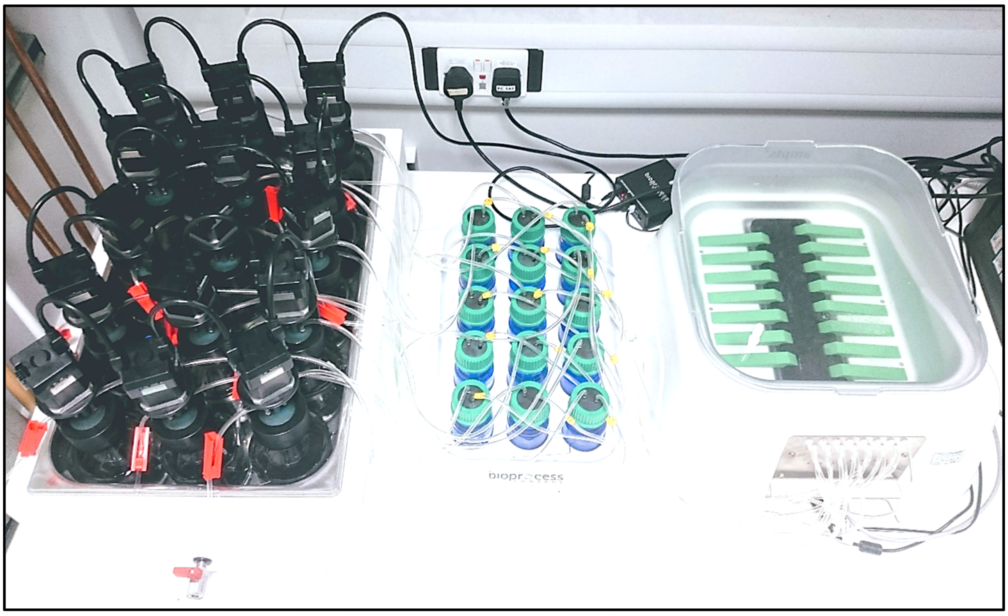

Figure 14. Biochemical methane potential test apparatus set-up.

Bottles were loaded with process water samples at 2 g COD in 200 mL of distilled water to give a concentration of 10 g COD per L and 200 mL of inoculum at a volatile solids (VS) concentration of 10 g VS per L, achieving a volumetric ratio of 1:1 of inoculum to substrate (ISR). This was then subsequently changed to an inoculum loading using COD, thereby achieving a true ISR of 1:1 according to guidelines for the standardisation of bio-methane potential tests [100]. Inoculum was obtained one month prior to use from the outlet of an anaerobic reactor for sludge digestion at Yorkshire Water's Esholt WWTW in Bradford, UK and stored refrigerated at 4 °C to allow exhausting of any endogenous methane production.

Initial tests were carried out under mesophilic conditions (37 ± 1 °C) for 15 days and stirred for 60 seconds every 600 seconds at 60 rpm. Subsequent tests were then carried out for 28 days or until daily methane production during three consecutive days was <1 percent of the accumulated volume of methane, as per standards. Prior to incubation all bottles were flushed with nitrogen for 20 seconds. Data was recorded by the AMPTS II software and transferred onto Microsoft Excel for data analysis.

3.7.3. Process water biodegradability indices

The rate at which substrates can be degraded are determined by its physical and chemical properties, such as particle size and biomass matrix, as well as its susceptibility to produce inhibitory intermediate products throughout the bioconversion process [101] . Therefore, the biomethane yield depends on the substrates' degree of biodegradability. The biodegradability for initial tests were calculated using Equation 8, utilising the experimental BMP (BMP_{exp}) and the theoretical BMP (BMP_{th}) values.

$$BD_{CH4}(\%) = \frac{BMP_{exp}}{BMP_{th}} \text{ x } 100 \tag{8}$$

However, to minimise inaccuracies of the theoretical BMP calculation, due to loss of volatiles during evaporation, the calculations of biodegradability index was modified (Equation 9) based on improvements made on the BMP tests as stated. Therefore, the biodegradability of process waters was calculated by difference of COD remaining after anaerobic digestion of the process waters, minus the inoculum COD added and was determined as:

$$BD_{CH4}(\%) = 50(-0.4 \times COD_{WD} + 4) \tag{9}$$

Where COD_{WD} is the COD value in g per L for the whole digestate after BMP testing. This method assumes no increase of microbial colonies within the inoculum during the digestion period.

3.8. Assessment of error and statistical analysis

Hydrothermal carbonisation experiments were performed in duplicate and the repeatability in solid yields was typically ±3 weight percent. All analyses of product streams were performed in duplicate. Average values are reported together with standard error in tables and figures. In addition, analysis using TOC was based on multiple sample injections until a maximum standard deviation of ± 2 percent was achieved. Experimental BMP tests were also performed in duplicate with blanks, positive, standards and inoculum controls.

3.9. Method limitations

Some methods described in this chapter have limitations with regards to data accuracy. XRF was utilised for the analysis of inroganics as it does not require sample dissolution, therefore allowing for non-destructive analysis compared to the methods of inductively coupled plasma optical emission spectrometry (ICP-OES) and atomic absorption spectrometry (AAS). However, limitations to XRF exist whereby a minimum of 10 to 20 part per million (ppm) is required for an accurate reading, whilst ICP-OES and AAS can detect very light elements at a finer resolution. Therefore, very low micro and heavy metal concentrations in the chars will not be detected running the risk of a false negative.

The lignocellulosic compositions in this study are based on a qualitative method. To be more accurate and for confidence in results the quantitative percentage content of cellulose, hemicellulose and lignin of the feedstock should be determined using wet detergent methods as described in Faithfull [102]. The methods include acid detergent fiber (ADF) which is required to determine the lignin content from the weight loss on oxidation by potassium permanganate. The residue from the oxidation step contains mainly cellulose and mineral ash. The cellulose content is determined as the weight loss on ashing of the residue. Nevertheless, the limitation and reliability of the detergent methods are dependent on the ash and bound protein content of the feedstock resulting an overestimation of cellulose [103].

The plant response test described was limited by the availability of space and equipment. The method (OFW004-006) requires each growing media test sample to use three separate germination trays, with each of the three tray having 10 seeds sown (30 in total). In this trial, seeds sown were reduced by a factor of 10 and each seedling was sown in their individual pot in three larger trays to avoid cross contamination. These measures had to be taking due to reduced equipment availability and laboratory space. As a result, the top growth of the plants were limited. However, relative plant masses are still valid as each seed was treated to the same growing conditions. Nevertheless, due to the level of experimental modification this test method is to be used for preliminary work.

3.10. Concluding remarks

All the analytical techniques for chemical composition and methods for assessing char behaviours during application are valid approaches to determine the objectives stated in this study. They have been chosen for their common use in literature, along with the resources and equipment that was available. All the methods were trained and verified by a professional technician for accuracy and repeatability. The improved methods and analytical techniques stated should be employed in further work if available.

CHAPTER IV

Characterisation of Digestate and Green Waste Feedstock

The characterisation of biomass materials is necessary to understand the variation of chemical composition of the starter materials (feedstock) and how this affects subsequent chemical reactions during conversion and chemical make-up of products. Biomass-based chars and liquid products after conversion are complex mixtures of mainly organic and inorganic compounds and water, the fractions of these are largely dependent on the feedstock composition.

4.1. Overview

The aim of this chapter is to understand how the composition varies between each feedstock examined in this study and to help forecast the physio-chemical properties of the products after thermochemical conversion. All the results from the characterisation experiments outlined in Chapter 3, section 3.2 are presented and examined in detail.

The objectives of this chapter are to:

- Characterise the digestate and green waste feedstock materials in order to understand their chemical composition, in particular to aid in the optimisation of the thermochemical conversion processes thereafter.
- Propose a blending strategy, by identifying a dissimilar digestate compared to that of the green waste materials based on its composition, to balance any negative properties and to aid in the engineering of the thermochemical conversion products.

4.2. Introduction

The uptake of conversion processes and technical advances in bioenergy generation has increased the competition of waste biomass as a feedstock resource. Waste biomass is a massively underutilised resource in the UK, as discussed in the introduction. To utilise this biomass feedstock, further knowledge of its physical properties is required for the optimisation of biomass conversion processes and output material flow. Importantly, the characterisation of biomass gives an understanding of the physio-chemical composition and how it is likely to behave during thermal treatment. Investigating the chemical composition and comparing differences opens the potential for synergetic benefits when it comes to blending materials, including the engineering of products for application purposes.

Therefore, the purpose of this study is to compare the chemical composition of four digestate materials, alongside the three green waste materials. The digestates; AGR, MSW, SS and VGF, as shown in Figure 15a, have been chosen due to their abundance and are representative of the most common feedstock materials used with AD facilities. The green waste materials; grass clippings, garden hedge cuttings and woodchip, shown in Figure 15b, have been chosen as they are the most common waste produced from parks and green spaces. Digestate normally ends up being disposed to land without fully extracting energy, and in the case of green waste any energy recovery at all.

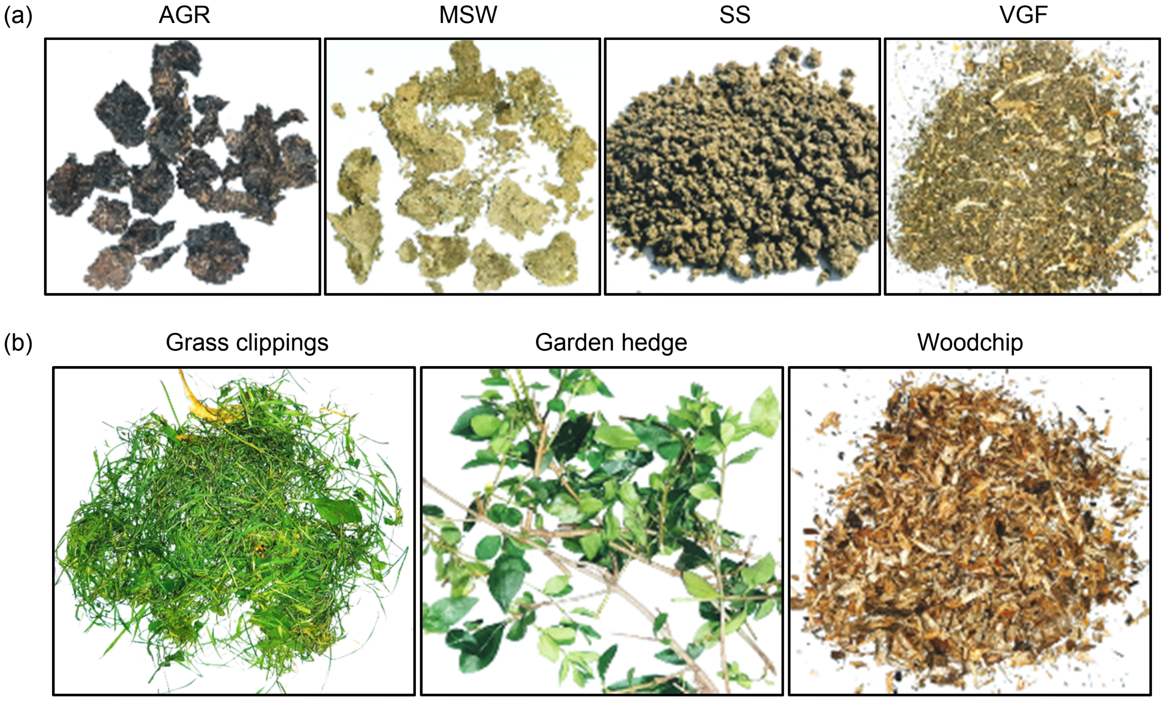

Figure 15. Visual images of the **a**) digestate and **b**) green waste materials.

The composition of biomass varies wildly. Complex in nature, their biochemical structure is largely comprised of carbohydrate polymers also known as lignocellulose. Lignocellulose is made up of cellulose, hemicellulose, lignin and a small number of other extractives (smaller organic molecules or polymers) and minerals (inorganic compounds) such as trace metals. Chemically speaking, these biochemical polymers are the most abundant biopolymers on earth [30,104]. These polymers are produced through the photosynthetic process which interact to build rigidity and structural integrity of cell walls within plants. In most plants, the cells are mostly aligned with the stem and are responsible for carrying minerals to the leaves as food for the growing plant. Figure 16 depicts the typical structure of lignocellulose found in plant materials.

The biopolymer composition of a cell wall is approximately 30 to 50 percent cellulose, 10 to 40 percent hemicellulose and 5 to 30 percent lignin [105]. Cellulose is a polymer of glucose units, linked by a glycosidic bond of a crystalline structure, which is highly resistant to enzymatic hydrolysis [106]. Hemicellulose makes up the plant's secondary cell walls, it is a heterogeneous polymer comprised of hexose, pentose and urgonic acids. Hemicellulose interacts with cellulose by covering the cellulose polymers, shielding it from enzymatic degradation [107]. Lignin is a cross-linked phenolic polymer which provides mechanical support to the plant cell walls as well as providing hydrophobicity properties [108]. Lignin encapsulates cellulose and hemicellulose, thereby further increasing the resistance to degradation [109]. The composition of these polymers, and in general the chemical composition of biomass directly affects their value and quality for further conversion and application.

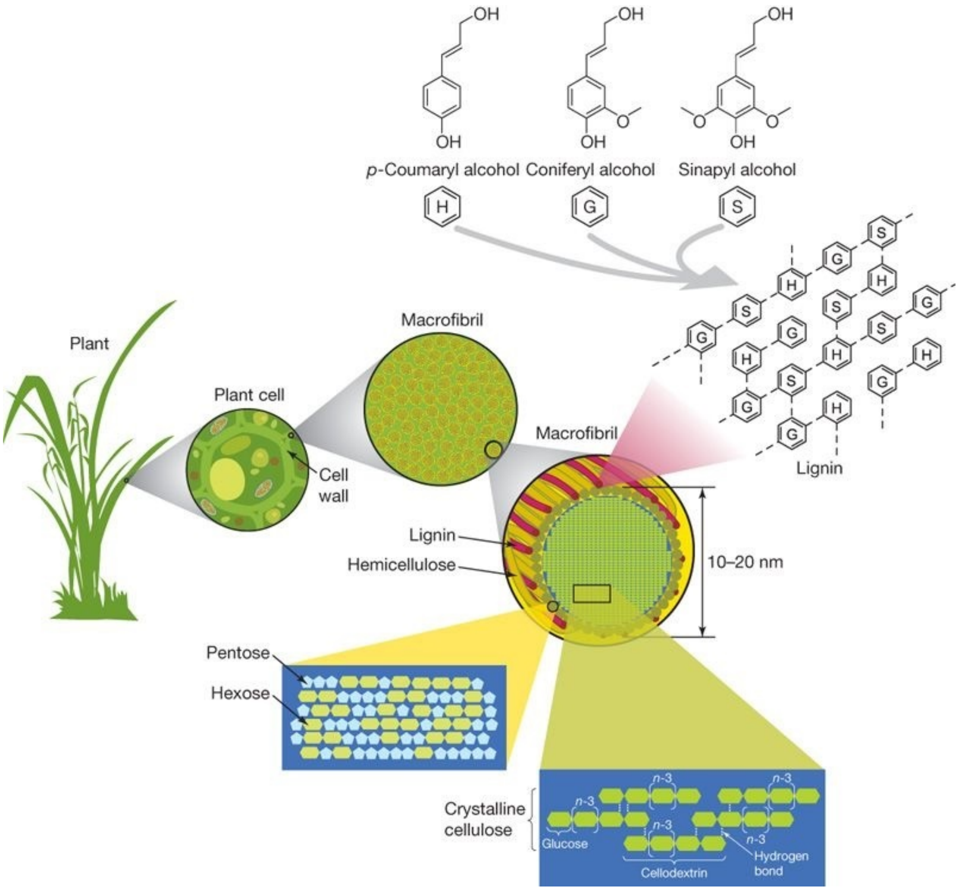

Figure 16. Typical structure of lignocellulose polymers in plant cell walls (sourced from [110]).

Waste biomass is even more heterogeneous in nature. Digestate and green waste materials can be vastly unalike; dissimilarities also exist within their own classifications. Table **9** shows digestate and green waste composition data found in the literature. The available data on chemical composition is generally given for ultimate and proximate analyses, and heating value. Less data is given for biochemical analysis and there is a significant lack of inorganic analyses. Additionally, the expression of units is not always consistent either, some are given in mass percentage or g/kg, including a variation of dry or dry ash free basis.

Literature data shows that the average volatile matter of digestate is 52 percent and the average ash content is 27.2 percent, but can be as high as 61 percent for the case of sewage sludge digestate. The carbon content of the digestates averages at 32.5 percent, with heating values averaging at 13.4 MJ/kg. For the green wastes, on average the volatile matter is 81.3 percent, ash content is 7 percent, carbon content 45.6 percent and HHV 17.4 MJ/kg. To put it succinctly, the greatest difference between the digestate and green waste material lies in the volatile matter, ash, carbon content and HHV.

Digestate materials are usually derived from high moisture food crops, which is preferable for AD. As digestate, these materials have already undergone a biological conversion process where microbes have metabolised available carbohydrates, proteins and fats. Therefore, the digestates will have a lower volatile matter and carbon content, plus a higher ash content than that of non-digested materials. The differences in volatile matter and carbon content can be attributed to the lignocellulosic content – however this is not clear from the available data. Additionally, digestate will also have a higher nitrogen content to that compared to lignocellulosic materials due to greater levels of proteins found in food crops. Green wastes are usually comprised of non-food crops and are normally utilised as a composting material due to their fibrous content. Both digestate and green wastes studied in literature have similar ranges of fixed carbon content, which indicates both materials may be recalcitrant for further biological processing in their current state. There is greater difference in the chemical composition of digestate due to the wider variety of origin material as a feedstock for AD, however high ash is a common trait. Green waste materials are generally high in carbon and low in ash content and they have less variance between them.

Table 9. Chemical composition of solid digestate and green waste materials found in literature.

Feedstock	Biochemical composition (wt%, db)				Proximate analysis (wt%, db)			Ultimate analysis (wt%, db)					HHV (MJ/kg, db)	Reference
	Cellulose	Hemi-cellulose	Lignin	Protein	VM	FC	Ash	C	H	N	S	O[a]		
Solid digestate														
Sewage sludge	-	-	-	-	34.4	3.3	61.2	18.3	2.9	2.7	0.3	14.6	7.8	[111]
Sewage sludge	-	-	-	-	55.8	7.8	31.8	34.8	3.9	5.0	1.2	20.3	16.6	[112]
SS+MSW	-	-	-	-	-	-	35.3	33.1	-	4.7	-	-	-	[113]
MSW	-	-	-	-	48.8	14.5	36.7	27.2	3.5	2.6	0.1	23.1	15.7	[114]
Maze silage	25.2	0.5	37.6	-	-	-	11.5	51.8[b]	6.8[b]	37.9[b]	-	37.9[b]	22.3[b]	[27]
Corn	-	-	-	-	-	-	23.7	39.2	5.0	3.4	-	30.5	-	[115]
Corn silage	-	-	-	-	-	-	-	-	-	-	-	-	-	[116]
Corn	-	-	-	-	-	-	-	42.0	5.4	1.6	-	36.5	-	[117]
Corn	-	-	-	-	-	-	19.6	40.7	5.5	2.4	-	31.7	-	[118]
Corn silage, manure	-	-	-	-	-	-	22.6	39.7	6.5	2.5	0.4	-	-	[119]
Corn, manure	-	-	-	-	-	-	10.7	52.1[b]	8.2[b]	2.3[b]	0.7[b]	36.8[b]	24.5[b]	[120]
Corn, grass, manure	35.8	4.0	24.9	13.4	48.3	16.4	24.9	50.6[b]	6.1[b]	4.2[b]	0.5[b]	34.4[b]	-	[121]
Wheat straw	44.6	18.9	21.3	-	-	-	-	-	-	-	-	-	-	[122]
Wheat straw	-	-	-	-	-	-	6.1	47.1	6.9	0.7	0.2	-	-	[119]
Straw	46.1	26.1	15.6	-	72.6	-	6.0	50.1[b]	6.9[b]	0.7[b]	-	41.8[b]	-	[123]
OWS Press cake	-	-	-	-	-	-	-	-	-	-	-	-	-	[124]
AD Press cake	-	-	-	-	-	-	63.9	17.8	2.3	0.3	0.0	12.1	-	[99]
Green waste														
Woodchip	-	-	-	-	-	-	-	46.1	6.3	0.1	-	47.5	16.1	[125]
Fallen leaves and deadwood	-	-	-	-	88.0	1.5	10.6	-	-	-	-	-	18.2	[126]
Tree, bushes and bamboo	-	-	-	-	76.1	15.7	8.2	47.1	6.9	0.8	-	37.1	18.3	[127]
Lawn grass	41.7	35.8	8.0	-	79.9	13.1	3.7	42.9	7.3	2.7	0.0	43.4	17.0	[128]
Grass	-	-	-	-	-	-	12.2	43.9	-	3.9	-	-	-	[115]
Straw	-	-	-	-	-	-	6.9	45.2	-	0.6	-	-	-	
Woodchips	-	-	-	-	-	-	0.7	48.8	-	0.2	-	-	-	

[a], measured by difference; [b] ,dry ash free (daf)

Four digestate and three green waste materials will be characterised for their chemical composition in this chapter. Similar digestates have been reported on in the literature; this investigation addresses the heterogeneous nature of these materials. Additionally, this study examines the chemical composition of three common green wastes material found in the Leeds City Region, not studied elsewhere. The outcomes of this chapter will aid in the understanding of how the chemical composition of digestate and green waste materials affect reactions during the thermochemical conversion processes HTC and pyrolysis in subsequent chapters. Specifically, it will show how physio-chemical properties of the biomass effects char and liquid yields, their properties and quality for application, including the potential for generating biogas from HTC process waters. This data can then support further work to develop a model to optimise an integrated conversion process and is a first step to engineering product properties.

4.3. Results and discussion

The feedstock used in this study will be characterised for their chemical composition which will aid in the understanding of how the composition affect reactions during HTC and pyrolysis thermochemical conversion.

4.3.1. Feedstock composition

The following sections will describe the chemical makeup of the feedstock of four digestate and three green waste through a number of characterisation techniques.

4.3.1.1. Proximate and gravimetric analysis

Proximate and gravimetric analysis techniques were performed to partition and classify chemical compounds within the digestate and green waste materials. Protein, moisture, volatile matter, fixed carbon and ash contents are listed in Table 10. The results show similar values to that found in the literature.

Protein analysis is particularly useful for the digestate materials as this provides an insight into the mesophilic bacteria’s metabolism and conversion performance of protein compounds present in the AD feedstock into volatile fatty acids (VFA) during the digestion process. The protein content is shown to vary significantly across the digestate. The greatest protein content, which remains undigested, was found within the secondary sludge digestate at 24.3 percent, followed by the agricultural residue, then vegetable, garden and fruit, with the least found in residual municipal solid waste digestate at 6.86 percent.

This data suggests the AD process did not achieve the highest efficiency in digestion as substrates were underutilised, therefore there is potential for further energy recovery via biological processing. The highest protein levels in the green waste found in grass clippings (21.9 percent), hedge then woodchip. This is due to the grass by nature largely comprised of green leaves [129].

After dewatering, oven and air drying methods digestate samples contained less moisture content (between 3.1 to 4.4 percent) than that of the green wastes (between 16.1 to 17.1 percent). Volatile matter generally represented the greatest fraction across all of the feedstock in this study, with the exception of MSW (lowest at 36.2 percent due to a very high ash content). Even higher levels of volatile matter were found in the green waste feedstock (between 71.1 and 76.7 percent) compared to that of the digestate (36.2 to 51.0 percent) with the exception of AGR digestate at 70.2 percent. This suggests that the AGR digestate shares similar biochemical composition to that of the green wastes and will be discussed later.

Table 10. Proximate and gravimetric analysis of the digestate and green waste feedstock.

	Digestate				Green waste		
	AGR	**MSW**	**SS**	**VGF**	**Grass**	**Hedge**	**Woodchip**
Protein (wt%, db)	17.7 ± 0.6	6.8 ± 0.3	24.3 ± 0.7	9.8 ± 0.5	21.9 ± 0.6	6.9 ± 0.3	2.5 ± 0.2
Moisture (wt%, ar)	5.7 ± 0.2	3.1 ± 0.0	6.6 ± 0.2	4.4 ± 0.0	16.6 ± 0.4	16.1 ± 0.4	17.1 ± 0.6
Volatile matter (wt%, db)	70.2 ± 0.3	36.2 ± 0.1	51.0 ± 0.1	47.2 ± 1.1	71.1 ± 0.1	76.7 ± 0.1	76.1 ± 0.2
Fixed carbon wt%, db)	13.8 ± 0.0	8.3 ± 0.0	2.1 ± 0.1	9.0 ± 0.2	16.6 ± 0.3	16.1 ± 0.2	17.1 ± 0.4
Ash[a] (wt%, db)	16.0 ± 0.3	55.5 ± 0.1	46.9 ± 0.0	43.8 ± 0.8	12.4 ± 0.4	7.2 ± 0.3	6.8 ± 0.6

ar, as received; db, dry basis; [a], calculated by difference

The digestate materials contain very high levels of ash, ranging from 40 to 55 percent. The exception is the AGR digestate which has a lower ash content of 16 percent, suggesting the initial starting material for AD was quite homogenous and had low contamination. Green waste, in comparison to the digestates, have much lower ash concentrations (6.8 to 12.4 percent) due to the typical composition of lignocellulose plant materials and very little contamination. The digestates exhibited somewhat lower fixed carbon content than the green wastes (between 8 and 13.8 percent, and between 16.1 and 17.1 percent respectively), likely correlated to their respective ash contents as shown in Figure 17. This observation was supported by a good negative correlation between ash and fixed carbon content (R^2=0.79).

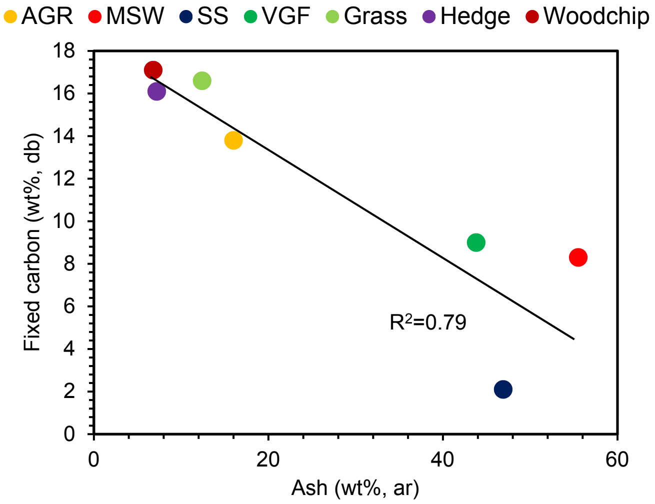

Figure 17. Correlation between fixed carbon and ash content of the digestate and green waste feedstocks.

Figure 18 illustrates ash, volatile matter and fixed carbon content for the all the feedstock in a ternary plot to allow comparison of all the proximate values on a dry basis. All data points are concentrated in the area defined by greater than 30 percent volatile matter, less than 20 percent fixed carbon and less than 60 percent ash content. Within this plot a cluster of four (AGR, grass, hedge and woodchip) is separated from a cluster of three (MSW, SS and VGF) by significant differences in volatile matter and ash contents. The major factor in the differences seen in volatile matter content is due to the biochemical composition of the feedstocks, in particular the cellulose, hemicellulose and lignin fractions of the biomass [130].

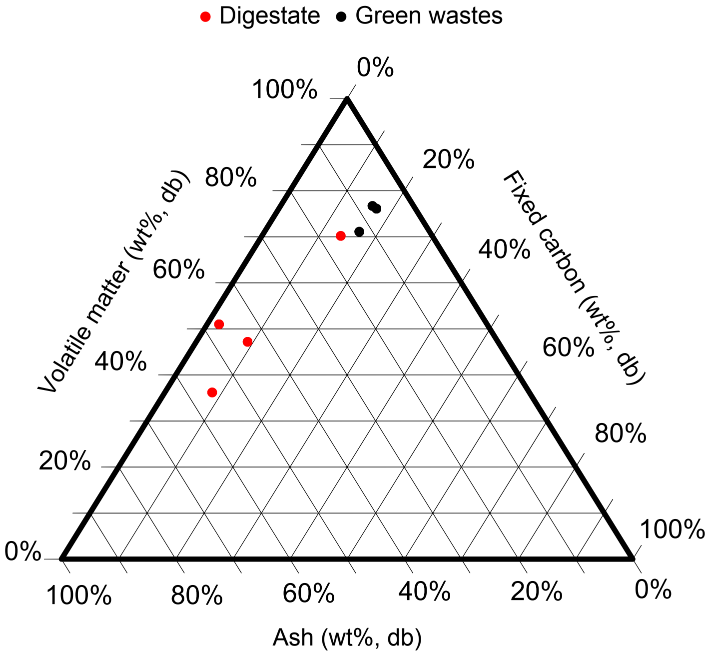

Figure 18. Ternary plot showing the relationship between ash, volatile matter and fixed carbon of the digestates and green waste feedstocks.

Figure 19 illustrates the biochemical composition of the digestate and green waste materials through differential thermogravimetric (DTG) curves obtained from TGA data (burning profiles). It should be noted that DTG used in this way is a qualitative assessment of the biochemical composition. Amongst the digestates, AGR exhibits the highest lignocellulosic content due to the peaks emerging between 1000 and 2000 seconds at 200 °C and 500 °C (Figure 19a). All green waste materials exhibit greater lignocellulosic content when compared to the digestate. Woodchip shows the largest proportion of cellulose and lignin (Figure 19b). Woodchip also has the largest fixed carbon content, supporting the positive correlation between lignin and fixed carbon content [131]. How the lignocellulosic makeup of the feedstocks affects their elemental composition will be discussed in the next section.

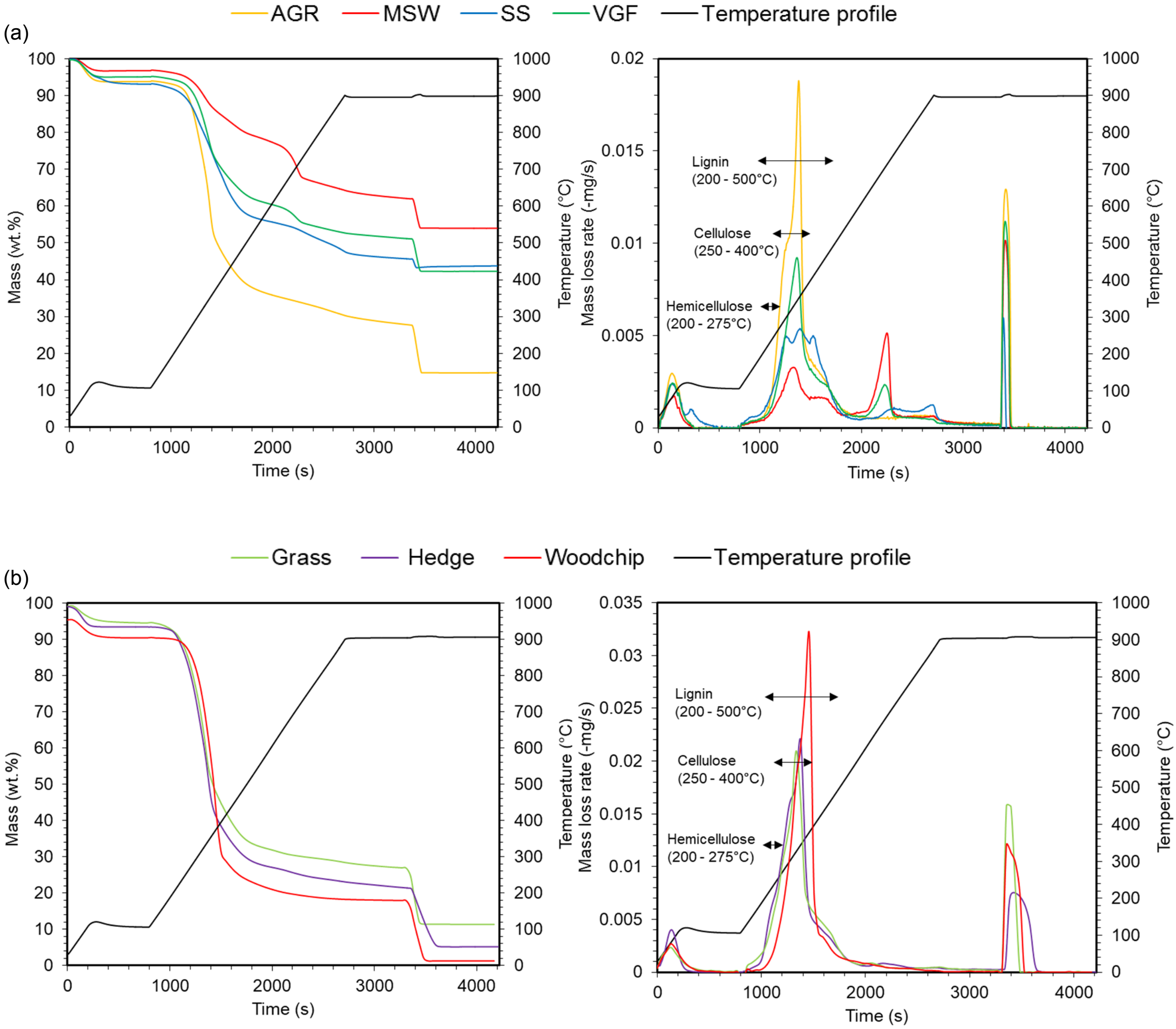

Figure 19. Thermal decomposition behaviour of the **a**) digestate and **b**) green waste feedstocks shown by thermogravimetric analysis (TGA) on the left and derivative thermogravimetric (DTG) curves on the right.

4.3.1.2. Ultimate analysis and energy density

Table 11 lists the carbon, hydrogen, nitrogen sulphur and oxygen contents, including atomic ratios and heating value and of the digestate and green waste feedstock. The results show similar elemental and heating values to that found in literature.

As shown in Figure 19, woodchip, hedge, grass and AGR digestate have the highest proportion of lignocellulosic compounds, this is reflected in high carbon contents (49.6, 46.7, 45.6 and 44.1 percent C respectively). AGR has the highest carbon content across the digestates, corresponding to a lower ash content of 16 percent. The SS digestate was generated from a digester incorporating thermal hydrolysis, therefore, the carbon content is slightly lower and the ash content is higher than a digestate not incorporating pre-treatment [112]. Higher hydrogen levels are also found with feedstock with the highest lignocellulosic compounds (typically in the range of 5.1 to 6.4 percent H).

Reflected in a high H/C ratio and lignocellulosic content, AGR achieves the greatest HHV across the digestates. Across the green wastes, woodchip achieves greatest HHV, again reflected in its even higher H/C ratio and lignocellulosic content, outperforming the energy content of AGR.

Table 11. Ultimate and heating analysis of the digestate and green waste feedstock on a dry basis.

	Digestate				Green waste		
	AGR	**MSW**	**SS**	**VGF**	**Grass**	**Hedge**	**Woodchip**
Ultimate analysis							
C (wt%, db)	44.1 ± 0.1	24.1 ± 0.0	28.6 ± 0.3	29.5 ± 0.1	45.6 ± 0.2	46.7 ± 0.0	49.6 ± 0.4
H (wt%, db)	5.1 ± 0.0	1.7 ± 0.0	3.1 ± 0.1	3.0 ± 0.1	5.3 ± 0.2	5.6 ± 0.1	6.4 ± 0.9
N (wt%, db)	3.2 ± 0.0	1.5 ± 0.0	3.4 ± 0.0	2.0 ± 0.0	3.5 ± 0.0	1.1 ± 0.0	0.4 ± 0.0
S (wt%, db)	0.3 ± 0.0	0.2 ± 0.0	1.5 ± 0.0	0.3 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
O[a] (wt%, db)	31.3 ± 0.3	16.9 ± 0.0	16.4 ± 0.3	21.3 ± 0.6	33.2 ± 0.9	39.4 ± 0.5	36.9 ± 0.7
H/C (daf)	1.38	0.83	1.30	1.22	1.37	1.42	1.55
O/C (daf)	0.53	0.53	0.43	0.54	0.55	0.63	0.56
Energy density							
HHV (MJ/kg db)[b]	17.8	15.6	14.9	14.9	18.4	18.6	19.9

db, dry basis; daf, dry ash free basis; [a], calculated by difference; [b], calculated according to Eq (1)

Figure 20a shows a graphical representation of the elemental composition as a whole of both digestates and green waste on a dry ash free basis, which is then further visualised by carbon and oxygen, and hydrogen and nitrogen in Figure 20b and 19c respectively. Sulphur is only represented in Figure 20a due to negligible content. Dry ash free values for all feedstocks are listed in Appendix Table 5.

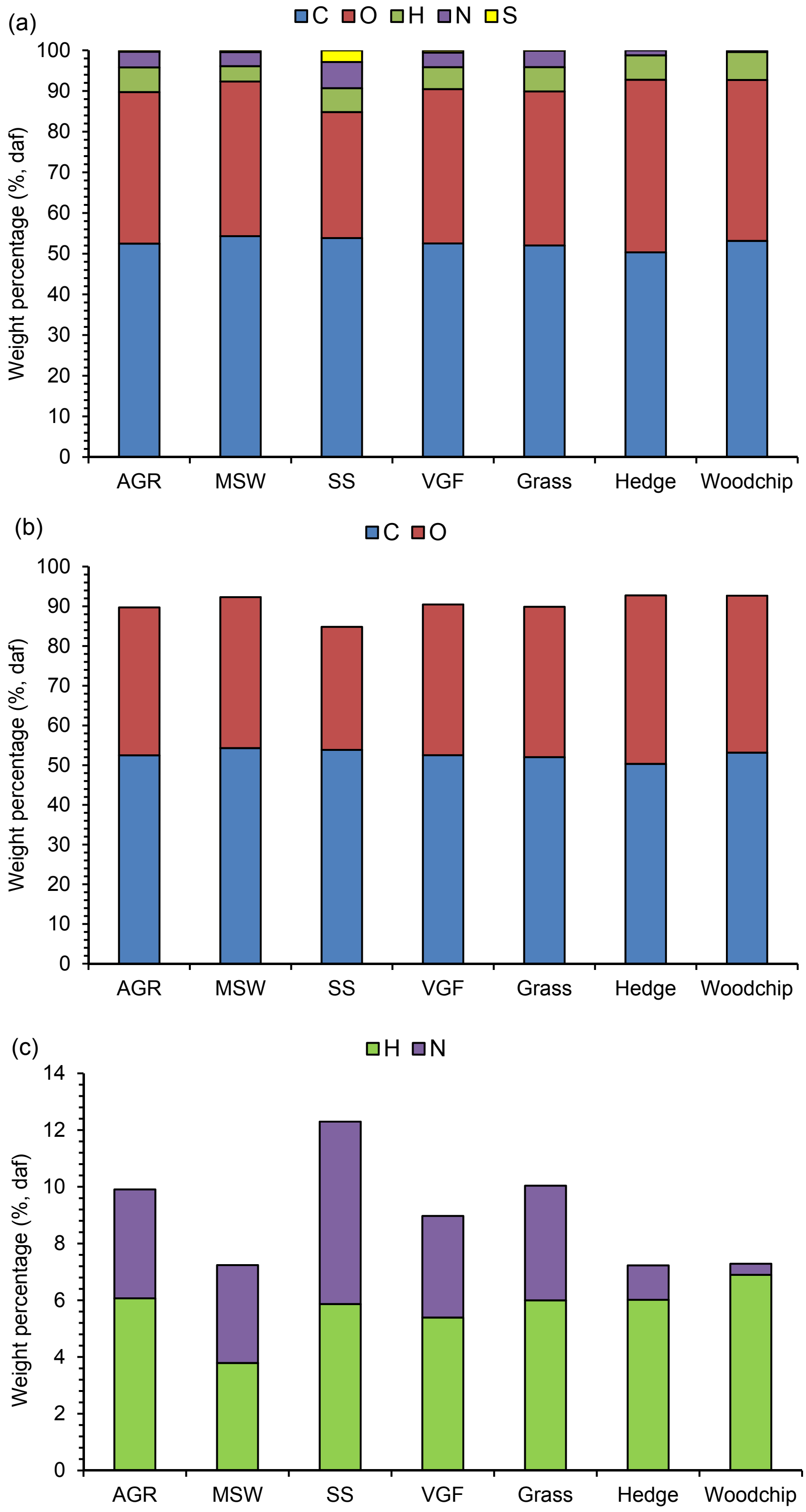

Figure 20. Comparison of **a**) carbon, oxygen, hydrogen, nitrogen and sulphur, **b**) carbon and oxygen and **c**) hydrogen and nitrogen of digestate and green waste feedstock on a dry ash free basis.

Dry ash free values are discussed here due to ash and moisture content not constituting as part of the chemical energy stored in the feedstock, and their removal is of little benefit to the energy content. However, drying of the feedstock increases the density of energy, though drying does not bring about any chemical change in the biomass. When the digestate and green waste are normalised for their CHNSO content, the carbon and oxygen contents begin to look quite similar, and as a result the energy density of the all the feedstock lie between the ranges of 20.2 and 22.3 HHV (MJ/kg, daf). The greatest hydrogen (daf) content is found in feedstocks that contain larger fractions of lignocellulosic compounds. This is due to the structure of cellulose being made up of hydrogen bonds [132].

The nitrogen content varies across the feedstock. Digestates typically have higher amounts of the nitrogen due to greater protein content, which is mainly attributed to microbial matter. Microbial matter, the methanogens, are present in large quantities during the digestion process, which are inevitably extracted along with digestate when removed. Amongst the green waste feedstock, grass has the highest nitrogen content. This is due to the grass taking up nitrogen at much greater levels during growth to create proteins for their entirely leafy structure [133].

The feedstock with the most inherent energy content is the SS digestate followed by woodchip, AGR digestate and grass at 22.3, 21.7, 21.5 and 21.3 HHV (MJ/kg, daf) respectively. Surprisingly, SS digestate has the highest energy density, due to exhibiting the lowest oxygen content of 31.0 percent (daf). However, the effect of ash content has a detrimental impact to the energy density as shown in Figure 21.

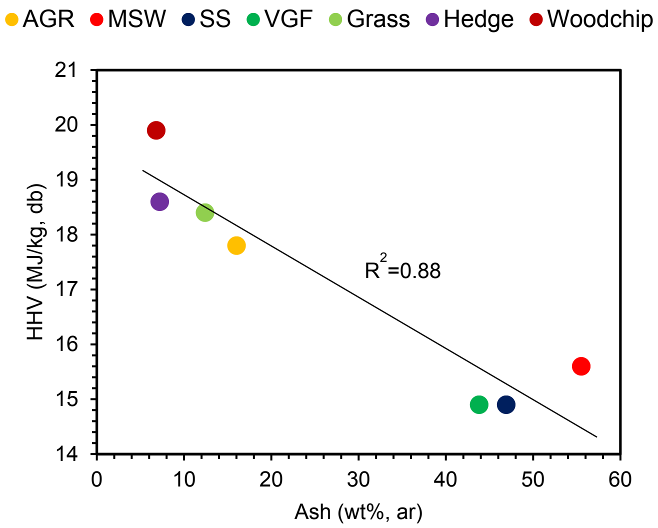

Figure 21. Comparison between HHV (dry basis) and ash content of digestates and green waste feedstock.

This observation shows a good negative correlation between heating value and ash content with R^2=0.88. Ash, the inorganic content is not separated prior to feedstock conversion and as a result the inorganic composition can also effect the yields of products during thermochemical transformation, this will be further discussed in Chapter 5.

4.3.1.3. Inorganic analysis

Analysing the inorganic composition of feedstock will help to gain an understanding of the applicability of the products created after thermochemical conversion. The major inorganic concentrations of digestate and green waste feedstocks are listed in Table 12. The ranking inorganic concentrations in order of decreasing content is shown in Table 13.

Table 12. Inorganic analysis of the digestate and green waste feedstocks.

Inorganic analysis (wt%, db)	Digestate				Green waste		
	AGR	MSW	SS	VGF	Grass	Hedge	Woodchip
Sodium, Na	0.3	0.9	0.5	0.7	0.3	0.2	0.1
Magnesium, Mg	0.7	1.4	0.9	0.7	0.4	0.1	0.0
Aluminum, Al	0.1	2.6	2.5	1.5	0.2	0.0	0.0
Silica, Si	1.8	10.2	7.6	12.0	1.8	0.4	0.2
Phosphorous. P	1.2	0.7	2.7	0.6	0.6	0.3	0.0
Potassium, K	1.6	1.6	0.7	1.2	1.4	1.5	0.0
Calcium, Ca	1.3	10.4	4.6	4.7	1.9	1.7	0.3
Iron, Fe	2.3	3.2	3.3	1.4	0.3	0.0	0.0

db, dry basis

The inroganic analysis shows that the digestate mineral matter is mainly comprised of silica, calcium and iron, whilst the green waste mineral matter is mainly comprised of calcium, silica and potassium. The largest concentration of inorganic, silica, is found in the VGF digestate (12 percent), this is due to the starter material (AD feedstock) being composed of garden waste, as silica is found in large concentrations within soil and sand [134]. The second largest concentration of inorganic, calcium, is found in the MSW digestate (10.4 percent); this is due to a fraction of animal bones found municipal food waste [135].

Table 13. The analysed inorganic elements ranked by decreasing content in the examined feedstock ashes.

Feedstock	Elements in decreasing order
AGR digestate	Fe > Si > K > Ca > P > Mg > Na > Al
MSW digestate	Ca > Si > Fe > Al > K > Mg > Na > P
SS digestate	Si > Ca > Fe > P > Al > Mg > K > Na
VGF digestate	Si > Ca > Al > Fe > K > Mg > Na > P
Grass clippings	Ca > Si > K > P > Mg > Fe > Na > Al
Garden hedge	Ca > K > Si > P > Na > Mg > Al > Fe
Woodchip	Ca > Si > Na > Al > Fe > Mg > K > P

Digestate contains comparatively higher amounts of iron due to the demand from mesophilic bacteria content, as iron is required for microbial growth [136]. The inorganic composition will be used to understand the fate of these compounds during thermochemical processing which is important to understanding how inorganics are fractionated in the products formed.

4.3.1.4. Macro nutrient content

This section presents specific analytes from previous analysis to compare and discuss the nutrient content of feedstock used in this study. Understanding the nutrient content is vital for quality and legislative purposes when disposing material to land for agricultural purposes. Figure 22 illustrates the macro nutrients; nitrogen, phosphorous and potassium content of the digestate and green waste feedstock.

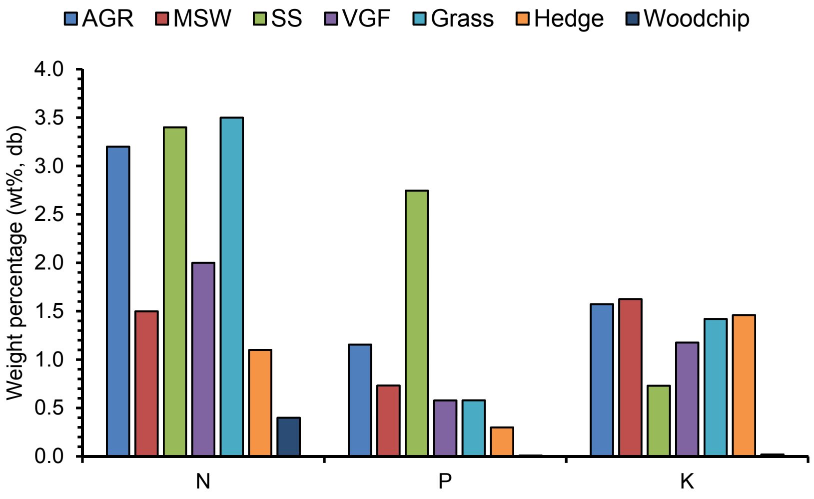

Figure 22. Macro nutrient content (nitrogen, phosphorous and potassium) of digestates and green wastes.

Overall, the greatest nutrient content is found in digestates compared to that of green wastes. This is largely due to the organic fractions of the AD feedstock being removed through substrate metabolism during the digestion process. Amongst the digestates, the greatest nitrogen and phosphorous content is found in the SS then AGR, with MSW digestate having the least. The potassium content is fairly similar across the feedstocks, with SS digestate having the least. The greatest levels of potassium is found in MSW digestate due to the starter material mainly being composed of food waste (diary, fish, fruit and vegetables, beans and legumes).

Amongst the green wastes, the overall nutrient content is lower than of digestates, with the exception of grass clippings. The highest nitrogen and phosphorous content across green wastes is found in grass due to its biochemical composition (high cellulose and protein content). The greatest potassium content is found in hedge and grass, this could be due to photosynthesis activity due to the high leaf content of these feedstocks. Woodchip contains very little nutrient content and as a result is usually applied as a mulching material in agriculture.

4.4. Chapter limitations and recommendations

The biochemical analysis of the feedstocks derived via DTG curves in this study only gives a qualitative comparison of lignocellulosic content between the biomass materials. Additionally, TGA burning profiles can also skew these results. Therefore, a single TGA burning profile was used. Nonetheless, using this method is suitable to be able to gain a general understanding of the differences of the lignocellulosic content between the feedstock. An improvement to this analysis would be to employ a quantitative method, i.e. a wet detergent chemical method. A wet chemical method [102] was developed and tested; however it was not fully carried out due to time constraints. On the other hand, the reliability of detergent methods is dependent on the ash and bound protein contents of the feedstock, these fractions and could result in an overestimation of cellulose, especially with complex biomass like digestate [137]. Furthermore, lignin is not directly measured. Additionally, determining the total lipid or fatty acids concentration would have provided a more complete picture of the biochemical compositions.

Whilst understanding the chemical properties of the feedstock has been the focus of this chapter, the physical properties i.e. particle size distribution, angle of internal friction and surface chemistry is absent. Providing this analysis would give a further understanding of how these materials would behave during storage and its mobilisation in the integration system, i.e. solids handling and material flow. However, this is proposed as further work and the analysis completed in this chapter is sufficient to understand the variation of chemical composition and its effect on chemical reactions during thermochemical processing in the following chapters.

4.5. Concluding remarks

The digestate feedstocks in this study show low parasitic moisture content after whole digestate dewatering, which suggests that they are more stable, and less degradation would occur if stored for long periods of time. However stable, the digestate materials exhibit large recalcitrant fractions (fixed carbon, ash and lignin content), along with undigested levels of carbohydrates and protein. This implies additional energy can be extracted via biological processing if these recalcitrant fractions are further mobilised.

Digestates generally have higher levels of ash content when compared to green wastes. This is due to the organic content (bio-available substrate) already having undergone hydrolysis and being metabolised by methanogens during AD. This negatively effects the energy density, as shown by low HHV's and higher inorganic levels. Stronger correlations can be seen with HHV and ash, compared to fixed carbon and ash content of the feedstock.

From the point of view of solid fuel and combustion for energy generation, a significant fraction of ash will remain in the hydrochar and pyrochar after conversion of a high ash content feedstock. When the chars are combusted, they would produce more fly ash and can possibly lead to greater fouling and slagging propensities within the combustion chamber. Inorganic analysis revealed that digestate materials have high levels of calcium, whilst green wastes exhibit higher contents of potassium. High calcium content is unfavourable, as they easily react with other elements, such as silica, to form alkali with very low melting points [138,139], increasing the potential for slagging and fouling.

Lignocellulosic feedstock (AGR digestate and green wastes) exhibited high hydrogen content. It is proposed that the energy density will be higher compared to that of low lignocellulosic feedstock (SS, MSW, VGF digestates) when converted into char. This is due to hydrogen's higher heating value being approximately seven times greater than that of carbon, which also lowers the oxidation state, thereby releasing more energy during the combustion process as there are more hydrogen atoms for every carbon atom [140].

The composition of the feedstock will affect the yields of products from HTC and pyrolysis. Feedstocks that are leafy in nature and high in protein (grass clippings) have resulted in higher nitrogen content. Previous studies have shown that feedstocks high in N typically generate a higher yield of char product when thermochemically converted [141]. SS digestate has low lignocellulosic, high protein and high N content. Therefore, it is likely to result in low hydrochar and pyrochar char yields, including higher levels of solubilisation into the process water during HTC.

Blending of dissimilar materials will help to increase or reduce targeted compounds. HTC blending has the opportunity to pre-treat and solubilise recalcitrant and high lignocellulosic feedstock to enhance AD biogas production. Additionally, if a high ash content digestate is blended, this has the potential to increase the calorific value and reduce inorganic concentrations thereby reducing slagging and fouling propensities in chars after conversion. Nutrient contents can also be balanced and be recycled after thermochemical processing for agricultural applications. Thus, the high ash and nutrient content of SS digestate has been selected for blending experiments.

The applicability of the products formed after HTC and pyrolysis will depend on the chemical reactions which govern product yields and chemical composition. The focus of the next chapter will be to explore integration concepts and examine the yields of products after thermochemical processing.

CHAPTER V

Integration Concepts and Effects of HTC Processing Compared to Pyrolysis

Obtaining continuous supply of biomass feedstock is necessary to realise the large-scale implementation of conversion technologies for the production of renewable fuels and functional materials. Barriers and challenges to this goal include variability in the physio-chemical properties of biomass which affect how they are handled and how these changes influence product yields when thermochemically converted.

5.1. Overview

The aim of this chapter is to understand the effect of feedstock composition, including HTC and pyrolysis operating variables on product yields to overcome these challenges. All the results from the thermochemical experiments outlined in Chapter 3, section 3.2 are presented and examined in detail.

The objectives of this chapter are to:

- Explore integration strategies with anaerobic digestion.
- Highlight the gaps in literature data for similar studies.
- Compare the effect of feedstock composition, including process variables of HTC and pyrolysis on product yields from the treatment of four digestate feedstocks.
- Compare the effect of feedstock composition, including process variables of HTC on product yields from the treatment of SS digestate blended with three green waste feedstocks.

5.2. Introduction

Digestate, the by-product of anaerobic digestion, is typically used in horticulture and agriculture as a fertiliser material. The digestate is typically high in available nitrogen, phosphorous and potassium; these are beneficial when applied for the cultivation of plants and crops which closes nutrient cycles. However, the introduction of British Standards Institution (BSI) Publicly Available Specification (PAS) 110 [23] has resulted in uncertainty over the recycling of digestate to land. PAS 110 describes a set of standards intended to ensure digestate complies with end of waste criteria, has a minimum quality and is fit for purpose to be applied as a fertiliser.

Digestate that does not meet this specification creates a material management challenge for the AD operators. It does this through the additional operational expenses (OPEX) from the costs of haulage, spreading, and disposal fees. As a result, there is a growing need to explore alternative digestate markets and land recycling, with emphasis on digestate enhancement technologies capable of adding value to the whole digestion process. Consequently, methods of transforming digestate into carbonaceous solid and liquid fractions for alternative utilisation using technologies such as hydrothermal carbonisation (HTC) [29,121,142] and pyrolysis [28,82,143–148] are now under investigation.

Hydrothermal carbonisation has evolved as an alternative approach for converting high moisture biomass into a “coal like” material (bio-coal) called hydrochar. It is gaining interest for the treatment of waste biomass and is being explored as a dewatering approach for sewage sludges [149–151]. HTC also produces a process water rich in solubilised organic material that can be biologically treated. Pyrolysis has been a common approach in the treatment of low moisture organic materials. In general, pyrolysis involves the charring or carbonisation of biomass, creating a solid residue called pyrochar and volatile products that remain gaseous or condense to create a liquid phase called bio-oil. The pyrolysis process is used heavily in the chemical industry, to produce coke from coal and other chemicals from either coal or petroleum.

The key to realising the full potential of biomass lies in the integration of processes, and maximising outputs for the sustainable production of bioenergy and bio-products. The bio-refinery concept integrates two or more biomass conversion processes to provide increased system efficiency, greater yields of products, and multiple energy vectors. Therefore, the integration of biological and thermochemical biomass conversion processes can provide improved material management, the production of different bioenergy vectors (i.e. a hybrid energy system) and value-added products.

Figures 23 and 24 illustrate the schematics of two potential integration concepts of AD and thermochemical conversion technology at the back and front end respectively. The back end approach illustrated in Figure 23 requires little adaptation to the current digestion operations as the incoming AD feedstock waste stream remains unchanged. Relative to the front end, the production of biogas is greater, owing to the incoming waste stream being biologically treated initially. This is also coupled with enhanced biogas production due to recycling of the thermochemical liquid phase which provides additional organic content mixed with the AD feedstock. Digestate also becomes more manageable since its volume is reduced after thermochemical treatment. Placing a thermochemical conversion technique at the back requires the solid content of whole digestate be increased to greater than ten percent solid matter prior to thermochemical treatment to avoid using energy to heat up large volumes of water. Therefore, dewatering of the digestate will need to be applied, and the discharge of water facilitated. The throughput of digestate will be limited to thermochemical conversion capacities and will need to be stored prior to processing.

Figure 24 illustrates a thermochemical conversion integrated at the front end of the AD process. Relative to the back end, this approach may improve the quality of char produced, owing to the direct conversion of a greater amount of organic content available from the incoming waste (as it has not been biologically converted initially). The resultant digestate after AD is easier to manage and pump since it will contain less solid matter, due to the initial thermochemical treatment and separation of char thereafter. This in turn will aid the degradation of the liquid phase in AD, since it is only water fed and contains little to no recalcitrant fibers. As a greater proportion of organics in the waste is converted to char this will lead to a reduction of biogas generation when the liquid phase is treated via AD, negatively impacting the whole system energy balance.

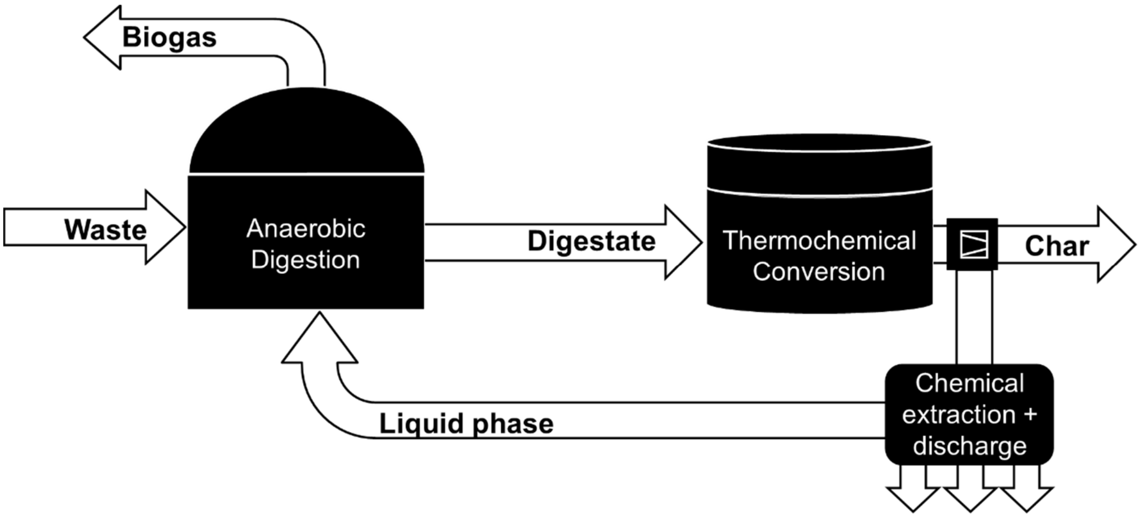

Figure 23. Schematic diagram of an integration strategy with thermochemical processing at the back end of AD plant.

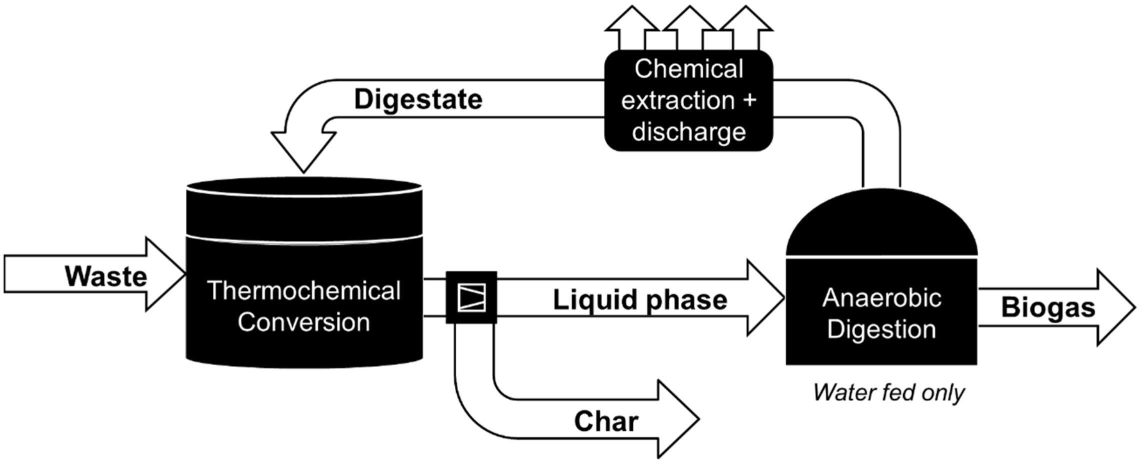

Figure 24. Schematic diagram of an integration strategy with thermochemical processing at the front end of AD plant.

With a focus on integrating HTC with AD, Figure 25 illustrates an approach with HTC at the back end. HTC is more favourable than pyrolysis as it is able to accept feedstock high in moisture. Again the AD facility would operate normally, with little adaptation required due to the HTC process waters being re-circulated. Additionally, re-circulation also reduces water demand for the hydrolysis stage in AD. At the HTC stage, co-processing and blending whole digestate with green waste materials removes the AD practice of fractionating the digestate (dewatering), this in turn will increase the solid matter content from 5 to 20 percent and above for efficient HTC practice by avoiding heating up large volumes of water. Co-processing can be advantageous in other ways. Theoretically, the resultant hydrochar has the potential to obtain greater HHV’s owing to greater lignin fraction converted to carbon and it can also reduce the inorganic concentrations, both increasing the quality of hydrochar as a solid fuel. Co-processing could also increase humic like substances within the hydrochar, which can improve the quality of hydrochar as a soil amendment product. Processing digestate with lignocellulosic materials by HTC would also remove barriers of introducing alternative recalcitrant AD feedstocks. With this approach, HTC would increase the solubilisation and degradability of the recalcitrant fractions prior to AD, a process that can be considered as a pre-treatment method, much like current thermal hydrolysis technology. This is the integration approach which is proposed in this study.

Due to the technology readiness level and scale of HTC processing, the capability of HTC and throughput of incoming waste is lower than that achievable by digesters. Therefore, biogas production is limited by the rate of HTC treatment. Biogas production could also be potentially limited by high concentrations of inhibitory compounds. For instance, the buildup of heavy metals through the repeated recirculation of process waters. To mitigate this, effluent water treatment technology will also need to be implemented.

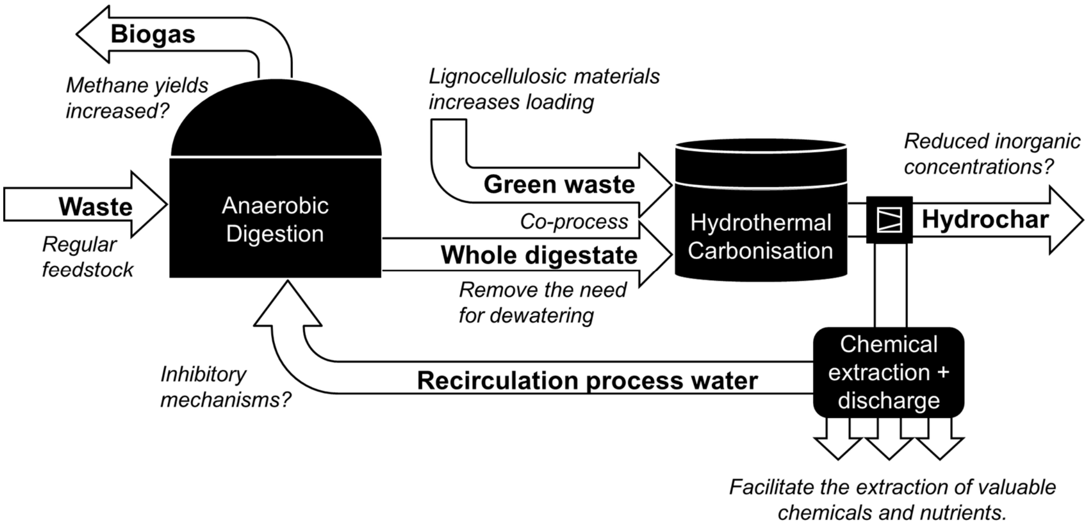

Figure 25. Schematic diagram of an integration strategy with HTC co-processing at the back end of AD plant.

Table 14 shows the typical HTC yield data and process parameters of a range of digestate, green waste and blended materials from literature. The data given for digestate materials have been selected to match the experimental conditions applied in this investigation (a retention time of an hour). The data shows that HTC solid loading used on average is around 15 w/w percent. The typical solid yield from HTC range is as low as 21.0 and as high as 80.7 percent for digestate (55 percent on average), 6.9 to 78.1 percent for green wastes (47 percent on average) and 43.7 to 60.1 percent for blended materials (53 percent on average). Typically, higher solid yields (dry basis) will be attributed to the digestate materials, due to their higher concentrations of inorganic levels (ash content). When blended with low ash content feedstock such as green waste, the solid yields should theoretically balance to the median, unless the composition of the combined feedstock acts as a catalyst for increased hydrochar polymerisation or solubilisation into the process water.

Table 15 shows the typical pyrolysis yield data and process parameters of a range of digestate materials from literature. The residence / retention times typically used are below or above an hour and temperatures of above 450 °C are common (with the exception of the study using corn stalk digestate at 220 °C and 240 °C). Pyrolysis solid yields are within the ranges of 33 to 85 percent (with an average of 46 percent), liquid yields in the range of 10.9 to 55.8 percent (with an average of 38 percent) and gas yields in the range of 5.3 to 43.6 percent (with an average 23 percent). Literature data shows that the pyrolysis of digestate solid and liquid yields on average are lower and gas yields on average are higher compared to that of HTC.

Table 14. HTC process parameters and yields of solid digestate, green waste and blended materials found in literature.

Feedstock	HTC parameters			Yields (wt%, db)			Reference
	Solid loading (w/w %)	Ret. time (hr)	Ret. temp (°C)	Solid	Liquid	Gas	
Solid digestate							
Sewage sludge	10	1	170	80.0	18.0	2.0	[111]
			250	66.0	32.0	2.0	
Sewage sludge		1	200	62.0	-	-	[99]
			250	51.0	-	-	
Sewage sludge + MSW	28	1	150	24.0	69.0	1.0	[113]
			200	21.0	71.0	4.0	
Corn, manure	13	1	180	80.7	-	-	[120]
			220	66.4	-	-	
			260	46.3	-	-	
Green waste							
Woodchip	7	6	200	60.6	-	-	[125]
Fallen leaves and deadwood	11	1	150	70.5	-	-	[126]
			170	61.7	-	-	
			190	50.4	-	-	
Tree, bushes and bamboo	5	1	150	78.1	-	-	[127]
			180	63.8	-	-	
			210	60.6	-	-	
			240	46.4	-	-	
Lawn grass	3	1	200	48.0	-	-	[128]
			240	37.0	-	-	
Grass	9	8	180	8.5	-	-	[115]
Straw			180	6.9	-	-	
Woodchips			180	23.4	-	-	
50/50 blends							
Swine manure & saw dust	15	10	220	58.9	-	-	[152]
Swine manure & corn stalk	15	10	220	56.3	-	-	
Sludge & sawdust	17	1	220	59.8	-	-	[153]
Food waste & sawdust		1	180	55.6	-	-	[154]
		1	220	53.7	-	-	
			260	43.7	-	-	
Sludge & sawdust	10	1	220	51.9	49.6	2.3	[155]
			260	49.3	46.6	2.7	
Sludge & corncob	10	1	220	60.1	57.6	2.6	
			260	48.2	45.2	3.0	
Sludge & cornstalk	10	1	220	57.7	54.7	3.0	
			260	52.0	48.6	3.5	
Sludge & rape straw	10	1	220	55.7	53.6	2.1	
			260	47.6	45.0	2.6	
Sludge & pine sawdust	12	0	220	58.1	-	-	[156]
Sludge & food waste	7	1	180	48.5	-	-	[157]
			230	50.5	-	-	

Table 15. Pyrolysis process parameters and yields of solid digestate materials found in literature.

Solid digestate	Pyrolysis parameters		Yields (wt%, db)			Reference
	Ret. time (hr)	Ret. temp (°C)	Solid	Liquid	Gas	
Corn silage and slurries	5 min	500	36.0	37.0	27.0	[158]
		550	33.0	35.0	32.0	
		600	33.0	33.0	34.0	
Food waste	4	500	42.5	52.2	5.3	[143]
Groats, olive, silage and manure	10 min	600	34.2	50.8	15	[82]
Manure, maize and cereal	10 min	600	34.0	55.8	10.2	
Sargassum	20 min	450	43.2	31.1	23.0	[159]
Corn stalk digestate	30 min	220	85.0	-	-	
		240	76.8	-	-	
Sugar beet	2	600	45.5	10.9	43.6	[160]

Although there are many studies of digestate conversion via HTC and pyrolysis, research in comparing a number of digestates, including the interlinked effects of both HTC and pyrolysis conversion remains limited. Studies are also lacking in the comparison of different solid loadings used within HTC. Furthermore, when reporting solid loading the units used are less consistent. In most of the HTC studies stated here, the process water and gas yields are not reported, thereby reducing our understanding of the degree of solubilisation. To the author's knowledge, garden hedge (privet) has not been investigated as a HTC feedstock. Current HTC blending work has focused on the co-processing of secondary sewage sludge (undigested) and lignocellulosic materials. No blending of digestate with lignocellulosics materials have been reported at the time of writing. A small number of mainly homogeneous digestates have been investigated for pyrolysis conversion, thereby lacking investigation of digestate from residual organic fraction of municipal solid waste. Additionally, pyrolysis residence times are either very short (less than 30 minutes) or very long (2 hours above) and there is an absence of studies using one hour.

This chapter addresses the need to compare the outputs of a range of digestate materials via HTC and pyrolysis conversion techniques and changing operating conditions. Additionally the blending of SS digestate with green waste via HTC co-processing is investigated, as this is only very briefly addressed in literature. The outcomes of this study will provide an understanding of how the feedstock composition can affect the reactions during thermochemical conversion, particular its yields, and in subsequent chapters the product composition.

5.3. Results and discussion

The feedstocks used in this study will be assessed for their behaviour during thermochemical processing via hydrothermal carbonisation and pyrolysis through product yields and material balance. Additionally, the processing parameters will also be evaluated on how chemical reactions also effect product yields. This will aid in understanding how these feedstocks could be utilised in a large-scale implementation for the production of renewable fuels and functional materials.

5.3.1. Digestate processing

Initially the results will focus on the comparison of yields from the processing of digestate materials via HTC and pyrolysis only to give a baseline understanding of the proposed integration approach (Figure 25).

5.3.1.1. HTC yields

The mass yields of the solid, liquid, and gaseous products from the HTC conversion of digestate is listed in Table 16. The values agree with the ranges of HTC yields found in literature. The error of hydrochar yields is under the limit of around 2.6 percent, suggesting that the homogeneity is of the feedstock when prepared is good and process conditions were repeatable and accurate.

In general, the data shows that the rate of solubilisation increases with temperature across all digestate feedstock, resulting in reduced hydrochar yields with increased liquid and gas yields. On the other hand, the rate of solubilisation decreases with solid loading, resulting in increased hydrochar yields and reduced liquid yields. The gas yields remain largely unaffected with increases in solid loading.

Table 16. Yields of products following hydrothermal carbonisation of digestate.

Feedstock and HTC process conditions	Yields (wt%, db)		
	Solid	Liquid[a]	Gas
AGR digestate			
150 °C at 20%	82.7 ± 2.2	15.2 ± 1.0	2.1 ± 1.2
200 °C at 10%	60.0 ± 2.6	36.6 ± 0.3	3.4 ± 2.2
200 °C at 20%	67.8 ± 1.5	26.9 ± 4.6	5.3 ± 3.1
200 °C at 30%	80.1 ± 1.7	16.8 ± 1.0	3.1 ± 0.7
250 °C at 10%	47.2 ± 0.1	50.1 ± 0.5	2.8 ± 0.4
250 °C at 20%	51.1 ± 2.9	45.7 ± 3.7	3.2 ± 0.8
250 °C at 30%	49.4 ± 1.1	45.6 ± 0.6	4.9 ± 0.5
MSW digestate			
150 °C at 20%	90.6 ± 2.1	8.1 ± 2.2	1.4 ± 0.1
200 °C at 10%	85.0 ± 0.2	10.2 ± 2.5	4.9 ± 2.3
200 °C at 20%	87.1 ± 0.2	9.5 ± 2.1	3.3 ± 1.9
200 °C at 30%	85.7 ± 0.8	11.1 ± 0.8	3.3 ± 0.1
250 °C at 10%	82.0 ± 0.0	15.0 ± 0.9	2.9 ± 0.9
250 °C at 20%	84.1 ± 1.3	12.1 ± 3.0	3.8 ± 1.8
250 °C at 30%	83.5 ± 1.0	5.4 ± 5.4	2.4 ± 2.4
SS digestate			
150 °C at 20%	87.1 ± 1.9	11.6 ± 2.0	1.3 ± 0.1
200 °C at 10%	72.6 ± 1.3	23.0 ± 1.8	4.4 ± 0.5
200 °C at 20%	76.1 ± 0.3	19.2 ± 0.4	4.7 ± 0.7
200 °C at 30%	78.0 ± 1.2	17.3 ± 4.3	4.7 ± 3.1
250 °C at 10%	65.6 ± 0.3	31.4 ± 0.3	3.0 ± 0.0
250 °C at 20%	67.9 ± 0.4	27.4 ± 1.2	4.7 ± 0.7
250 °C at 30%	69.5 ± 0.1	25.4 ± 0.2	5.1 ± 0.3
VGF digestate			
150 °C at 20%	89.0 ± 0.2	9.8 ± 0.2	1.2 ± 0.0
200 °C at 10%	79.5 ± 0.1	19.1 ± 0.2	1.4 ± 0.2
200 °C at 20%	80.9 ± 1.0	16.6 ± 0.2	2.5 ± 0.8
200 °C at 30%	79.8 ± 1.3	15.3 ± 1.6	4.9 ± 2.9
250 °C at 10%	71.1 ± 0.5	20.5 ± 5.8	8.4 ± 5.3
250 °C at 20%	71.4 ± 1.4	25.5 ± 0.7	3.1 ± 0.7
250 °C at 30%	73.7 ± 0.1	21.4 ± 1.1	4.9 ± 1.2

[a], calculated by difference

5.3.1.1.1. Effect of HTC temperature

Figure 26 illustrates the effect of HTC temperature on solid, liquid and gaseous product yields. There are subtle differences between the feedstocks, however the differences in yields are more profound at the higher temperatures. As the temperature increases, the yield of hydrochar reduces for all feedstocks, however the most dramatic decrease is seen with AGR digestate, as shown in Figure 26a. This is due to AGR digestate chemical composition, which exhibited the lowest ash and the largest lignocellulosic content which is more thermally degradable at higher temperatures. Significant degradation of cellulose occurs between 200 °C and 250 °C and lignin degrades between 220 °C and 260 °C [104], which would account for the lower solid yields achieved at 250 °C compared to 200 °C for AGR digestate, and in another study [99].

On average, the decreasing rate of hydrochar formation with increasing temperature is highest with AGR (-0.32 percent per °C), followed by SS (-0.19 percent per °C), VGF (-0.18 percent per °C), then MSW digestate (-0.07 percent per °C). The yields of extractable material from the MSW digestate were the lowest out of the four digestates attributed to its highest ash content.

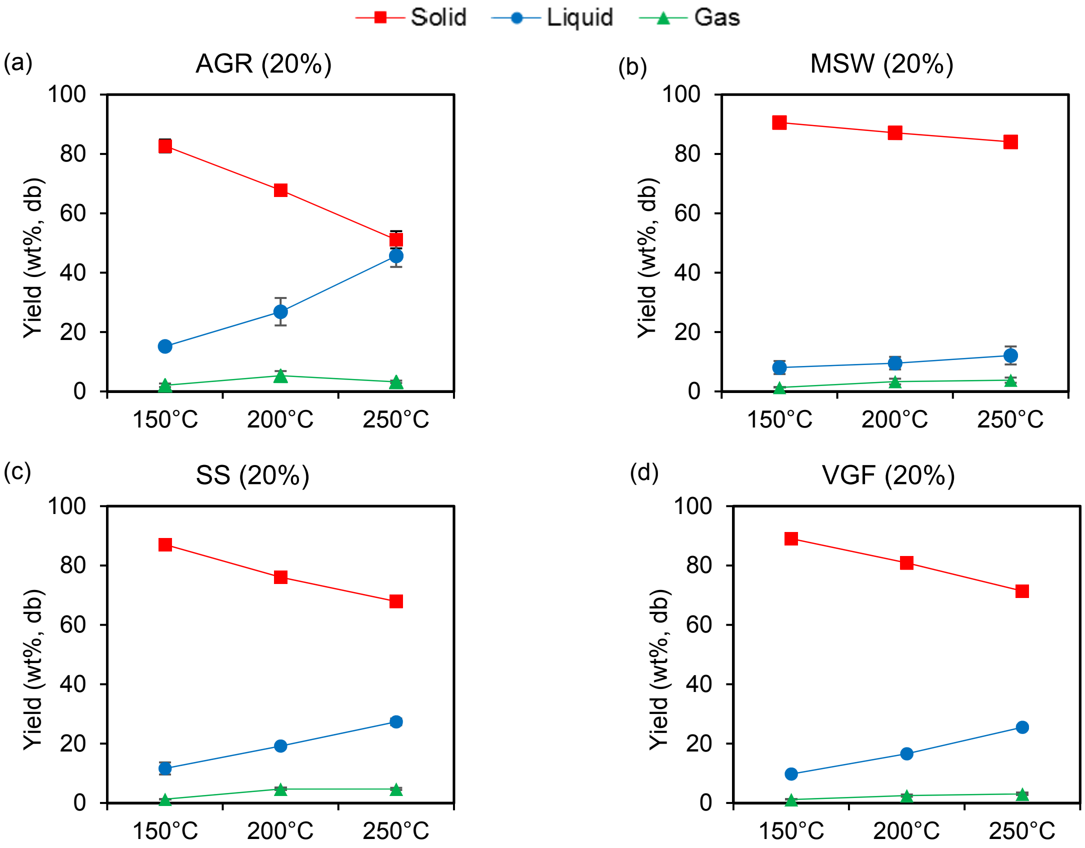

Figure 26. Influence of temperature on product yields at 20 percent loading for **a**) agricultural residue (AGR), **b**) municipal solid waste (MSW), **c**) sewage sludge (SS), and **d**) vegetable, garden and fruit (VGF) digestates on a dry basis (db), based on duplicate data and error bars represent deviation around the mean.

Protein generally starts to degrade at temperatures above 200 °C [161] and produce high levels of soluble amino acids which begin to polymerise to produce char and oil at 250 °C [72]. Previous reports of the HTC of sewage sludge derived feedstocks generally show an increase in solubilisation with higher temperatures, leading to high levels of soluble carbon in the process waters [112,162,163].

On average, with increasing temperatures the rate of solubilisation of digestate material into the liquid phase is highest with AGR (0.30 percent per °C), followed by SS and VGF (both at 0.16 percent per °C), then MSW digestate (0.04 percent per °C). The rate of gas production ranges within 0.01 to 0.03 yield percent per °C, therefore gas yields remain largely unaffected by increasing temperatures.

5.3.1.1.2. Effect of HTC solid loading

Figure 27 illustrates the effect of HTC solid loading (10, 20 and 30 percent) on product yields at 200 °C and 250 °C for the digestate materials. The results show that the effect of solid loading on yields is now feedstock dependent. Increasing the solid loading lowers the rate of solubilisation across all the digestate materials, resulting in an increase in hydrochar yield.

On average, the greatest rate of hydrochar production with increasing solid loading is found with AGR and SS at 200 °C (0.20 and 0.05 percent per solid loading respectively). The increasing rate of hydrochar production for AGR at 200 °C can be attributed to the amount of lignin not being degraded, therefore remaining in the solid phase hydrochar. Compare this to that of AGR at 10 percent solid loading treated at 250 °C, Figure 27b, where a large fraction of the digestate (lignin) is solubilised, resulting in a higher liquid yields.

The greatest reduction in solubilisation with increasing solid loading is found with AGR treated at 200 °C, followed by MSW digestate treated at 250 °C (-0.20 and -0.10 percent per solid loading respectively). This reduction of liquid yields can be attributed to a saturation effect, where solubilised compounds re-polymerise into hydrochar. The levels and average rate of gas production remains relatively stable with increased solid loadings (between ±0.03 yield percent per solid loading).

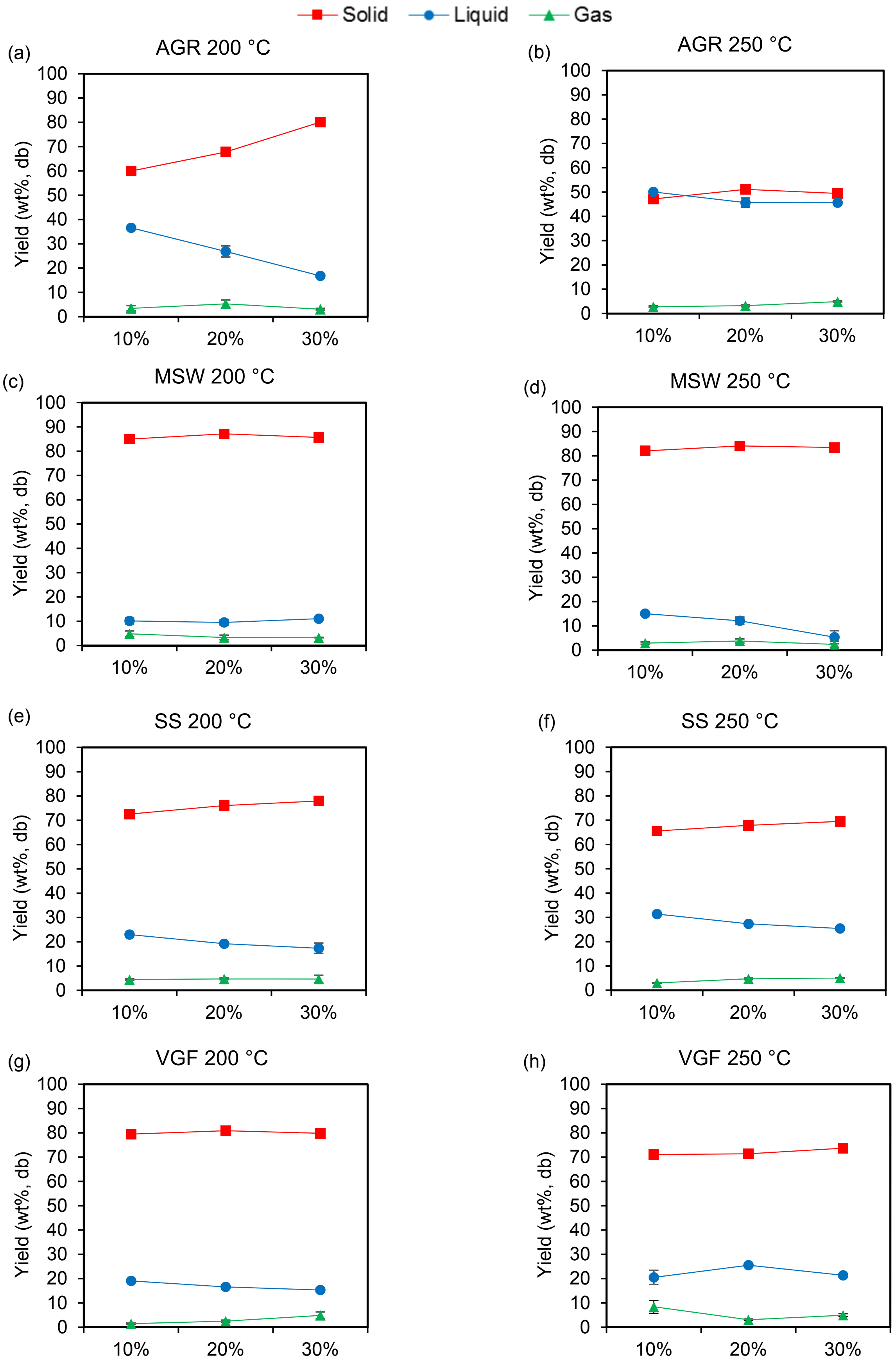

Figure 27. Influence of loading on HTC product yields, or **a**) AGR at 200 °C, **b**) AGR at 250 °C, **c**) MSW at 200 °C, **d**) MSW at 250 °C, **e**) SS at 200 °C, **f**) SS at 250 °C, **g**) VGF at 200 °C, **h**) VGF at 250 °C on a dry basis (db), based on duplicate data and error bars represent deviation around the mean.

5.3.1.2. Pyrolysis yields

The mass yields of solid, liquid and gaseous products from the pyrolysis conversion of digestate is listed in Table 17. The pyrolysis yield values agree with the ranges found in literature. At lower temperatures all four digestate exhibit similar yields. At 200 °C, solid yields are in the range of 89.9 to 92.8 percent, liquid 0.2 to 3.3 percent and gas 5.4 to 8.3 percent. At pyrolysis temperatures above 200 °C the differences become larger, and even more profound at 600 °C. Therefore, the wide temperature range used with pyrolysis experiences severe rates of conversion.

Table 17. Yields of products following pyrolysis of digestate.

Feedstock and pyrolysis process conditions	Yields (wt%, db)		
	Solid	**Liquid**	**Gas**[a]
AGR digestate			
200 °C	91.0 ± 3.2	3.3 ± 0.8	5.7 ± 2.4
400 °C	43.3 ± 0.5	38.7 ± 5.4	18.0 ± 4.9
600 °C	33.5 ± 3.0	42.4 ± 1.3	24.1 ± 1.7
MSW digestate			
200 °C	92.8 ± 0.3	0.2 ± 0.0	6.9 ± 0.3
400 °C	79.8 ± 0.6	4.3 ± 1.6	15.9 ± 2.1
600 °C	74.4 ± 1.5	8.9 ± 1.1	16.6 ± 2.5
SS digestate			
200 °C	89.9 ± 3.5	1.8 ± 0.2	8.3 ± 3.3
400 °C	54.9 ± 1.0	18.8 ± 4.5	26.3 ± 3.5
600 °C	47.7 ± 1.6	25.6 ± 0.1	26.7 ± 1.5
VGF digestate			
200 °C	92.0 ± 0.3	2.6 ± 2.6	5.4 ± 2.3
400 °C	66.8 ± 0.6	12.6 ± 2.5	20.6 ± 1.9
600 °C	62.0 ± 0.4	10.8 ± 5.9	27.2 ± 6.2

[a], calculated by difference

5.3.1.2.1. Effect of pyrolysis temperature

Figure 28 shows the effect of temperature on pyrolysis product formation. The rate at which the feedstock is transformed changes rapidly with increasing temperatures. The formation of solid yield, pyrochar, reduces for all digestates as temperature increases. From 200 °C to 400 °C, this change of increase is rapid due to the degradation of organic fractions. The largest step change is seen in the AGR digestate as shown in Figure 28a, attributed to AGR's greater lignocellulosic and low ash content.

In general, the rate of pyrolysis product formation between 200 °C and 600 °C is not linear. The greatest average pyrochar reduction rate with increasing temperature is found with AGR (-0.58 percent per °C), followed by SS (-0.42 percent per °C), VGF (-0.30 percent per °C) then MSW digestate (-0.18 percent per °C). The greatest average liquid phase production rate with increasing temperature is found with AGR (0.39 percent per °C), followed by SS (0.24 percent per °C), MSW (0.09 percent per °C) then VGF digestate (0.08 percent per °C). This results in AGR digestate exhibiting the lowest solid and highest liquid yield at 600 °C. Additionally, greater liquid yields were produced than solid yields from AGR digestate at 600 °C.

The levels of gas generated is greater than the liquid yields, with the exception of AGR at 400 °C and 600 °C. This is due to oxygen and hydrogen formed gases from the volatilisation of lignin and cellulosic fractions of AGR re-condensing into pyrolysis oils [164]. The greatest average gas production rate with increasing temperature is found in VGF (0.22 percent per °C), followed by AGR and SS (both 0.18 percent per °C) then MSW digestate (0.10 percent per °C). At 600 °C, the greatest gas yields were produced with VGF (medium confidence due to error bars) followed by SS, AGR then MSW digestate. It is unknown why the rate of gas production with increasing temperatures is highest for VGF than AGR and SS digestate.

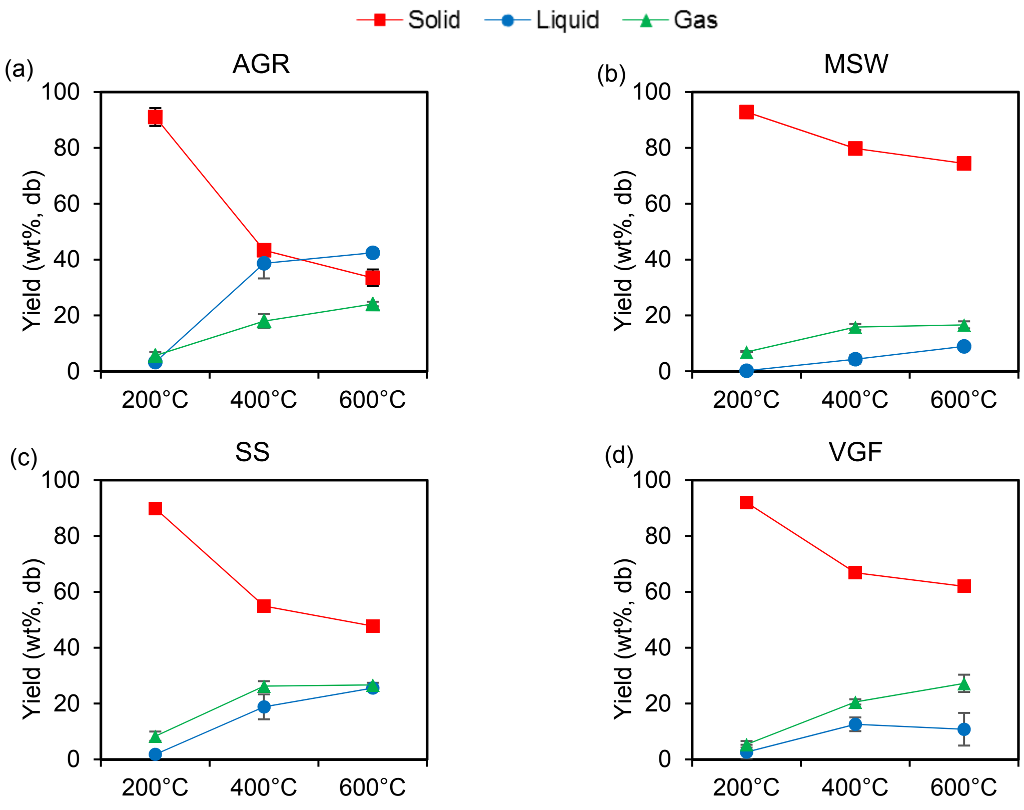

Figure 28. Influence of temperature on pyrolysis product yields for **a**) agricultural residue (AGR), **b**) municipal solid waste (MSW), **c**) sewage sludge (SS), and **d**) vegetable, garden and fruit (VGF) digestates on a dry basis (db), based on duplicate data.

5.3.1.3. Comparison of HTC and pyrolysis conversion of digestate

For the direct comparison of thermochemical methods Figures 29, 30, 31 and 32 illustrate the products yields from the conversion of digestate via HTC and pyrolysis. In general, the formation of products with HTC are more linear than that of pyrolysis. However, HTC has a smaller temperature range. Therefore, this linear observation of HTC yields with increasing temperatures could be potentially representing a section of an exponential curve.

AGR digestate readily degrades in both thermochemical processes, illustrated in Figure 29. This is shown in the reduction of solid yields with increasing temperature, and corresponding increases in liquid and gas yields. The largest liquid yield is achieved with HTC at 250 °C, whilst the greatest AGR digestate gas yields are found from pyrolysis processed at all temperatures. The increasing pyrolysis gas yields results in a loss of solid yields, whilst the liquid yield remains largely unaffected. This is attributed to the operation of pyrolysis, whereby phase separation occurs due to the mechanics of the technology and as a result the liquid and gas products do not chemically react with all three phases. Across the digestate materials, AGR exhibits the most readily thermally degradable feedstock, as exhibited by large liquid and gas yields, due to its large organic fraction.

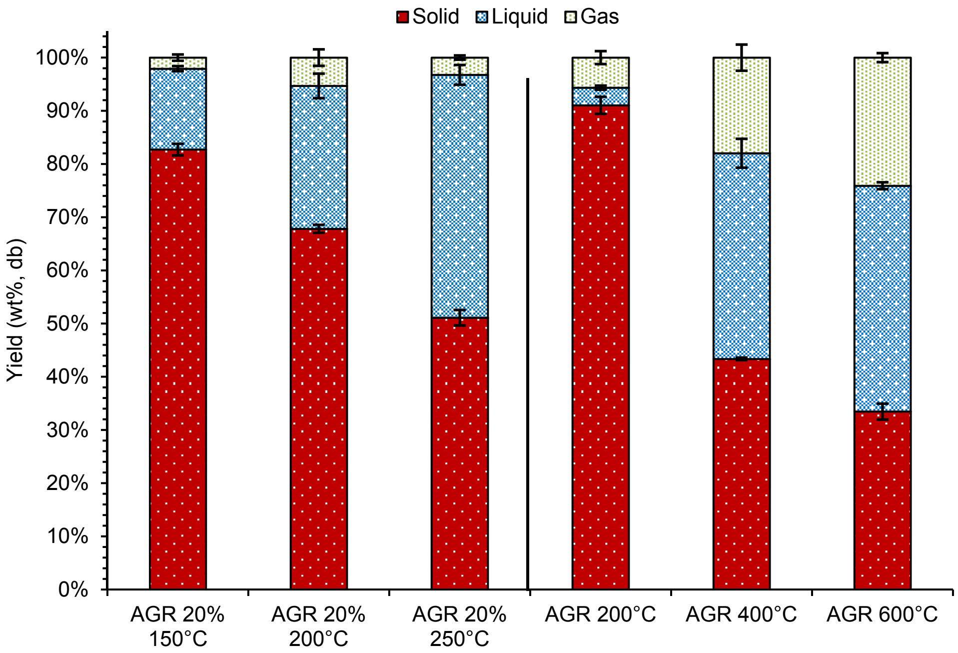

Figure 29. Comparison of the product yields from HTC and pyrolysis of AGR digestate.

MSW is characterised by the highest ash content across all the digestates and as a result shows little transformation during both thermochemical processes, as shown in Figure 30. The greatest MSW solid and liquid yields are derived from HTC, whilst pyrolysis generates the greatest gas yields again. Most of the solubilisation during HTC occurs at lower temperatures (small step changes in increasing temperatures). The largest MSW liquid yield is achieved with HTC processing at 250 °C. Compared to pyrolysis, MSW degrades mostly to gas with increasing temperatures. In terms of thermochemical processing, the behaviour of MSW digestate shows this is the most recalcitrant feedstock.

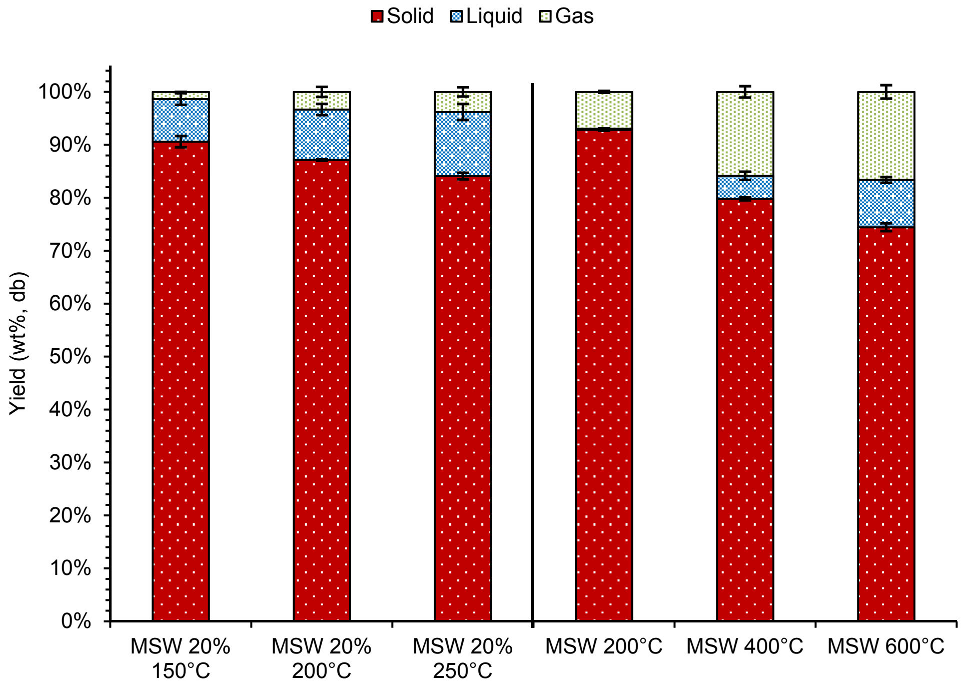

Figure 30. Comparison of the product yields from HTC and pyrolysis of MSW digestate.

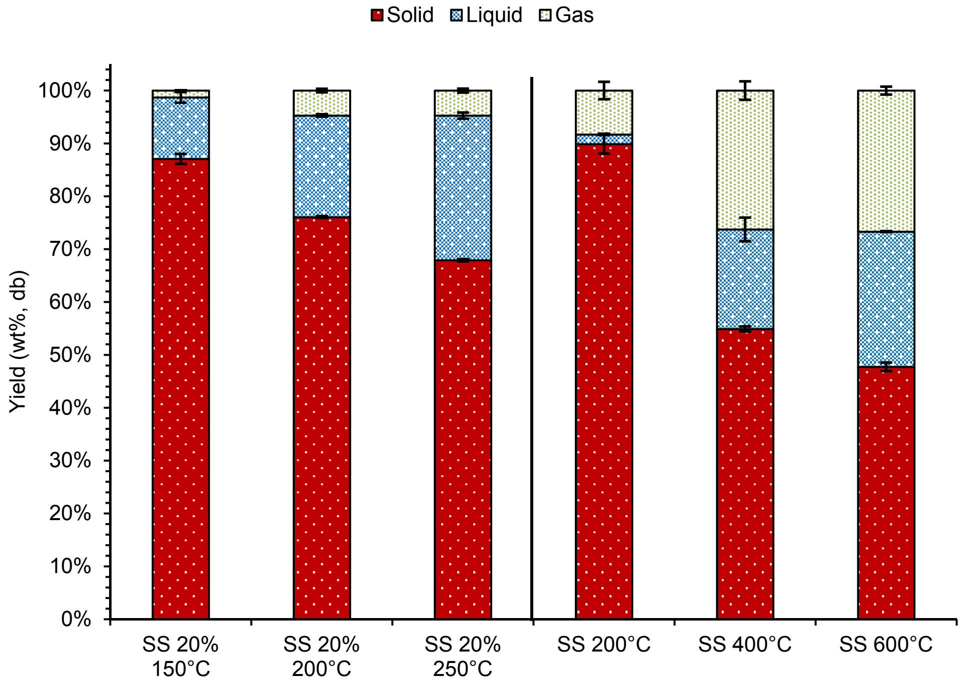

Figure 31. Comparison of the product yields from HTC and pyrolysis of SS digestate.

SS digestate also readily degrades (much like AGR) in both thermochemical processes, as shown in Figure 31. A greater step change is seen in pyrolysis with increasing temperatures, as exhibited by the large increase in gas yields between 200 °C and 400 °C. This can be attributed to SS digestates fraction of protein volatilising above 200 °C forming aromatic hydrocarbons [165]. Between 400 °C and 600 °C pyrolysis gas yields from SS digestate remain stable, however there is an increase in liquid phase, most visibly from an increase of pyrolysis bio-oil. This is assumed to be the fat content of SS digestate volatilising into a gas containing oxygen and hydrogen forms, which re-condense into bio-oil [164]. The largest SS liquid yield is achieved with HTC 250 °C. This result supports the argument that the biochemical make-up of SS digestate is more readily solubilised via HTC than it is volatilised to form liquids via pyrolysis.

The VGF digestate product yields from HTC and pyrolysis are shown in Figure 32. Even though VGF has lower ash content than SS, VGF exhibits lower liquid and gas product formation compared to SS digestate during both conversion processes (compare Figure 32 with Figure 31). VGF is therefore more recalcitrant than SS during thermochemical conversion. For the case of pyrolysis, VGF exhibits little transformation into liquid phase. The reduction of VGF pyrolysis solid yields is due to an increase of gas yields with increasing temperatures. During pyrolysis, VGF behaved more like MSW. However, during HTC, VGF behaved more similarly to SS digestate. The mechanism underpinning the behaviour of VGF in both processes is unknown. The largest VGF liquid yield is achieved with HTC at 250 °C. Therefore, as with SS digestate, VGF exhibits a tendency to be more easily solubilised via HTC than volatilised to form liquids via pyrolysis.

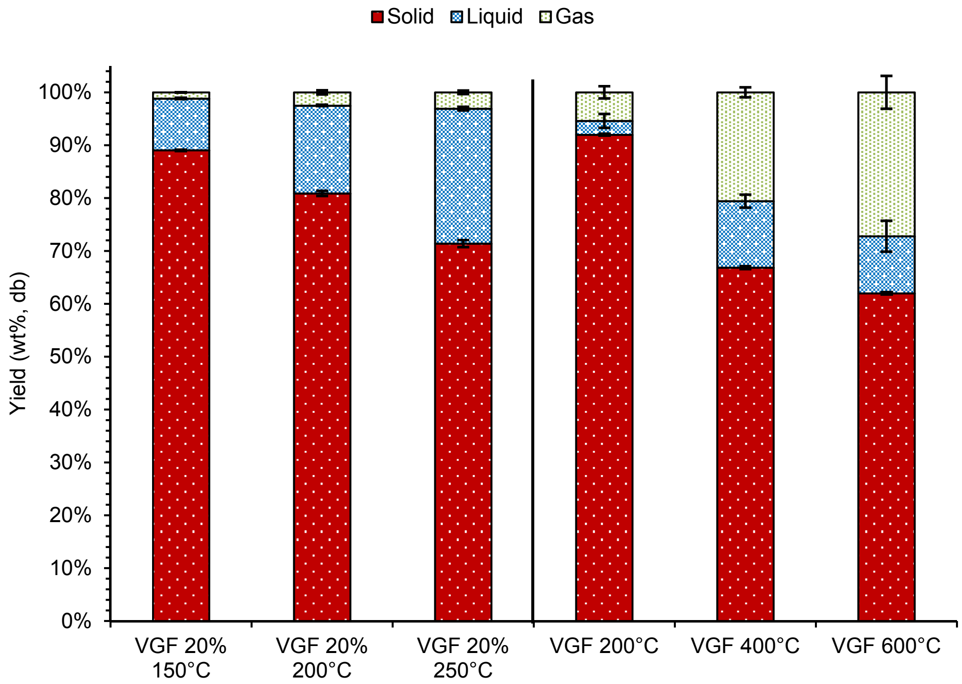

Figure 32. Comparison of the product yields from HTC and pyrolysis of VGF digestate.

5.3.2. Green waste processing and blends in HTC

In Chapter 4, SS digestate was selected for blending with green wastes for HTC co-processing due to its resource availability and dissimilar chemical composition to the lignocellulosic type green waste materials. The feedstocks for blending are characterised by large dissimilarities in protein, volatile matter, ash, and fixed carbon, carbon, sulphur, oxygen and HHV. The strategy for co-processing as part of the integration concept illustrated in Figure 25 will be simulated and yields will be discussed in the following sections.

5.3.2.1. HTC yields

The mass yields of the solid, liquid and gas products from the HTC of green waste and SS digestate blends is listed in Table 18.

Table 18. Yields of products following hydrothermal carbonisation of green waste and SS digestate and green waste blends at 50 percent.

Feedstock and HTC process conditions	Yields (wt%, db)		
	Solid	Liquid[a]	Gas
Green wastes			
Grass clippings			
150 °C	68.7 ± 2.4	30.7 ± 2.4	0.5 ± 0.0
200 °C	59.8 ± 0.5	39.0 ± 0.4	1.1 ± 0.1
250 °C	51.4 ± 0.3	46.1 ± 0.4	2.4 ± 0.0
Garden hedge			
150 °C	65.2 ± 0.2	33.8 ± 0.2	0.9 ± 0.0
200 °C	56.5 ± 1.2	41.8 ± 1.2	1.8 ± 0.1
250 °C	46.6 ± 0.6	51.0 ± 0.6	2.5 ± 0.1
Woodchip			
150 °C	85.5 ± 1.2	14.1 ± 1.1	0.3 ± 0.1
200 °C	73.8 ± 0.6	25.7 ± 0.3	0.5 ± 0.3
250 °C	56.5 ± 0.5	41.8 ± 0.4	1.7 ± 0.0
Blended (SS and green wastes)			
SS and grass 50/50			
150 °C	81.0 ± 0.4	18.4 ± 0.1	0.6 ± 0.2
200 °C	67.9 ± 0.1	30.8 ± 0.2	1.3 ± 0.3
250 °C	56.0 ± 1.4	42.3 ± 1.6	1.7 ± 0.2
SS and hedge 50/50			
150 °C	75.7 ± 0.2	23.7 ± 0.3	0.6 ± 0.2
200 °C	65.8 ± 0.1	32.5 ± 0.1	1.7 ± 0.0
250 °C	56.8 ± 0.5	41.3 ± 0.5	1.9 ± 0.0
SS and woodchip 50/50			
150 °C	87.4 ± 0.3	11.8 ± 0.7	0.8 ± 0.4
200 °C	75.4 ± 0.1	23.5 ± 0.4	1.1 ± 0.4
250 °C	62.9 ± 1.4	35.5 ± 1.5	1.5 ± 0.1

[a] calculated by difference

The solid yields from the HTC of grass clippings were in the range of 51.4 to 68.7 percent, garden hedge 46.6 to 65.2 percent and woodchip 56.5 to 83.5 percent. The values here match the HTC solid yields of green waste found in literature, with the exception of the values given by the study that processes grass, straw and woodchip [115] due to the incorrect reporting of yields. Compared to the HTC of the digestates, the solid yields of the green wastes mimic that of AGR digestate (in the range of 51.1 to 82.7 percent). Even though AGR has less lignocellulosic content, the increased ash content of the AGR digestate makes up this difference.

Figure 33 shows the effect of temperature on product formation during the HTC of green wastes and their blends with SS digestate. Garden hedge exhibits greater solubilisation across all temperatures, especially at 250 °C where liquid yield is greater than the solid yield by 3.4 percent as shown in Figure 33c. The next topmost solubilising green waste feedstock is grass clippings, followed by woodchip. This is correlates with greater hemicellulose and cellulose contents found in garden hedge to that of grass clippings, followed by the lowest in woodchip as shown in Chapter 4, Figure 19b.

The product yields obtained from the HTC of woodchip is largely dissimilar to grass and hedge at 150 °C and 200 °C. However, at 250 °C woodchip yields become similar, compare Figure 33a, c and e. On average the reduction rate of solid yield with increasing temperature is highest with woodchip (-0.29 percent per °C), followed by hedge (-0.19 percent per °C) then grass (-0.17 percent per °C). On average the rate of solubilisation of material into the liquid phase with increasing temperature is highest with woodchip (0.28 percent per °C), followed by hedge (0.17 percent per °C) then grass (0.15 percent per °C). The rate of gas production with increasing temperatures remains stable of between 0.01 to 0.02 percent per °C. Therefore, woodchip is more recalcitrant to degradation, followed by hedge then grass, and increasing the severity of HTC reduces the recalcitrant behaviour.

When green waste feedstock is blended with SS digestate for co-processing the yields of hydrochar is increased and the levels of soluble matter into the liquid phase are reduced when compared to the single processing of grass, hedge and woodchip, as shown in Figure 33b, d and f. Co-processing also reduces the rate of gas production, but this is minimal averaging at 0.01 percent per °C.

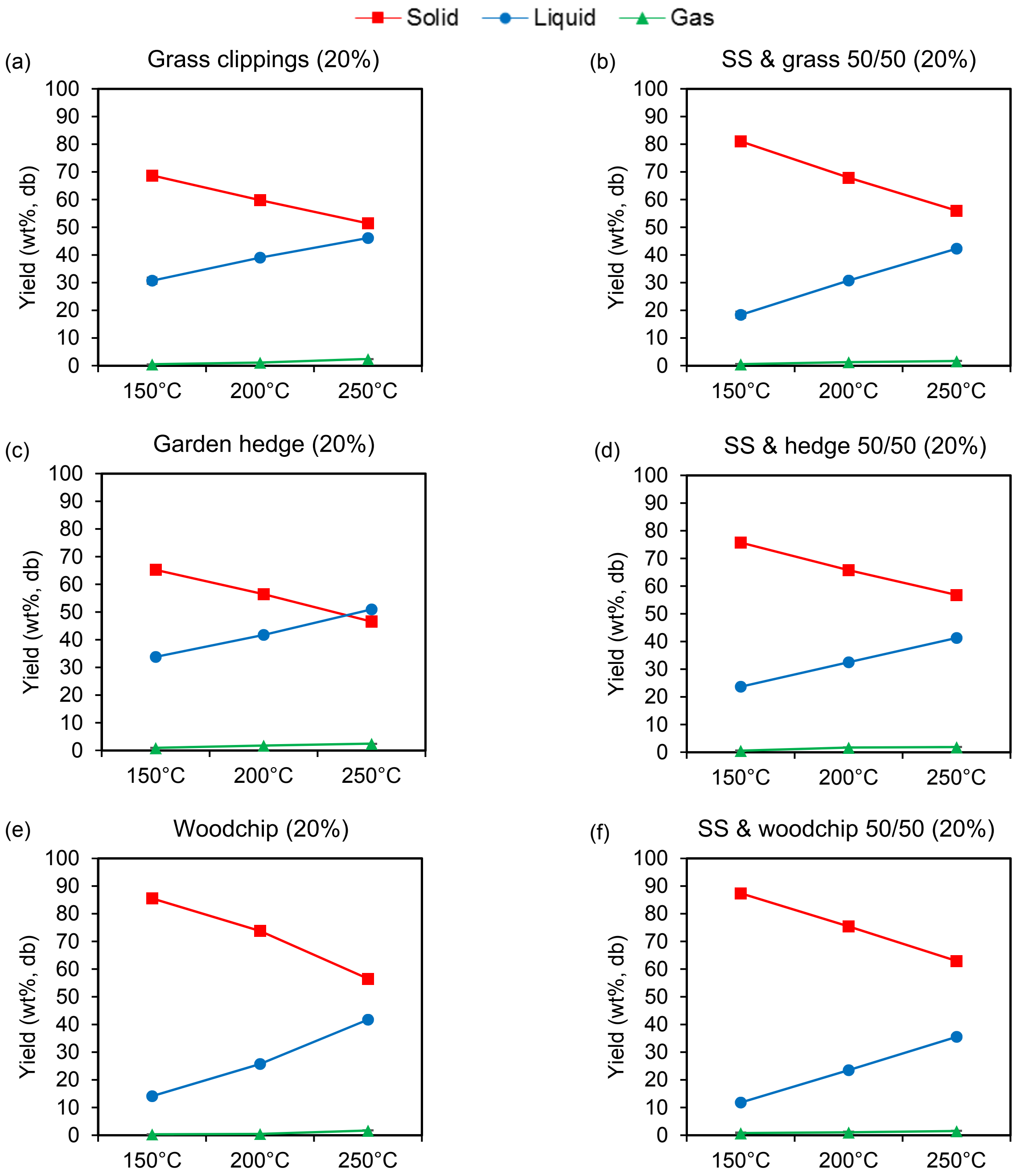

Figure 33. Influence of temperature on product yields at 20 percent loading for **a**) grass clippings, **b**) SS digestate and grass clippings 50/50, **c**) garden hedge, **d**) SS digestate and garden hedge 50/50, **e**) woodchip and **f**) SS digestate and woodchip 50/50 on a dry basis (db), based on duplicate data and error bars represent deviation around the mean.

Figures 34, 35, 36 show the yields of products of 0, 50 and 100 percent blending ratios of SS digestate to the three green wastes to illustrate the effect of blending and HTC co-processing. The effect of blending (at 50 percent) exhibits a linear relationship with the solid and liquid yields. The absolute differences between theoretical and actual yields of the blended feedstocks are listed in Table 19. The only instance where there is a difference between the theoretical and actual yields is exhibited with SS digestate and grass clippings at 250 °C, where solid yields are about 5 percent lower and liquid yields are about 5 percent higher than expected.

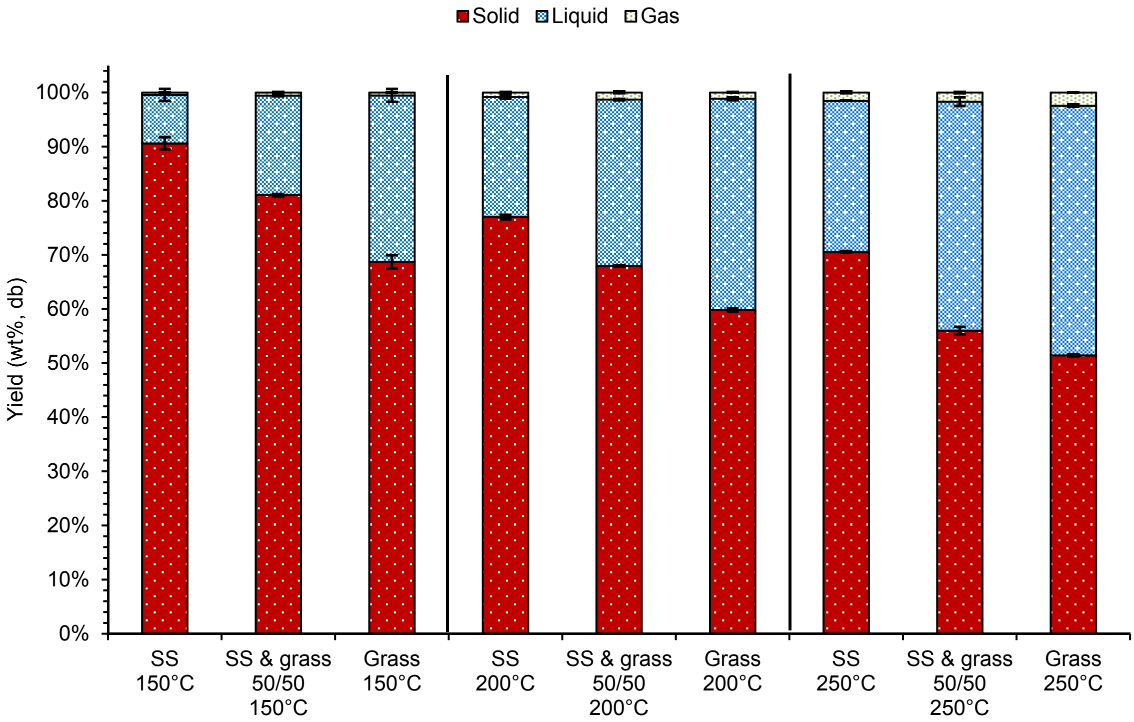

Figure 34. Comparison of the product yields from HTC of SS digestate, grass clippings and their blends.

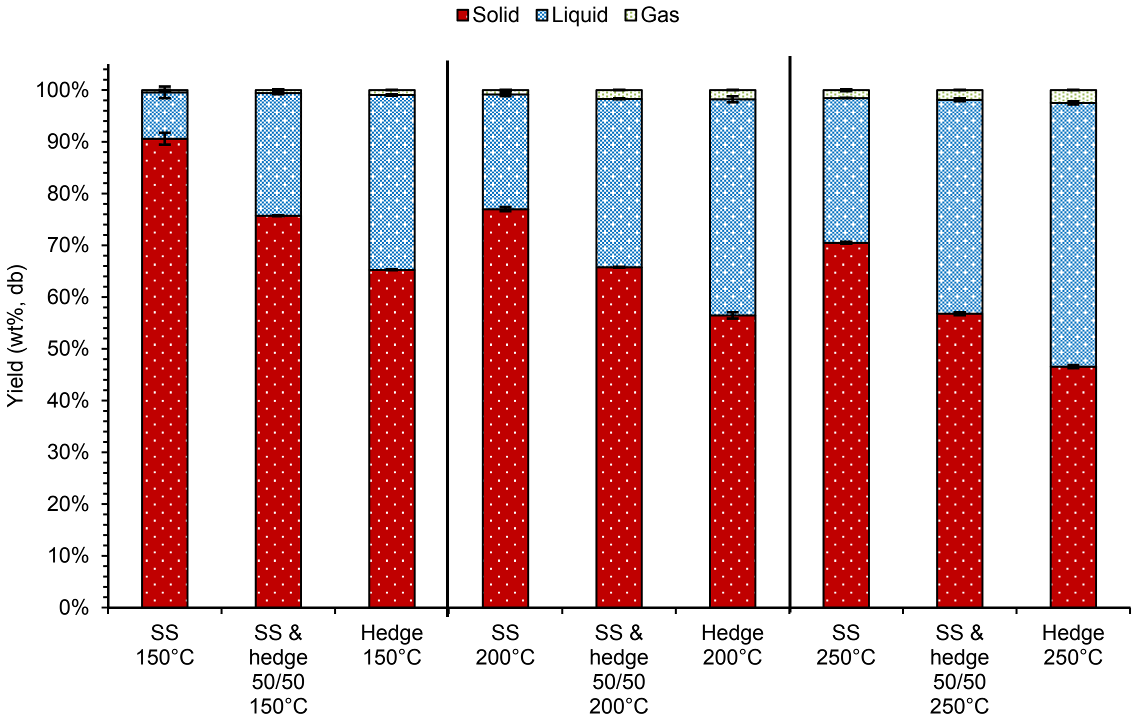

Figure 35. Comparison of the product yields from HTC of SS digestate, garden hedge and their blends.

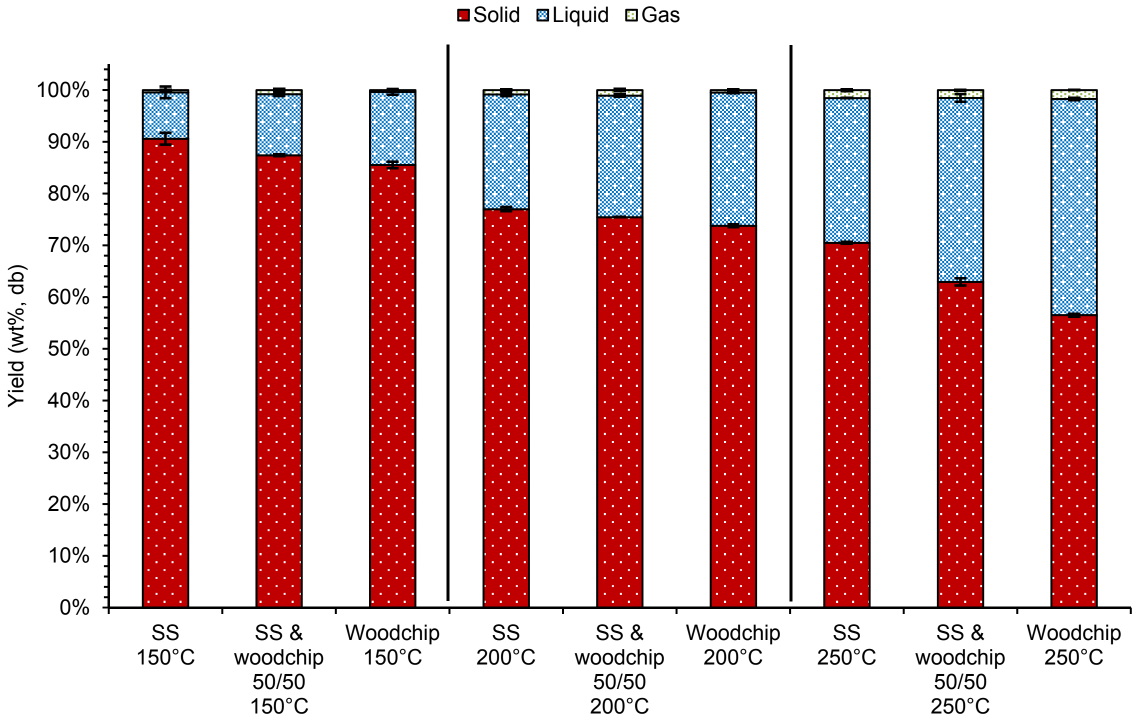

Figure 36. Comparison of the product yields from HTC of SS digestate, woodchips and their blends.

Furthermore, from the point of view of adding of SS digestate to the green waste this increases the average rate of solubilisation with increasing temperature of grass (from 0.15 to 0.24 percent per °C, Figure 34), and with hedge (from 0.14 to 0.18 percent per °C, Figure 35). On the other hand, the average rate of solubilisation of wood chip is decreased (from 0.28 to 0.24 percent per °C, Figure 36). Therefore, this observation suggests that blending SS digestate with grass clippings exhibits an acceleration of solubilisation with increasing temperatures. This could lend itself to a catalytic effect with the combined inorganic composition of SS digestate and grass materials. However, this statement is expressed with low confidence and statistical significance due to the error value associated with both SS digestate and grass clippings product yields processed at 150 °C.

Table 19. Theoretical, actual and absolute difference of product yields following hydrothermal carbonisation of SS digestate and green waste blends.

HTC 50/50 blends	Solid yield (wt%, db)			Liquid yield (wt%, db)			Gas yield (wt%, db)		
	Theoretical	Actual	Absolute difference	Theoretical	Actual	Absolute difference	Theoretical	Actual	Absolute difference
SS & grass 150 °C	79.67	81.04	1.37	19.84	18.38	1.46	0.49	0.57	0.09
SS & grass 200 °C	68.39	67.93	0.47	30.62	30.78	0.16	0.99	1.29	0.31
SS & grass 250 °C	60.96	56.02	4.94	37.05	42.29	5.24	1.99	1.70	0.30
SS & hedge 150 °C	77.92	75.74	2.19	21.38	23.69	2.31	0.69	0.58	0.12
SS & hedge 200 °C	66.72	65.77	0.95	31.97	32.53	0.56	1.31	1.70	0.39
SS & hedge 250 °C	58.52	56.81	1.71	39.47	41.30	1.83	2.00	1.88	0.12
SS & woodchip 150 °C	88.07	87.40	0.67	11.54	11.82	0.28	0.40	0.78	0.39
SS & woodchip 200 °C	75.38	75.43	0.05	23.97	23.51	0.46	0.65	1.06	0.40
SS & woodchip 250 °C	63.51	62.94	0.57	34.87	35.54	0.68	1.62	1.52	0.11

5.4. Chapter limitations

A limitation of this chapter is the retention time used for thermochemical conversion and its effects on the yield of the products. Nevertheless, to compare HTC and pyrolysis using a retention time of one hour is sufficient to see the optimum transformation of the feedstock to obtain stable solid yields of hydrochar [166–168] and pyrochar [169,170] . One hour is also representative of the residence time used in literature to trade-off energy usage and hydrochar quality for efficient HTC operation.

Further understanding of how solid loading affects the HTC yields from feedstock blends is also limited. Only 20 percent solid loading was used for the blends to focus on how blending effects HTC yields. Additionally, the understanding of the different blending ratios effect on yields is also limited (i.e. increased frequency of step changes, for instance 25 and 75 percent ratios). However, this is wider than the scope of the study and is more beneficial when investigating the engineering of product properties for application. Furthermore, this study does not investigate HTC processing with the re-circulated process water (as shown in Figure 25), and its effect on the yields of HTC. This is also out of the scope of this study, however the further study of recirculation effects on the entire integration approach is recommended for whole systems behaviour and analysis.

5.5. Concluding remarks

Performing HTC and pyrolysis on four digestate materials has given an understanding of how the digestate composition, conversion process and process parameters effect product yields. The blending of SS digestate with green wastes has also given an understanding of how HTC co-processing affects product yields.

With a focus on the conversion process, low temperature operation exhibited similar product yields for both HTC and pyrolysis of digestate. At higher process temperatures the solid yields reduced and liquid yields increased for both HTC and pyrolysis. An increase in gas yields with temperature is only exhibited with pyrolysis. For HTC, higher temperature treatment results in increasing organic material solubilised into the water phase. The increased solubilisation with higher temperature is a result of both solubilisation of the biochemical components and the solubilisation of inorganic compounds [99]. Solubilisation of organic material into the water phase creates an opportunity for recycling of the process waters back into anaerobic digestion, potentially increasing biogas yields.

Therefore, depending on the chemical makeup, the process waters generated from HTC of digestate lends itself for AD treatment.

The lower yields of hydrochar obtained at 250 °C indicate that the decarboxylation and dehydration reactions are more favourable. However, higher solid loadings in HTC effects hydrochar yields positively. The increase in hydrochar yields with solid loading can be attributed to the saturation of the process waters and an increase in polymerisation reactions during HTC. Product formation with increasing temperatures is observed to be more linear with HTC than that of pyrolysis, however this cannot be said with confidence due to the different range of temperatures used. Pyrolysis generated greater levels of gaseous products, whilst HTC generated greater liquid yields. With that said, at higher HTC temperatures (250 °C) the solid and liquid phase yields are comparable to that of pyrolysis also at higher temperatures (600 °C). When digestate is pyrolysed most of the transformation of occurs before 400 °C, little difference to yields are made when over processing over 400 °C. Pyrolysis is advantageous for the reduction of digestate volume as most of the material is converted into a gas phase. However, pyrolysis is less environmentally friendly as gasses that are flued still contain polluting emissions, even after clean up.

With a focus on the behaviour of digestate during processing, the AGR and SS digestate degrades more rapidly than MSW and VGF, thus creating high liquid and gas yields in both HTC and pyrolysis. MSW experiences the least amount of liquid yields, especially with pyrolysis, therefore this material would not be beneficial for the integration of pyrolysis or HTC with AD to maximise biogas generation. With increasing process temperatures, AGR exhibits the lowest char yields followed by SS, VGF and MSW digestate for both HTC and pyrolysis. Therefore AGR digestate has a high propensity for volume reduction via thermochemical conversion to improve material management.

The processing of green waste feedstock by HTC has shown that the degradation of woodchip at high temperature HTC results in similar product yields to that of other green wastes and AGR digestate, due to their large lignocellulosic content. This can be attributed to high lignin fractions found this these particular feedstocks by which lignin degrades at high temperatures. Lignin degrades between 220 °C and 260 °C, which contributes to the increase in solubilisation with temperature.

The effect of blending in the HTC co-processing of feedstocks made little or no difference to the theoretical yields. SS digestate and grass clippings, however, is the exception, where a small catalytic effect is shown. The effect of blending feedstocks and HTC co-processing will be more apparent in the analysis of product properties and their subsequent application. For that reason, the next chapter will characterise the chemical composition of the solid products (hydrochar and pyrochar) and liquid products (HTC process waters) and understand the influence from feedstock composition and process variables.

CHAPTER VI

Characterisation of Products: Hydrochar, Pyrochar and HTC Process Water Composition

To successfully scale up the integration of thermochemical processes with AD it is necessary to understand how biomass feedstock behaves during conversion for effective product application. Any variation in the system will affect productivity and overall system efficiency. Barriers to system efficiency and effectiveness include irregularity in the chemical and physical properties of biomass and their effect, including operating parameters, on chemical reactions and product properties for application. Furthermore, physio-chemical properties such as moisture content, acidity, density, heating value and stability are important in term of its storage, utilisation, and handling of products.

6.1. Overview

The aim of this chapter is to understand the effect of feedstock composition, including HTC and pyrolysis operating variables on product properties. All the results from the characterisation experiments outlined in Chapter 3, section 3.2 are presented and examined in detail.

The objectives of this chapter are to:

- Highlight the gaps in literature for similar studies.
- Compare the effect of feedstock composition and process variables of the solid properties from HTC and pyrolysis and HTC liquid properties from the treatment of the four digestate feedstocks.
- Compare the effect of feedstock composition and process variables of HTC on solid and liquid product properties from the treatment of SS digestate blended with three green waste feedstocks.

6.2. Introduction

Pyrolysis and HTC thermochemical technologies have been identified as potential conversion routes for digestate enhancement, but their system efficiency and product effectiveness requires further investigation in order for successful large-scale industrial implementation. Most issues of system efficiency and product effectiveness arise from feedstock materials used for the processes, especially if they are complex biomass.

The pyrolysis conversion of digestate, a complex biomass, has been studied but remains a challenge due to high ash and high nitrogen contents of this feedstock resulting in high ash pyrochar [82,143,158] and pyrolysis liquids high in heterocyclic nitrogen [28,171,172] which are problematic in application. While some studies show that pyrochar from anaerobically digested sewage sludge contains high levels of mineral matter and plant nutrients [173,174], there is uncertainty with other biomass pyrochar as to whether they are effective in agricultural application, specifically whether nutrients levels are readily or crop available (i.e., bioavailable) when added to soils [82]. There are also uncertainties regarding the eco-toxicity of digestate derived pyrolysis liquids [175]. Furthermore, uncertainties for the application of both pyrochar and hydrochar from other biomass feedstock also exist [176,177].

The HTC of biomass typically results in energy densification, resulting in a hydrochar with a higher calorific value than the starting material [78]. This can typically increase the higher heating value (HHV) from around 15 to 17 MJ/kg on a dry basis for the starting biomass to an energy densification up to 1.5 [178,179], and as high as 30 MJ/kg for the hydrochar [168,180,181].

Demineralisation also occurs, improving the ash chemistry of the biomass which reduces the propensity for slagging and fouling during combustion for greater biomas boiler performance [99,168,179]. Hydrochar has an increased hydrophobicity which enhances dewatering and is highly friable, meaning it can be ground more easily than the starting biomass, improving its handling properties [182]. Hydrochar has also been shown to have improved combustion properties compared to its pyrochar equivalent [177,183], largely due to its reduced mineral content.

HTC is therefore a potential route for digestate enhancement, although energy densification is not always observed with all feedstocks. Sewage sludge for instance generally results in a low calorific value (CV) hydrochar, whereas feedstocks containing higher biochemical content generally produce a higher CV hydrochar [184]. Solubilisation of organic material into the water phase creates an opportunity for recycling of the process waters back into anaerobic digestion, potentially increasing biogas yields. The process waters from HTC are rich in dissolved organics and can facilitate nutrient and chemical recovery [73,75,78]. However, the HTC of high ash and complex biomass and product application still remains a challenge similar to that in pyrolysis and requires further investigation.

Table 20 shows the typical chemical properties of hydrochar produced from solid digestate, green wastes and blended materials and Table 21 shows the typical chemical properties for pyrochar produced from solid digestate. Data has been acquired from the studies identified in the previous chapters to match the process conditions applied in this study to aid in comparison.

Table 20 shows that the HHV of hydrochar from digestate material is typically lower (average of 15.3 MJ/kg) than that of green wastes and blended materials (average of 20.2 and 19.1 MJ/kg respectively) due to the differences in lignin and fixed carbon content, as described previously. Table 21 shows that there is limited data available on the calorific value of digestate pyrochar produced from similar operating parameters of this study.

The ash content of hydrochar in the literature varies from low as 9.6 to as high as 81.4 percent. Specifically, the average ash content of hydrochar generated from digestate is 47.6 percent, 6.1 percent for from green wastes and 28.8 percent from blended materials. Digestate pyrochar ash content also varies from 7.7 to as high as 55.1 percent, with an average of 24.1 percent. The carbon content is similar for both hydrochar a pyrochar generated from digestate (average of 35.2 and 37.9 percent respectively).

Green waste and blend hydrochar exhibit greater carbon content than that of digestate hydrochar (average of 51.4 and 50.6 percent respectively). The greater carbon and energy density of the green wastes and blends compared to the digestate hydrochar is attributed to the biochemical composition, in particular the increased levels of lignin found in green wastes which boosts the calorific value of hydrochar when co-processed. The data shows that an increase of temperature increases the calorific value and carbon content of the resultant pyrolysis and HTC chars.

Table 20. Hydrochar properties from the HTC of solid digestate, green waste and blended materials found in literature.

Hydrochar feedstock	Proximate and ultimate analysis (wt%, db)								HHV (MJ/kg, db)	Reference
	VM	FC	Ash	C	H	N	S	O^a		
HTC of solid digestate										
Sewage sludge	20.6	0.7	78.3	12.0	1.8	1.0	0.2	6.6	5.5	[111]
	17.4	1.1	81.4	10.0	1.4	0.6	0.2	6.4	4.3	
Sewage sludge	-	-	74.8	14.0	1.4	0.5	0.1	9.3	9.1	[99]
	-	-	72.2	22.5	1.8	0.7	0.0	7.1	7.7	
Sewage sludge + MSW	-	-	38.2	35.5	-	3.9	-	-	-	[113]
	-	-	44.0	35.4	-	3.0	-	-	-	
Corn, manure	-	-	9.6	55.2	7.1	1.9	0.7	35.2	24.1	[120]
	-	-	13.4	62.1	6.8	2.3	0.7	28.1	26.8	
	-	-	16.7	69.8	6.4	3.2	0.8	19.8	29.9	
Green waste										
Woodchip	-	-	-	48.7	6.2	0.1	-	44.9	17.3	[125]
Fallen leaves and deadwood	-	-	-	-	-	-	-	-	19.9	[126]
	-	-	-	-	-	-	-	-	21.0	
	-	-	-	-	-	-	-	-	23.0	
Tree, bushes and bamboo	76.4	16.2	7.4	47.8	6.4	0.8	-	37.6	13.4	[127]
	73.9	19.7	6.4	51.3	6.5	0.8	-	35.1	20.3	
	72.1	23.8	4.7	53.3	6.4	0.6	-	35.0	22.0	
	64.5	30.0	5.5	61.6	6.3	0.9	-	25.7	25.1	
Lawn grass	-	-	-	-	-	-	-	-	-	[128]
	-	-	-	-	-	-	-	-	-	
Grass	-	-	14.5	47.4	-	2.3	-	-	-	[115]
Straw	-	-	2.6	49.6	-	0.4	-	-	-	
Woochip	-	-	1.9	51.6	-	0.2	-	-	-	
50/50 blends										
Swine manure & saw dust	67.4	19.7	12.9	-	-	-	-	-	23.3	[152]
Swine manure & corn stalk	68.0	19.3	13.4	-	-	-	-	-	23.8	
Sludge & sawdust	55.8	17.0	27.2	41.1	4.7	2.2	0.3	24.6	16.2	[153]
Food waste & sawdust	78.5	11.3	10.2	53.2	6.6	0.9	-	39.4	19.1	[154]
	60.3	30.4	9.3	60.9	6.1	1.4	-	31.6	22.5	
	45.4	47.8	6.7	68.6	6.3	1.3	-	23.7	26.8	
Sludge & sawdust	58.2	14.6	27.2	3.4^b	4.2^b	3.0^b	0.6^b	26.5^b	13.5^b	[155]
	36.2	15.8	48.0	40.7^b	3.8^b	2.6^b	0.5^b	4.4^b	17.8^b	
Sludge & corncob	44.2	22.1	33.7	48.4^b	4.9^b	3.4^b	0.7^b	9.0^b	20.9^b	
	40.0	23.7	36.4	50.1^b	4.9^b	3.3^b	0.6^b	4.7^b	22.2	
Sludge & cornstalk	47.5	13.4	39.2	37.2^b	4.0^b	3.0^b	0.7^b	16.0^b	14.7^b	
	37.5	14.5	48.1	37.5^b	3.7^b	2.5^b	0.6^b	7.7^b	15.9^b	
Sludge & rape straw	56.8	10.2	33.1	39.0^b	5.3^b	2.9^b	0.6^b	19.1^b	16.4^b	
	47.0	10.9	42.1	39.4^b	4.6^b	2.9^b	0.5^b	10.5^b	17.2^b	
Sludge & pine sawdust	64.6	22.6	12.8	50.9	5.6	2.7	-	27.2	-	[156]
Sludge & food waste	45.4	15.0	39.7	42.2	5.0	2.7	0.2	10.3	18.7	[157]
	36.2	14.3	49.5	37.1	4.1	2.6	0.1	6.6	16.0	

^{a}, calculated by difference; ^{b}, dry ash free

Table 21. Pyrochar properties from the pyrolysis of solid digestate materials found in literature.

Pyrochar feedstock	Proximate and ultimate analysis (wt%, db)								HHV (MJ/kg, db)	Reference
	VM	FC	Ash	C	H	N	S	O[a]		
Solid digestate										
Food waste	12.6	32.3	55.1	35.3	1.2	4.0	0.5	3.9	13.0	[143]
Groats, olive, silage and manure	91.0	1.3	7.7	42.5	6.1	1.4	0.1	42.1	-	[82]
Manure, maize and cereal	89.5	1.0	9.5	43.0	6.2	1.3	0.1	39.5	-	
Sugar beet	-	-	-	30.8	1.4	2.7	0.5	39.9	-	[160]

[a], calculated by difference; [b], dry ash free

Table 22 shows the liquid properties from the HTC of solid digestate, green wastes and blended materials from the studies identified in Table 20. Limited data is given on the properties of the process waters as much of the studies have focused on the characteristics of the solid materials and their application. In general, the pH of the process waters are acidic. HTC process waters from digestate are slightly less acidic to those from green wastes. No pH data is available on the process waters from blended materials. The data available on the process waters generated from similar materials and operating parameters used in this study is lacking in the literature, in particular the TN, TOC, COD, VFA and phenolic content. These analytes provide useful information on the biodegradability and inhibition mechanisms experienced during anaerobic digestion.

Table 22. Liquid properties from the HTC of solid digestates, green wastes and blended materials found in literature.

Process water feedstock	pH	TN (g/L)	TOC (g/L)	C:N ratio	COD (g/L)	Total VFA (g/L)	Total phenols (g/L)	Reference
HTC of solid digestate								
Sewage sludge	5.1	19.56	65.74	3.36	-	-	-	[111]
	7.7	18.61	62.35	3.35	-	-	-	
Corn, manure	4.8	-	-	-	-	-	b.d	[120]
	4.4	-	-	-	-	-	b.d	
	4.4	-	-	-	-	-	0.02	
Green waste								
Grass	5.7	15.50	1.40	-	-	-	-	[115]
Straw	4.4	15.10	5.00	-	-	-	-	
Woodchips	3.9	0.26	5.70	-	-	-	-	

[a], calculated by difference; b.d, below detection limit

There are substantial gaps in the literature; little has been done to compare a number of digestate materials and the effects of both feedstock on the one hand and HTC and pyrolysis parameters on the other hand on the product properties. Whilst comparison of a number of blend materials has been reported via HTC, albeit not with digestate, there currently lacks any investigation on chemical properties of the process waters generated from co-processing. The hydrochar and pyrochar composition through proximate and elemental analysis is usually well documented, however inorganic analysis is also missing.

Again, there is a lack of data available on the process waters of digestate, and green waste or blends that are similar to the experimental design in this study.

In this chapter, the hydrochar, pyrochar and HTC process water will be characterised for their chemical composition. Outcomes of this chapter will aid in the understanding of how HTC process conditions, such as solid loading and temperature, including pyrolysis affect product composition and properties of the hydrochar and process waters, and how they are utilised for application in subsequent chapters. Additionally, the outcomes of this chapter will explore the potential benefits of blending digestate with other feedstocks containing lignocellulosic biomass as this may increase the calorific value of the resulting hydrochar and allow more recalcitrant biomass to be treated for biogas generation.

6.3. Results and discussion

The thermochemical conversion products generated in this study will be characterised for their chemical composition. This will aid in understanding the influence of feedstock and HTC and pyrolysis operating variables on product variability.

6.3.1. Digestate conversion products

Following the structure of previous chapters, initially the focus will be on the composition of the products from HTC with comparison with the pyrolysis of digestate, to give a comparison between enhancement methods and give a baseline for the proposed integration concept.

6.3.1.1. Hydrochar analysis

Hydrochar obtained from the HTC of digestate material will be discussed in terms of its proximate and ultimate analysis, energy density and inorganic composition against the operating parameters of temperature and solid loading.

6.3.1.1.1. Proximate, ultimate analysis and energy density

The proximate, ultimate analysis, including higher heating value and H:C and O:C atomic ratios for digestate hydrochar are listed in Table 23. The values agree with the chemical composition data found in the literature and the accuracy is good, generally within ± 2 percent.

Table 23. Ultimate, proximate, and heating analysis of solid digestate hydrochar.

Digestate hydrochar	Ultimate analysis (wt%, db)					Proximate analysis (wt%, db)			HHV (MJ/kg, db)	H/C (daf)	O/C (daf)
	C	H	N	S	O^a	VM	FC	Ash^a			
AGR digestate											
150 °C at 20%	44.2 ± 1.9	4.8 ± 0.3	3.1 ± 0.1	0.0 ± 0.0	27.5 ± 0.5	62.2 ± 3.2	17.5 ± 0.6	20.4 ± 2.7	17.9	1.29	0.47
200 °C at 10%	52.0 ± 0.4	6.9 ± 1.4	3.1 ± 0.5	0.1 ± 0.1	23.1 ± 3.5	69.4 ± 1.5	15.9 ± 2.8	14.7 ± 1.4	21.6	1.59	0.33
200 °C at 20%	50.8 ± 0.8	6.0 ± 0.7	3.3 ± 0.5	0.1 ± 0.1	24.4 ± 3.3	67.4 ± 0.5	17.3 ± 1.9	15.3 ± 1.4	20.7	1.40	0.36
200 °C at 30%	51.2 ± 1.2	6.1 ± 0.5	3.5 ± 0.2	0.0 ± 0.0	22.8 ± 2.5	66.7 ± 0.3	17.0 ± 1.3	16.3 ± 1.0	20.9	1.42	0.33
250 °C at 10%	57.3 ± 1.4	6.3 ± 1.1	3.6 ± 0.3	0.2 ± 0.0	11.5 ± 1.9	56.7 ± 0.1	22.3 ± 0.9	21.0 ± 0.8	24.0	1.32	0.15
250 °C at 20%	57.1 ± 1.4	6.6 ± 1.5	3.9 ± 0.3	0.2 ± 0.0	12.0 ± 3.1	58.2 ± 0.0	21.6 ± 0.1	20.2 ± 0.1	24.2	1.39	0.16
250 °C at 30%	56.7 ± 0.4	5.8 ± 0.4	3.8 ± 0.0	0.3 ± 0.0	12.7 ± 0.7	56.2 ± 0.8	23.1 ± 0.9	20.7 ± 0.1	23.3	1.21	0.17
MSW digestate											
150 °C at 20%	23.8 ± 1.7	2.1 ± 0.3	1.2 ± 0.1	0.0 ± 0.0	19.0 ± 4.5	39.4 ± 6.8	6.6 ± 0.5	54.0 ± 6.3	15.2	1.04	0.60
200 °C at 10%	22.6 ± 0.1	1.6 ± 0.0	0.7 ± 0.0	0.1 ± 0.1	11.7 ± 1.7	32.0 ± 2.3	4.7 ± 0.9	63.4 ± 1.5	15.5	0.85	0.39
200 °C at 20%	21.4 ± 0.2	1.6 ± 0.0	0.9 ± 0.0	0.1 ± 0.0	13.9 ± 0.1	32.3 ± 0.8	5.6 ± 0.7	62.1 ± 0.1	15.6	0.87	0.49
200 °C at 30%	24.0 ± 1.4	1.8 ± 0.1	0.9 ± 0.0	0.1 ± 0.0	12.2 ± 0.4	32.4 ± 1.0	6.5 ± 0.2	61.1 ± 1.2	15.4	0.90	0.38
250 °C at 10%	23.0 ± 2.8	1.6 ± 0.2	0.7 ± 0.1	0.2 ± 0.2	9.7 ± 2.0	28.3 ± 4.6	6.9 ± 0.7	64.9 ± 5.3	15.6	0.83	0.32
250 °C at 20%	21.7 ± 1.5	1.6 ± 0.1	0.8 ± 0.0	0.0 ± 0.0	7.9 ± 0.3	25.7 ± 3.1	6.3 ± 1.2	68.0 ± 2.0	15.6	0.88	0.28
250 °C at 30%	23.4 ± 0.7	1.7 ± 0.0	0.9 ± 0.0	0.0 ± 0.0	7.8 ± 0.9	26.9 ± 0.2	6.8 ± 0.4	66.3 ± 0.2	15.5	0.85	0.25
SS digestate											
150 °C at 20%	33.4 ± 1.8	4.4 ± 0.6	3.2 ± 0.2	0.3 ± 0.1	15.0 ± 2.3	50.5 ± 4.7	5.7 ± 0.2	43.8 ± 4.9	15.0	1.56	0.34
200 °C at 10%	34.0 ± 1.2	4.2 ± 0.2	2.1 ± 0.0	0.8 ± 0.1	13.0 ± 1.0	47.9 ± 0.5	6.1 ± 0.0	46.0 ± 0.4	15.0	1.48	0.29
200 °C at 20%	34.0 ± 1.1	4.2 ± 0.2	2.4 ± 0.1	0.9 ± 0.1	14.0 ± 0.6	49.1 ± 0.9	6.5 ± 0.2	44.4 ± 0.7	15.1	1.47	0.31
200 °C at 30%	35.2 ± 0.7	4.4 ± 0.1	2.9 ± 0.0	1.2 ± 0.0	12.7 ± 0.1	49.4 ± 0.8	6.9 ± 0.1	43.7 ± 0.9	15.4	1.48	0.27
250 °C at 10%	34.4 ± 0.3	4.0 ± 0.2	2.2 ± 0.2	0.8 ± 0.0	9.2 ± 0.7	44.3 ± 0.6	6.2 ± 0.3	49.5 ± 0.9	15.2	1.39	0.20
250 °C at 20%	34.7 ± 0.4	4.1 ± 0.0	2.4 ± 0.1	0.7 ± 0.3	10.6 ± 0.6	45.9 ± 0.5	6.6 ± 0.2	47.5 ± 0.3	15.3	1.42	0.23
250 °C at 30%	36.4 ± 0.8	4.3 ± 0.1	2.8 ± 0.0	0.9 ± 0.3	9.0 ± 0.7	46.6 ± 0.6	6.8 ± 0.0	46.6 ± 0.6	15.7	1.40	0.19
VGF digestate											
150 °C at 20%	29.7 ± 1.8	3.0 ± 0.1	1.9 ± 0.1	0.0 ± 0.0	12.2 ± 1.2	37.6 ± 0.7	9.3 ± 0.0	53.1 ± 0.7	15.0	1.22	0.31
200 °C at 10%	26.3 ± 1.6	2.7 ± 0.2	1.1 ± 0.0	0.2 ± 0.0	14.4 ± 3.2	37.5 ± 0.7	7.2 ± 0.7	55.3 ± 1.4	14.8	1.22	0.41
200 °C at 20%	32.2 ± 1.9	3.3 ± 0.2	1.5 ± 0.1	0.3 ± 0.0	13.3 ± 0.0	41.7 ± 1.5	9.0 ± 0.7	49.4 ± 2.3	15.1	1.23	0.31
200 °C at 30%	30.4 ± 1.5	3.1 ± 0.1	1.4 ± 0.1	0.2 ± 0.0	12.5 ± 1.3	39.3 ± 1.8	8.4 ± 1.1	52.3 ± 3.0	14.9	1.23	0.31
250 °C at 10%	26.4 ± 0.6	2.6 ± 0.1	1.2 ± 0.1	0.1 ± 0.1	8.3 ± 0.1	30.4 ± 0.6	8.2 ± 0.1	61.3 ± 0.7	14.8	1.17	0.24
250 °C at 20%	27.8 ± 0.7	2.7 ± 0.0	1.4 ± 0.0	0.1 ± 0.1	9.0 ± 1.6	31.7 ± 1.7	9.2 ± 0.7	59.0 ± 2.4	14.9	1.14	0.24
250 °C at 30%	29.1 ± 2.1	2.9 ± 0.4	1.5 ± 0.2	0.1 ± 0.1	5.4 ± 1.5	30.4 ± 0.4	8.6 ± 0.7	61.0 ± 1.1	15.0	1.17	0.14

^{a}, calculated by difference; ^{b}, calculated according to Equation (1)

Figure 37a, b, c and d illustrates normalised C, H, N, O and ash content, including energy densification of AGR, MSW, SS and VGF digestates along with the resultant hydrochar plotted against increasing HTC temperature and solid loading. Normalisation has been performed so that the composition is equal to the solid yields of hydrochar and to aid in the fate of elemental composition. Normalisation was calculated by the masses of C, H, N and O of the hydrochar divided by the mass of the initial feedstock.

Elemental composition of the hydrochar produced at all three temperatures show an increase of carbon and decrease of oxygen content compared to the raw feedstock. These results show that the decrease of solid mass yields with increasing temperature was caused largely by the mass loss of oxygen i.e. deoxygenation. This trend has also been observed in the literature [128,179]. The reduction of oxygen mass is accompanied by increases of carbon and hydrogen content. The largest increase in carbon is seen with AGR digestate from 44.2 percent at 150 °C to 57.1 percent at 250 °C. Therefore, the rate of reaction for deoxygenation increases with higher temperatures.

The removal of oxygen and increase in carbon and hydrogen promotes energy densification. Only a subtle increase of energy densification is shown with MSW, SS and VGF (less than a factor of 1.1), whilst AGR digestate processed at 250 °C densifies up to a factor of 1.4, with an increase of HHV from 17.9 MJ/kg at 150 °C to 24.2 MJ/kg at 250 °C. Some sewage sludge products, such as primary sludge and digestate that are generated without thermal pre-treatment methods can produce higher degrees of energy densification [112], but it is still generally low compared to lignocellulosic derived feedstocks. AGR digestate contains the largest lignin content and the lowest ash content which explains the significant energy densification. Energy densification is not observed for the other digestate samples largely due to the high ash content. Additionally, AGR digestate hydrochar has resulted in the greatest volatile matter content as shown in Table 23. This may be from the lignocellulosic content promoting re-adsorption of volatile fragments absorbed in the process water onto the surface of the char, which remains when separating the products for analysis after HTC.

The increase in solid loading at both 200 °C and 250 °C also corresponds to a higher carbon content in the hydrochar and a slight increase in HHV (Table 23). This slight increase in HHV with solid loading, however, does not promote a substantial change in energy densification at both temperatures, largely due to the retention of ash content. In the case of the SS digestate, there was a significant increase in water soluble products with increasing temperature and solid loading as discussed later, as a result this was not accompanied by an energy densification in the hydrochar. The nitrogen content of the hydrochar also increase with solid loading, as does the overall ash content of the chars. Generally, increasing the solid loading reduces the volatile matter in the hydrochar with a corresponding increase in fixed carbon (Table 23). Therefore, this observation points to the solubilisation of the volatile matter as highlighted before and this will be discussed in section 6.3.1.4.

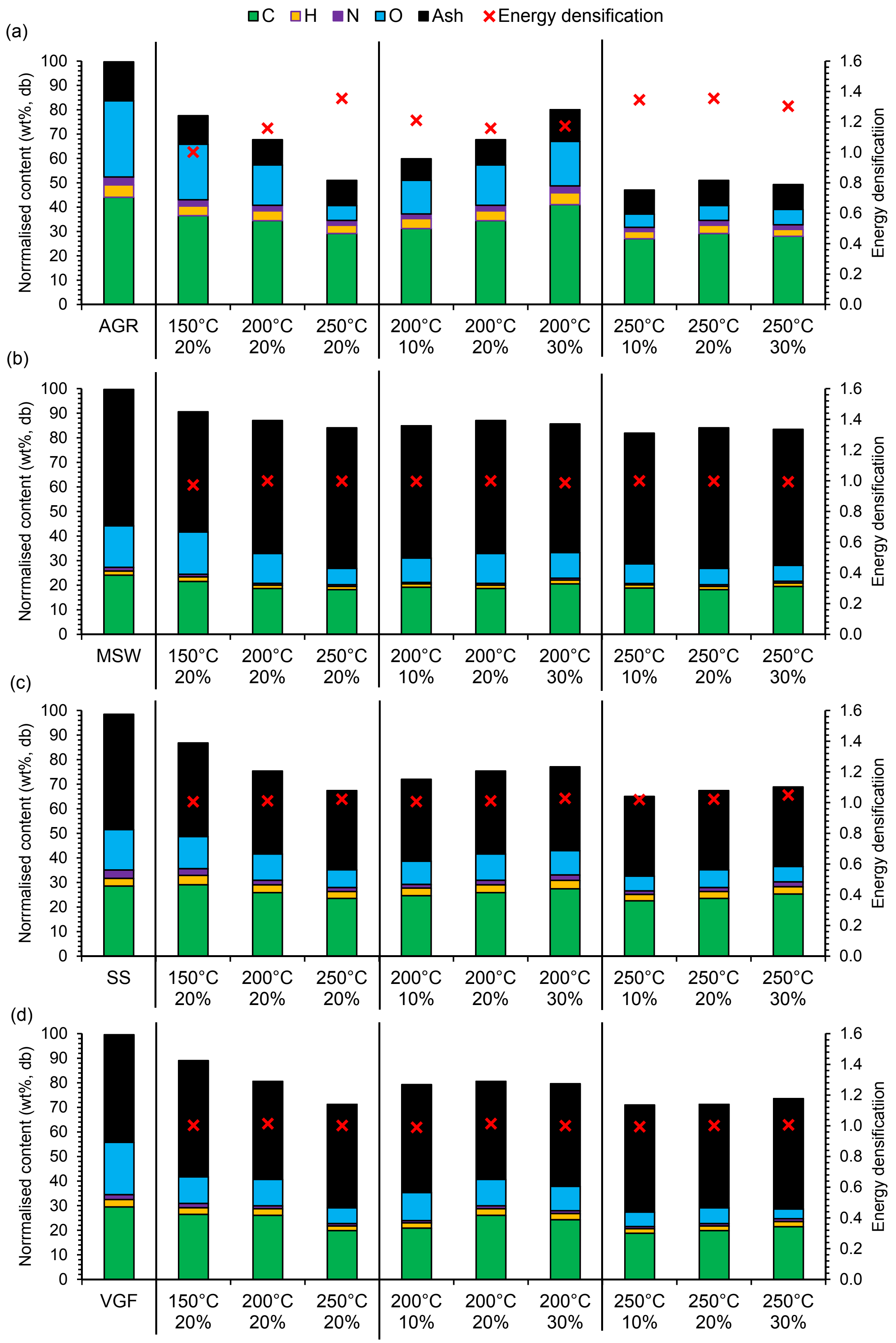

Figure 37. Normalised C, H, N, O and ash content, including energy densification of **a**) AGR, **b**) MSW, **c**) SS and **d**) VGF feedstock and respective hydrochar against increasing HTC temperature and solid loadings.

6.3.1.1.2. Inorganic analysis

Table 24 lists the major ash forming elements found in the digestate hydrochar. The major inorganic constituents of the digestate hydrochar are silica and calcium followed by iron.

Table 24. Inorganic analysis of the solid digestate hydrochar.

Digestate hydrochar	Inorganic analysis (wt%, db)							
	Na	**Mg**	**Al**	**Si**	**P**	**K**	**Ca**	**Fe**
AGR digestate								
150 °C at 20%	0.34	0.97	0.14	2.59	1.55	2.90	2.12	0.79
200 °C at 10%	0.27	0.50	0.14	2.27	1.17	1.13	1.71	0.68
200 °C at 20%	0.24	0.59	0.11	2.21	1.15	1.75	1.60	0.60
200 °C at 30%	0.26	0.65	0.12	2.17	1.24	2.03	1.72	0.66
250 °C at 10%	0.22	1.14	0.18	2.97	1.98	0.75	2.83	1.09
250 °C at 20%	0.14	0.99	0.16	3.33	1.69	1.02	2.34	0.95
250 °C at 30%	0.10	1.09	0.15	3.36	1.81	1.04	2.47	0.90
MSW digestate								
150 °C at 20%	0.55	1.48	2.30	7.03	0.95	0.91	14.85	3.60
200 °C at 10%	0.58	1.65	2.91	10.93	0.96	1.41	13.91	3.62
200 °C at 20%	0.52	1.69	2.96	10.33	1.11	1.11	13.53	3.85
200 °C at 30%	0.57	1.63	2.95	10.01	1.05	1.12	13.42	3.84
250 °C at 10%	0.47	1.75	2.80	8.92	1.18	0.86	17.57	4.10
250 °C at 20%	0.32	1.57	4.67	12.15	3.62	1.01	5.43	4.46
250 °C at 30%	0.92	1.65	3.16	13.46	0.90	1.34	11.92	3.42
SS digestate								
150 °C at 20%	0.38	0.96	3.11	8.40	2.12	0.70	3.26	2.48
200 °C at 10%	0.22	0.99	3.29	8.90	2.25	0.72	3.32	2.78
200 °C at 20%	0.25	0.94	3.03	8.40	2.31	0.67	3.37	2.73
200 °C at 30%	0.38	0.95	2.98	8.32	2.16	0.72	3.22	2.58
250 °C at 10%	0.58	1.19	2.28	9.72	0.73	0.93	9.45	2.59
250 °C at 20%	0.41	1.07	3.30	8.81	2.47	0.74	3.66	2.84
250 °C at 30%	0.23	1.07	3.21	8.77	2.38	0.73	3.52	2.75
VGF digestate								
150 °C at 20%	0.62	1.08	1.96	13.51	1.03	1.05	7.15	1.66
200 °C at 10%	0.26	0.83	1.93	16.12	0.96	0.72	5.83	1.67
200 °C at 20%	0.22	0.84	1.84	13.45	0.93	0.83	5.73	1.58
200 °C at 30%	1.23	0.88	1.85	14.25	0.83	0.91	5.56	1.43
250 °C at 10%	0.50	0.99	2.09	18.21	0.94	0.87	5.88	1.79
250 °C at 20%	0.29	1.03	2.03	17.06	0.92	0.78	6.38	1.82
250 °C at 30%	0.60	1.05	2.17	17.26	1.01	0.92	6.42	1.90

Figure 38 illustrates the fate of the inorganics, described as the percentage of the inorganics remaining in the solid yield after HTC treatment of the feedstock. In general, HTC treatment is seen to reduce the mass of ash and this effect is greater with increasing temperatures as shown in Figure 38a, d, g and j. The rate of reduction and specific removal of inorganics is feedstock dependent. Magnesium, aluminium, silica, phosphorous is not affected by HTC treatment, nor does increasing temperatures affect the removal of these particular inorganics.

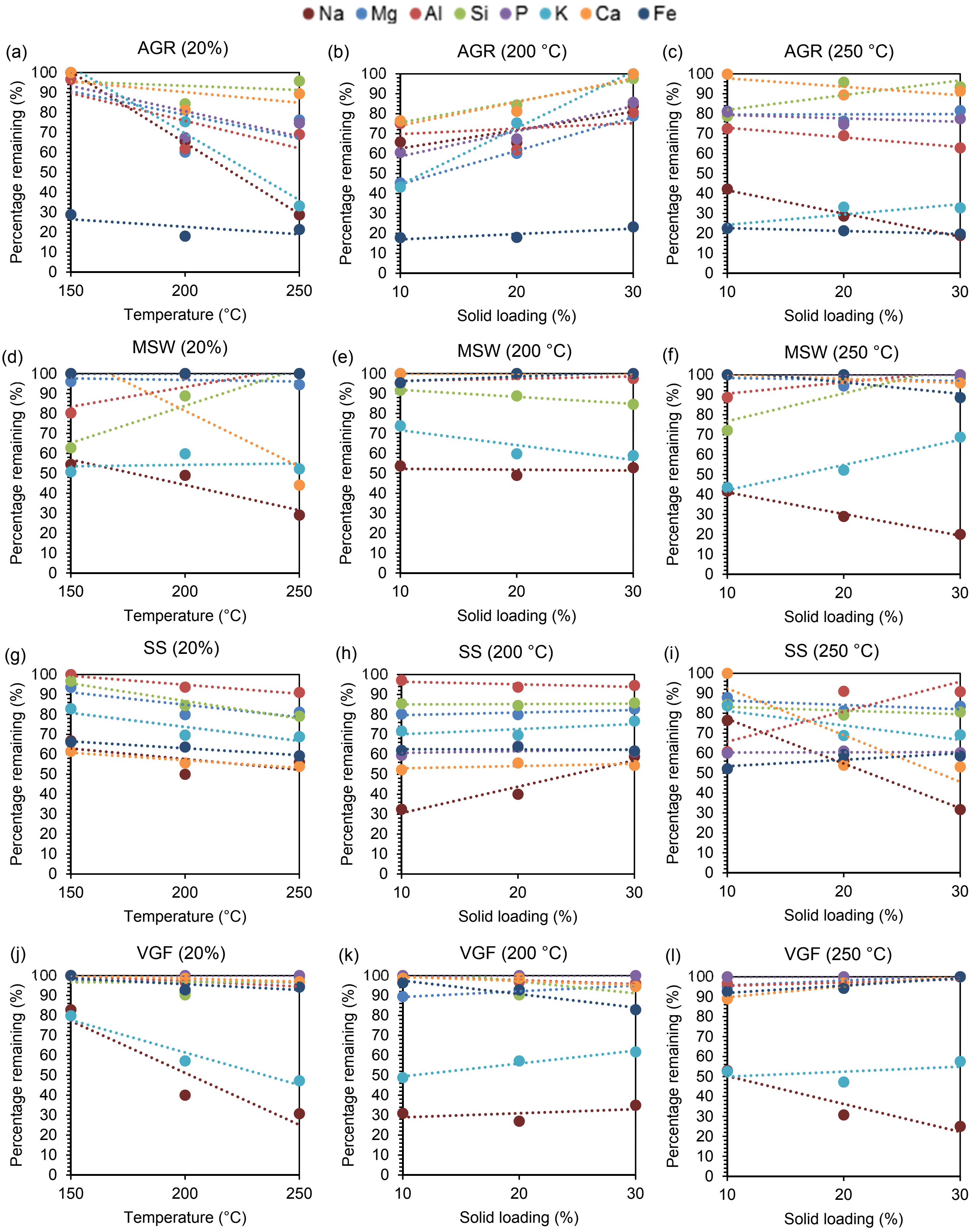

Figure 38. Fate of inorganics against HTC temperature, solid loading at both 200 °C and 250 °C for AGR **a**), **b**) and **c**), MSW **d**), **e**) and **f**), SS **g**), **h**) and **i**), and VGF **j**), **k**) and **l**) respectively.

HTC treatment does however reduce the iron, sodium, potassium and calcium content across all digestate materials. At 150 °C AGR digestate exhibits a reduction of up to 70 percent of iron, MSW exhibits a reduction of up to 50 percent for potassium and sodium (the 35 percent reduction of silica here is most likely an anomaly due to reducing extraction rates at higher temperatures), whilst SS exhibits a reduction of around 40 to 30 percent of calcium, sodium, iron and up to 20 percent reduction in potassium, lastly VGF digestate exhibits up to 20 percent reduction in sodium and potassium.

The effect of temperature is seen to greatly accelerate the extraction of sodium in all feedstock as shown in Figure 38a, d, g and j, with the greatest rate of reduction found in AGR and VGF digestate. AGR and VGF digestate exhibits a large reduction of sodium of 65 and 45 percent respectively from 150 °C to 250 °C (Figure 38a and j). Large extraction rates are also exhibited for potassium with increasing temperatures. AGR and VGF digestate exhibited K removal from 150 °C to 250 °C of up to 60 and 30 percent respectively. The large extraction of sodium and potassium may be due to AGR and VGF digestates comparatively high lignocellulosic content.

Generally, there was no discernible effect of solid loading on the inorganic composition of the solid digestate hydrochar. When processing at 200 °C the effect of increasing solid loading on the percentage remaining of the inorganics remain stable, with the exception of AGR, where most of the inorganics see an increasing rate of retention rather than reduction with higher solid loading. Most notably, a sharp increase of potassium retention within AGR hydrochar is seen between solid loadings of 10 and 30 percent. At 200 °C sodium retention is increased with higher solid loading, exhibited especially with SS digestate (Figure 38h).

When processing at 250 °C the effect of increasing solid loading shows an influence on the rate of retention of potassium, most notably with MSW and AGR digestate. The greatest rate of potassium retention is exhibited by MSW (40 to 70 percent) and AGR (20 to 30 percent) as shown in Figure 38c and f respectively. For sodium the opposite trend is seen when processing at 250 °C compared to 200 °C with increasing solid loading. Sodium at this temperature is now extracted with increasing solid loading across all digestate materials (compare Figure 38b, e, h and j with c, f, i and l). Therefore, the fate of sodium during the influence of solid loading is temperature dependent. It is not known why this phenomenon occurs.

6.3.1.2. Pyrochar analysis

To enable the comparison of thermochemical processes the pyrochar obtained from pyrolysis of digestate material will be discussed in terms of its proximate, ultimate analysis, energy density and inorganic compositions influenced by temperature.

6.3.1.2.1. Proximate, ultimate analysis and energy density

Table 25 lists the ultimate, proximate and heating analysis of pyrochar produced from digestate. The chemical composition values agree with the ranges found in the literature, however the HHV values calculated in this study are between 2 to 4 MJ/kg greater, this is due to the different stoichiometric equations used to calculate the calorific values. The accuracy of the composition data is good, generally within ±2 percent.

Table 25. Ultimate, proximate, and heating analysis of solid digestate pyrochar.

Digestate pyrochar	Ultimate analysis (wt%, db)					Proximate analysis (wt%, db)			HHV (MJ/kg, db)	H/C (daf)	O/C (daf)
	C	H	N	S	O^{a}	VM	FC	Ash^{a}			
AGR digestate											
200 °C	43.7 ± 0.4	5.1 ± 0.2	3.4 ± 0.3	0.2 ± 0.1	31.7 ± 3.5	67.0 ± 2.8	17.1 ± 0.8	15.9 ± 3.6	17.7	1.39	0.54
400 °C	51.2 ± 1.0	2.7 ± 0.0	3.2 ± 0.2	0.1 ± 0.0	15.4 ± 0.4	29.9 ± 0.2	42.7 ± 0.6	27.4 ± 0.8	19.5	0.64	0.23
600 °C	52.7 ± 1.8	1.2 ± 0.2	2.5 ± 0.3	0.1 ± 0.0	10.0 ± 3.3	18.1 ± 0.4	48.5 ± 0.7	33.5 ± 1.1	19.2	0.27	0.14
MSW digestate											
200 °C	22.3 ± 0.5	1.6 ± 0.1	1.4 ± 0.0	0.2 ± 0.1	17.8 ± 0.2	34.9 ± 1.0	8.5 ± 0.7	56.7 ± 0.3	15.6	0.86	0.60
400 °C	22.9 ± 0.7	1.0 ± 0.1	1.0 ± 0.1	0.2 ± 0.1	8.4 ± 3.9	23.5 ± 1.6	10.0 ± 1.3	66.5 ± 2.9	16.2	0.54	0.27
600 °C	23.4 ± 3.1	0.6 ± 0.2	1.7 ± 1.1	0.6 ± 0.5	2.4 ± 6.5	20.7 ± 3.2	8.0 ± 4.7	71.2 ± 1.5	16.8	0.30	0.08
SS digestate											
200 °C	34.4 ± 2.0	4.4 ± 0.2	4.1 ± 0.0	0.8 ± 0.8	20.2 ± 1.0	55.9 ± 0.5	8.0 ± 0.8	36.1 ± 0.2	15.3	1.53	0.44
400 °C	31.7 ± 0.9	3.1 ± 0.2	3.3 ± 0.0	0.3 ± 0.3	7.9 ± 2.1	30.0 ± 5.4	16.2 ± 2.3	53.8 ± 3.1	15.4	1.16	0.19
600 °C	26.0 ± 0.3	0.9 ± 0.2	2.6 ± 0.1	0.9 ± 0.2	1.8 ± 1.3	14.7 ± 0.6	17.4 ± 1.3	67.9 ± 0.7	16.5	0.41	0.05
VGF digestate											
200 °C	30.9 ± 2.5	3.3 ± 0.5	2.1 ± 0.4	0.3 ± 0.1	13.1 ± 0.0	41.0 ± 2.6	8.8 ± 0.9	50.2 ± 3.5	15.0	1.28	0.32
400 °C	27.7 ± 1.8	1.5 ± 0.1	1.6 ± 0.1	0.1 ± 0.1	5.9 ± 0.7	19.9 ± 1.1	16.8 ± 0.1	63.3 ± 1.2	15.9	0.66	0.16
600 °C	22.8 ± 1.7	0.5 ± 0.1	1.0 ± 0.1	0.1 ± 0.1	1.8 ± 1.4	10.9 ± 0.0	15.4 ± 0.4	73.8 ± 0.4	16.7	0.28	0.06

^{a}, calculated by difference; ^{b}, calculated according to Equation (1)

Figure 39a, b, c and d illustrate normalised C, H, N, O and ash content, including energy densification of AGR, MSW, SS and VGF digestate and respective pyrochar against increasing pyrolysis temperature. Normalisation has been performed so that the total proximate and ultimate composition data is equal to the yield of the pyrochar.

The results show that the decrease of solid mass with increasing temperature was caused by the reduction of oxygen, hydrogen, nitrogen and volatile matter compared to the raw feedstock. Whilst, elemental carbon, fixed carbon and ash content increase with pyrolysis temperature. The increase of carbon and reduction of oxygen results in greater of pyrochar HHV which increases with temperature. The increase in HHV also correlates with an increase in energy densification. However, energy densification is minimal (up to a factor of 1.1) with the greatest increase of HHV exhibited by AGR from 17.7 to 19.2 MJ/kg (Figure 39a and Table 25). The ash concentrations of the pyrochar also increase with temperature.

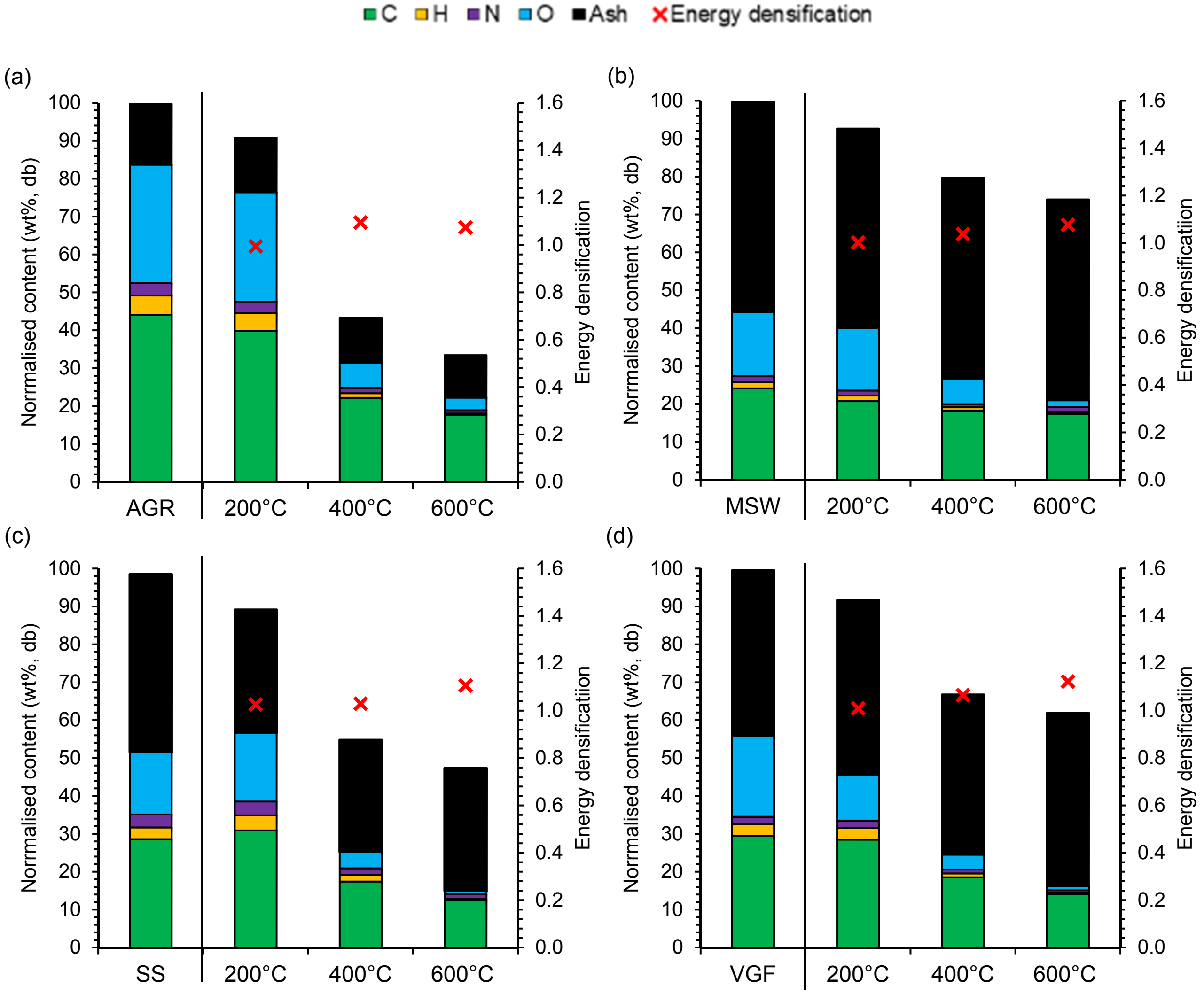

Figure 39. Normalised C, H, N, O and ash content, including energy densification of **a**) AGR, **b**) MSW, **c**) SS and **d**) VGF feedstock and respective pyrochar against with increasing pyrolysis temperature.

6.3.1.2.2. Inorganic analysis

Table 26 lists the major ash forming elements found in the digestate pyrochar. The major components of inorganic compounds of the pyrochar are silica, calcium and iron. Figure 40 illustrates the fate of the inorganics when processing via pyrolysis. The fate of inorganics is described as the percentage of these compounds remaining in the solid yield after pyrolysis treatment of the feedstock. In general, pyrolysis treatment reduces the ash concentrations compared to that of the starting material.

Table 26. Inorganic analysis of the solid digestate pyrochar.

Digestate pyrochar	Inorganic analysis (wt%, db)							
	Na	Mg	Al	Si	P	K	Ca	Fe
AGR digestate								
200 °C	0.35	0.67	0.09	1.82	1.04	3.15	1.32	0.00
400 °C	0.34	1.07	0.18	3.09	1.96	2.36	2.48	4.21
600 °C	0.34	1.19	0.25	4.22	2.25	2.87	2.84	5.10
MSW digestate								
200 °C	0.79	1.58	2.49	8.14	0.96	1.00	13.38	3.51
400 °C	0.72	1.83	3.03	10.03	1.12	1.25	15.53	4.12
600 °C	0.89	1.98	3.29	10.79	1.24	1.26	16.38	4.42
SS digestate								
200 °C	0.28	0.77	2.50	7.01	1.74	0.65	2.67	1.95
400 °C	0.35	1.20	3.75	10.47	2.58	0.95	4.00	2.88
600 °C	0.47	1.53	4.68	12.99	3.36	1.24	5.10	3.74
VGF digestate								
200 °C	0.48	0.77	1.60	14.70	0.76	1.32	5.13	0.01
400 °C	1.10	1.01	1.97	17.49	1.03	1.59	7.03	1.63
600 °C	0.82	1.15	2.36	20.65	1.20	2.03	8.26	1.91

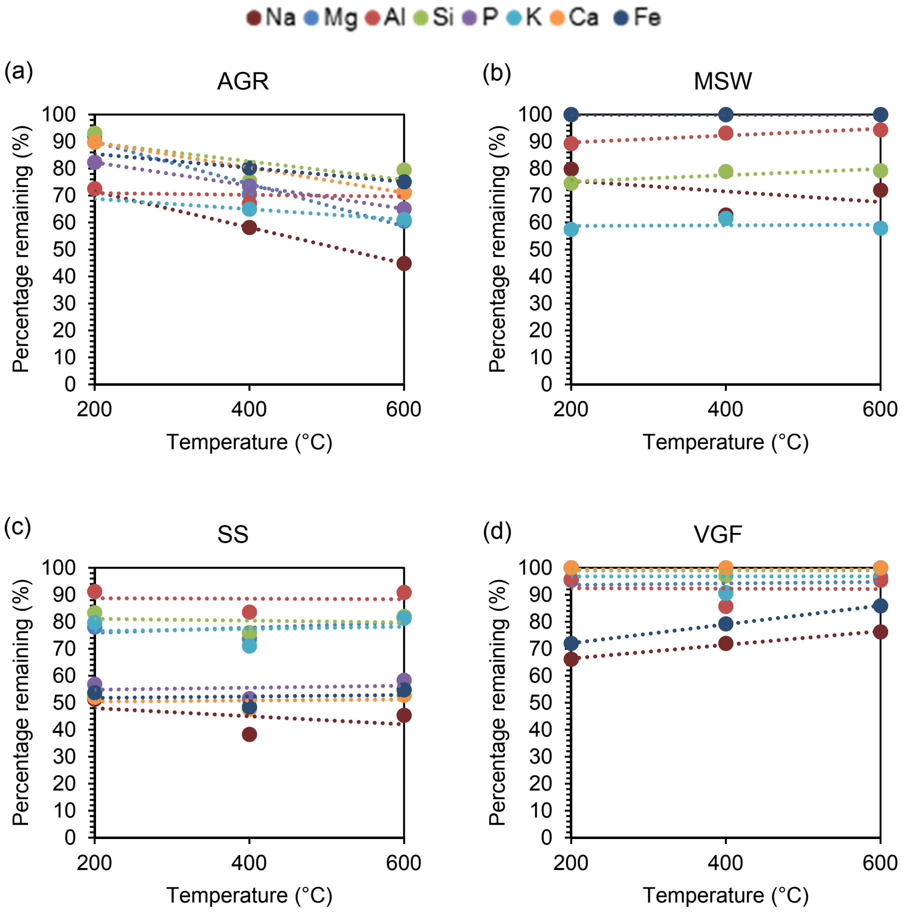

Figure 40. Fate of inorganics against pyrolysis temperature **a**) AGR, **b**) MSW, **c**) SS and **d**) VGF.

Levels of sodium, potassium, iron in particular is predominantly reduced for SS and VGF digestate, followed by a significant reduction of calcium for SS digestate. More specifically, AGR digestate at 200 ˚C exhibits a reduction of up to 30 percent of sodium, aluminium and potassium (Figure 40a), up to 40 percent reduction of potassium and up to 25 percent reduction in silica and sodium for MSW digestate (Figure 40b). SS digestate sees up to 45 percent reduction in sodium, calcium, phosphorous and iron (Figure 40c), whilst VGF digestate shows up to a 35 percent reduction in sodium and iron (Figure 40d). The effect of increasing temperature beyond 200 ˚C does not lend itself to further extraction of inorganics. However, the exception is AGR digestate, where the rate of extraction increases with temperature as shown in Figure 40a (up to 20 percent at 200 ˚C and up to 35 percent at 600 ˚C).

VGF digestate shows an opposite trend of the retention of sodium and iron with increasing temperatures (Figure 40d). Therefore, these observations of differing extraction and retention of inorganics, including the rates of which this occurs with increasing temperature show to be feedstock dependent. This further supports the theory that the fate of inorganics is influenced by the physical structure of the biomass feedstocks.

6.3.1.3. Comparison of HTC and pyrolysis solid products

In order to compare the treatment of digestate enhancement technologies, the chemical composition of both hydrochar and pyrochar have been plotted against each other. A ternary diagram, shown in Figure 41 compares proximate analysis and a Van Krevelen diagram shown in Figure 42 compares the elemental and heating analysis.

The ternary diagram shows that all data points are concentrated in the area defined by less than 70 percent volatile matter, less than 50 percent fixed carbon and less than 80 percent ash. The hydrochar, as a collective, exhibit closer clustering that that of pyrochar. Specifically, the hydrochar are concentrated in the area defined by less than 70 percent volatile matter, less than 30 percent fixed carbon and less than 70 percent ash. Whilst the pyrochar are concentrated in the area defined by less than 70 percent VM, less than 50 percent fixed carbon and less than 75 percent ash. The two outliers are AGR pyrochar at 400 ˚C and 600 ˚C, with fixed carbon contents of around 42 and 49 percent respectively. This is due to the high lignocellulosic content of AGR digestate, which experiences greater carbonisation at higher temperatures.

Therefore, the main differences of proximate composition between hydrochar and pyrochar is the fixed carbon (20 percent greater in some cases) and ash content (5 percent greater in some cases).

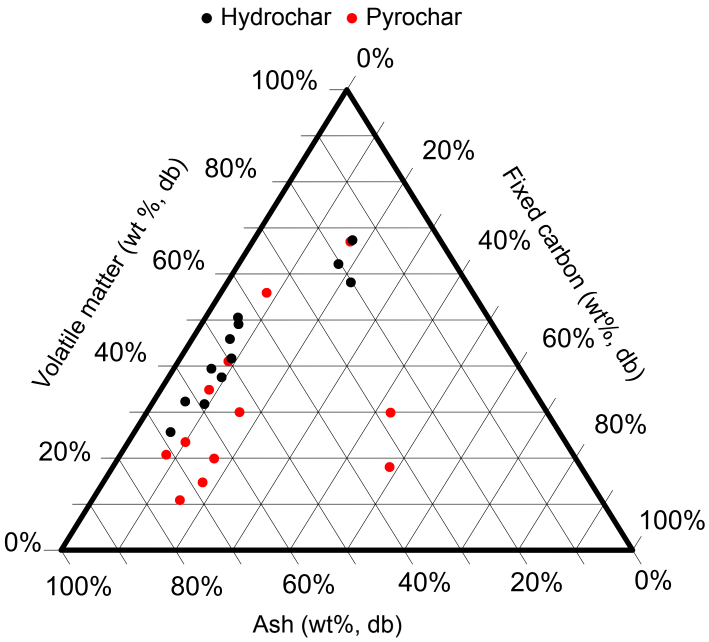

Figure 41. Ternary plot showing the relationship between ash, volatile matter and fixed carbon of the hydrochar and pyrochar from the HTC and pyrolysis of digestate.

The Van Krevelen diagram, drawn in Figure 42, compares the atomic H:C and O:C ratios of the raw feedstock, hydrochar (produced at 150 ˚C, 200 ˚C and 250 ˚C at 20 percent solid loading), pyrochar (produced at 200 ˚C, 400 ˚C and 600 ˚C) and typical low and high grade coals. The atomic ratios are based on dry ash free values and the diagram is typically used to illustrate the degree of maturity and aromacity of char materials [185]. Increasing temperatures for both thermochemical processes favours the reduction of oxygen (reduction) and hydrogen (dehydrogenation) and an increase carbon, therefore resulting in an increase in char HHV as described before. The hydrochar present higher H:C ratios than that of pyrochar and therefore follow a different trajectory with increasing processing temperatures.

When comparing the atomic ratios with a focus of temperature, hydrothermal carbonisation at 150 ˚C and 200 ˚C produces similar ratios to that of pyrolysis at 200 ˚C, whilst HTC at 250 ˚C achieves similar ratios to that of pyrolysis at 400 ˚C. Pyrochar produced at 600 ˚C achieves similar, if not better morphology to that of low grade bituminous and lignite coals.

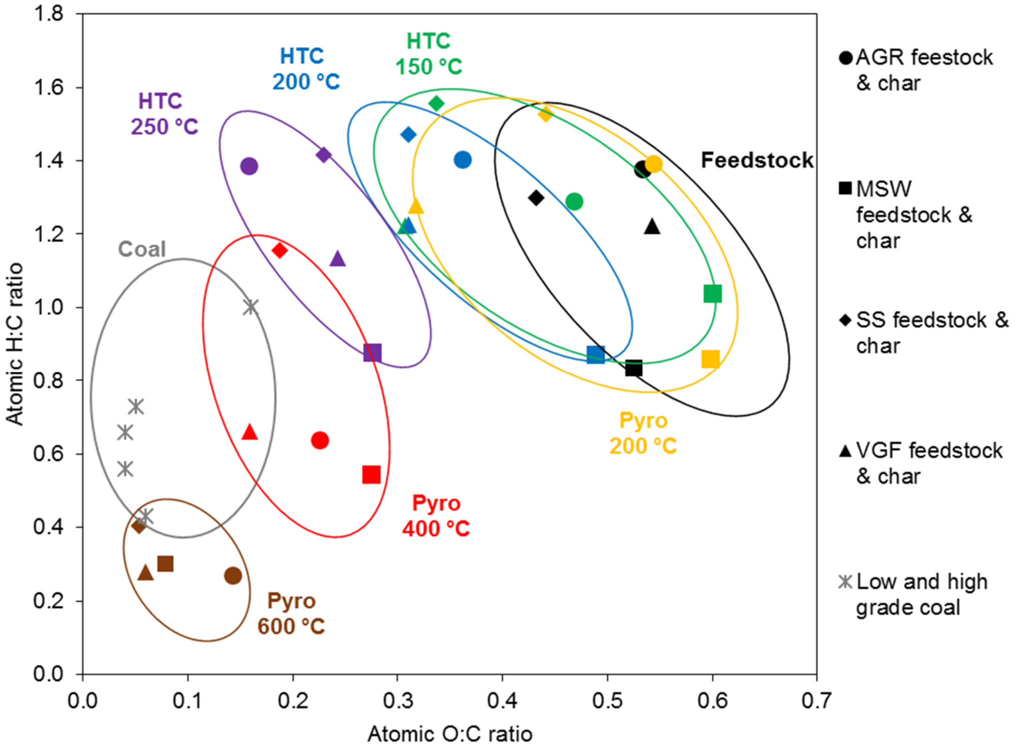

Figure 42. Van Krevelen diagram for digestate feedstock and resultant hydrochar (produced at 20 percent loading) and pyrochar on a dry ash free basis.

6.3.1.4. HTC process water analysis

Understanding the composition of the HTC process waters will also help determine the influence of feedstock character and HTC operating parameters, including its application in the following chapters. Composition analysis of the process waters generated from the HTC of digestate materials is listed in Table 27.

Table 27 shows that the pH of the process waters are between 6 and 8. High ash and nitrogen feedstocks produce basic process waters at a higher temperatures (MSW and SS digestate), and acidic process waters are produced from higher fractions of lignocellulosic feedstock (see AGR and VGF values in Table 27). Higher ash and nitrogen containing feedstock has also been reported in the literature to produce basic process waters, which may be responsible for lowering solid yields by reducing the level of polymerisation for hydrochar [141]. This is observed with SS digestate, resulting in high liquid yields as shown in the previous chapter. In general, the pH of the process waters is feedstock dependent and is linked to the inorganic and nitrogen content of the process waters. The levels of nitrogen in the process waters are highest for the SS digestate as expected, reflecting the high protein content of this feedstock.

Table 27. Composition analysis of the process waters derived from HTC of digestate.

Digestate process waters	pH	TN (g/L)	TOC (g/L)	COD (g/L)	Total VFA (g/L)
AGR digestate					
150 °C at 20%	6.7	3.1	13.9	45.5	1.8
200 °C at 10%	6.9	1.6	9.2	25.2	1.3
200 °C at 20%	6.2	1.9	14.9	42.2	2.1
200 °C at 30%	5.8	3.3	18.8	54.6	2.0
250 °C at 10%	5.7	1.4	10.9	29.1	2.5
250 °C at 20%	6.1	2.2	16.5	46.3	4.2
250 °C at 30%	6.5	2.9	17.3	56.6	6.1
MSW digestate					
150 °C at 20%	6.5	1.1	3.4	22.6	0.7
200 °C at 10%	7.2	0.9	3.1	10.7	0.9
200 °C at 20%	7.1	2.4	5.7	18.1	0.9
200 °C at 30%	7.4	2.4	8.7	23.4	1.5
250 °C at 10%	7.1	1.0	2.7	9.4	1.3
250 °C at 20%	7.8	1.7	6.0	16.4	1.3
250 °C at 30%	7.5	3.4	6.1	21.2	1.9
SS digestate					
150 °C at 20%	5.6	2.4	16.6	31.0	1.1
200 °C at 10%	5.2	2.6	7.8	21.0	1.4
200 °C at 20%	6.2	4.5	17.1	38.9	1.8
200 °C at 30%	5.6	6.2	21.0	48.7	2.8
250 °C at 10%	7.2	2.4	7.1	23.4	3.5
250 °C at 20%	7.6	4.7	18.4	43.6	5.3
250 °C at 30%	7.5	6.5	20.3	51.6	5.5
VGF digestate					
150 °C at 20%	6.5	1.0	5.7	11.9	0.9
200 °C at 10%	6.1	1.1	4.2	12.0	1.2
200 °C at 20%	5.7	1.4	8.5	22.5	1.1
200 °C at 30%	6.0	1.7	10.3	31.5	1.3
250 °C at 10%	6.4	0.9	4.2	16.1	1.4
250 °C at 20%	6.4	1.5	9.8	27.8	2.2
250 °C at 30%	6.7	2.1	10.6	36.9	2.6

Figure 43 illustrates the influence of temperature and solid loading on the yield, TOC and COD contents, including theoretical TOC values for the process waters produced from varying solid loading. Theoretical TOC assumes additive behaviour from the feedstock added at increments of 10 percent into the HTC process. For all process waters the TOC content increases with temperature. The highest TOC was observed for the SS digestate followed by the AGR, VGF, and then MSW digestate. Figure 43c shows that additive TOC behaviour is observed for sewage sludge digestate at lower solid loadings (10 to 20 percent) for both temperatures, but at higher solid loading (30 percent) the levels of TOC decrease, possibly due to saturation of the process water.

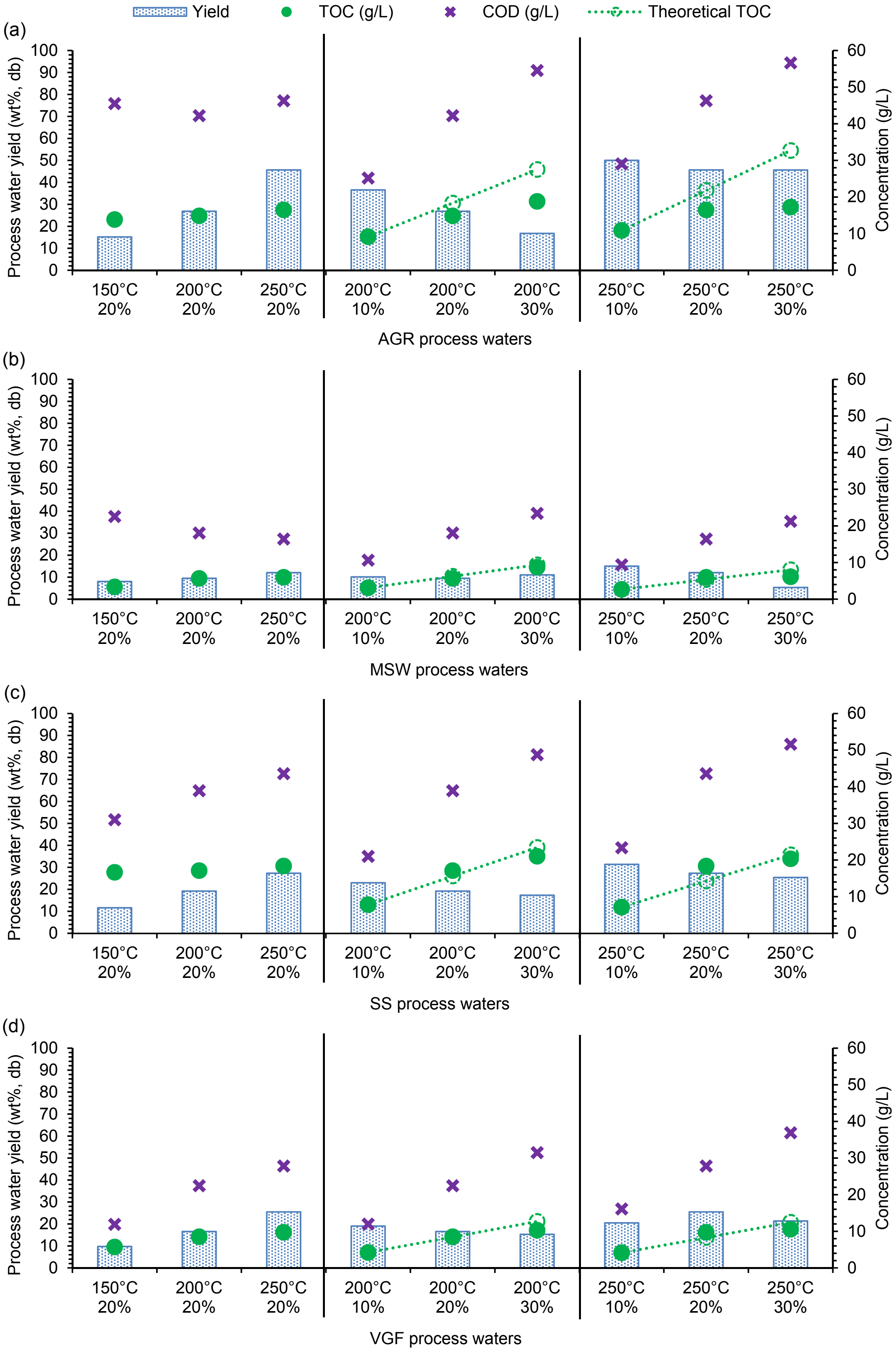

Figure 43. Influence of temperature and solid loading on process water composition for **a**) AGR, **b**) MSW, **c**) SS and **d**) VGF.

However, for the case of AGR digestate process waters (Figure 43a), TOC is non-additive and the rate of solubilisation decreases with high solid loading. The COD content of the process waters is shown to increase with solid loading at both 200 ˚C and 250 ˚C for all digestate. However, for rising temperature COD is shown to increase for SS and VGF, be stable for AGR and decrease for MSW digestate. Therefore, the level of COD is dependent on the feedstock composition. The VFA content is shown to increase both with temperature and solid loading variables, this correlates with the loss of oxygen in the hydrochar, where organic acids form and dissolve in the liquid phase [72,79]; this reaction is also accompanied by a release of CO_2 which constitutes a fraction of the HTC gas yields. High levels of VFA are inhibitory to anaerobic digestion and are likely to reduce biogas yields [186], this will be discussed further in Chapter 8.

6.3.2. Green waste and blend conversion products

Following the structure of the previous chapters, the focus will now be of the composition of the products from the HTC of green waste and SS digestate blends to understand the effect of co-processing in the proposed integration concept.

6.3.2.1. Hydrochar analysis

Hydrochar obtained from the HTC of green waste and blends will be discussed in terms of its proximate, ultimate analysis, energy density and inorganic composition against HTC temperature.

6.3.2.1.1. Proximate, ultimate analysis and energy density

The proximate, ultimate analysis, including higher heating value and H:C, O:C atomic ratios for green waste and blend hydrochar are listed in Table 28. The chemical composition values agree with the ranges found in the literature. The accuracy of the composition is very good, generally within ±1 percent.

Figure 44 illustrates a ternary diagram to compare the relationship of volatile matter, fixed carbon and ash of the green waste and to show changes to composition when blended. All data points are concentrated in the area defined by greater than 50 percent volatile matter, less than 40 percent fixed carbon and less than 40 percent ash. There is clear clustering of two groups, separating the green wastes to that of the blend hydrochar. The green waste hydrochar are concentrated in the area defined by greater than 55 percent volatile matter, less than 40 percent fixed carbon and less 20 percent ash content.

Table 28. Ultimate, proximate, and heating analysis of green waste and blend hyrdochar.

Green waste and blend hydrochar	**Ultimate analysis (wt%, db)**					**Proximate analysis (wt%, db)**			**HHV (MJ/kg, db)**	**H/C (daf)**	**O/C (daf)**
	C	**H**	**N**	**S**	**O[a]**	**VM**	**FC**	**Ash[a]**			
Grass clippings											
150 °C	49.4 ± 0.1	6.1 ± 0.0	3.1 ± 0.0	0.0 ± 0.0	3.1 ± 0.0	72.5 ± 0.2	17.0 ± 0.2	10.5 ± 0.1	20.0	1.48	0.35
200 °C	53.1 ± 0.4	6.0 ± 0.0	3.2 ± 0.0	0.0 ± 0.0	3.2 ± 0.0	69.2 ± 0.3	16.6 ± 0.2	14.2 ± 0.5	21.6	1.34	0.27
250 °C	61.4 ± 0.0	6.1 ± 0.1	3.1 ± 0.0	0.1 ± 0.0	3.1 ± 0.0	61.5 ± 0.0	25.0 ± 0.1	13.5 ± 0.1	25.7	1.18	0.18
Garden hedge											
150 °C	51.7 ± 0.4	6.1 ± 0.1	2.0 ± 0.1	0.0 ± 0.0	2.0 ± 0.1	76.1 ± 0.3	18.2 ± 0.0	5.7 ± 0.4	20.9	1.41	0.38
200 °C	58.4 ± 0.2	5.9 ± 0.0	1.7 ± 0.0	0.0 ± 0.0	1.7 ± 0.0	69.3 ± 0.1	24.9 ± 0.0	5.8 ± 0.0	23.8	1.20	0.32
250 °C	65.2 ± 0.2	5.9 ± 0.0	2.2 ± 0.1	0.1 ± 0.0	2.2 ± 0.1	60.5 ± 0.4	33.8 ± 0.1	5.6 ± 0.5	27.4	1.08	0.24
Wood chips											
150 °C	51.2 ± 1.7	6.0 ± 0.1	0.3 ± 0.0	0.0 ± 0.0	0.3 ± 0.0	82.3 ± 0.3	15.9 ± 0.3	1.8 ± 0.0	20.5	1.41	0.46
200 °C	55.8 ± 0.8	5.7 ± 0.1	0.3 ± 0.0	0.0 ± 0.0	0.3 ± 0.0	75.2 ± 0.3	21.2 ± 0.2	3.7 ± 0.1	22.3	1.22	0.40
250 °C	69.2 ± 0.4	5.5 ± 0.1	0.5 ± 0.0	0.0 ± 0.0	0.5 ± 0.0	58.2 ± 0.9	38.5 ± 1.0	3.3 ± 0.1	28.8	0.95	0.26
SS & grass 50/50											
150 °C	41.9 ± 0.1	5.2 ± 0.0	3.6 ± 0.0	0.6 ± 0.1	3.6 ± 0.0	64.0 ± 0.1	10.5 ± 0.2	25.5 ± 0.3	17.2	1.48	0.31
200 °C	43.4 ± 0.2	4.9 ± 0.0	2.9 ± 0.0	0.7 ± 0.0	2.9 ± 0.0	59.4 ± 0.8	10.5 ± 0.2	30.1 ± 0.6	17.6	1.35	0.25
250 °C	44.0 ± 0.0	4.5 ± 0.0	3.0 ± 0.1	0.7 ± 0.0	3.0 ± 0.1	51.8 ± 0.3	12.3 ± 0.0	35.8 ± 0.2	17.8	1.23	0.18
SS & hedge 50/50											
150 °C	42.0 ± 0.4	5.1 ± 0.1	2.7 ± 0.0	0.5 ± 0.0	2.7 ± 0.0	65.0 ± 0.1	10.0 ± 0.1	25.0 ± 0.2	17.1	1.44	0.33
200 °C	45.7 ± 0.1	5.0 ± 0.0	2.4 ± 0.0	0.5 ± 0.0	2.4 ± 0.0	59.1 ± 0.1	13.4 ± 0.0	27.6 ± 0.1	18.3	1.31	0.26
250 °C	47.5 ± 0.4	4.7 ± 0.0	2.6 ± 0.0	0.6 ± 0.0	2.6 ± 0.0	53.3 ± 0.0	15.4 ± 0.1	31.3 ± 0.1	18.9	1.19	0.19
SS & wood 50/50											
150 °C	42.9 ± 0.6	5.7 ± 0.3	2.0 ± 0.1	0.4 ± 0.0	2.0 ± 0.1	66.7 ± 0.1	11.9 ± 0.7	21.4 ± 0.7	17.2	1.57	0.34
200 °C	46.9 ± 0.1	5.1 ± 0.1	1.8 ± 0.0	0.5 ± 0.0	1.8 ± 0.0	62.3 ± 0.2	15.2 ± 0.4	22.5 ± 0.2	18.7	1.29	0.31
250 °C	51.3 ± 0.0	4.8 ± 0.1	2.3 ± 0.0	0.5 ± 0.0	2.3 ± 0.0	51.6 ± 0.3	21.2 ± 0.1	27.2 ± 0.2	20.3	1.12	0.20

[a],calculated by difference

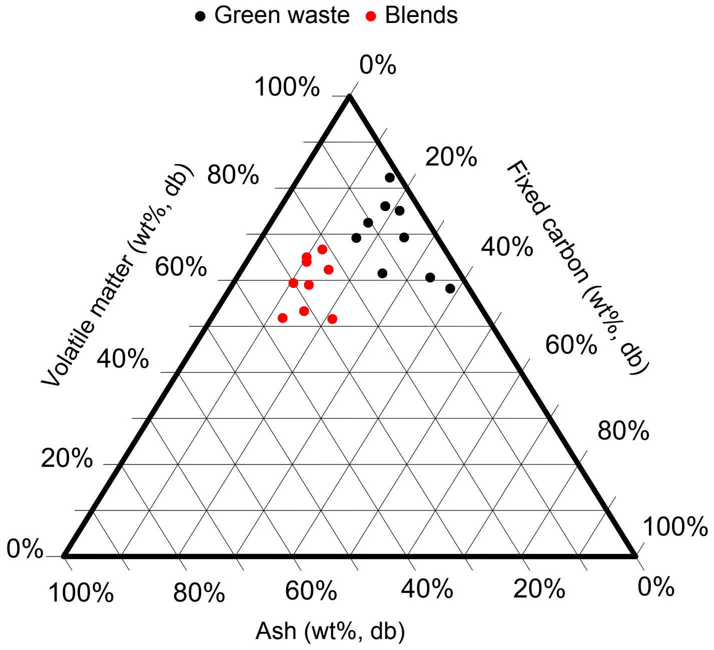

Figure 44. Ternary plot showing the relationship between ash, volatile matter and fixed carbon of the hydrochar from the HTC of green waste and blends.

The blend hydrochar are concentrated in the area defined by less than 70 percent volatile matter, less than 25 percent fixed carbon and less than 40 percent ash content. Clearly, the act of blending the green waste with SS digestate has reduced the spread of the proximate composition and the ash content distinctly separates the two groups. SS digestate hydrochar has a range of ash content between 43.8 to 47.5 percent and when blended with comparatively low ash green waste this has reduced the ash content to between 21.4 to 35.8 percent, a reduction in the range of 11.7 to 22.4 percent.

Figure 45 illustrates normalised C, H, N, O and ash content, including energy densification of the green wastes and blends, together with the resultant hydrochar against temperature. The largest carbon content is found with the woodchip hydrochar, this correlates with woodchip having the largest lignocellulosic content. As a result woodchip hydrochar generated at 250 °C achieves the greatest HHV at 28.8 MJ/kg. On the other hand, the HHV of green waste hydrochar are similar at lower HTC temperatures (20.0 to 20.9 MJ/kg at 150 °C, and 21.6 to 23.8 MJ/kg at 200 °C).

Therefore, if improving the green wastes quality as a solid fuel, it is recommended that HTC is operated above 200 °C for higher calorific value hydrochar. As expected, the levels of nitrogen in the hydrochar are highest from the grass clippings, reflecting the high protein content, as a result of the feedstocks leafy structure. The highest ash content of the hydrochar is also found in the hydrochar generated from grass clippings.

Results from co-processing also show that the addition of green wastes to SS digestate reduces the carbon and hydrogen content and increases oxygen and sulphur content of the resultant hydrochar. This is due to the larger fraction of ash material present in the SS digestate influencing the atomic ratios. Consequently, the energy density is reduced in the blend hydrochar along with a reduction of the rate of energy densification. The increase of HHV of the blends with temperature is minimal. Table 28 shows that the largest calorific value step change with temperature is found in the hydrochar produced from SS and woodchip followed by SS and hedge then SS and grass (from 17.2 to 20.3, 17.1 to 18.9 and 17.2 to 17.8 MJ/kg respectively).

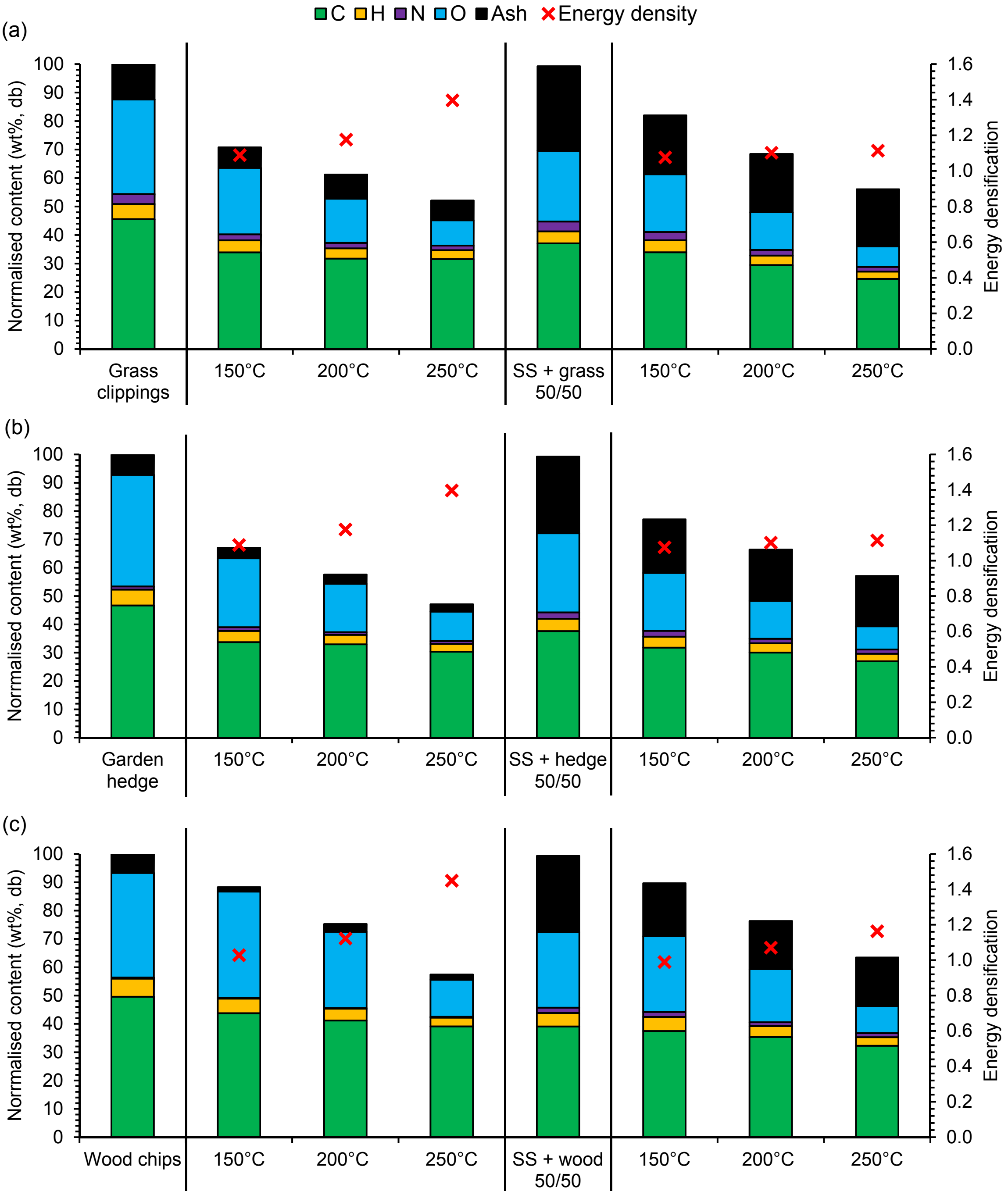

Figure 45. Normalised C, H, N, O and ash content, including energy densification of **a**) Grass and SS + grass blends, **b**) hedge and SS + hedge blends and **c**) wood chip and SS + woodchip blends against with increasing HTC temperature.

A Van Krevelen diagram shown in Figure 46, is given to compare the H:C and O:C atomic ratios of the green wastes and SS digestate feedstock along with the resultant hydrochar generated at 150 °C , 200 °C and 250 °C, accompanied by typical low and high grade coals.

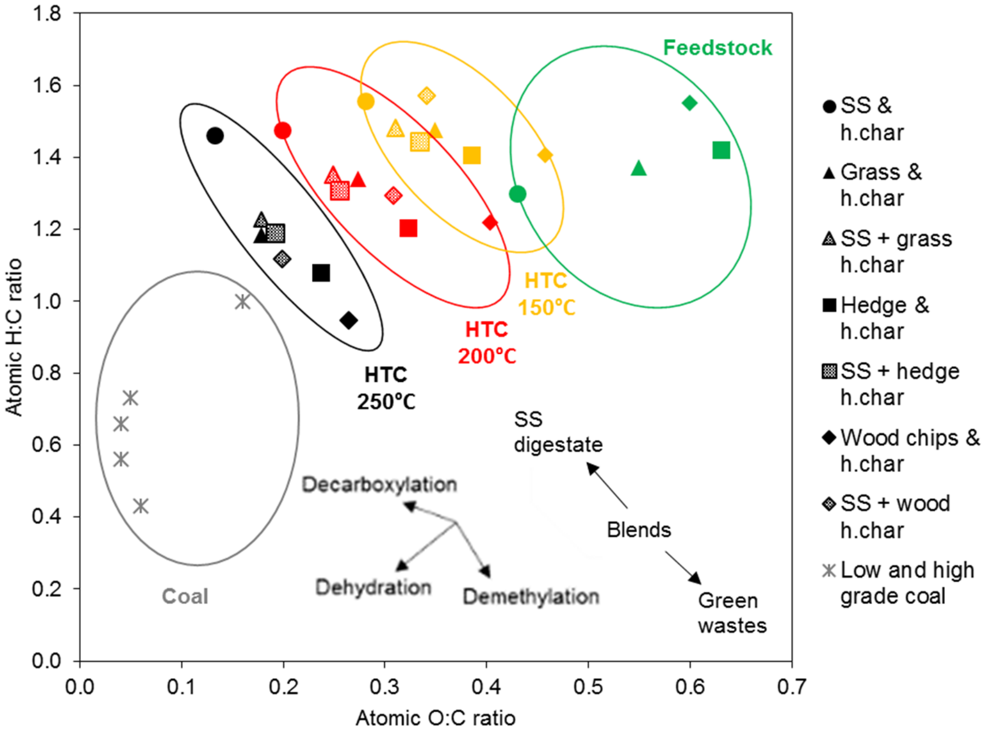

Figure 46. Van Krevelen diagram for green waste, SS digestate feedstock and resultant hydrochar, including blends on a dry ash free basis.

The atomic ratios of the hydrochar follow the same trajectory as shown in the previous Van Krevelen diagram (Figure 42). SS digestate hydrochar exhibits higher H:C ratios and lower O:C ratios compared to the green waste hydrochar at each temperature. This trend is also observed with the other high ash digestates in this study (Figure 42) and in other studies [118], confirming that high inorganic content feedstock hydrochar favour decarboxylation, compared to low inorganic content feedstock hydrochar which favour dehydration reactions. Blending SS digestate with green wastes centralises the atomic ratios, reducing the spread of variability. SS digestate and grass blend hydrochar exhibits the least atomic ratio change from its grass clipping hydrochar counterpart and the increase in temperature reduces this gap. The blend hydrochar produced at 250 °C exhibits very similar morphology to that of low grade coal.

6.3.2.1.2. Inorganic analysis

Table 29 lists the major ash forming elements found in the green waste and blend hydrochar. The major components of inorganic compounds of the green waste hydrochar are calcium, silica, potassium and phosphorous, in that order. Whilst the major components of the blend hydrochar in descending order are silica, calcium, aluminium and iron.

Table 29. Inorganic analysis of the green waste and blend hydrochar.

Green waste and blend hydrochar	Inorganic analysis (wt%, db)							
	Na	Mg	Al	Si	P	K	Ca	Fe
Grass clippings								
150 °C	0.18	0.25	0.08	1.78	0.55	1.21	1.83	0.06
200 °C	0.20	0.28	0.11	2.71	0.82	1.18	2.35	0.08
250 °C	0.21	0.30	0.11	2.37	0.90	0.65	2.69	0.08
Garden hedge								
150 °C	0.14	0.09	0.03	0.30	0.29	0.77	1.80	0.02
200 °C	0.07	0.07	0.03	0.22	0.40	0.73	1.87	0.02
250 °C	0.07	0.08	0.03	0.12	0.50	0.39	1.92	0.02
Woodchip								
150°C	0.04	0.03	0.07	0.31	0.01	0.02	0.39	0.05
200°C	0.04	0.05	0.18	0.69	0.02	0.05	0.63	0.13
250°C	0.18	0.04	0.13	0.63	0.02	0.13	0.39	0.09
SS & grass 50/50								
150 °C	0.46	0.55	1.46	4.54	1.26	1.13	2.23	1.28
200 °C	0.27	0.64	1.71	5.44	1.50	1.11	2.81	1.47
250 °C	0.26	0.81	2.07	6.54	1.96	0.90	3.27	1.89
SS & hedge 50/50								
150 °C	0.23	0.45	1.60	4.62	1.04	1.72	1.95	1.19
200 °C	0.18	0.53	1.81	4.92	1.29	0.81	2.52	1.40
250 °C	0.21	0.63	2.06	5.68	1.47	1.20	2.63	1.60
SS & woodchip 50/50								
150 °C	0.21	0.44	1.45	4.12	1.03	0.54	1.57	1.29
200 °C	0.18	0.46	1.54	4.36	0.98	0.65	1.63	1.24
250 °C	0.34	0.56	1.96	5.33	1.17	0.68	1.79	1.43

Figure 47 illustrates the fate of inorganics with temperature when processing green wastes and blends of SS digestate and green wastes. The inorganic composition of raw blend of SS digestate and green wastes was not directly measured, instead these are assumed from the average percentages of each inorganic compound analysed.

In general, HTC treatment reduces the mass of ash, through the reduction of iron, sodium, potassium and aluminium. However, the rate of inorganic removal remains relatively stable with increasing temperatures as shown with grass and woodchip (Figure 47a and e). Garden hedge exhibits the greatest removal efficiencies with increasing temperature (Figure 47c). Whilst, woodchip exhibits increasing Na and P retention with increasing temperatures.

The influence of blending shows greater removal efficiencies of the inorganics overall, between the range of 50 to 80 percent removal. Blends of SS digestate with grass and hedge show an increased rate of sodium and potassium removal with increasing temperatures (Figure 47b and d) whilst the removal rate in general remains stable with the blends of SS digestate and woodchip. The increased removal of inorganics from the grass and hedge materials compared to that of woodchip, may be due to the increased levels of hemicellulose and cellulose contents in the former, which is less strongly bounded than lignin by nature as discussed in Chapter 4.

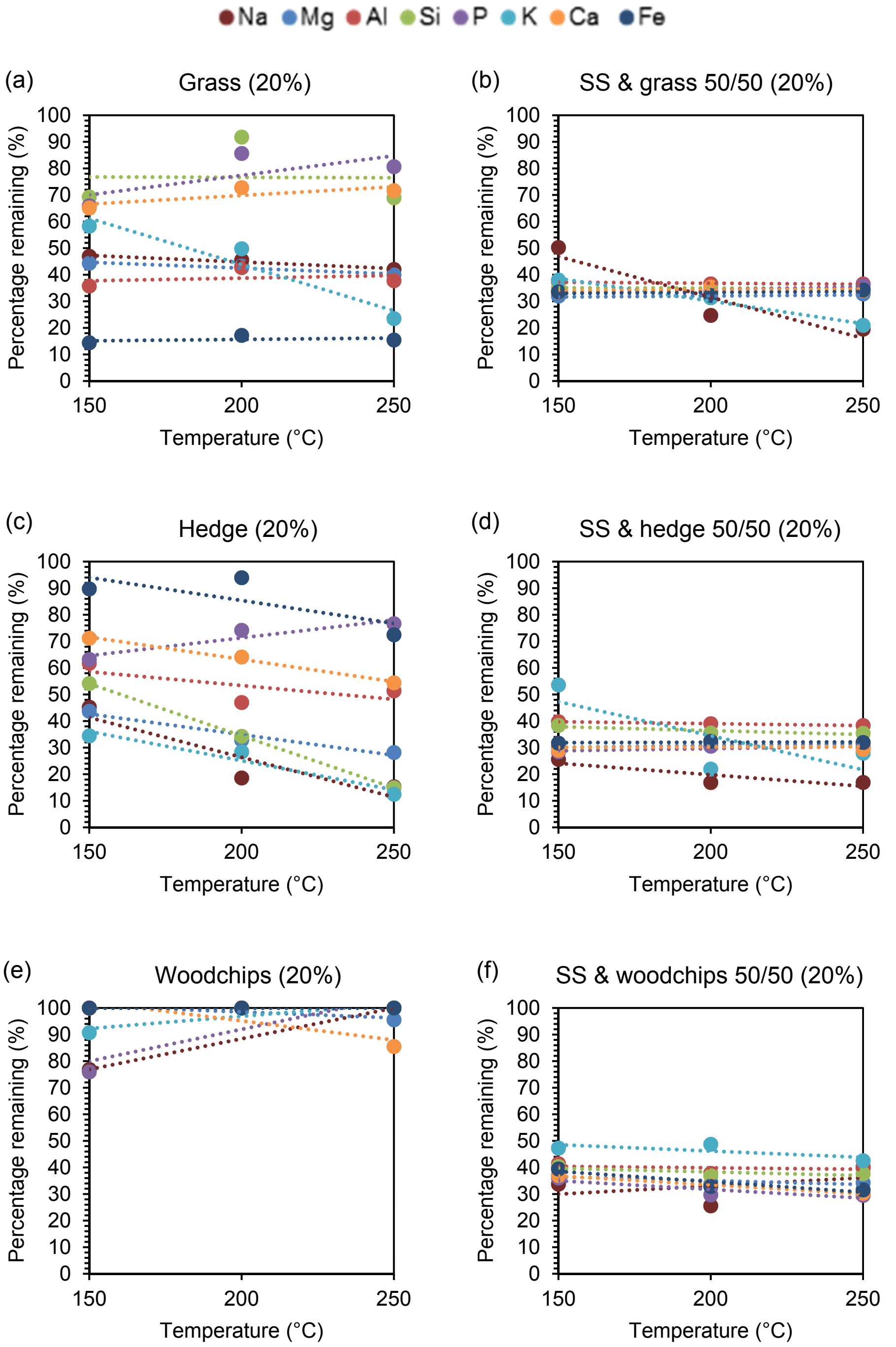

Figure 47. Fate of inorganics against pyrolysis temperature for **a**) grass, **b**) SS + grass, **c**) hedge, **d**) SS + hedge, **e**) woodchip and **f**) SS + woodchips, all at 20 percent solid loading.

6.3.2.2. HTC process water analysis

Analysis of the process waters generated from the HTC of green waste and blended materials will aid in the understanding of the influence on co-processing to the composition of the process waters and subsequent application. Table 30 lists the pH, total nitrogen, total organic carbon, chemical oxygen demand and total volatile fatty acids found in the process waters generated from green waste and blends.

Table 30. Composition analysis of the liquids derived from HTC of green waste and blends.

Green waste and blend process water	pH	TN (g/L)	TOC (g/L)	COD (g/L)	Total VFA (g/L)
Grass clippings					
150 °C	5.8	1.6	19.6	54.3	1.5
200 °C	4.6	2.8	18.0	49.3	3.6
250 °C	6.2	8.6	78.0	10.1	4.7
Garden hedge					
150 °C	5.2	0.6	26.4	94.4	2.2
200 °C	3.8	2.1	22.4	66.3	7.1
250 °C	5.4	0.8	20.7	62.2	8.2
Woodchip					
150 °C	4.0	3.0	8.1	20.3	0.9
200 °C	4.0	2.9	10.6	30.0	3.2
250 °C	4.0	0.2	12.6	32.6	4.8
SS & grass 50/50					
150 °C	5.8	1.8	13.9	39.0	1.5
200 °C	4.7	2.0	15.4	44.7	2.9
250 °C	6.9	3.4	15.6	45.1	4.1
SS & hedge 50/50					
150 °C	5.5	1.7	19.7	58.7	1.2
200 °C	4.3	2.2	17.9	49.8	3.9
250 °C	5.9	2.0	16.6	46.0	1.5
SS & wood 50/50					
150 °C	5.6	1.2	8.1	22.8	0.9
200 °C	4.1	4.4	9.8	26.0	2.1
250 °C	5.1	1.4	10.8	30.1	3.7

The pH of the green waste process waters, as listed in Table 30, range from 3.8 to 6.2, this is particularly acidic and is due to the high lignocellulosic content found in the feedstock. Blending results in less acidic and more neutral process waters, which range from 4.1 and 6.9. Notably, the pH of the 200 °C process waters are more acidic than 150 °C and 250 °C process waters. Additionally, the acidic process waters from the HTC of woodchip does not neutralise with increasing temperatures as it does with the grass clippings and garden hedge, especially as VFA content increases. From the data collected, there is insufficient information to understand why these phenomena occur. The acidity of woodchip process waters results in increasing polymerisation for hydrochar during HTC reactions, also exhibited in another study [141], therefore its solid yields are far greater than its liquid yields. The levels of TN in the process waters are highest for grass as expected due to solubilisation, reflecting the high protein content of the feedstock.

Figure 48 illustrates the influence of temperature on the yield, including levels of TOC and COD of the single and blended feedstocks.

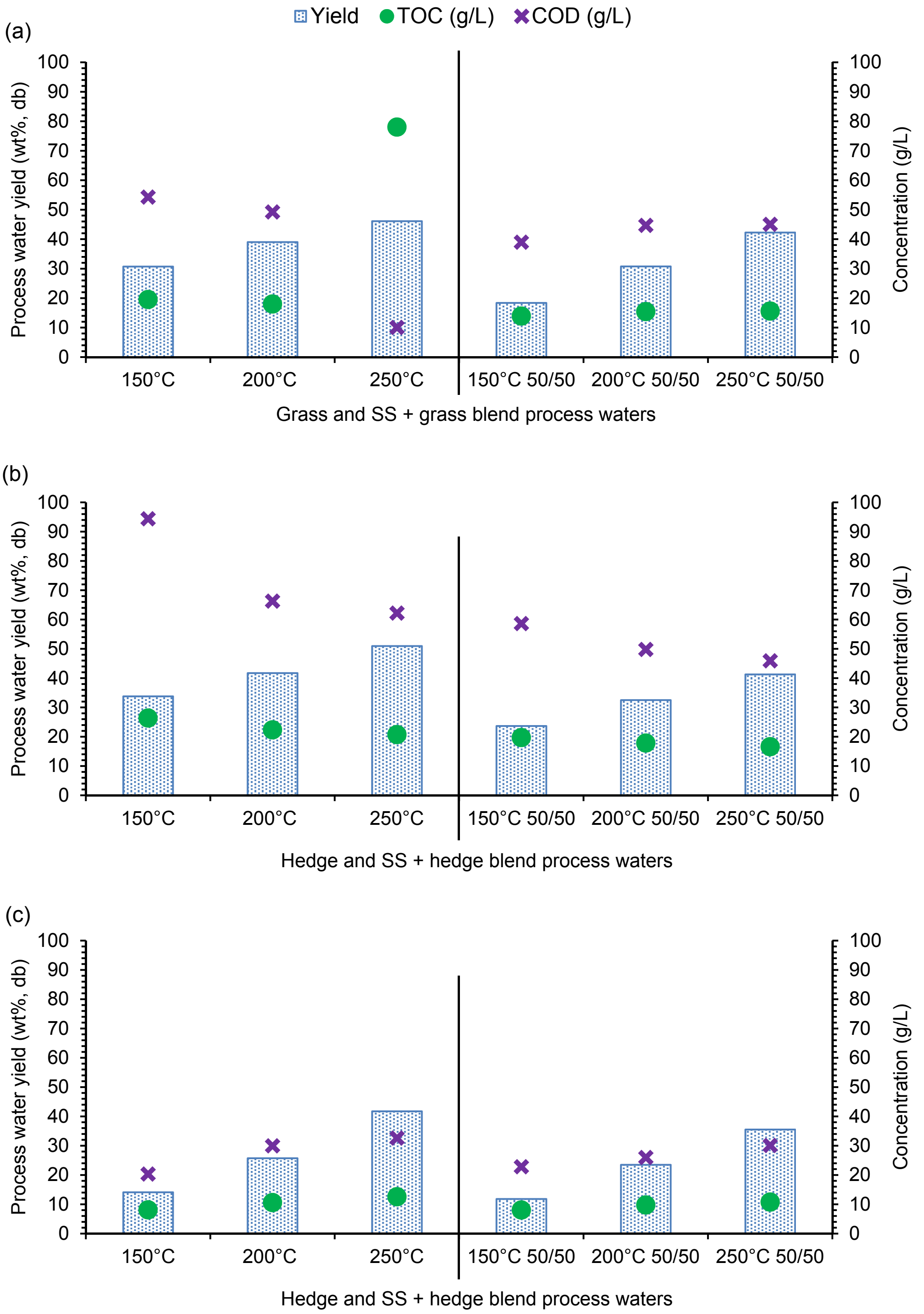

Figure 48. Influence of temperature on process water composition for **a**) grass and SS + grass blend, **b**) hedge and SS + hedge blend and **c**) woodchips and SS + woodchips all from 20 percent solid loading.

For all process waters, the levels of TOC remain fairly constant with increasing temperature, with the exception of grass at 250 °C as shown in Figure 48a , where TOC reaches to 78 g/L. Hedge exhibits a strong negative correlation of COD with increasing HTC temperatures (Figure 48b), whilst woodchip shows a weak positive correlation of COD with increasing temperatures (Figure 48c). Therefore, the COD content of the process waters is feedstock dependent. The VFA content however is generally shown to increase with temperature for all feedstock as shown in Table 30, due to increased oxygen reduction reactions and the formation of organic acids form that dissolve into the process waters [72].

6.4. Chapter limitations and recommendations

A limitation of this chapter is the analysis missing on the physical properties of the hydrochar and pyrochar materials i.e. hydrophobicity, surface chemistry and cation-exchange capacity (CEC) to understand porosity. These analyses help to understand how the materials will behave during handling and preparation for further application. However, the focus of this study has been on the chemical characteristics of the materials and the analysis provided in this study is sufficient to understand the effect of thermochemical reactions on the chemical composition variation of the products.

To further develop this chapter, the addition of pyrolysis GCMS would be beneficial to understand the chemical compositions of solid products by obtaining data on non-volatile compounds, including the determination of its microstructure. Washing hydrochars may also improve the accuracy of the chemical composition, as process waters may be absorbed into the surface of the hydrochars during product separation. However, this may also wash away other analytes and affect the chemical composition. Additionally, analysis of the gas phase would also improve the understanding of how feedstock materials and operating variables transforms biomass feedstock, including requirements for flue gas clean up at industrial scale.

6.5. Concluding remarks

Performing HTC and pyrolysis has given an understanding of how feedstock composition and process parameters affects product composition. The blending of SS digestate with green wastes has also given an understanding of how HTC co-processing affects the product composition.

The chemical composition of both hydrochar and pyrochar depends on conversion conditions, including the composition of the initial feedstock materials. During HTC and pyrolysis the mass loss of oxygen occurs, also called deoxygenation, a reaction that increases with temperatures. Deoxygenation causes the solid yields to decrease, and in the case of HTC the creation of VFA in the process waters and CO_2.

Concentrations of volatile matter are similar for both digestate hydrochar and pyrochar. The effect of energy densification is greatest with AGR digestate due to its larger lignin content across both conversion processes. There is little point in processing MSW, SS and VGF digestate via pyrolysis above 200 °C due to little enhancement being made to the carbonisation of the feedstock. Above these temperatures the increase in calorific value is minimal and an even larger fraction of ash is retained in the pyrochar. However, the main benefit to the pyrolysis of digestate in this study is obtaining a char material with a high fixed carbon content, thereby increasing carbon sequestration or producing a high quality bio-coal product. Furthermore, according to the guidelines given by the European Biochar Certificate (EBC) [187] and the International Biochar Initiative (IBI) Standards [188] on H:C and O:C ratios, the pyrochars presented in this study could be considered as certified biochars.

In terms of HTC, there is little benefit to processing SS digestate over 150 °C as little improvement is made to the hydrochar energy density for application as a solid fuel. In general, the ash content in the hydrochar increases with both temperature and solid loading due to increased solubilisation of the organic material into the process waster. Increasing temperatures also results in the extraction of inorganic content into the process waters.

For digestates, higher temperature HTC processing increased liquid yields, including concentrations of TOC which is beneficial for process water treatment and biogas production. Additionally, higher solid loading of digestate material reduced the liquid yields and increased the TOC content in a non-additive way for some digestates. Ultimately, the effect of solid loading relies heavily on the feedstock composition and has more of an effect on the characteristics of process water than hydrochar.

In terms of HTC co-processing, when blending SS digestate with green wastes, the greatest change exhibited is with a reduction of inorganic content, followed by a reduction of volatile matter in the hydrochar. The elemental composition of grass hydrochar is not greatly affected by the addition of SS digestate. The addition of SS digestate to the green wastes slightly increases the TOC concentration with temperature, as TOC levels remained stable for green wastes alone. The concentration of COD in the process waters is heavily feedstock dependent. COD decreases with temperature for hedge, though COD increases for SS digestate. This could be due to the higher fraction of hemicellulose present in garden hedge that polymerise into hydrochar at higher temperatures, reducing the concentration of COD. Hedge blended with SS reduces this strong negative correlation.

Overall, the extraction of inorganics from feedstock materials is shown to occur at greater degrees with HTC than pyrolysis. The extraction of particular inorganics during HTC is feedstock dependent and can be attributed to the physical structure of the biomass itself. On the whole, HTC reduces iron, sodium, potassium and calcium content. The fate of sodium is dependent on both temperature and solid loading. A high solid loading at lower temperature will retain sodium within the hydrochar whilst a high solid loading and high temperature will extract sodium into the liquid phase. The ability for HTC to extract inorganics can be beneficial for hydrochar application.

A number of different factors and patterns have emerged from the conversion of digestate, green waste and blends via HTC and pyrolysis. Therefore, the next two chapters will focus on the application of the products. Chapter 7 will focus on the application of solid products hydrochar and pyrochar as a solid fuel and soil amender product, and Chapter 8 will focus on the treatment and application of HTC process waters for the generation of bio-methane.

CHAPTER VII

Application of Hydrochar and Pyrochar

To successfully market the solid products obtained from the thermochemical conversion of waste materials, it is necessary to understand application opportunities and how chemical makeup affect their performance. This in turn allows for the engineering of these products through the tuning of system operations. Barriers to marketing include the understanding of the complex mechanisms affecting their stability, handling and behaviour during application, whilst adhering to quality standards.

7.1. Overview

The aim of this chapter is to understand the effect of the composition of hydrochar and pyrochar on behaviour for a number of potential applications and to assess their suitability and quality. All the results from the char application experiments outlined in Chapter 3, section 3.2 are presented and examined in detail.

The objectives of this chapter are to:

- Highlight recent advancements in literature that investigate stability, handling and behavioural mechanisms for the application of hydrochar and pyrochar as a solid fuel and soil product.
- Compare the effect of hydrochar and pyrochar from digestate, including green waste and blend hydrochar composition on solid fuel properties, in particular the behaviour of ash during combustion via slagging and fouling indices.
- Compare the effect of macro, micro nutrients, including heavy metals, and phytotoxicity to germination and growth of tomato plants of SS digestate and green waste blend hydrochar in order to assess quality criteria as a soil product.

7.2. Introduction

A potential route of utilisation for hydrochar and pyrochar is in the generation of heat and electricity from their combustion. When compared to pyrochar, hydrochar has an increased hydrophobicity, enhancing dewatering and is highly friable meaning it can be more easily ground than the starting biomass, potentially improving its handling properties [189].

However, the generation of electrical energy from the combustion of hydrochar from digestate as applied as a solid fuel remains a challenge due to its inherently high levels of inorganic materials. The char from HTC has been shown to have improved combustion properties compared to its pyrochar equivalent [177,183]. Additionally, at higher temperature HTC the fraction of inorganic levels are further reduced (demineralisation) within the hydrochar, however overall yields of hydrochar are also decreased due to greater solubilisation of organic matter into the process water as seen in previous chapters. The process of demineralisation also improves the ash chemistry resulting in the reduction of the slagging and fouling propensities during combustion [99,190].

A number of indices have been formulated to understand slagging and fouling propensities, these are summarised in Methodology section 3.5.4. To re-iterate, the alkali index (AI) expresses the amount of alkali oxides (K_2O and Na_2O) in the fuel per unit of fuel energy. Alkali metals react with silica contained in the ash, forming silicates with a very low melting point, less than 800 °C. Therefore, if biomass or resultant chars are found with large contents of silica and potassium this can result in the formation of potassium silicates which create deposits in the boiler which operate in excess of 1,200 °C [191]. Studies have reported the alkali index to be of significant importance to predict the occurrence of slagging and fouling, therefore the levels of metals are monitored [192].

During combustion, loosely bound particles can become denser and come together to form compact and hard particles, this mechanism is called ash sintering. The bed agglomeration index (BAI) gives an indication of the degree of ash sintering and agglomeration occurring during combustion. The oxides in ash can be classified into acidic and base oxides (SiO_2, Al_2O_3, TiO_2 and Fe_2O_3, CaO, MgO, Na_2O, K_2O respectively). The propensity for ash deposition is evaluated in terms of a base-to-acid ratio (R b/a). The R ba ratio is an indication of the fusion behaviour and slagging potential of ash and ash-containing metals to combine during combustion to produce low temperature melting salts. Slagging refers to the formation of deposits generated from the adhesion of sticky, melted or softened ash particles on heat transfer surfaces exposed to radiant heat within boilers. The slagging index (SI) of a solid fuel is used to indicate the slagging propensity of the ash, similar to the R b/a ratio. Fouling refers to the dry deposition of ash particles or condensation of volatile inorganic components on heat transfer surfaces. The fouling index (FI) of a solid fuel is a measure of the fouling propensity of ash. The slag viscosity index (SVI) is one index used to predict the slagging tendency as it leads to an understanding of the structure of slag.

Table 31 lists these slagging and fouling indices for waste biomass and resultant hydrochar and pyrochar, including sub-bituminous coals found in the literature. The literature shows HTC improves slagging and fouling indices compared to pyrolysis.

Table 31. Slagging and fouling indices for both feedstock and resultant hydrochar and pyrochar from wastes, including sub-bituminous coal.

Feedstock	Feed. slagging & fouling indices						Process & parameters				Char slagging & fouling indices						Ref.
	AI	BAI	R b/a	SI	FI	SVI	Pro.	Load (%)	Temp (°C)	Time (hr)	AI	BAI	R ba	SI	FI	SVI	
Sub-bituminous coal 1	-	-	1.85	0.8	5.0	27	HTC	25	300	1	-	-	1.66	0.5	1.7	29	[153]
Sub-bituminous coal 2	-	-	1.95	0.4	11.0	26					-	-	1.88	0.3	2.0	25	
Sub-bituminous coal 3	-	-	1.38	0.7	9.2	37					-	-	1.16	0.4	1.1	39	
Sub-bituminous coal 4	-	-	2.30	2.1	18.8	25					-	-	1.91	1.0	2.9	26	
AD press cake	1.14	0.90	0.10	0.0	0.2	92	HTC	10	200	1	0.95	2.62	3.20	0.0	2.1	0	[99]
									250		0.30	4.65	0.10	0.0	0.0	89	
Sewage sludge	1.71	3.95	0.30	0.6	0.5	80			200		1.67	7.20	0.20	0.6	0.2	82	
									250		0.88	6.93	0.20	0.0	0.3	80	
Municipal wastes	0.66	0.63	0.60	0.3	2.9	59			200		0.40	1.43	0.60	0.1	1.8	55	
									250		0.10	5.01	0.30	0.0	0.2	73	
Willow	0.16	0.03	2.10	0.2	39.4	6			200		0.04	0.11	0.60	0.1	9.9	4	
									250		0.05	0.14	1.00	0.1	25.4	3	
Olive mill	0.66	-	-	-	-	-	HTC	30	200	2	0.40	-	-	-	-	-	[193]
									225		0.21	-	-	-	-	-	
									250		0.07	-	-	-	-	-	
Canned artichoke	1.09	-	-	-	-	-			200		0.80	-	-	-	-	-	
									225		0.74	-	-	-	-	-	
									250		0.50	-	-	-	-	-	
Orange wastes	0.53	-	-	-	-	-			200		0.12	-	-	-	-	-	
									225		0.26	-	-	-	-	-	
									250		0.16	-	-	-	-	-	
Mixed waste digestate	1.28	-	1.14	-	-	-	Not performed				-	-	-	-	-	-	[194]
Municipal sewage sludge	-	-	-	1.1	1.2	56	Pyro	-	500	1	-	-	-	0.9	1.3	56	[195]
									600		-	-	-	0.9	1.3	55	
									700		-	-	-	1.0	1.2	56	
Industrial sewage sludge	-	-	-	0.7	1.0	64			500		-	-	-	0.6	1.0	65	
									600		-	-	-	0.6	1.0	64	
									700		-	-	-	0.6	1.1	63	

An increasing number of studies are now focusing on the agronomical properties of char for its use as a ‘biochar’ i.e. placed in the ground. Biochar applications in agriculture are based on physiochemical properties such as stability, conditioning and hydraulic properties, bioavailability of nutrients, including sorption of GHG and phosphorous, and phytotoxicity to germination and plant growth including abnormalities. Importantly, all of these factors contribute to the understanding of biochars long term environmental sustainability (biogeochemistry). The effect of char on soil conditioning (amelioration or amendment), has been of interest to improve soil fertility, hydraulic properties, physical properties and nutrient use efficiency. However, due to the complexity of the physio-chemical properties of chars, most studies remain unsettled.

The attitude towards HTC char application in soils is undecided because of inconclusive results, largely due to the variation of feedstock materials, processing and operating conditions and complexity of the physiochemical properties of charcoal-like materials. The content of labile carbon, especially water extractable organic carbon content is a sensible indicator of soil organic matter quality. Greater fractions of labile carbon has been reported to be found in hydrochar compared to that of pyrochar of the same starter material [117,196]. Hydrochar also exhibits similar recalcitrant carbon fractions to that of pyrochar made from lower temperature pyrolysis as shown in Chapter 6 Tables 23 and 25 (see fixed carbon content values), this carbon fraction persists in soil for longer therefore exhibits stability. The fertility of soils is determined to be largely dependent on the content of humic substances. The main fractions of humic substances are comprised of humic acid and fulvic acid. These acids generate mechanisms that provide soils and plants with concentrated doses of essential nutrients, vitamins and trace elements [197]. Humic materials have been characterised with high cation-exchange-capacities (CEC) [198], which is a measure of how many cations (nutrients) can be retained and exchanged on material particle surfaces. The CEC of hydrochar has been reported to be greater to that compared to pyrochar [199], therefore hydrochar can be seen as a ‘humic’ like material [200]. For these reasons, the pyrochars generated in this study will not be investigated in the forthcoming results and discussion section. Additionally, the high CEC value of hydrochar also helps to increase water retention and has been reported to have greater water holding capacities (WHC) compared to pure quartz sand by a factor of 5 to 10 [201].

The bio-availability of nutrients (nitrogen, phosphorous and potassium) and the stability of char are important factors if used as a soil amender, fertiliser, compost or peat like product. A number of studies have investigated the fate of macro and micro nutrients, including heavy metals during HTC and pyrolysis of digestate and other biomass materials, as shown in Table 32. It was found that the majority of nitrogen (N) compounds, such as ammonia (NH_3) and phosphorous (P) are retained in the solid hydrochar [113], whilst potassium (K) is largely transferred into the liquid phase [119] also validated in Chapter 6. The rate of P immobilisation in hydrochar has been shown to be feedstock dependent and linked to the presence of Ca, Mg and Fe which increases with high temperature processing due to precipitation of phosphate salts [111]. However, the plant availability of P was found to be low due to the digestate levels of iron and aluminium salts [113]. The mineralisation of hydrochar has been found to more stable compared to the raw digestate material [115] and stability has been linked to multiple factors, including O:C and H:C atomic ratios, C:N ratios, pH and lignin content. On the other hand, a study by Schulze et al. (2016) could not confirm the correlation of lignin content with hydrochar stability, though the stability was significantly increased through the recirculation of HTC process waters [123]. Nevertheless, there are challenges for the use of hydrochar for agricultural purposes. Becker et al. (2013) studied concentrations of harmful volatile organic compounds (VOC) to soil ecology from hydrochar created from a number of biomass feedstock, including digestate. Results show that level of benzens, phenols, furans, ketones and aldehydes increase with process temperatures. The research suggests restraint on the application of fresh hydrochar within soils [122].

Another facet to the agronomical use of char is the need to assess the risk to plant germination and growth i.e. plant response. Limited studies have been conducted in this area, especially with chars generated from digestate materials. The genotoxicity and phytotoxicity effects of a wide range of biomass waste hydrochar were studied by Busch et al., (2013) and it was found that mostly negative genotoxic results were exhibited and total germination inhibition occurred at additions above five percent v/v [176]. However, the same hydrochars exhibited growth stimulating effects after biological post-treatment by co-composting with agri-residues. The same negative results were also found by Bargmann et al., (2014) for the germination of barley after hydrochar application. It was found however, that the negative effects were diminished when sowing barely nine weeks after the application hydrochar. The study concludes that the germination-inhibiting substances were removed during the nine weeks after soil incorporation [116]. Hydrochar also has the capacity for adsorption of gas emissions. Methane and nitrous oxide adsorption capacities have been reported to be greater for hydrochar compared to that of pyrochar on rice paddy fields [202]. Another study by Takaya et al., (2016) investigated the phosphate and ammonium adsorption capacities of hydrochar and pyrochar from a range of waste materials to remediate soils [124]. It was found that hydrochar derived from digestate slightly outperformed pyrochar from the same material. However, it remains unclear as to whether the surface area of char is the most important factor influencing ammonium uptake. Nevertheless, the outcomes of research highlight the potential of hydrochar to also remediate and adsorb emissions from the composting process.

Table 32. Macro, micro nutrients and heavy metals of feedstock and resultant char found in literature for agronomical analysis.

	Feedstock macro and micro nutrients, and heavy metals (db)														Process & parameters				Char macro and micro nutrients, and heavy metals (db)														
Feedstock	**N**	**P**	**K**	**Ca**	**Mg**	**Na**	**Fe**	**Cu**	**Mn**	**Zn**	**Mo**	**Cr**	**Ni**	**Pb**	**Pro.**	**Load**	**Temp**	**Time**	**N**	**P**	**K**	**Ca**	**Mg**	**Na**	**Fe**	**Cu**	**Mn**	**Zn**	**Mo**	**Cr**	**Ni**	**Pb**	**Ref.**
	(g/100g)						**(mg/kg)**					**(mg/kg)**				**(%)**	**(°C)**	**(hr)**	**(g/100g)**						**(mg/kg)**					**(mg/kg)**			
Corn digestate	3.40	-	4.25	2.40	0.08	2.40	280	-	-	-	-	-	-	-	HTC	9	180	8	1.82	-	0.25	0.98	0.20	0.05	1940	-	-	-	-	-	-	-	[115]
Grass	3.87	-	3.00	0.70	0.16	0.04	240	-	-	-	-	-	-	-					2.28	-	0.25	1.28	0.23	0.04	110	-	-	-	-	-	-	-	
Straw	0.63	-	2.04	0.22	2.04	0.17	10	-	-	-	-	-	-	-					0.43	-	0.04	0.19	0.04	0.04	400	-	-	-	-	-	-	-	
Woodchips	0.18	-	0.07	0.12	0.04	0.06	20	-	-	-	-	-	-	-					0.17	-	0.04	0.08	0.04	0.03	590	-	-	-	-	-	-	-	
Straw digestate	0.7^{b}	-	-	-	-	-	-	-	-	-	-	-	-	-	HTC	10	210	6	1.10	-	-	-	-	-	-	-	-	-	-	-	-	-	[123]
																	230		1.60	-	-	-	-	-	-	-	-	-	-	-	-	-	
																	250		1.80	-	-	-	-	-	-	-	-	-	-	-	-	-	
SS digestate	2.70	1.64	0.41	2.36	0.51	0.64	3091	-	-	-	-	-	-	-	HTC	10	250	1	0.60	1.93	0.30	2.81	0.71	0.39	3877	-	-	-	-	-	-	-	[111]
Swine manure	3.00	1.56	0.81	3.68	0.96	0.40	104	-	-	-	-	-	-	-					2.70	2.96	0.02	5.59	0.98	0.52	220	-	-	-	-	-	-	-	
Chicken manure	5.70	1.29	2.03	2.43	0.65	0.37	42	-	-	-	-	-	-	-					4.90	2.44	0.04	4.78	1.13	0.56	151	-	-	-	-	-	-	-	
MSW digestate	4.70	2.45	0.63	4.76	0.49	-	2690	138	278	452	3	29	17	11	HTC	28	150	1	3.90	2.42	0.45	4.52	0.48	-	2650	151	299	467	4	29	19	467	[113]
																	200		3.00	2.78	0.45	5.09	0.56	-	2990	179	345	540	5	36	24	540	
Corn digestate	1.57	-	-	-	-	-	-	-	-	-	-	-	-	-	HTC	n.g	200	6	2.59	-	-	-	-	-	-	-	-	-	-	-	-	-	[117]
																	250		2.98	-	-	-	-	-	-	-	-	-	-	-	-	-	
															Pyro	-	750	0.8	0.90	-	-	-	-	-	-	-	-	-	-	-	-	-	
Woodchip	0.78	-	-	-	-	-	-	-	-	-	-	-	-	-	HTC	n.g	200	6	1.07	-	-	-	-	-	-	-	-	-	-	-	-	-	
																	250		1.22	-	-	-	-	-	-	-	-	-	-	-	-	-	
															Pyro	-	750	0.8	0.89	-	-	-	-	-	-	-	-	-	-	-	-	-	
Silage & manure digestate	2.33	-	-	-	-	-	-	-	-	-	-	-	-	-	HTC	11	180	1	7.08	-	-	-	-	-	-	-	-	-	-	-	-	-	[120]
																	220		6.75	-	-	-	-	-	-	-	-	-	-	-	-	-	
																	260		6.42	-	-	-	-	-	-	-	-	-	-	-	-	-	
															Pryo	-	400	0.5	3.69	-	-	-	-	-	-	-	-	-	-	-	-	-	
																	600		2.83	-	-	-	-	-	-	-	-	-	-	-	-	-	
																	800		2.12	-	-	-	-	-	-	-	-	-	-	-	-	-	
Greenhouse waste	1.10	-	-	-	-	-	-	-	-	-	-	-	-	-	HTC	10	250	1	3.10	2.00	7.00	16.00	2.00	0.00	-	-	-	-	-	-	-	-	[124]
															Pyro	-	400		1.20	4.00	41.00	36.00	9.00	4.00	-	-	-	-	-	-	-	-	
																	600		0.90	4.00	50.00	45.00	12.00	4.00	-	-	-	-	-	-	-	-	
MSW digestate	1.50	-	-	-	-	-	-	-	-	-	-	-	-	-	HTC	10	250	1	0.90	5.00	2.00	27.00	6.00	0.30	-	-	-	-	-	-	-	-	
															Pyro	-	400		0.90	6.00	12.00	39.00	6.00	4.00	-	-	-	-	-	-	-	-	
																	600		0.90	5.00	11.00	36.00	5.00	4.00	-	-	-	-	-	-	-	-	
Municipal press cake	1.20	0.36	0.74	2.60	0.29	0.18	8534	47	206	202	2	67	31	98	Pyro	-	400	15	0.90	0.55	1.07	3.31	0.45	0.28	12217	76	260	265	4	92	46	100	[203]
																	600	15	0.64	0.51	0.99	2.99	0.40	0.26	11399	76	260	265	4	102	48	112	

^{b}, daf; n.g, not given

By in large, these studies show that the application of hydrochar to land will need further investigation, including an application strategy that fits in with agricultural practice. The literature contains a number of knowledge gaps on the application of hydrochar and pyrochar as solid fuel and soil amendment products. A number of studies assessing the combustion behaviour of both hydrochar and pyrochar generated from biomass wastes have been conducted, however research on the slagging and fouling behaviour of raw digestate and chars produced from both HTC and pyrolysis remains limited. Furthermore, there is an absence of research for hydrochar application in agriculture; specifically, studies on phytotoxicity causing delays to seed germination, including inhibition and adverse effects on plant growth. Moreover, studies that assess the quality of hydrochar against compost quality criteria are missing. Therefore, the purpose of this chapter is to understand the functionality of HTC and pyrolysis chars for their applicability in solid fuel and incorporation into soils. Combustion analysis via slagging and fouling indices have been performed on all hydrochar and pyrochar to indicate which thermochemical process enhances the solid fuel properties of digestate materials, including co-processed feedstock, to understand how the addition of lignocellulosic materials affects the indices. The outcomes of this investigation will aid in the understanding of whether high ash chars should be utilised as a solid fuel. Additionally, this chapter also assesses the potential application of hydrochar as a soil product via analysis of the agronomic properties, which include nutrient and heavy metal concentrations and plant response tests. The hydrochar will also be evaluated against the PAS 100 quality criteria for compost (listed in Table 33) on potentially toxic elements, including weed seeds and physical contaminants.

Table 33. PAS100 quality criteria for application as a compost product (sourced from [204]).

Item	Parameter	Test method	Unit	Upper limit
Pathogens				
1	Escherichia coli	BS ISO 16649-2	CFU / g fresh mass	1000
2	Salmonella spp	BS EN ISO 6579	25 g fresh mass	Absent
PTE's				
3	Cadmium (Cd)	BS EN 13650	mg / kg dry matter	1.5
4	Chromium (Cr)	BS EN 13650	mg / kg dry matter	100
5	Copper (Cu)	BS EN 13650	mg / kg dry matter	200
6	Lead (Pb)	BS EN 13650	mg / kg dry matter	200
7	Mercury (Hg)	BS ISO 16772	mg / kg dry matter	1
8	Nickel (Ni)	BS EN 13650	mg / kg dry matter	50
9	Zinc (Zn)	BS EN 13650	mg / kg dry matter	400
Stability / maturity				
10	Microbial respiration rate	ORG 0020	mg CO2 / g	16
Weed seeds and propagules				
11	Germinating weed seeds or propagule regrowth	OFW004-006	mean number / litre of compost	0
Physical contaminates				
12	Total glass, metal, plastic and any ‘other’ non-stone fragments > 2 mm	AfOR MT PC&S	% mass / mass of “air-dry” sample	0.25 of which 0.12 is plastic
Stones				
13a	Stones > 4 mm in grades other than “mulch”	AfOR MT PC&S	% mass / mass of “air-dry” sample	8
13b	Stones > 4 mm in “mulch” grade	AfOR MT PC&S		10

The outcomes of this latter investigation are in support of the HTC co-processing integration approach (Figure 25), which can be conceptualised as a compost accelerating process due to the reported humic like character of hydrochar.

7.3. Results and discussion

The chars generated in this study will be assessed for their behaviour during combustion from the analysis of energy yields, and slagging and fouling indices, including hydrochar's behaviour within soil from the analysis of nutrient and heavy metal concentrations and tomato plant response tests. This will aid in the understanding of how well suited the chars are for the application as a solid fuel and soil incorporation product. Pyrochar will not be assessed for their agronomic properties as outlined in section 7.2 Introduction.

7.3.1. Application as a solid fuel

Slagging and fouling indices are used to understand the behaviour of char-like materials during combustion. The inorganic composition data as given in Chapter 6 has been used to calculate the indices using equations given in Chapter 3 section 3.5.4. The slagging and fouling indices have been applied to the digestate chars (both hydrochar and pyrochar) and to the hydrochar produced from green wastes only, including SS digestate and green waste blends, to understand any improvements from co-processing with lignocellulosic materials. Table 34 shows an overview of the indices' interpretation, with key indicator colours used in the following results section.

Table 34. Key and summary of the propensities for each slagging and fouling indices used [99].

Key	Interpretation	Slagging and fouling indices					
		AI	BAI	R b/a	SI	FI	SVI
🟩	Low / safe	<0.17	>0.15	<0.5	<0.6	<0.6	>72
🟨	Medium / likely	>0.17<0.34	<0.15	>0.5<0.7	>0.6<2.0	>0.6<40	>65<72
🟥	High / certain	>0.34	-	>0.7	>2.0	>40	<65

7.3.1.1. Digestate hydrochar and pyrochar combustion behaviour

Table 35 lists the slagging and fouling indices and coloured indicators for their propensities for both the digestate raw material and resultant chars (hydrochar and pyrochar) created with varying process parameters. The energy yields, which indicate the amount of energy retained after thermochemical treatment, are also listed. In general, the increase in HTC and pyrolysis process temperature lowers energy yields for the digestate feedstock mainly due to the loss of solid material through solubilisation or volatisation as shown in Chapter 5.

Table 35. Slagging and fouling indices for hydrochar and pyrochar from digestate material.

	Digestate and resultant chars	Energy yield (%)	Slagging and fouling indices					
			AI	BAI	R b/a	SI	FI	SVI
	AGR digestate		1.25	1.46	2.10	0.6	29.2	38
Hydrochar	150 °C at 20%	82.9	2.21	0.29	1.66	0.1	32.2	49
	200 °C at 10%	72.6	0.80	0.56	1.15	0.1	13.6	54
	200 °C at 20%	78.6	1.18	0.35	1.32	0.2	20.9	54
	200 °C at 30%	94.0	1.34	0.34	1.48	0.0	25.5	51
	250 °C at 10%	63.5	0.50	1.29	1.28	0.3	7.4	46
	250 °C at 20%	69.3	0.59	0.95	1.03	0.2	7.3	53
	250 °C at 30%	64.5	0.60	0.93	1.06	0.3	7.1	52
Pyrochar	200 °C	90.5	2.40	0.17	1.95	0.4	52.4	51
	400 °C	47.5	1.69	1.83	2.09	0.1	25.1	37
	600 °C	36.0	2.04	1.86	1.80	0.1	21.1	41
	MSW digestate		2.05	1.44	0.92	0.2	5.3	50
Hydrochar	150 °C at 20%	88.1	1.21	2.80	1.53	0.0	5.2	35
	200 °C at 10%	84.7	1.60	2.09	1.02	0.1	4.0	46
	200 °C at 20%	87.1	1.31	2.70	1.04	0.1	3.4	45
	200 °C at 30%	84.6	1.37	2.60	1.06	0.1	3.7	44
	250 °C at 10%	82.0	1.07	3.52	1.41	0.3	3.6	36
	250 °C at 20%	83.9	1.06	3.88	0.48	0.0	1.2	61
	250 °C at 30%	82.9	1.84	1.72	0.77	0.0	3.3	54
Pyrochar	200 °C	93.0	1.46	2.20	1.27	0.2	5.1	40
	400 °C	82.8	1.54	2.37	1.20	0.2	4.5	41
	600 °C	80.2	1.62	2.32	1.18	0.7	4.5	42
	SS digestate		1.04	3.00	0.63	1.0	2.1	56
Hydrochar	150 °C at 20%	87.6	0.90	2.62	0.43	0.1	1.3	65
	200 °C at 10%	73.1	0.78	3.40	0.42	0.3	1.1	65
	200 °C at 20%	76.9	0.75	3.43	0.44	0.4	1.1	64
	200 °C at 30%	80.2	0.89	2.68	0.44	0.5	1.4	65
	250 °C at 10%	66.9	1.25	1.94	0.82	0.7	3.2	52
	250 °C at 20%	69.4	0.95	2.81	0.46	0.3	1.4	63
	250 °C at 30%	73.0	0.75	3.32	0.44	0.4	1.1	64
Pyrochar	200 °C	92.2	0.76	2.39	0.42	0.3	1.4	66
	400 °C	56.5	1.05	2.56	0.42	0.1	1.2	66
	600 °C	52.8	1.29	2.50	0.43	0.4	1.4	65
	VGF digestate		1.55	0.85	0.42	0.1	2.2	73
Hydrochar	150 °C at 20%	89.4	1.41	1.13	0.49	0.0	2.0	67
	200 °C at 10%	78.7	0.83	1.95	0.34	0.1	0.8	74
	200 °C at 20%	82.1	0.86	1.73	0.40	0.1	1.1	71
	200 °C at 30%	79.9	1.84	0.74	0.41	0.1	2.2	73
	250 °C at 10%	70.7	1.16	1.49	0.33	0.0	0.9	76
	250 °C at 20%	71.6	0.89	1.96	0.36	0.1	0.8	73
	250 °C at 30%	74.2	1.28	1.42	0.37	0.0	1.2	73
Pyrochar	200 °C	92.8	1.49	0.79	0.36	0.1	1.6	75
	400 °C	71.2	2.15	0.68	0.42	0.0	2.2	73
	600 °C	69.6	2.12	0.77	0.40	0.0	1.9	73

Figure 49 illustrates the energy yield, alkali index, bed agglomeration index and base-to-acid ratios of the digestate materials and resultant chars. These three indices have been chosen due to their popularity. For example, the AI is a useful guide to fouling, the BAI is an indicator of how ash can form together create hard deposits without melting (ash sintering) and R b/a is a good guide for biomass slagging, however it should be noted that the interpretation is different for coal [205]. With regards to HTC, the effect of solid loading on energy yields remains stable, with the exception of AGR digestate processed at 200 ˚C, where the energy yield increases with solid loading, as shown in Figure 49a.

No significant reduction has been made to the alkali index from both thermochemical treatments on all digestate samples as values remain above 0.34, which means almost certain fouling (Tables 34 and 35). However, the alkali index propensity is shown to reduce with increasing HTC temperature (Figure 49a and d). Pyrolysis shows the opposite trend where AI values increase with temperature.

The bed agglomeration index of the char has reduced in some cases compared to the starter digestate material. The data suggests that BAI is not affected by variation in process parameters, however for the case of AGR digestate, the risk is increased through HTC processing. Nonetheless, generally all values remain above 0.15 indicating the likelihood of bed agglomeration as low. Improvements are made to the base to acid ratio (R b/a) from the initial materials, except for MSW digestate. The R b/a values are reduced from a medium risk to a low risk of slagging for SS digestate from both treatments (the value for SS digestate hydrochar produced at 250 ˚C at 10 percent solid loading appears to be an anomaly).

In general, the base-to-acid ratio is reduced with increasing HTC temperatures. Increasing HTC solid loading and pyrolysis temperatures did not affect R b/a values. Improvements to the slagging index (SI) propensity are made on all digestate feedstock regardless of the treatment process. Where raw materials are at medium risk, such as AGR and SS digestate, improvements are made by both HTC and pyrolysis to reduce the risk to low, as shown in Table 35. No significant effect of treatment is made to the fouling index (FI). Where FI has improved is through the HTC of AGR and VGF digestate compared to the raw materials. However, the reductions made are not significant as all cases remain at medium risk. An improvement in the slag viscosity index (SVI) is only seen with pyrochar derived from SS, changing from high to medium risk (however this cannot be said with confidence due to the small step change exhibited).

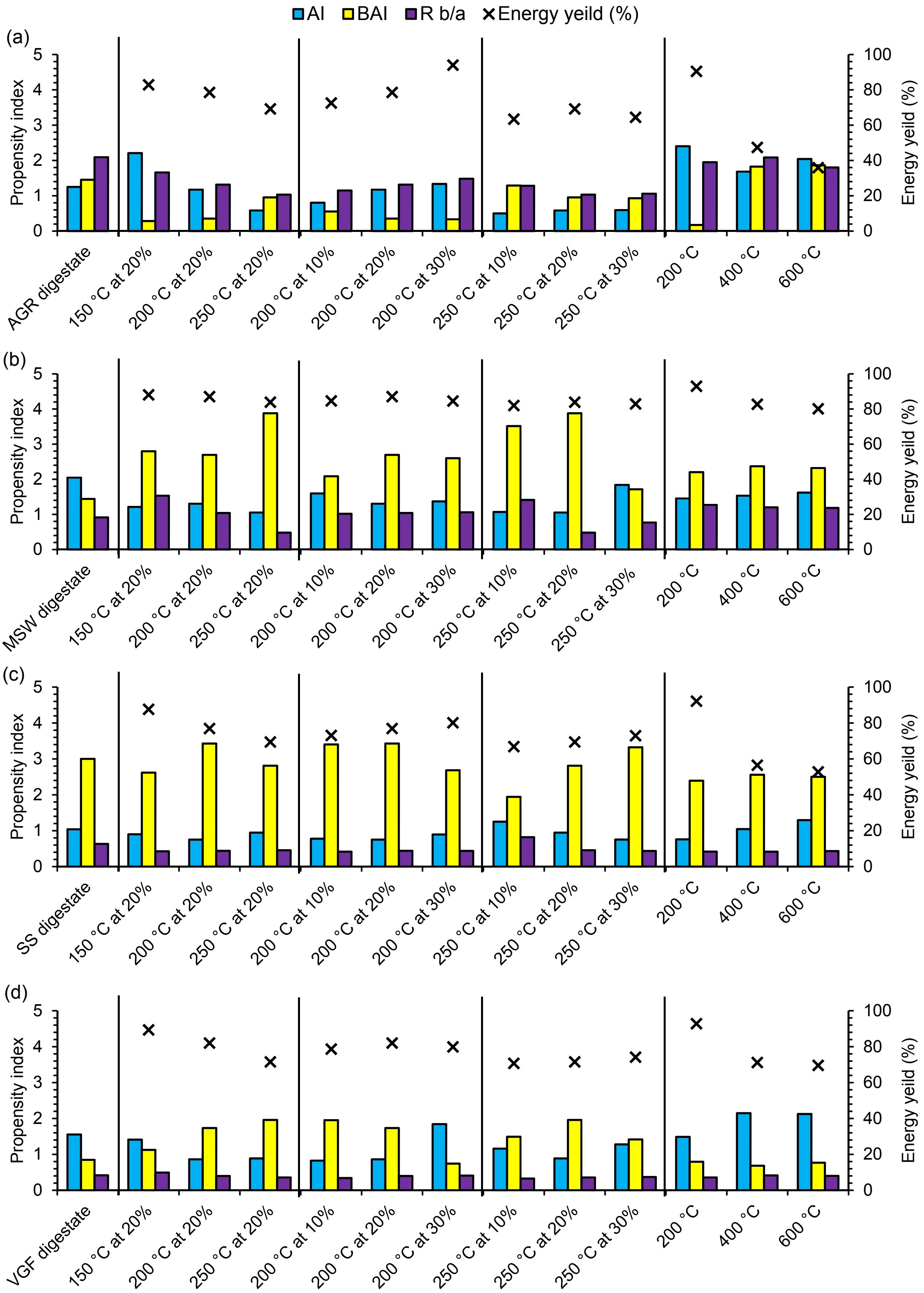

Figure 49. Energy yield, alkali index, bed agglomeration and base-to-acid ratio propensities for digestate materials and resultant hydrochar and pyrochar obtained from **a**) AGR, **b**) MSW, **c**) SS and **d**) VGF through differing operating parameters.

7.3.1.2. Green waste and blend hydrochar combustion behaviour

Table 33 shows the slagging and fouling indices used to evaluate the influence of the ash composition and chemistry behaviour during combustion for hydrochar produced from green wastes and blends with SS digestate. SS digestate alone has been included for the purpose of comparison.

Figure 50 shows how HTC temperatures affect energy yield, alkali index for fouling, bed agglomeration for ash sintering, and base-to-acid ratio for slagging propensities. As seen previously, the increase of temperature lowers energy yields largely due to solubilisation of the solid material into the liquid phase. The reduction rate of energy yields with temperature is greater with the blended materials than their single counterparts, especially with SS digestate and grass clippings as shown on Figure 50a. This is due to the fraction of SS digestate and lignocellulosic content experiencing greater solubilisation at higher temperatures.

Table 36. Slagging and fouling indices for hydrochar from SS digestate, green wastes and blends

Feedstock and resultant hydrochar	Energy yield (%)	Slagging and fouling indices					
		AI	BAI	R b/a	SI	FI	SVI
SS digestate		1.23	2.19	0.47	0.7	1.8	64
150 °C	87.6	0.83	2.69	0.43	0.4	1.4	65
200 °C	76.9	0.97	2.63	0.44	0.5	1.4	64
250 °C	69.4	1.15	2.47	0.48	0.4	1.7	63
Grass clippings		1.13	0.19	1.42	0.0	24.4	50
150 °C	74.8	0.84	0.05	1.20	0.1	19.3	55
200 °C	70.3	0.78	0.07	0.93	0.0	11.0	60
250 °C	71.8	0.42	0.11	1.03	0.1	8.1	54
SS & grass 50/50		1.87	0.56	0.83	0.6	8.7	57
150 °C	87.2	1.15	0.93	0.58	0.3	4.5	62
200 °C	74.9	0.97	1.23	0.55	0.4	3.1	62
250 °C	62.4	0.81	1.89	0.52	0.4	2.1	62
Garden hedge		1.10	0.01	5.52	0.0	163.8	23
150 °C	73.4	0.53	0.02	5.49	0.0	107.1	19
200 °C	72.4	0.41	0.03	7.28	0.0	121.6	14
250 °C	68.6	0.20	0.06	11.00	0.8	109.0	8
SS & hedge 50/50		2.70	0.26	1.36	1.0	22.8	46
150 °C	77.2	1.40	0.71	0.55	0.3	5.2	66
200 °C	71.7	0.67	1.64	0.50	0.3	2.2	62
250 °C	64.0	0.91	1.32	0.51	0.3	2.8	63
Woodchip		0.04	0.49	1.27	0.0	9.9	43
150 °C	87.9	0.04	0.86	0.92	0.0	4.2	50
200 °C	82.8	0.05	1.72	0.68	0.0	2.0	56
250 °C	81.9	0.14	0.30	0.71	0.0	8.7	65
SS & woodchip 50/50		0.80	1.06	0.79	0.6	4.6	53
150 °C	86.5	0.54	1.98	0.45	0.2	2.0	65
200 °C	80.8	0.55	1.74	0.44	0.2	2.0	66
250 °C	73.2	0.63	1.61	0.41	0.2	1.9	68

No significant improvements are made to the alkali index (AI) for green wastes (slight decrease with temperature) and blending with SS digestate increased the AI index. Notably, however the AI index value for woodchip is increased when blended with SS digestate, from a low to high risk. On the other hand, improvements are made to the BAI of green waste hydrochar due to co-processing with SS digestate, turning grass clippings and garden hedge from likely to safe when co-processed at all temperatures.

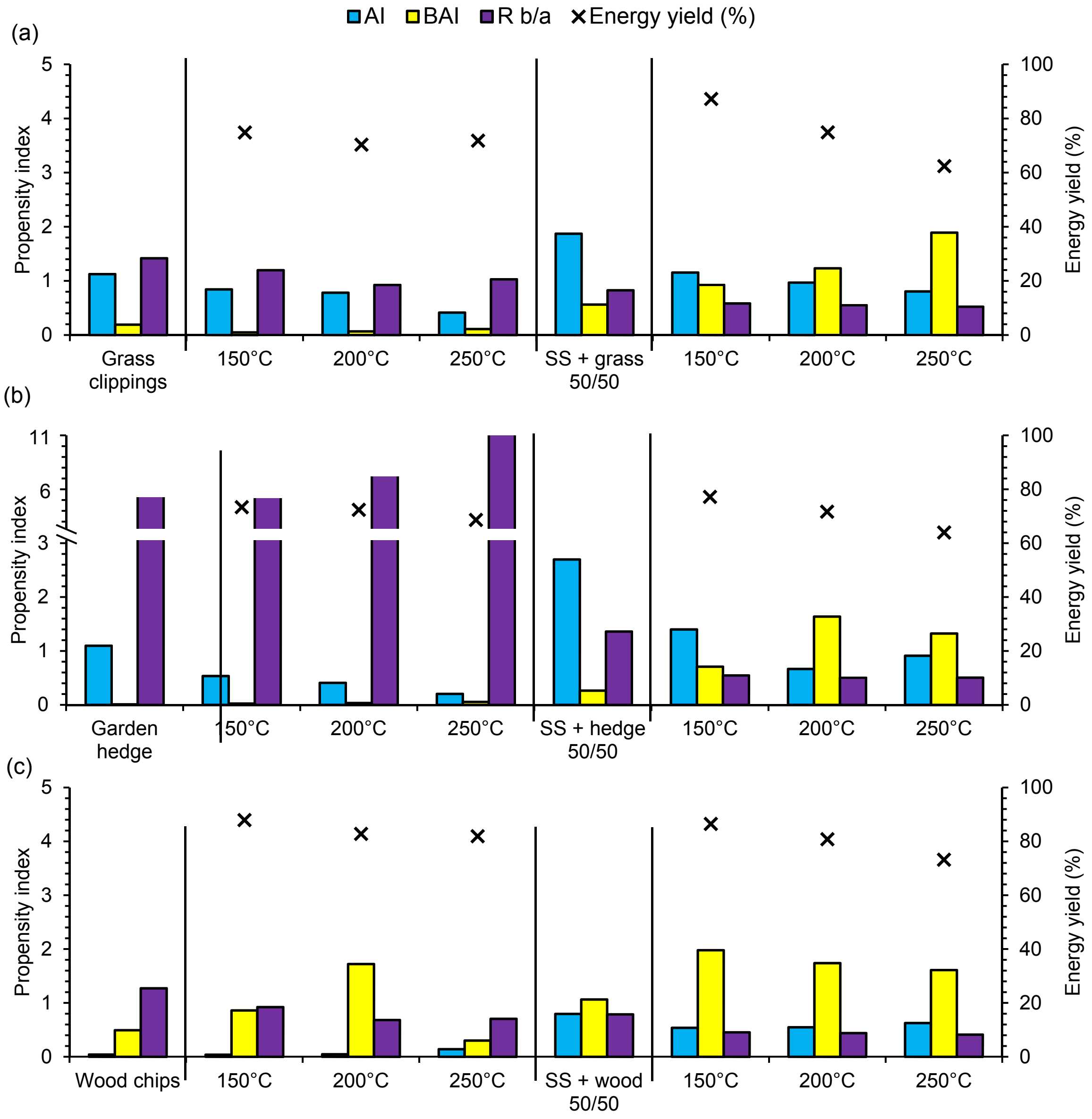

Figure 50. Energy yield, alkali index, bed agglomeration and base-to-acid ratio propensities for green waste and blends with SS digestate resultant hydrochar obtained from **a**) grass clippings, **b**) garden hedge and **c**) woodchip with increasing temperature.

Improvements are also made to the base-to-acid ratio as a result of co-processing, from a high risk of slagging for green wastes to medium and low risk of slagging when blended with SS digestate. Figure 50b also shows a significant improvement made to garden hedge when co-processed with SS digestate. The R b/a values are reduced from around 11 to 0.5

as shown in Table 36, this is due to garden hedge containing a high concentration of basic oxides, in particular calcium and potassium which are diluted when blended and further diluted when processed via HTC.

In general, HTC made no significant improvement to the slagging index (SI) of the green wastes. However, the exception is with SS digestate blended with garden hedge processed at all temperatures, where the risk is reduced from medium to low, as shown in Table 36. On the other hand, the fouling index (FI) for the green wastes is improved through co-processing with SS digestate. However, improvements are only made for high risk cases, such as grass and hedge, were blending has reduced the fouling risk from high to medium. An improvement in SVI is only seen with SS digestate and woodchip blends, where a high risk is reduced to a medium risk when processed at 150 ˚C and further reduced to a low risk when processed at 250 ˚C.

7.3.2. Hydrochar application in agriculture

As illustrated in Chapter 4, Figure 25, the latter half of the proposed HTC with AD integration concept, specifically where digestate and green waste is co-processed, can be conceptualised as accelerating the composting process. To allow a proof of this concept this investigation will assess the suitability of SS digestate and green waste hydrochar for its application as a 'biochar'.

The following sections will analyse the agri-environmental behaviour of the hydrochars. Specifically, they will examine the nutrient and heavy metal concentrations for potentially toxic elements, preliminary plant response tests to understand phytotoxicity to germination and abnormalities during plant growth, and finally assess again the PAS 100 quality criteria for compost. It should be noted that hydrochar from blended feedstock will not be included in the discussion here, due to time constraints which resulted in a smaller sample for the plant response test. However, the data on nutrient and heavy metals, including quality criteria for the blend hydrochar are provided within the appendix as discussed later.

7.3.2.1. Nutrients and heavy metals

Table 37 lists the macro (N, P, K, Ca, Mg, Na) and micro nutrients (Fe, Cu, Mn, Zn, Mo), including heavy metals (Cr, Ni, Pb) content of the hydrochar produced from SS digestate alone and green wastes at 20 percent solid loading at 150 °C, 200 °C and 250 °C process temperatures.

The data for the raw feedstock, including blends of the same are shown in Appendix Table 6. Boron (B) and Cadmium (Cd) could not be quantified due to equipment constraints.

Table 37. Concentration of macro and micro nutrients, including heavy metals SS digestate and green waste hydrochar (dry basis).

Hydrochar	Macro nutrients (g/100 g, db)						Micro nutrients (mg/kg, db)					Heavy metals (mg/kg, db)		
	N	P	K	Ca	Mg	Na	Fe	Cu	Mn	Zn	Mo	Cr	Ni	Pb
SS 150 °C	3.70	1.95	0.70	2.78	0.83	0.31	23747	272.5	1251	766	n.d	n.d	90.7	140.2
SS 200 °C	2.62	2.23	0.75	3.38	0.98	0.42	26979	350.9	1454	890	n.d	265.8	84.7	147.6
SS 250 °C	2.42	2.58	0.93	3.78	1.09	0.47	30317	351.3	1697	977	n.d	302.3	105.7	147.9
Grass 150 °C	3.11	0.55	1.21	1.83	0.25	0.18	581	22.4	112	60	25.2	33.6	16.5	n.d
Grass 200 °C	3.24	0.82	1.18	2.35	0.28	0.20	796	45.1	139	90	29.5	n.d	20.5	n.d
Grass 250 °C	3.10	0.90	0.65	2.69	0.30	0.21	833	25.1	155	82	28.3	n.d	13.9	n.d
Hedge 150 °C	2.00	0.29	0.77	1.80	0.09	0.14	192	23.1	121	106	n.d	n.d	8.6	n.d
Hedge 200 °C	1.67	0.40	0.73	1.87	0.07	0.07	232	23.4	130	127	n.d	n.d	9.8	n.d
Hedge 250 °C	2.23	0.50	0.39	1.92	0.08	0.07	217	18.8	149	129	n.d	n.d	12.5	n.d
Woodc. 150 °C	0.28	0.01	0.02	0.39	0.03	0.04	490	12.5	71	40	n.d	32.3	14.8	n.d
Woodc. 200 °C	0.29	0.02	0.05	0.63	0.05	0.04	1295	22.3	104	64	n.d	54.1	37.5	n.d
Woodc. 250 °C	0.45	0.02	0.13	0.39	0.04	0.18	858	15.8	81	45	n.d	42.9	17.5	n.d

n.d, not detected

Figure 51a, b and c illustrate the concentrations of macro and micro nutrients, and heavy metals of the hydrochar materials assessed in this section. In general, the largest fraction of macro nutrients within the hydrochar are calcium and nitrogen. Levels of iron and magnesium dominate the micronutrients concentration and chromium shares the greatest fraction of heavy metals for all hydrochar.

SS digestate hydrochar contains the greatest concentrations of micro and macro nutrients, including heavy metals compared to that of green waste hydrochar. Amongst the green waste, the largest fractions of nutrients and heavy metals are held in grass clippings, garden hedge then woodchip hydrochar. SS digestate hydrochar contains significantly larger fractions of phosphorous calcium and magnesium (around 2, 3 to 4 and 1 g per 100 g respectively). The hydrochar from SS digestate also contains large amounts of iron (23.7 g per kg), this is at least 23 times more than levels found in green wastes and up to 10 times more chromium and nickel as shown in Figure 51b. The heavy metal lead (Pb) is only found in SS digestate hydrochars, between levels of 140 to 147 mg per kg (Table 37).

Furthermore, high temperature HTC of SS digestate enriches these nutrient and heavy metals concentrations due to solubilisation of biochemical components as shown in Chapter 5, it is also further enriched due to the reduction of nitrogen as shown in Figure 51a.

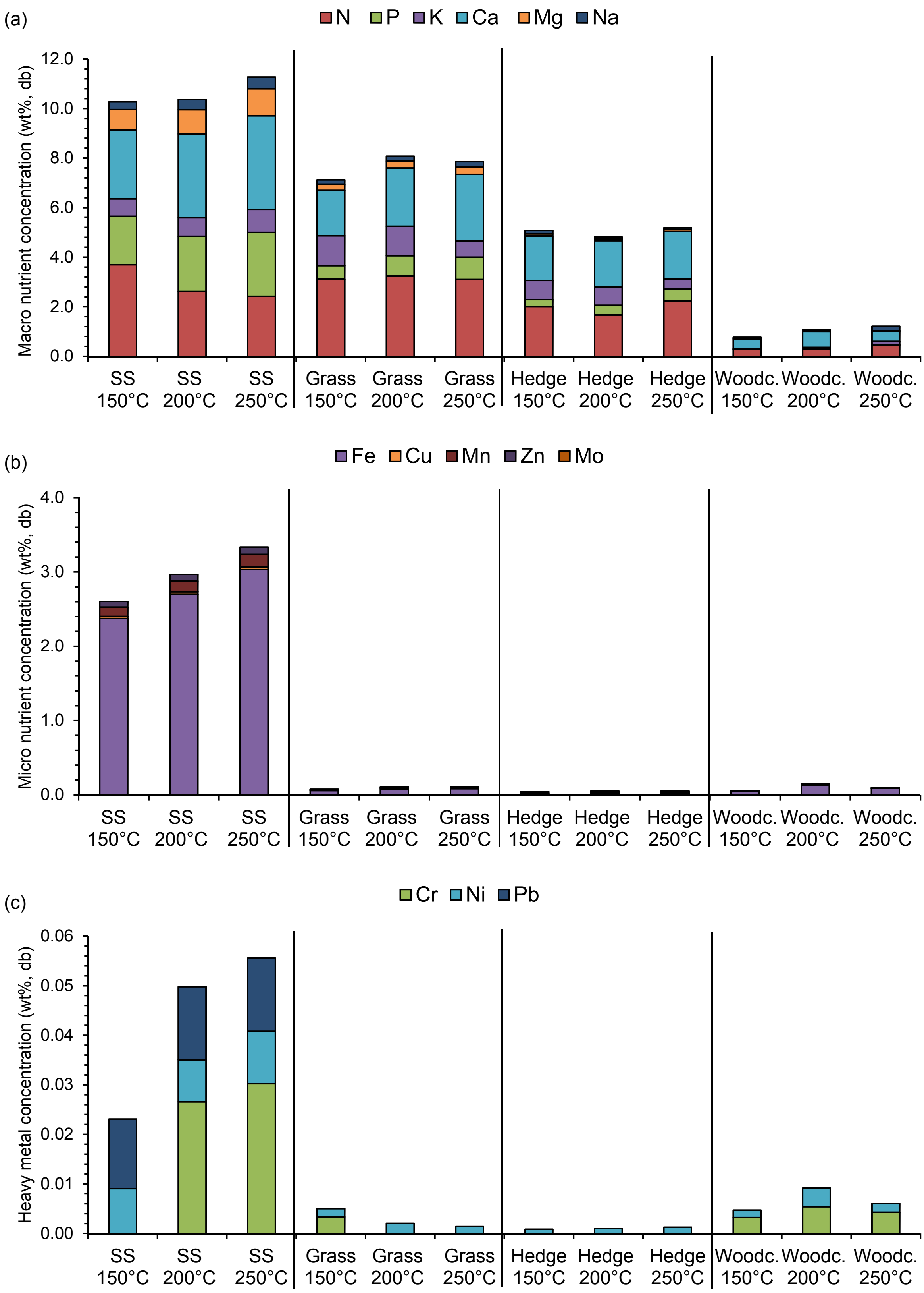

Figure 51. SS digestate and green waste hydrochar produced at 20 percent solid loading at 150 ˚C, 200 ˚C and 250 ˚C concentrations of **a**) micro, **b**) macro nutrients and **c**) heavy metals as a weight percentage of the initial material (dry basis).

However, this trend is not seen with the hydrochars from green wastes where nitrogen levels remain stable, leading to an overall stability of macro and micro nutrients, including heavy metals concentrations. It should be noted that chromium was undetected for SS digestate hydrochar produced at 150 ˚C and is considered an anomaly due to positive reading from higher temperatures.

7.3.2.2. Plant response tests (preliminary work)

The chemical composition of the hydrochars have revealed concentrations of compounds that may be harmful to plants. Therefore, it is necessary to carry out plant response tests using the hydrochar as a growing medium to ascertain any phytotoxic effects to germination and plant growth. Due to the modifications applied to the plant response tests as described in the methodology, this test is preliminary work to gain more understanding of the applicability of hydrochar in agriculture. The results of this test is listed in Table 38 and visual images are represented in Figures 52 to 57.

The phytotoxicity of the hydrochar materials were evaluated by the germination index of F1 Shirley hybrid tomato cultivar. Germination success was measured through seedling emergence after 10 days (G10) and 14 days (G14) of sowing. SS digestate and grass clipping hydrochar showed nearly 100 percent G10, with the exception of 150 °C temperature hydrochars exhibiting 67 percent G10. This observation shows that 150 °C hydrochars from SS digestate and grass clippings have a greater phytotoxicity to germination. Woodchip and garden hedge hydrochar as growing media showed the lowest germination index after 10 days, therefore exhibiting high phytotoxicity to germination. After 14 days, the germination index (G14) improved amongst garden hedge and woodchip hydrochar growth media, however this indicates slow germination and initial plant growth (see Figures 55 and 56, and Figures 53 and 54 respectively). Garden hedge hydrochar eventually reached 100 percent germination index after 14 days. The lowest relative plant mass was exhibited by woodchip (see Figures 53 and 54) followed by garden hedge and grass clippings hydrochar growing media (see Figures 54, 55 and 56) after 28 days as, as shown in Table 38.

On average, the highest relative plant mass was obtained by the growing media comprised of SS digestate hydrochar produced at lower HTC temperatures. However, the standard deviation for these values are wide, therefore confidence cannot be given to the results. Garden hedge and woodchip hydrochar from 200 ˚C and 250 ˚C HTC processing did not perform well in terms of relative plant mass values, as shown in Figures 56 and 54 (relative plant masses of 9 and 8 percent for garden hedge and 9 and 2 percent for woodchip respectively). Therefore, high temperature hydrochar from garden hedge and woodchip used as growing media are phytotoxic to plant growth.

Table 38. Germination indices, relative plant mass, number of weeds and abnormalities from hydrochar produced from SS digestate and green wastes.

Peat and hydrochar mixtures (2:1 ratio)	Replicate	No. germ. (10 days)	No. germ. (14 days)	G_{10} (%)	G_{14} (%)	Top growth mass after 28 days (mg)	Mean top growth mass (mg)	Relative plant mass (%)	No. weeds	Abnormalities		
										Stem	Leaf	Mould
Control (peat only)	1	3	3	-	-	140	140 ± 5.2	-	0			
	2					134						
	3					147						
Peat + SS digestate 150 °C	1	2	2	67	67	381	491 ± 110.1	350	0			
	2					601					■	
	3					NG						
Peat + SS digestate 200 °C	1	3	3	100	100	443	371 ± 68.0	265	0			
	2					280						
	3					392						■
Peat + SS digestate 250 °C	1	3	3	100	100	420	343 ± 75.1	245	0			■
	2					241						■
	3					369						■
Peat + Grass clippings 150 °C	1	2	2	67	67	NG	27 ± 9.1	19	0			■
	2					36				■		■
	3					18				■		■
Peat + Grass clippings 200 °C	1	3	3	100	100	20	25 ± 4.5	18	0			■
	2					26						■
	3					31					■	■
Peat + Grass clippings 250 °C	1	3	3	100	100	29	131 ± 144.5	93	0		■	■
	2					335						■
	3					28						■
Peat + Garden hedge 150 °C	1	1	3	33	100	17	15 ± 4.7	11	0			■
	2					8						■
	3					19						■
Peat + Garden hedge 200 °C	1	0	3	0	100	20	13 ± 5.8	9	0			■
	2					14						■
	3					6						■
Peat + Garden hedge 250 °C	1	1	3	33	100	5	11 ± 4.4	8	0			■
	2					12						■
	3					15						■
Peat + Woodchips 150 °C	1	0	3	0	100	27	29 ± 2.6	21	0		■	
	2					33						
	3					27						
Peat + Woodchip 200 °C	1	1	2	33	67	6	12 ± 6.8	9	0			
	2					19						
	3					NG						
Peat + Woodchip 250 °C	1	1	2	33	67	NG	2 ± 0.3	2	0			
	2					3						
	3					2						

NG, no growth

Figure 52. Pictures of plant growth from control and SS 150 ˚C soil test samples (picture of the third seedling is missing).

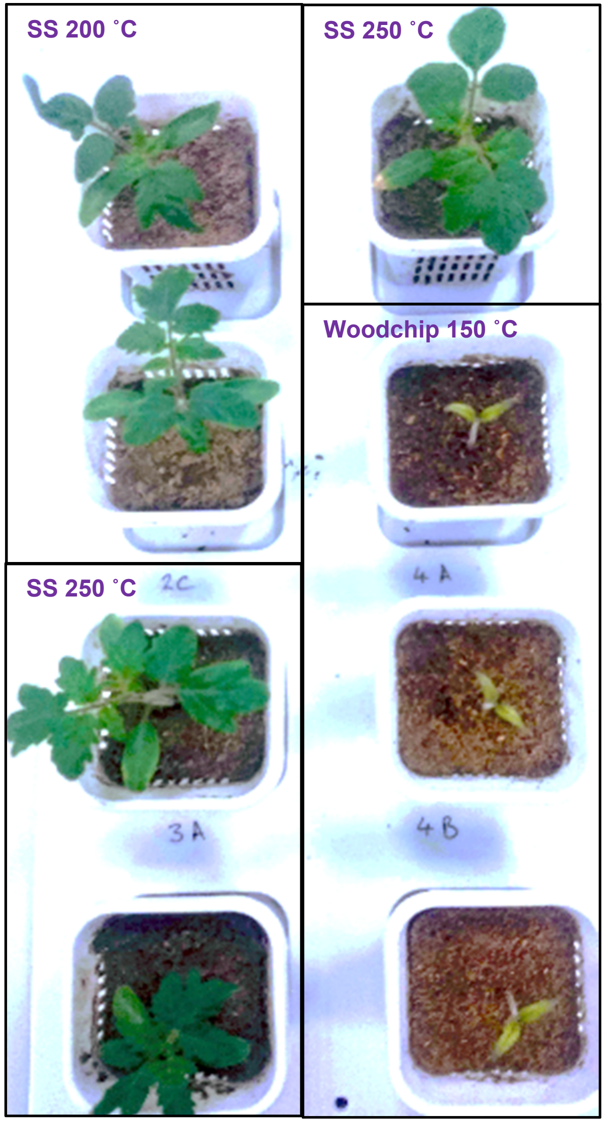

Figure 53. Pictures of plant growth from SS 200 ˚C, SS 250 ˚C and woodchip 150 ˚C soil test samples.

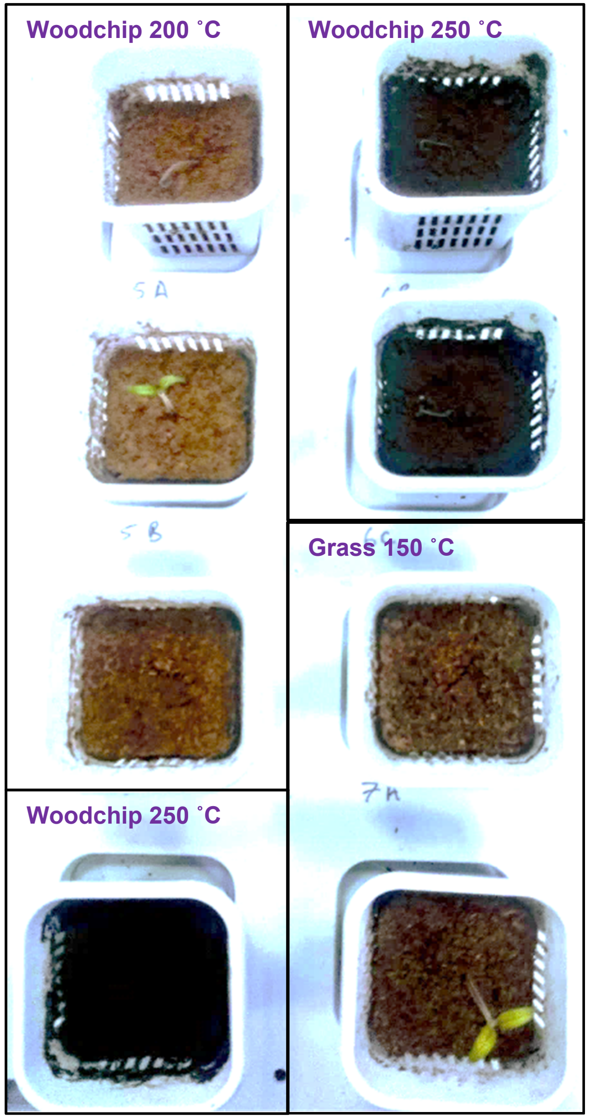

Figure 54. Pictures of plant growth from woodchip 200 ˚C and 250 ˚C, and grass 150 ˚C soil test samples.

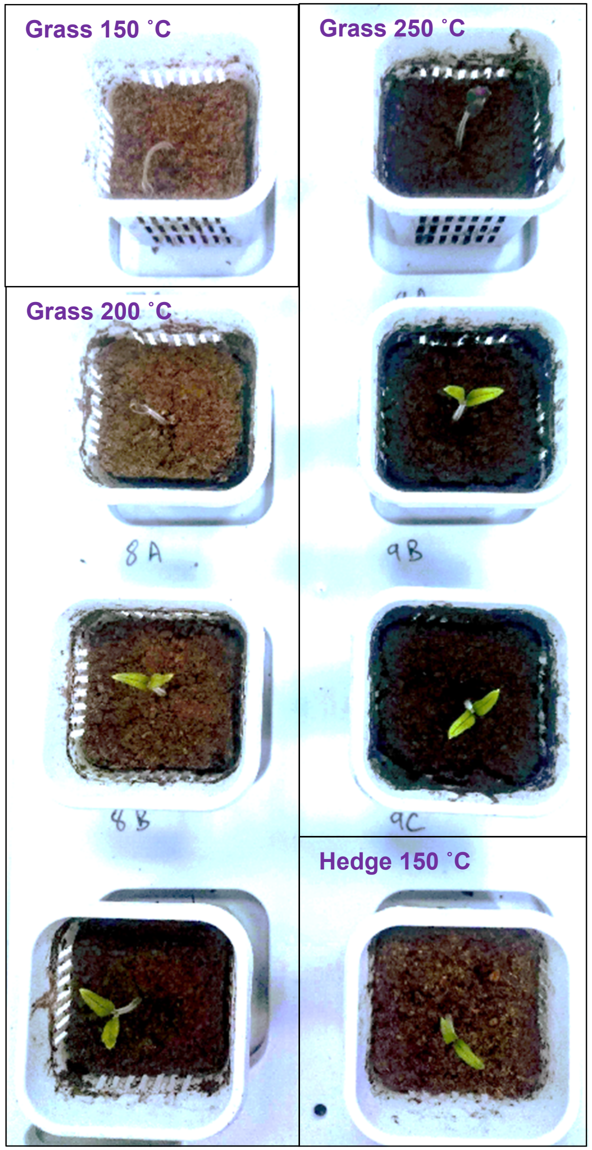

Figure 55. Pictures of plant growth from grass 150 ˚C, 200 ˚C and 250 ˚C, and hedge 150 ˚C test samples.

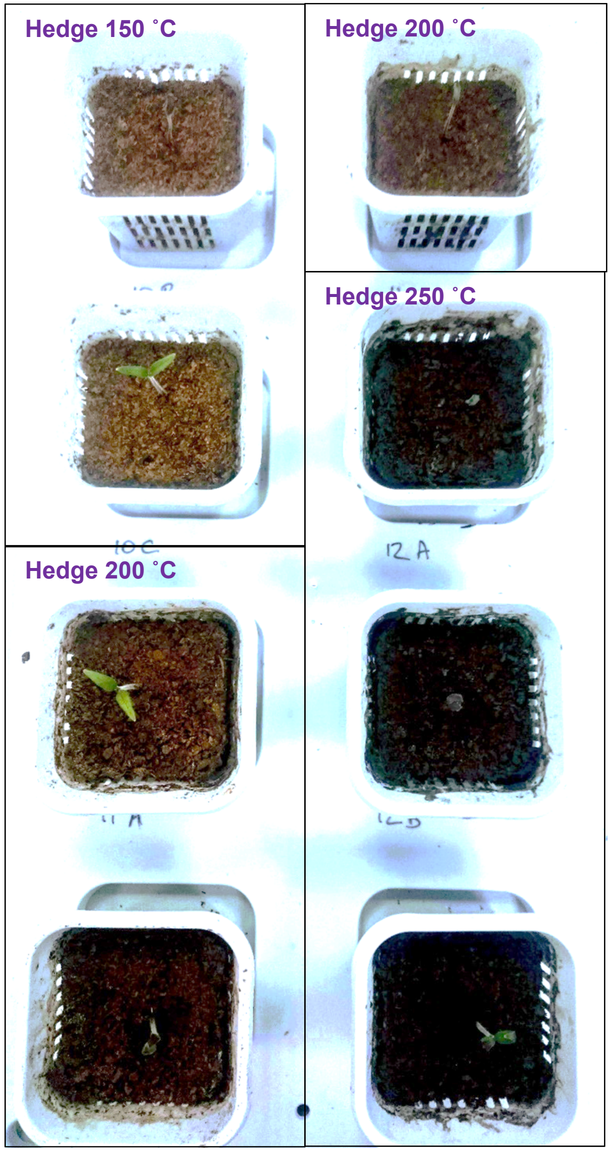

Figure 56. Pictures of plant growth from hedge 150 ˚C, hedge 200 ˚C and hedge 250 ˚C soil test samples.

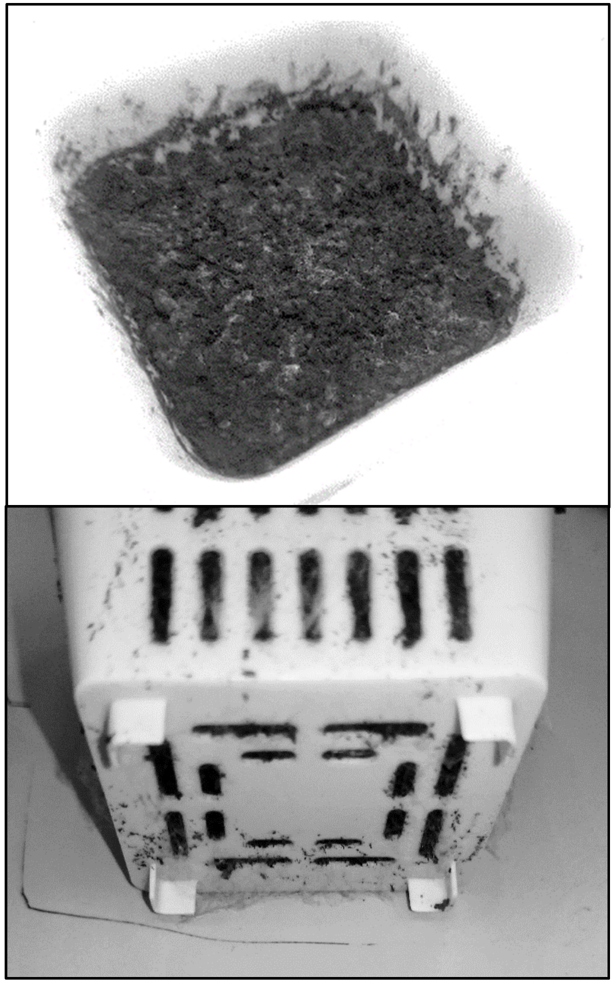

Figure 57. Pictures of mould growth found on the top and bottom of soil test pots.

In general, the growing media samples from green waste hydrochar exhibited the greatest phytotoxicity to overall plant growth, with higher temperature hydrochar exhibiting even greater levels of inhibition. No correlations of relative plant mass with nutrient and heavy metal concentrations can be made to explain the slow and low top growth mass of garden hedge and woodchip hydrochar, since SS digestate contains higher concentrations of the compounds measured and achieved relatively higher plant mass values.

The inhibition to overall plant growth could be attributed to other toxic compounds, organic pollutants for instance, such as volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAH) and 5-hydroxymethylfufural (HMF). High levels of these compounds have found to be phytotoxic, genotoxic and cytotoxic [73,176,206–208] and this finding requires further plant response investigation.

Additionally, no weeds were exhibited with any of the test samples, however abnormalities were observed during the 28-day period of growth. Stem abnormalities, such as severe bending of the stem was observed with 150 °C grass clippings hydrochar for two of the growing media samples, whilst the third did not germinate (see Figures 54 and 55). Leaf abnormalities, such as yellow spotting were exhibited by growing media samples from SS digestate hydrochar processed at 150 °C for one seedling, including one seedling from grass clipping hydrochar processed at 200 °C and 250 °C, and woodchip hydrochar processed at 150 °C (Figure 52, and Figures 54 and 55 respectively). Another unexpected abnormality was observed. Mould growth was found in growing media samples from SS digestate hydrochar processed at 250 °C and for grass clippings and garden hedge hydrochar at all temperatures as shown in Figure 57.

7.3.2.3. End of waste quality criteria

The Publically Available Specification for composted materials (PAS 100) is a document for the end of waste criteria for compost, meaning that when met, waste materials are no longer subject to regularity controls and have achieved product status. The hydrochar used in the plant response tests have been assessed against the quality criteria found in PAS 100, as listed in the introduction section.

Table 39 shows a matrix that scores the hydrochar used in the plant response, including raw feedstock materials, against criteria items 1 to 13b, with green as pass, red as fail and grey as not applicable. Appendix Table 7 includes PAS 100 scoring for co-processed hydrochar (SS digestate and green waste blends). It should be noted that item 11 (weeds) has been greyed out for the raw feedstock materials and blend hydrochar since the plant response tests were not conducted for these samples.

Table 39. PAS 100 quality criteria matrix for SS digestate and green waste hydrochar at all temperatures.

	PAS 100 criteria items (Table 33)													
Feedstock + hydrochar	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13a**	**13b**
SS digestate	▨	▨	▨	🟥	🟥	🟩	▨	🟥	🟥	▨	▨	🟩	🟩	🟩
150 °C	🟩	🟩	▨	🟩	🟥	🟩	▨	🟥	🟥	▨	🟩	🟩	🟩	🟩
200 °C	🟩	🟩	▨	🟥	🟥	🟩	▨	🟥	🟥	▨	🟩	🟩	🟩	🟩
250 °C	🟩	🟩	▨	🟥	🟥	🟩	▨	🟥	🟥	▨	🟩	🟩	🟩	🟩
Grass clippings	▨	▨	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	▨	🟩	🟩	🟩
150 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
200 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
250 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
Garden hedge	▨	▨	▨	🟥	🟥	🟩	▨	🟥	🟥	▨	▨	🟩	🟩	🟩
150 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
200 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
250 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
Woodchip	▨	▨	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	▨	🟩	🟩	🟩
150 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
200 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
250 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩

Green = pass, red = fail, grey = not applicable / not analysed

Table 39 assumes that the hydrochar do not contain any pathogens (items 1 and 2), since the HTC temperatures are higher than the recommended temperatures required to inactivate E.coli and Salmonella of 70 ˚C [209]. However, the pathogen content of the raw feedstock cannot be assumed and therefore are greyed out as enumeration tests were not investigated. Upper limits for cadmium (item 3), mercury (item7) and microbial respiration rate (item 10) are also greyed out due to the absence of the analysis.

The matrix shows that the raw SS digestate feedstock and resultant hydrochar at all temperatures, including the garden hedge feedstock, would fail PAS 100 quality criteria. Table 9 shows red areas based on exceeding the upper limits for chromium (item 4), copper (item 5), nickel (item 8) and zinc (item 9). What is more, the nutrient and heavy metal concentrations of the raw SS digestate feedstock materials, listed in Appendix Table 6 would also fail to meet the quality standards for digestate to be used as a fertiliser product (PAS 110).

Grass clippings, garden hedge and woodchip hydrochar all satisfy the PAS 100 quality criteria as a compost product. The failing criteria for raw garden hedge feedstock becomes satisfactory after HTC treatment. Nevertheless, as shown in the previous experiment, all green waste hydrochar resulted in a high degree of phytotoxicity to plant growth.

7.4. Chapter limitations and recommendations

The assessment of the application of chars in this study has limitations. The slagging and fouling indices are theoretical assumptions based on inorganic composition which were originally developed to predict ash behaviour and deposition during the combustion of brown and bituminous coal. The composition of biomass composition varies considerably and an even greater variation with biomass wastes compared to that of coal. Therefore, a large margin of error will be associated with the slagging and fouling propensities of the raw feedstock materials and the resultant chars produced via thermochemical processing in this chapter. However, no other indices are available as an alternative, therefore all of the slagging and fouling indices available in the literature have been represented. It is recommended that ash fusion tests be carried out to provide actual analysis of combustion behaviour.

For agricultural purposes, this chapter lacks the bioavailable nutrient content (minerisable N, P, K and S), electrical conductivity and cation exchange capacity (CEC) of the hydrochar. These analyses can help further understand the suitability and behaviour of the application of hydrochar in agriculture. Additionally, analysis for cadmium (Cd), boron (B), total extractable organic carbon (TEOC), water extractable organic carbon (WEOC), polycyclic aromatic hydrocarbons (PAH) volatile organic compounds (VOC) and water holding capacity (WHC) would have strengthened this chapter, by ways of understanding the biogeochemical behaviour of the hydrochar.

The plant response test, conducted to understand any phytotoxic effects to seedling germination and plant growth, was heavily modified due to bottlenecks of the space and equipment available at the time of experimentation. Essentially, the number of seeds sowed were a factor of 10 less than what is required in standard plant response tests. Furthermore, the seedling pots used will have reduced the space available for seedling root systems to spread, thereby inhibiting the rate of plant growth. The minimum requirement for the plant response test method (OFW004-006) is that plants have a minimum of fresh weight of 2 g in order to be inclusive of test results.

Additionally, the peat material selected to comprise the growing media used in the plant response tests was not characterised. Toxic compounds found in the peat material could also inhibit germination and plant growth combined with the concentrations from hydrochar. It is recommended that the raw biomass feedstock materials should also be tested for plant response to provide an understanding of the benefits to hydrothermal conversion. It should be noted that some growing media samples were more dense and compacted than others, which made water and root penetration more difficult. This is due to the preparation of hydrochar i.e. powdering of the material, combined with hydrophobic properties. Therefore, it is recommended that the plant response test be repeated with a greater number of seeds, without pots and in growing media prepared with larger hydrochar particle size.

For the assessment of PAS 100 quality criteria, E.coli or Salmonella enumeration tests were not performed to assess the pathogen content in the raw material or hydrochar. The assumption that pathogens are destroyed based on the HTC temperatures used does not take into account any contamination that may occur during handling or storage of the material.

7.5. Concluding remarks

Assessing the combustion and agronomic behaviour of the solid products after thermochemical treatment has given an understanding of the potential routes of application for hydrochar and pyrochar.

Hydrochar and pyrochar produced solely from digestate material is not recommended as a solid fuel, as the ash chemistry and predicted slagging and fouling behaviour is less than ideal for combustion and boiler efficiency. There is little benefit to processing digestate at high temperature due to the piecemeal enhancement of fuel properties.

However, processing hydrothermally does demineralise biomass feedstocks, though as shown there is little advantage in improving the ash behaviour of already very high ash feedstocks. Reducing the concentration of ash through the means of co-processing with lignocellulosic feedstock does have the potential of reducing the slagging and fouling behaviour whilst increasing the calorific value of the resultant hydrochar. In this study, the co-processing of SS digestate and green waste improved the ash chemistry to a certain degree, due to SS digestates' high aluminosilicate, calcium and phosphorous content, thereby reducing ash melting temperatures [138]. However, further blending ratios should be investigated to further reduce the likelihood of slagging and fouling, and be validated by ash fusion testing.

Another application route of hydrochar lies in the agriculture industry, potentially replacing the market for digestate as a fertiliser product. In plant response tests, SS digestate hydrochar growth media produced the greatest germination indices, mean top growth and relative plant mass levels. However, it did not fully meet quality criteria as a compost product due to exceeding Cr, Cu, Ni and Zn upper limits. Whilst green waste hydrochar met all upper limits safely, the mean top growth and relative plant mass values does not lead to seeing these single feedstock hydrochar as good compost products. There is potential, however, in meeting the quality criteria via hydrochar engineering, though the tuning of blending ratios, including varying operating parameters of temperature and solid loading. Additionally, phytotoxicity to plant growth could be reduced through further stabilisation techniques, such as co-composting hydrochar with typical composting materials. It is advised that field trials be conducted to fully understand carbon and nitrogen dynamics, bio-aerosols and other emissions after applying hydrochar in soil.

The potential for hydrochar to be used in agriculture has given an opportunity to develop the concept of an accelerating composting process, as part of the HTC co-processing integration with AD approach. This concept benefits from diverting materials away from composting, thereby reducing material volume and time for aerobic digestion, including the capturing of gas emissions from the mitigation of disposal to land and from the solubilised organic content in the HTC process waters. To this end, and to complete the proof of concept for the proposed integration approach, Chapter 8 will investigate the potential for biogas production from the HTC process waters generated in this study via anaerobic digestion.

CHAPTER VIII

Anaerobic Digestion: Treatment and Application of HTC Process Water

For the successful integration of HTC with AD, it is necessary to understand the subsequent treatment and application behaviour of the liquid product generated during HTC. The process waters are rich in soluble organics as shown in previous chapters and therefore have the potential to enhance biogas production when co-digested with regular AD feedstock. To assess process water performance and to avoid AD shutdown it is vital that the underlying mechanism for metabolism and cause of inhibition during digestion is understood.

8.1. Overview

The aim of this chapter is to assess the behaviour of process waters using biochemical methane potential (BMP) tests. An understanding of how the composition of the process water is influenced by the feedstock and HTC process conditions on biogas yields, including any inhibitory effects to microbial metabolism will also be investigated. Mesophilic test results from HTC process water application experiments outlined in Chapter 3, section 3.2 are presented and examined in detail.

The objectives of this chapter are to:

- Highlight similar studies on the BMP performance of HTC process water.
- Compare the composition of the process waters as substrates for digestion, highlighting inhibitory compounds.
- Compare the effect of co-processing on the BMP performance and to assess the viability of recirculating process waters in the integration of HTC and AD.

8.2. Introduction

Interest has grown in exploring methods to introduce alterative feedstock materials for AD and treating digestate to reduce volumes, functionalise and generate energy via biogas production. Exploring alternative materials is key for reducing market competition to obtain AD feedstock resource. However, lignocellulosic compounds are recalcitrant and these fractions are a challenging issue for digestion. Breaking down high lignin fractions can be employed by thermochemical treatment, such as HTC, where recalcitrant compounds are thermally degraded and solubilised into a liquid phase, i.e. HTC process water, as demonstrated in Chapter 6. Solubilisation of organic material into the water phase thereby creates an opportunity for recycling of the process waters back into anaerobic digestion, potentially increasing biogas yields [210,211]. The process waters from HTC contain both dissolved organics and inorganics and can facilitate nutrient and chemical recovery [73,75,78,211]. Biodegradability is a measure of how well a material can be digested by microbes i.e. metabolised. Initial studies have shown that lower temperature hydrothermal process waters typically have higher biodegradability than higher temperature process waters [211–214]. To improve biodegradability, the main challenges include ensuring the stability of microbes and digestion environment by safeguarding digestion parameters and the levels of inhibitory compounds.

Substrate, is the term used for the surface or material on or from which a microbe lives, grows, or obtains its nourishment. To ensure that microbial metabolism of substrate is kept positive it is vital to keep sources of inhibition low during the AD process. Inhibition in AD can be caused from a number of sources, such as ammonia, sulphur, light and heavy metals, oxygenated and organic compounds, including poor operational and environmental conditions. Ammonia is released from the degradation of nitrogenous matter in the form of ammonium (NH_4^+) and free ammonia (NH_3) acts as a strong inhibitor [215]. The production of free ammonia nitrogen (FAN) varies depending on the amount of total ammonium nitrogen (TAN) which is dependent on the C:N ratio and pH value of the substrate. High sulphur present in the substrate is also an inhibitor of the digestion process [210]. Sulphur present as sulphate is reduced to hydrogen sulphide by sulphate-reducing bacteria (SRB). A high level of hydrogen sulphide is toxic to methanogens [216]. Inhibition from light metals is caused by the toxicity of salt to microorganisms. Microbial cells become dehydrated and experience osmotic pressure due to the high salt content (sodium toxicity) present in the substrate [217]. Other light metals include potassium, magnesium and calcium which can create toxicity in the AD process via removal of cations [218]. Inhibition from heavy metals such as Cr, Co, Cu, Zn, Cd, Ni and Fe can disrupt the enzymic function of microbes [219]. Organic compounds and chemicals are also inhibitors to the digestion process. Whilst VFA are not themselves inhibitory, high levels of VFA lowers pH, in turn creating a toxic environment which causes process instability [220,221]. Hydroxymethylfurfural (HMF) and furfaral derivatives (formic acid, levulinic acid) are generated during high temperature treatment of biomass; these are generally produced at higher concentrations if pre-treated with acid. Furfural is a stronger inhibitor than HMF in the AD process [222]. Lignin derivatives are also highly toxic to methanogens when they are present with aldehyde groups, such as phenolic compounds [219,223,224]. Table 40 shows upper limits of a number of compounds and chemicals that cause AD inhibition.

Table 40. Inhibition limits of compounds and chemicals in the AD process, sourced from [210].

Substance	Moderately inhibitive (mg/L)	Strongly inhibitive (mg/L)
Calcium (Ca)	1500–4500	8000
Ammonia Nitrogen (NH_3-N)	1500–3000	3000
Sodium (Na)	3500–5500	8000
Magnesium (Mg)	1000–1500	3000
Potassium (K)	2500–4500	12000
Sulphur (S)	200	200
Zinc (Zn)	-	1.0 (soluble)
Copper (Cu)	-	50–60 (total)
Nickel (Ni)	-	30 (total)
Chromium (Cr)	-	180–420 (total)
Chromium VI (Cr(VI))	-	200–250 (total)

Table 41 shows the typical bio-methane yields produced via mesophilic anaerobic digestion from a number of HTC process waters created using different solid loadings, temperatures and retention times from literature.

Table 41. Biomethane yield from mesophilic anaerobic digestion of HTC process waters found in literature.

Substrate (HTC process waters)	HTC parameters			Biomethane yields		Ref.
	Load (%)	Temp (°C)	Time (hr)	mlCH$_4$/gVS	mlCH$_4$/gCOD	
Sewage Sludge Digestate	-	-	-	-	175	[112]
	4.5	160	0.50	-	260	
		220		-	277	
		250		-	226	
Sewage sludge digestate	n.g	200	6.00	-	103-178	[225]
Corn sillage	n.g	220	6.00	-	236	[95]
Thin stillage	7.2	220	1.25	-	295	[226]
Sewage sludge	15.0	208	1.00	-	98	[227]
Primary & secondary sludge	10.0	170	1.00	257	-	[228]
Primary & secondary sludge	15.0	208	1.00	-	99-177	[229]
Microalgal biomass	66.0	180	1.00	356	-	[230]
		210		226	-	
		240		188	-	
Fecal simulant	10	140	0.50	-	126	[231]
			1.00	-	168	
			1.50	-	146	
			4.00	-	97	
		170	1.00	-	158	
		180	0.50	-	106	
			1.50	-	93	
			2.00	-	209	
		200	0.50	-	26	
Food waste		260	4.00	-	69	[232]

n.g, not given

An assessment of experimental biochemical methane potential (BMP) has been performed by many, although the majority of studies have focused on sewage sludge [112,225,229,233–236]. The studies show the levels of BMP from sewage sludge digestate process waters increase with HTC temperature and generally peak around 180 °C to 220 °C. In general, HTC temperatures lower than 220 °C result in greater BMP levels than higher temperature process waters. On the other hand, levels of BMP from process waters from the HTC of micro algal biomass decrease with increasing temperatures. This suggests different inhibitory compounds are present in the process waters, which is both temperature and feedstock dependent.

There are knowledge gaps in the literature and discrepancies between the standards used for BMP tests, along with the reporting of result units. This inevitably makes it difficult to compare results amongst other studies. Additionally, only limited studies are available for BMP tests of HTC process waters from digestate materials [87,212,228,232] and there is less emphasis on the effect of solid loading. There is an absence of BMP studies for HTC process waters made from woody or lignocellulosic biomass. There are also minimal studies showing the effect of HTC co-processing of biomass wastes on BMP.

Therefore, the purpose of this chapter is to understand the effect of the process conditions, such as solid loading and temperature on the levels of BMP and concentrations of inhibitory compounds from the process waters produced from the HTC of digestate and green waste feedstock. Furthermore, the process waters from the HTC co-processing of SS digestate with green wastes will also be investigated to understand the effect of blending recalcitrant lignocellulosic fractions on bio-methane generation and inhibition. The outcomes of this investigation will help in understanding how much additional energy can be extracted from the biomass waste feedstocks and contribute to the completion of the proof of concept integration approach.

8.3. Results and discussion

The HTC process waters generated in this study will be assessed for their behaviour during anaerobic digestion. The waters will be analysed for the chemical composition of soluble compounds, biomethane potential tests and biodegradability to understand the opportunity to recycle the waters back into AD, as illustrated in the integration concept in Figure 25.

8.3.1. BMP of digestate HTC process waters

The focus of the results and discussion section will initially be of the anaerobic digestion of the HTC process waters created from AGR, MSW, SS and VGF digestate materials.

The pH; C:N ratio; COD; total VFA; sugars and phenols; theoretical and experimental BMP including a biodegradability index for AGR, MSW, SS and VGF digestate process waters are listed in Table 42. The assays of solvents, VFA and sugars that make up the total concentrations can be seen in Appendix Table 8. It should be noted that the biodegradability index for the digestate process waters are based on Equation 8, which takes into account the theoretical BMP to give an understanding of the maximum methane potential. Methods for calculating biodegradability have been improved in the next section, as described later.

Table 42. Liquid analysis, theoretical and experimental biochemical methane potential (BMP), including biodegradability of digestate HTC process waters.

Digestate process waters	pH	C:N ratio	COD (g/L)	Total VFA (g/L)	Total sugars (g/L)	Total phenols (g/L)	BMPth (CH_4/gVS)	BMPexp (NmlCH_4/gCOD)	Biodegradability (BI %)
AGR digestate									
150 °C at 20%	6.7	4.5	45.5	1.8	2.2	1.4	224.3	100.0 ± 8.0	45
200 °C at 10%	6.9	5.6	25.2	1.3	1.1	1.1	302.3	136.0 ± 48.5	45
200 °C at 20%	6.2	8.0	42.2	2.1	0.0	1.6	327.8	180.7 ± 1.1	55
200 °C at 30%	5.8	5.8	54.6	2.0	0.6	2.2	326.7	178.6 ± 2.9	55
250 °C at 10%	5.7	7.6	29.1	2.5	0.1	0.8	314.3	139.5 ± 34.5	44
250 °C at 20%	6.1	7.4	46.3	4.2	0.0	0.8	302.9	155.5 ± 1.3	51
250 °C at 30%	6.5	5.9	56.6	6.1	0.0	0.9	312.0	166.3 ± 6.2	53
MSW digestate									
150 °C at 20%	6.5	3.1	22.6	0.7	0.7	0.3	220.5	84.6 ± 1.5	38
200 °C at 10%	7.2	3.4	10.7	0.9	0.0	0.2	249.2	129.0 ± 29.1	52
200 °C at 20%	7.1	2.4	18.1	0.9	0.2	0.4	284.5	137.7 ± 1.6	48
200 °C at 30%	7.4	3.7	23.4	1.5	0.2	0.5	275.7	157.2 ± 11.4	57
250 °C at 10%	7.1	2.7	9.4	1.3	0.2	0.3	231.8	154.0 ± 12.3	66
250 °C at 20%	7.8	3.6	16.4	1.3	0.5	0.6	268.3	134.6 ± 2.8	50
250 °C at 30%	7.5	1.8	21.2	1.9	0.9	0.6	238.1	151.8 ± 6.6	64
SS digestate									
150 °C at 20%	5.6	6.9	31.0	1.1	0.6	0.2	335.7	100.2 ± 5.4	30
200 °C at 10%	5.2	3.0	21.0	1.4	0.2	0.3	358.6	163.5 ± 13.1	46
200 °C at 20%	6.2	3.8	38.9	1.8	1.2	0.9	389.5	181.7 ± 7.6	47
200 °C at 30%	5.6	3.4	48.7	2.8	3.5	0.9	402.7	196.9 ± 43.0	49
250 °C at 10%	7.2	3.0	23.4	3.5	0.5	0.5	448.9	146.3 ± 9.9	33
250 °C at 20%	7.6	3.9	43.6	5.3	0.7	0.8	456.8	151.9 ± 12.4	33
250 °C at 30%	7.5	3.1	51.6	5.5	1.8	0.9	501.8	163.2 ± 6.7	33
VGF digestate									
150 °C at 20%	6.5	5.9	11.9	0.9	1.2	0.3	343.3	121.4 ± 16.3	35
200 °C at 10%	6.1	3.8	12.0	1.2	0.1	0.4	383.7	142.0 ± 10.4	37
200 °C at 20%	5.7	6.3	22.5	1.1	0.8	0.9	355.2	158.6 ± 3.1	45
200 °C at 30%	6.0	5.9	31.5	1.3	0.1	1.2	355.7	144.4 ± 8.2	41
250 °C at 10%	6.4	4.7	16.1	1.4	0.7	0.7	477.4	128.0 ± 0.1	27
250 °C at 20%	6.4	6.5	27.8	2.2	1.2	1.2	384.1	125.1 ± 1.8	33
250 °C at 30%	6.7	5.0	36.9	2.6	0.0	1.5	380.4	113.0 ± 4.2	30

Figures 58 and 59 illustrate the cumulative methane yields of the digestate process waters obtained via BMP tests for comparison against HTC temperature and solid loading respectively. Figure 60 illustrates the biodegradability as curves for all digestates as a function of temperature and solid loading. Appendix Figures 3 to 14 show spectograms and tables of volatile compounds identified via GCMS liquid injection of 20 percent solid loading process waters generated from the HTC of AGR, MSW, SS and VGF at 150 °C, 200 °C and 250 °C temperatures. The chemical composition of the soluble compounds show that the C:N ratio of the process waters are below 10, which is still considered to be within efficient digestion operational parameters [237,238]. In general, the phenol content of the process waters rises with increasing temperature and is highest for the AGR digestate as expected, as it has the highest level of lignocellulosic content. The next greatest amount of phenolic content is exhibited by VGF, then SS, followed by MSW process waters. High levels of phenolic compounds are inhibitory to the digestion process. However, the concentrations of phenols contained in these process waters are below upper limits of digestion inhibition [239].

The levels of BMP and biodegradability are shown to peak at 200 °C for all digestate process waters as shown in Figures 58 and 60 respectively. Overall, the process waters generated at 150 °C produced the least amount of biomethane and exhibited the lowest biodegradability, with the exception of VGF 150 °C. However, the VGF 150 °C process water could be an outlier due to the error of ±16.3 associated with the BMP result. Additionally, the results for the experimental BMP show large standard error, therefore the biodegradability indices cannot be given with great confidence (an improved method was utilised in the next section). Understanding any links and correlation between the levels of BMP and measured analytes has proven difficult. Process waters exhibiting high total sugar content suggests they would generate the greatest levels of biomethane. Whilst this is true for SS digestate, the correlation between BMP and sugar content is weak for other digestates.

The biomethane production for AGR and MSW digestate process waters is shown to be similar when comparing solid loadings at both 200 °C and 250 °C (Figure 59). However, for the SS and VGF digestate, the lower temperature processing at 200 ˚C produces significantly higher methane yields than at 250 °C for the same solid loading.

Generally, the influence of solid loading does not have a substantial effect of BMP across the digestate process waters. However, for the case of process waters from SS digestate, increasing the solid loading at 200 °C results in an increase in methane production (Figure 59e), whereas at 250 °C, an increase of solid loading results in a minimal increase in levels of BMP (Figure 59f). On the other hand, the BMP data for AGR digestate process waters suggests that the levels of methane reduce as the solid loading increases beyond 20 percent; however this change is minimal and is associated with margins of error. These observations suggest the minimal effect of solid loading on the biomethane yields is influenced by both temperature and feedstock.

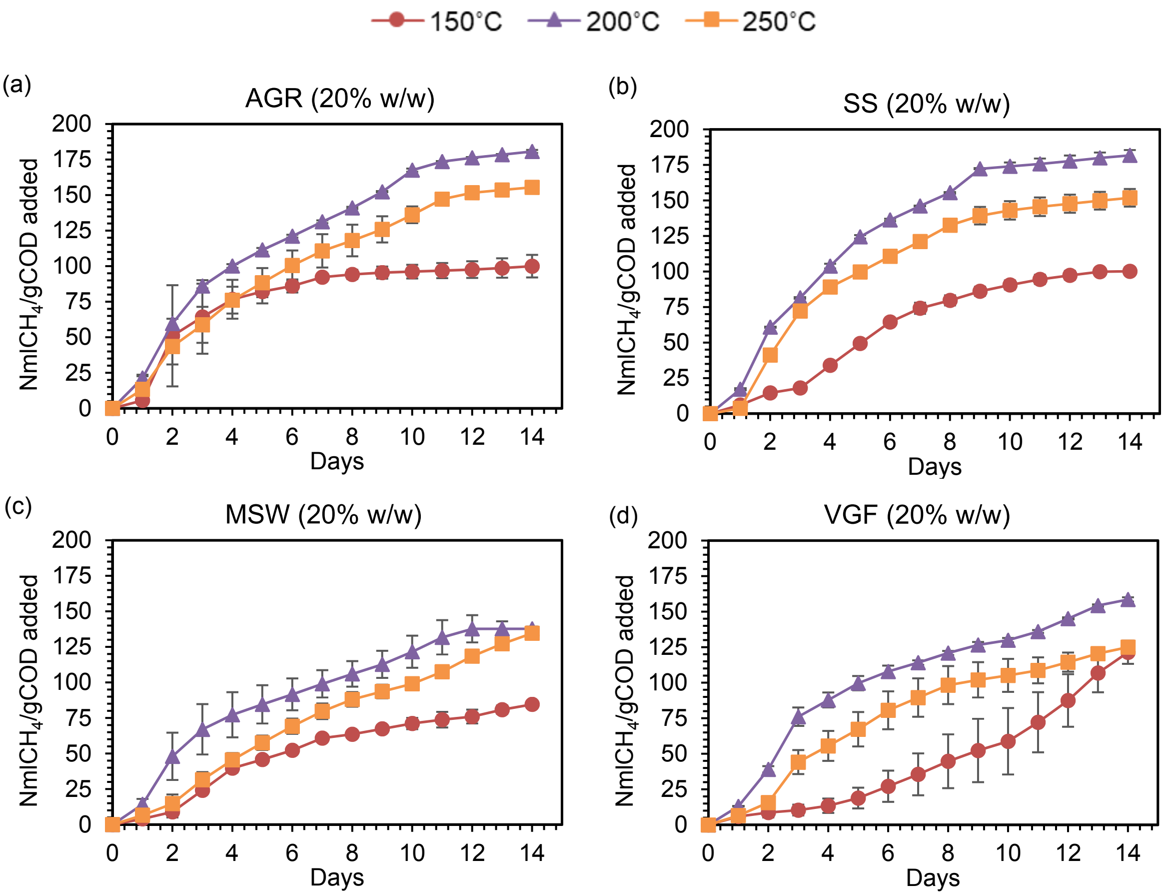

Figure 58. Cumulative methane yield for **a**) AGR, **b**) MSW, **c**) SS and **d**) VGF at 150 °C, 200 °C and 200 °C at 20 percent solid loading. Error bars represent standard error from the mean.

In terms of biomethane production, higher temperature process waters exhibit low BMP levels, despite increasing COD (and TOC as shown in Table 27), suggesting that high temperature process waters have greater levels of inhibitory compounds. Even though levels of light and heavy metals were not measured for the process waters, the fate of inorganics as illustrated in Figure 38 show that the increasing transfer of Na, K, Ca, Mg into the process waters could be the cause of this inhibition. However, this does not explain why process waters obtained at 200 °C generate the highest BMP and as a result a higher biodegradability index as shown in Figure 60.

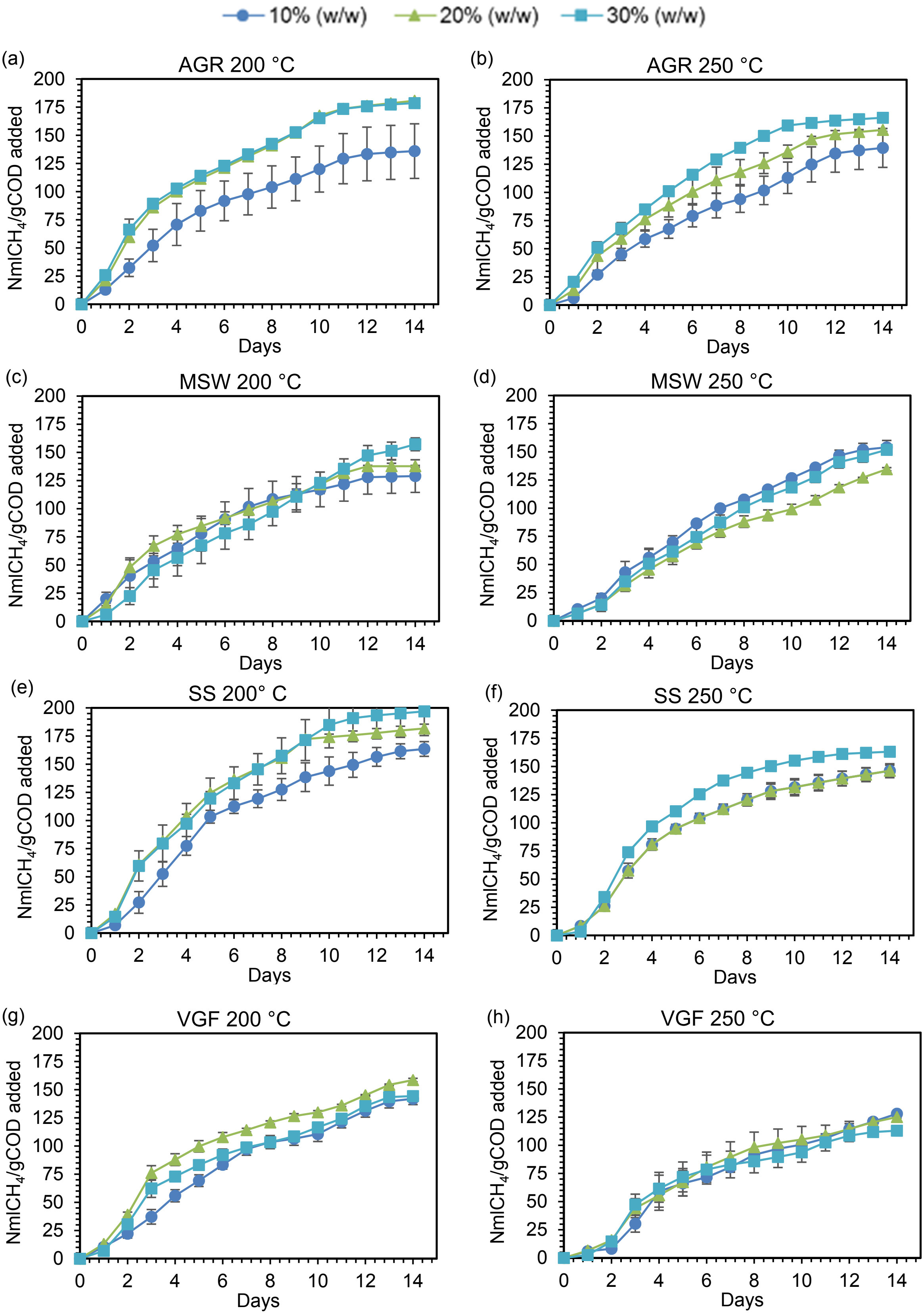

Figure 59. Cumulative methane yield for **a**) AGR 200 °C, **b**) AGR 250 °C, **c**) MSW 200 °C, **d**) MSW 250 °C, **e**) SS 200 °C, **f**) SS 250 °C, **g**) VGF 200 °C and **h**) VGF 250 °C at 10, 20 and 30 percent solid loading. Error bars represent standard error from the mean.

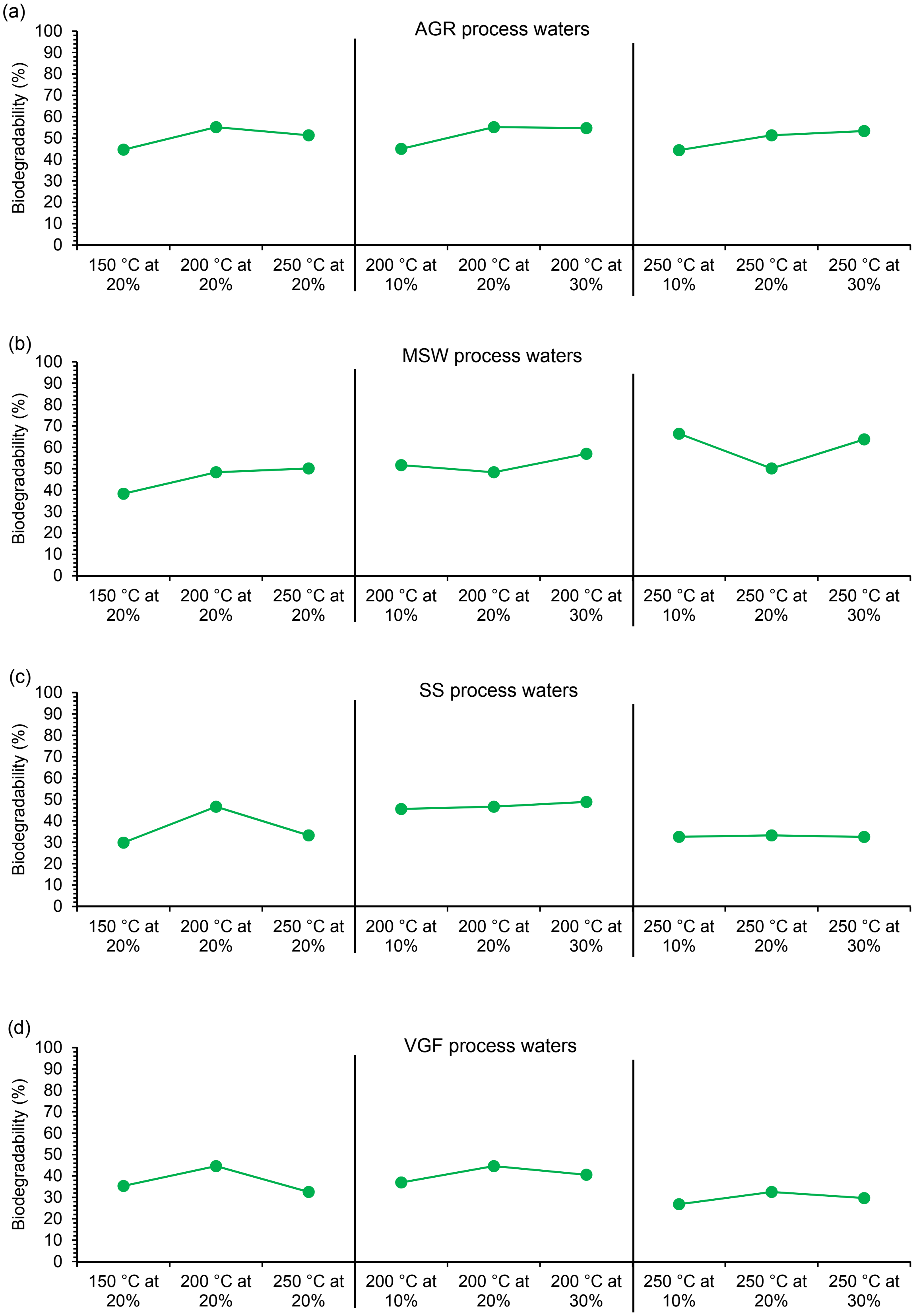

Figure 60. Biodegradability curves for **a**) AGR, **b**) MSW, **c**) SS and **d**) VGF process waters with increasing temperatures (150 °C, 200 °C and 300 °C) and solid loading (10, 20 , 30 percent) at both 200 °C and 250 °C.

Analysis of the GCMS spectra does highlight a possible cause of inhibition from 150 °C process waters. Appendix Figures 3, 6, 9 and 12 show that there are more furan derivatives for 150 °C compared to 200 °C and 250 °C process waters. As discussed in the introduction, furan derivatives such as furfural and 5-hydroxymethylfurfural are inhibitory and should be quantified as part of further work.

8.3.2. BMP of green wastes and blends HTC process water

This section of the results and discussion section will focus on the anaerobic digestion of the HTC process waters created from green waste, including SS digestate and green waste blends, to understand the effect of HTC co-processing in the proposed integration concept.

The pH; C:N ratio; COD; total VFA; sugars and phenols; levels of BMP; COD removed, including biodegradability for SS digestate; grass clippings; garden hedge; woodchips and blends are listed in Table 43. It should be noted that for this set of BMP tests, inoculum was loaded at a COD basis, to match of that the loading of the substrate, i.e. a true inoculum to substrate ratio (ISR) of 1:1. The BMP tests were also extended to 28 days, to make sure any delays and lagging to metabolism was compensated for, to ensure exhaustion of the production of methane. It should also be noted that the biodegradability method has been modified so that it is based on the amount of COD removed from the COD added from the inoculum and substrate mixtures (Equation 9). This improved method avoids the errors associated with the calculation of theoretical BMP from the loss on evaporation for elemental analysis of the process waters (further discussed in the limitation section 8.4).

The assays of solvents, VFA and sugars that make up the total concentrations can be seen in Appendix Table 9. Figure 61 illustrates the cumulative methane yields from positive and standard controls and blanks used for the following BMP tests for confidence and reliability of the results. Powdered laboratory grade cellulose was used as a positive control and HTC process water created from food waste was used as a standard control (high in COD and TOC) to validate the BMP tests. Results as shown in Figure 61 show that the cellulose was digested in an efficient manner, reaching a maximum of about 380 ml CH_4 after 14 days. The standard control reached a similar maximum after 18 days. There was also no endogenous methane production from the blank tests. Therefore, the inoculum used for these tests had been properly prepared and stored for application.

Figures 62 and 63 illustrate respectively the cumulative methane yields and biodegradability curves for SS digestate, green wastes and blend process waters.

Table 43. Liquid analysis, experimental biochemical methane potential (BMP) and biodegradability of SS digestate, green waste and blend HTC process waters.

SS, green waste and blend process waters	pH	C:N ratio	COD (g/L)	Total VFA (g/L)	Total sugars (g/L)	Total phenols (g/L)	BMPexp ($NmlCH_4/gCOD$)	COD removed (per 2g)	Biodegradability (BI_{COD}%)
SS digestate									
150 °C	6.5	1.7	18.8	0.2	n.d	0.2	98.2 ± 8.2	0.74	37
200 °C	5.1	1.9	36.5	1.8	0.5	0.5	159.2 ± 5.6	1.16	58
250 °C	8.0	3.2	37.8	4.0	n.d	0.2	141.8 ± 0.4	1.11	55
Grass clippings									
150 °C	5.8	12.2	54.3	1.5	33.4	0.3	165.0 ± 3.7	1.49	74
200 °C	4.6	6.5	49.3	3.6	21.7	1.3	188.5 ± 0.1	1.41	71
250 °C	6.2	9.1	10.1	4.7	n.d	0.1	45.5 ± 7.0	0.36	19
SS + grass 50/50									
150 °C	5.8	7.6	39.0	1.5	21.0	0.2	165.6 ± 0.5	1.48	74
200 °C	4.7	7.8	44.7	2.9	0.4	0.3	184.4 ± 9.8	1.66	83
250 °C	6.9	4.6	45.1	4.1	6.8	0.4	129.7 ± 2.7	1.36	68
Garden hedge									
150 °C	5.2	42.3	94.4	2.2	n.d	0.5	61.7 ± 4.2	0.63	32
200 °C	3.8	10.7	66.3	7.1	n.d	0.5	112.4 ± 0.1	0.74	37
250 °C	5.4	26.1	62.2	8.2	n.d	0.9	96.9 ± 0.5	1.22	61
SS + hedge 50/50									
150 °C	5.5	11.8	58.7	1.2	n.d	0.5	116.1 ± 14.7	1.28	64
200 °C	4.3	8.2	49.8	3.9	14.9	0.4	39.2 ± 3.1	0.31	15
250 °C	5.9	8.1	46.0	1.5	23.9	0.7	122.0 ± 3.9	1.22	61
Woodchip									
150 °C	4.0	2.7	20.3	0.9	12.0	0.4	97.8 ± 7.7	0.59	30
200 °C	4.0	3.6	30.0	3.2	9.1	0.2	16.2 ± 0.3	0.45	22
250 °C	4.0	67.1	32.6	4.8	1.0	0.3	18.6 ± 2.1	0.26	13
SS + wood 50/50									
150 °C	5.6	6.9	22.8	0.9	0.7	0.1	142.9 ± 1.1	1.44	72
200 °C	4.1	2.2	26.0	2.1	1.0	0.7	172.4 ± 0.9	0.98	49
250 °C	5.1	8.0	30.1	3.7	n.d	0.3	92.5 ± 17.0	0.52	26

n.d, not detected

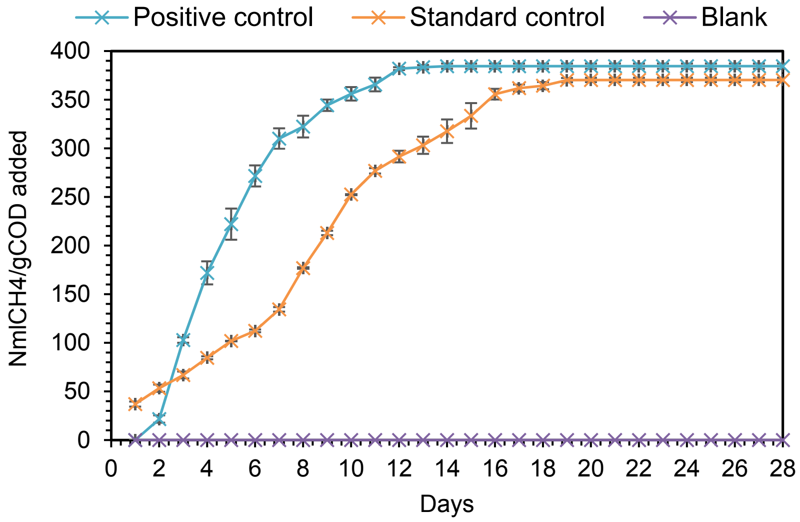

Figure 61. Cumulative methane yield for positive control (cellulose), standard control (food waste process water) and blank inoculum during green waste and blend HTC process BMP tests.

Figures 62a and 63a shows that SS digestate process waters perform similarly to that of previous tests, where the greatest levels of BMP and biodegradability are exhibited at 200 °C. The C:N ratio of the green wastes are more wide-ranging when compared to the digestate process waters and are within digestion operational parameters [27]. The greatest BMP levels are achieved from the 150 °C and 200 °C grass clipping process waters; this correlates with the greatest hemi-cellulose content exhibited by the feedstock and as a result the highest total sugar content (carbohydrates) of up to 33.4 g/L within its process waters.

The 250 °C grass clippings process water exhibited low BMP due to the sugar content of the process waters (originally derived from the hemicellulose fractions) decomposing into furan compounds (such as 5-HMF and furfural) at temperatures above 170 °C [240]. This is validated with the total sugar content reducing with increasing HTC temperature, and found to be nil for the process water generated at 250 °C as shown in Table 43.

Garden hedge and woodchip process waters generally exhibited long lag periods and overall low biogas production. Even though woodchip contains the largest fraction of lignin, the total phenolic content of the woodchip process waters is lower than that of hedge and grass process waters and to that of digestate materials (Tables 43 and 42 respectively). This behaviour indicates that process waters derived from high lignin feedstock are inhibitory to the AD process, albeit not owing to the phenolic content of the process waters. Inhibition is likely to be due to the combination of acidic process waters (woodchip as low as 4.0 pH) and other compounds, such as furans, which increase in concentration with HTC temperature.

Ultimately, process waters generated from green wastes do not have high biochemical methane potential, with the exception of grass clippings at 200 °C (reaching up to 188 $mlCH_4$ per g COD). BMP and biodegradability are now shown to be dependent on the type of green waste treated rather than HTC temperature (Figure 63). For instance, grass and woodchip process waters generated more biogas at 150 °C compared to 250 °C, whereas the opposite is true with digestate process waters.

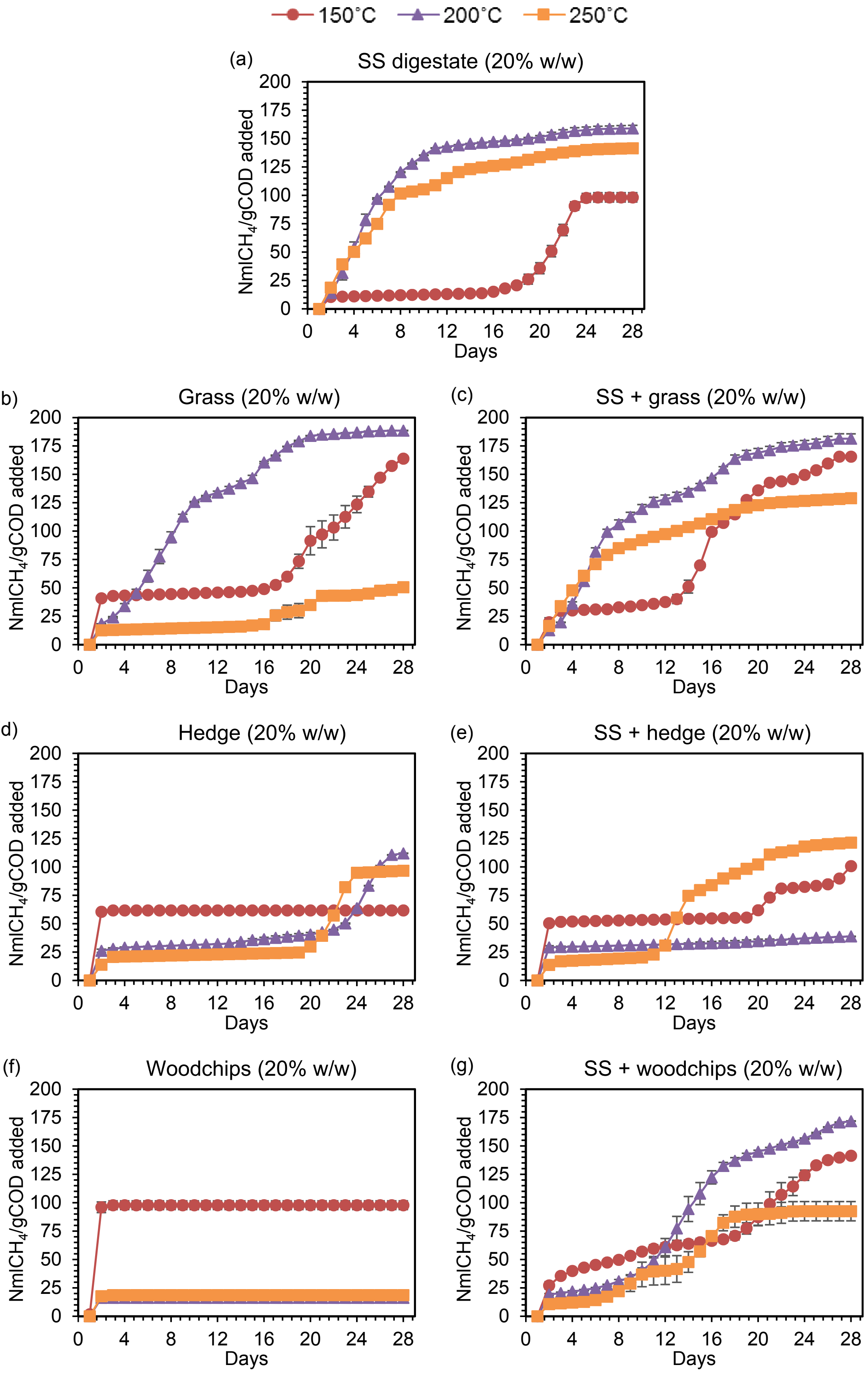

Figure 62. Cumulative methane yield for **a**) SS digestate, **b**) Grass, **c**) SS + grass 50/50, **d**) Hedge, **e**) SS+ hedge 50/50, **f**) Woodchips and **g**) SS + woodchips 50/50 for 150 °C, 200 °C and 200 °C at 20 percent solid loading. Error bars represent standard error from the mean.

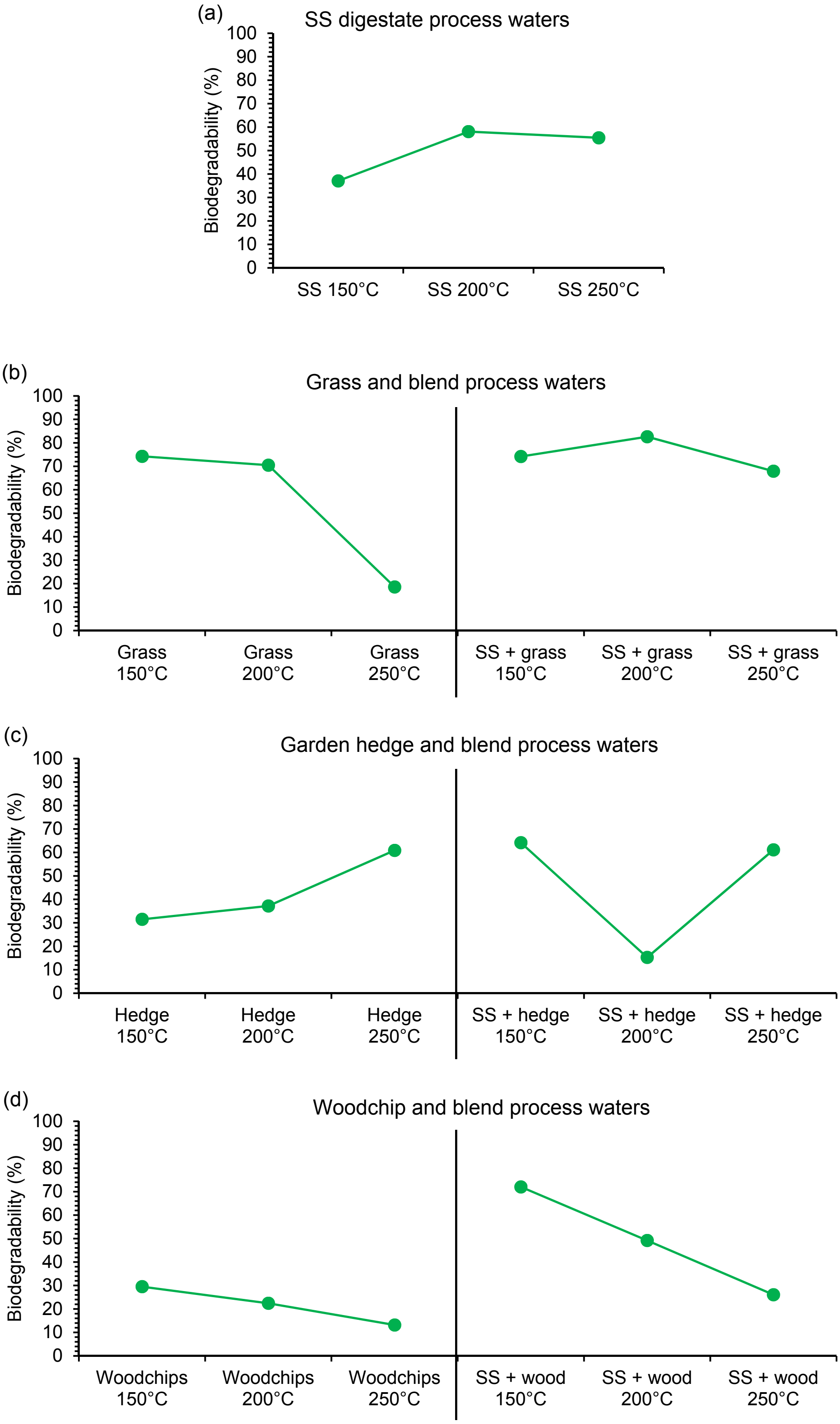

Figure 63. Biodegradability curves for **a**) SS digestate, **b**) grass and SS + grass blends, **c**) garden hedge and SS + hedge blends and **d**) woodchips and SS + woodchip blend process waters with temperature of 150 °C, 200 °C and 250 °C at a fixed solid loading of 20 percent.

Co-processing SS digestate with green wastes does result in the significant improvement of biomethane generation when compared to green waste process waters alone. Where process waters have not performed well, for instance low BMP levels from 250 °C and 150 °C (less than 100 mlCH_4 per g COD), positive effects to the levels of BMP are made via co-processing (above 100 mlCH_4 per g COD in most cases) as seen in Figure 62c, e and g. For the case of woodchip, blending with SS digestate improves the biomethane generation for all temperatures, thereby indicating a lowering of concentration of inhibitory compounds. However, the majority of the process waters still exhibit significant lag time, as shown in Figure 62g, indicating a level of toxification which requires further investigation.

8.4. Chapter limitations

Due to the nature of liquid analysis and biological processing this chapter has some limitations, predominantly associated with section 8.3.1 BMP of digestate HTC process waters.

The usage of theoretical BMP (on digestate process waters) has a wide range of error due to being based on a stoichiometric equation using elemental CHNS values. The elemental values were derived from dried process waters which inherit large errors. The large error is associated with the preparation of the dried process waters, with volatiles being lost during evaporation when drying at 60 °C. This results in an under-estimation of the theoretical BMP value. Additionally, the oxygen content is calculated by the difference of the measured elemental percentages and the ash percentage. An over-approximation of the ash content occurs due to the oxidation of sodium which results in a gain in ash mass. This results in an under-approximation of oxygen when calculated by difference. A way to circumnavigate this issue would be to obtain CHNS and O values directly by elemental analysis via liquid injection.

For the actual BMP tests, the inoculum concentration was loaded using volatile suspended solids (VSS) and process water concentrations were loaded using COD for the initial investigations. Therefore, the ISR ratios were not truly 1:1 for the digestate process waters BMP tests. Additionally, the digestate process water BMP tests were only conducted for 14 days due to equipment capacity issues. This was subsequently extended to 28 days for the green waste and blend process water BMP tests and loaded using COD for both inoculum and process waters, to represent a true 1:1 inoculum to substrate ratio.

For the green wastes and blend process waters, biodegradability was based on the amount of COD removed by the methanogens. This method has a small error associated with its calculation, as it does not take into account the additional accumulation of COD attributed to the increase of microbial flora. Therefore, by 28 days the increasing population of microbes may increase the COD content of inoculum to above 2 grams. As a result of this, the biodegradability index is an under-approximation.

8.5. Concluding remarks

Assessing the composition of the HTC process waters and biochemical methane potential has given an understanding of the potential treatment and application via AD, including an insight into which processes' waters are inhibitory to digestion.

Process waters from the HTC of digestate at 150 °C was found to generate lower levels of BMP and exhibited lower biodegradability than that of 200 °C and 250 °C process waters, indicating near or exceeding limits of inhibitory compounds present in the process waters. Changing the solid loading during the HTC of the digestate feedstock had little to no effect on the BMP levels generated from the process waters. Therefore, it can be inferred that biogas production was not negatively affected when increasing solid loading of up to 30 percent.

Considering the improvements in the energetics of HTC when operating at higher solid loading (avoiding heating up of a larger fraction of water), it appears that high solid loading and using temperatures lower than 250 °C would be most suitable for HTC processing of single digestate feedstocks. From the data gathered, it is not known why 200 °C process waters exhibit greater levels of BMP and biodegradability. In general, green waste process waters show lower BMP levels than digestate process waters, with the exception of the process waters generated from the HTC of grass clippings. Garden hedge and woodchip performed poorly, attributed to inhibitory compounds, such as furans formed from the degradation of lignin at higher fractions compared to grass clippings. The levels of BMP are improved for the majority of green waste 150 °C and 250 °C process waters when co-processed with SS digestate. This indicates a balancing of the readily available substrate for microbial metabolism through the reduction of inhibitory compounds concentrations. However, some degrees of inhibition still exist and therefore further investigation of blending ratios is required.

In summary, the results highlight the potential for energy recovery when digestate and green wastes are solubilised during HTC and subsequently metabolised to produce bio-methane. Additional composition analysis and BMP tests are required with SS digestate and green waste blends to understand low methane generation performance in some cases. Nonetheless, the integration of HTC is beneficial to treat digestate and enhance biogas yields via anaerobic digestion of process waters, exhibiting technology synergy towards a bio-refinery concept.

CHAPTER IX

Conclusions, Research Limitations, Recommendations and Direction

This study set out to explore the concept of a new integrated waste management process, through technology synergy, for increased bioenergy generation and production of functional materials, including mitigation of greenhouse gas emissions when digestate and waste biomass are disposed to land. Empirical research was conducted to understand the opportunities from integrating hydrothermal carbonisation with anaerobic digestion to valorise digestate and other waste biomass, compared to the integration with pyrolysis, the competing thermochemical technology.

The following sections will conclude how the research objectives and aim were met, discuss the limitations of the research, and recommend any changes and additional analysis to strengthen the work carried out. Finally, areas of interest are highlighted in for other fields for further work to develop HTC with AD systems.

9.1. Overview

The main empirical findings are chapter-specific and were summarised within their respective chapters;

Chapter 4. Characterisation of digestate and green waste feedstock;
Chapter 5. Integration concepts and effects of HTC processing compared to pyrolysis;
Chapter 6. Characterisation of products; hydrochar, pyrochar and process water composition;
Chapter 7. Application of hydrochar and pyrochar;
Chapter 8. Anaerobic digestion; treatment and application of HTC process waters.

9.2. Synthesis and conclusions

This section will synthesise the empirical findings to fulfil the following research objectives;

Understand the effect of feedstock composition on product yields and composition.
Chapter 4 established the varying nature of the feedstock used in this study, this was due

to the differing sources of biomass and stages of pre-treatment applied to the material. Composition analysis shows that the digestate materials exhibit higher levels of ash compared to that of green wastes. This is primarily due to the available carbon metabolised by the mesophilic anaerobes during anaerobic digestion. As a result, Chapter 5 found that feedstock with high ash content produced high solid yields, particularly in pyrolysis, mainly owing to the high fraction of inorganic content retained in the solid char products, predominantly comprised of silica, calcium and iron (Chapter 6). Additionally, Chapter 6 showed that hydrochar produced from digestate materials exhibit lower calorific value compared to that of green wastes. Literature reports that chars with high levels of ash negatively affect its performance as a solid fuel.

AGR digestate and green waste have high lignin content (Chapter 4). Chapter 6 showed that these high lignin feedstocks generated high volatile matter, fixed and elemental carbon content hydrochar and pyrochar, thereby resulting in greater energy densification compared to the starting material. Chapter 6 also shows that high lignin feedstock, such as woodchip, generated acidic HTC process waters, which can negatively affect bio-methane production as reported by the literature.

Chapter 4 also revealed SS and AGR digestate and grass feedstocks possess high levels of nitrogen and protein due to the typical makeup of faecal matter and the leafy nature of agricultural residues and grass respectively. Furthermore, AGR digestate, grass clippings, garden hedge and woodchip also exhibited high cellulose content. As a result in Chapter 5, these feedstocks generated high liquid yields due to the solubilisation of protein and cellulose. Feedstocks with high protein and cellulose levels generated process waters resulting in high TOC and COD concentrations, as presented in Chapter 6.

Understand the effect of process type and process conditions on product yields and composition.

Chapter 5 revealed low temperature HTC and pyrolysis provided similar product yields. At higher process temperatures the char yields reduced and liquid yields increased for both thermochemical processes. Gas yields remained stable with HTC, whilst pyrolysis exhibited an increase in gas yields with temperature. Generally, HTC produced a similar liquid yield to that of pyrolysis, but using much lower temperatures, due to the solubilisation process of HTC.

Chapter 6 showed that the solubilisation process of HTC allowed greater removal of inorganic compounds. Typically, sodium was removed from all digestate materials and transferred into the process water. The extraction of inorganics is mainly feedstock dependent, specifically the physical structure of the biomass itself. HTC also generated comparable energy densification to that of low temperature pyrolysis, however high temperature pyrolysis increased the content of fixed carbon and ash in the resulting pyrochar.

There is little benefit in processing high ash feedstock, such as SS digestate at high temperature processing, as greater parasitic energy is required to obtain any significant improvements in energy density and fixed carbon contents, especially with pyrolysis treatment above 400 °C.

Chapter 6 also revealed the effect of temperature on the composition of HTC process waters. The levels of organic carbon within the process waters increased with temperature when processing digestate, but remained stable with green wastes. The effect of HTC solid loading on hydrochar is minimal, whilst the effects on process water characteristics rely heavily on the initial feedstock material (feedstock dependent).

Understand the effect of blending digestate with three types of recalcitrant lignocellulosic biomass on the product yield and composition.

In Chapter 4, SS digestate was chosen to be blended with green wastes for HTC co-processing due to resource abundance and composition dissimilarities (low lignocellulose, high phosphorous, high sulphur and high ash content) to that of lignocellulosic feedstock (high lignocellulose, low phosphorous, low sulphur and low ash content). HTC's ability to solubilise recalcitrant lignin fractions also gave an opportunity for green wastes to become an alternative AD feedstock via HTC pre-treatment.

Chapter 5 showed that the actual yields from co-processing were very close to theoretical yields (linear relationship), with the exception of SS digestate blended with grass clippings, where increased rate of solubilisation occurred at higher temperatures, indicating a catalytic effect. The rate of solubilisation at higher temperatures is also slightly increased for SS digestate and garden hedge blends, whilst the opposite is true for SS digestate and woodchip blends. Chapter 6 showed that the effect of co-processing on process water characteristics is dependent on feedstock composition.

Chapter 6 also revealed the effect of co-processing on hydrochar composition. A decrease of ash concentrations of up to a quarter was exhibited and the rate of inorganic removal was stabilsed, with at least 50 percent of all inorganics removed. The effect of blending also increased the energy densification of SS digestate hydrochar due to the addition of lignocellulosic compounds from the green wastes. Together these benefits are thought to promote the combustion performance of the hydrochar as a solid fuel.

Understand potential routes of application of pyrochar and hydrochar.

In Chapters 4, 5 and 6 it was found that the atomic ratios of high temperature hydrochar and pyrochar from digestate and green waste were similar to that of low grade coals. This is due to high lignocellulosic, fixed carbon and volatile matter contents. Therefore, these particular chars are suited for potential application as solid fuel in theory. However, Chapter 7 showed that the combustion behaviour of the high ash concentrated digestate chars make them unfavourable as a solid fuel due to very high slagging and fouling propensities. Additionally, few improvements are made to the digestate via HTC and pyrolysis when altering operating conditions. Whilst HTC did slightly perform better than pyrolysis in reducing these propensities, the high levels of ash present in the digestate feedstock was detrimental for their suitability as a solid fuel in the first place.

Chapter 7 however, did show some improvements made to the combustion behaviour by HTC co-processing. Nonetheless, levels of reduction were not significant enough to eradicate slagging and fouling behaviour. As such there is little point trying to optimise for production of a solid fuel and it is more sensible optimising for recovery of energy from recycling process waters back into the digester.

Additionally, Chapter 7 investigated the application of hydrochar as a soil amendment and potentially as an alternative compost product. SS digestate in particular as a feedstock exhibited high levels of micro and macro nutrients (Chapter 4), and the subsequent hydrochar exhibited the greatest levels of N, P, K, Ca and Mg compared to the green wastes (Chapter 6 and 7). During plant response tests, the SS digestate hydrochar growing media showed improvement to the fresh mass yield as compared to the control. However, SS digestate hydrochar did not meet PAS 100 quality criteria, mainly due to breaching the upper limits for heavy metal concentrations. Green waste hydrochar was also investigated, and whilst green waste hydrochar meets PAS100 quality criteria, phytotoxicity to germination was observed. A clear need to investigate further blend ratios is required, along with methods to stabilise hydrochar via co-composting (discussion to follow).

Understand potential applications for process waters.

Chapter 8 assessed the anaerobic digestion behaviour of HTC process waters using biochemical methane potential (BMP) tests. The HTC process waters generated from digestate materials at 200 °C achieved the greatest cumulative BMP levels and biodegradability, particularly with SS digestate, whereas the 150 °C process waters were the most inhibitory. Analysis of the process water composition did not reveal the potential cause of inhibition at this temperature (Chapter 6 and 8). Additionally, the levels of BMP were not significantly affected when by solid loading. Therefore, increasing solid loading did not affect inhibition levels for them to reach the upper limits of inhibitory compounds, as described in Chapter 8.

Green waste process waters exhibited low cumulative BMP levels compared to the digestates, with the exception of grass clippings due to its high hemi-cellulose fractions, which degrade to carbohydrates (Chapter 4 and 8). The inhibition exhibited by green wastes can be attributed to the high lignin content of the feedstock (Chapter 4), plus low pH of the process waters (Chapter 6). In Chapter 8, it was shown that process waters generated from the co-processing of SS digestate with green wastes improved lag times and BMP levels compared to green wastes process waters 150 °C and 250 °C. As a result biodegradability was also improved. It was concluded that higher solid loading and mid temperatures (200 °C) would be most suitable for better energetic performance of the proposed integrated HTC and AD system.

9.2.1. Holistic thinking - the bigger picture

The aim of understanding the opportunities of valorising digestate and green waste biomass through the integration of hydrothermal and anaerobic digestion was met. Additionally, the benefits and disadvantages of HTC vs pyrolysis were also highlighted. Overall, the pyrolysis of high ash feedstock is not favorable, additionally the process would be accompanied by higher operational expenses due to the parasitic energy required to remove moisture from organic wastes and high operating temperatures. Additionally, if the pyrolysis gas phase is not utilised then this would be detrimental to the energy and carbon balance of the system, as well being less environmentally friendly.

On the other hand, the HTC co-processing aspect of the proposed integrated system is limited by batch processing, including a requirement for manual loading of waste streams if operating at 20 percent and higher solid loading, also known as heavy slurries. Heavy slurries affect performance as they nearly exceed current capabilities of pumping technologies. Pumping performance is also dependent on the degree of slurry homogeneity, therefore feedstock preparation will be required, especially of lignocellulosic feedstock, reducing the efficiency of the integrated system.

However, the empirical work in this study has shown that this integration approach delivers a promising method to convert digestate into a safer, higher quality product with multiple uses whilst improving waste management operations. The approach also improves AD efficiency and operator revenue by enhancing biogas yields and costs are saved from the disposal of non-fit-for-purpose digestate. Additionally, co-processing digestate with green wastes introduces alternative recalcitrant AD feedstock via HTC pre-treatment, which alleviates competition as feedstock is becoming more difficult to source.

Furthermore, this integrated waste management process also helps to meet renewable energy targets and creates opportunities for significant economic gain to the bioenergy and bio-economy sector. Benefits to the environment are also made. Fugitive greenhouse gas emissions are mitigated compared to composting and anaerobic digestion operations, as illustrated in Figure 64.

Additionally, heavy metal leaching and eutrophication are also mitigated by reducing the disposal of digestate and green waste to land. It also has the potential to provide additional supply chains for solid fuel and a soil amender, alternative compost or slow-release fertiliser product. The integrated processing of biomass wastes can also mobilise organic and inorganic compounds to facilitate the recovery of nutrients, metals and production of chemicals, aligning with goals set by the UK Government in the waste to resource productivity report [31], helping to move toward a circular economy.

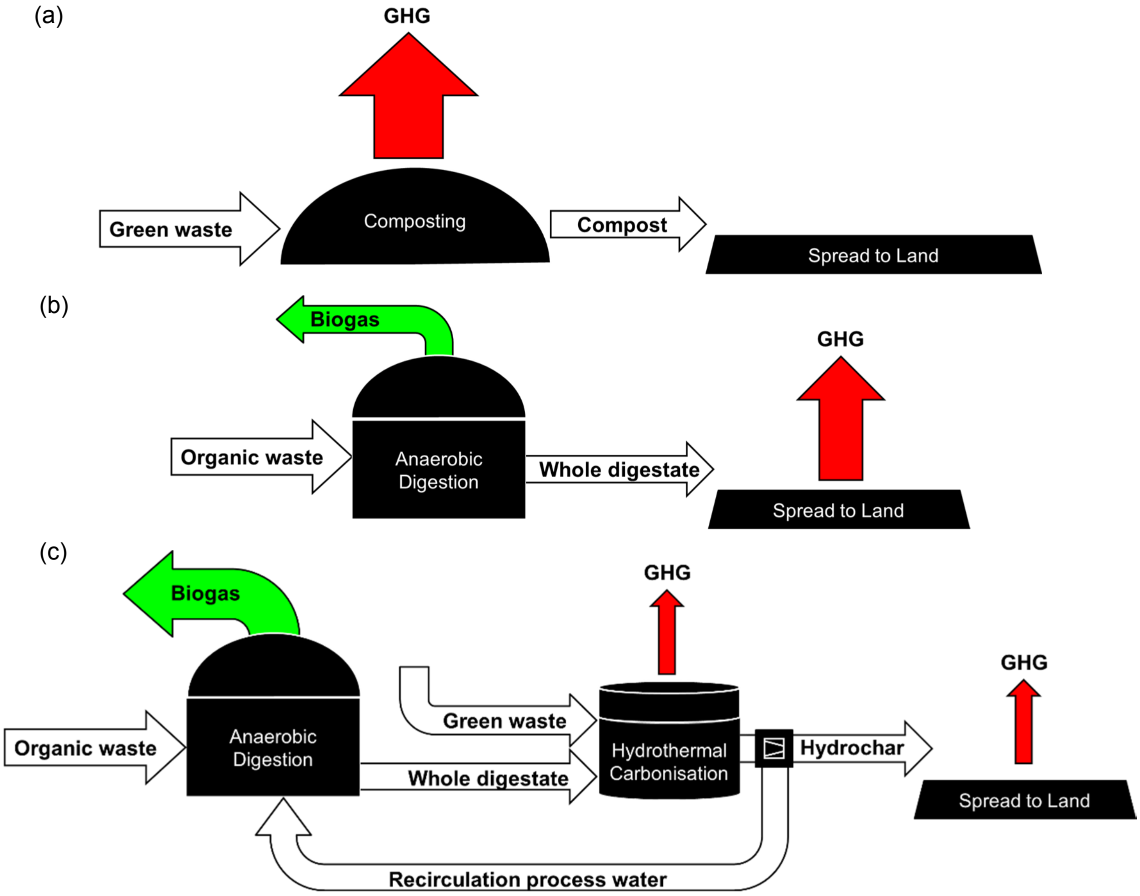

Figure 64. General assumptions of operational greenhouse gas emissions from **a**) composting, **b**) anaerobic digestion and **c**) integrated AD and HTC facilities.

9.3. Research limitations

Due to the availability of digestate material at the time of experimental design, only dewatered and dried solid digestate was procured and investigated. This, therefore, limits the research conducted in this study by providing an underestimate of the potential opportunity for energy generation from solid fuel combustion and enhanced bio-methane production, including availability of minerals as a soil amender or alternative compost product. This is due to the loss of soluble organic and inorganic matter during the fractionation of whole digestate at AD facilities. Fractionation occurs for logistical and treatment purposes. Dewatered digestate, also referred to as press cake and solid digestate, is cheaper and easier to transport. The subsequent reduction in weight and volume, and removal of hydrolysed products allows the ability for storage in limited spaces and the ability to store for longer periods due to the reduced organic content.

Furthermore, when MSW solid digestate was received it was further fractionated in the laboratory, by manually removing pieces of glass, plastic and masonry. Not all of these inorganic fragments would have been removed either due being concealed within the organic fractions. Therefore, the MSW digestate used in this study is not a true representation of the MSW digestate that leaves AD facilities and would require pre-treatment efforts to ensure homogeneity.

The digestate and green waste samples used in this study are also a snapshot of composition in time. Seasonal changes will affect the composition of these feedstock, especially if the anaerobic digestate operators change suppliers of organic waste material throughout the year for full AD operational capacity. Furthermore, midway through the experimental programme additional AGR and VGF digestate material was procured due to exhausting supplies. Therefore, to ensure accuracy and homogeneity, the remainder AGR and VGF material was mixed with the newly procured material. The subsequent values for ultimate and proximate analysis only differed slightly, but still remained within the errors associated of the previous analysis given. Additionally, the composition and structure of green waste feedstock will change throughout the year, due to summer and winter months affecting moisture and leafy content, affecting the lignocellulosic composition and ash concentrations of the biomass.

Another limitation of this study is a lack of detailed information of the digestate materials used. Having information of the whole digestate, in terms of the HACCP procedures and assessment of quality criteria would have helped to understand the extent of remediation via thermochemical processing. Additionally, the composition data of the original feedstock material for AD and output biogas levels achieved within the digestate prior to treating the digestate would have given more of an understanding of the proposed integration approach energy balance (empirical energy calculations).

Lastly, not all analytical techniques were performed in duplicate, in particular XRF for inorganic analysis, and in triplicate for BMP tests to understand biodegradability and inhibition. This was due to equipment availability and capacity issues. Due to these bottlenecks, the experimental analysis was spread out over the course of the study and as a result the materials were stored for prolonged periods of time. Nevertheless, to ensure accuracy and repeatability the experimental and environmental conditions were acutely monitored to reduce instability and variability. Recommendations are made in the following section to alleviate these issues.

9.4. Recommendations for further work

The degree to which digestate is dewatered differs according to the type of AD facilities. Therefore, it is recommended that an assessment of the effect of digestate dewatering and dry matter content on thermochemical processing and product composition should be conducted. This would also allow additional data for the energy required to dewater for pyrolysis and a truer representation of the concept of increasing the dry matter content of the digestate when blending green wastes for HTC co-processing. As solid digestate was utilised in this research, the findings lend themselves to a 'worst' case scenario to the opportunities and benefits from the integration of HTC and AD.

It is also recommended that the variation of feedstock composition for digestate and green waste is assessed to identify if there are seasonal changes, and how this may affect the composition of thermochemical products thereafter. For better representation of conversion processes, the HTC chamber should be purged with nitrogen to remove any oxidation effects during reactions, and be controlled via pressure regulation to avoid the potential for residence temperature overshoot during exothermic reactions. Moreover, HTC should be performed with additional temperature increments. This will aid in the understanding of why 200 °C HTC processing generates greater levels of BMP and biodegradability. This will also aid in the optimisation for biogas generation through process water composition analysis. To obtain greater accuracy of the chemical composition of the products generated, it is recommended that products be analysed within short timeframes (within two weeks) to mitigate any degradation effects during storage of the hydrochar and process water.

Moreover, further study is suggested on assessing the variation of HTC plant operation on product composition, such as; temperature, heating rate and methods; pressures; solid loading and residence times to optimise at large scale industrial processing. It is also recommended that more agri-environmental analysis and behavioural testing of HTC hydrochar as a soil amendment product is conducted to understand biological toxicity, leaching of pollutants, emissions and soil respiration mechanisms. Finally, it is recommended that the continuous recycling of HTC process water be investigated. This will aid in the understanding of the influence of recycling on the effect of HTC product composition and build-up of potentially toxic elements (PTE), such as heavy metals and other organic pollutants, which can be detrimental to the digestion process. Additionally, the digestion of HTC process water with regular AD feedstock should also be investigated to understand the effect of co-digestion on the levels of BMP and inhibition mechanisms, including the auxiliary effect of process water recycling. The hydrochar produced from the proposed series of tests thereafter should then be investigated for its potential applications stated in this research and further research topics highlighted in the next section.

9.5. Future research direction

Hydrothermal carbonisation of biomass and waste residues has been recognised as having the potential to become an environmentally-friendly conversion process for the production of hydrochar, including production of a process water by-product rich in dissolved organics. The products of HTC have been identified as materials with a range of functional attributes for a range of applications. The challenge to remove limitations of the application of HTC products rests on the continued investigations of the physiochemical characteristics, stability and decomposition mechanisms. These also include investigations required on the indirect effects, such as residual greenhouse gas patterns of both hydrochar [73] and process waters, including social behaviours and engaging in communication between producers, users and regulators to influence properties and to ensure quality standards that are fit for purpose to minimise environmental harm.

To help focus the continuation of investigations, four areas of research topics and interests have been recognised for the application of hydrochar and HTC process water. The research topics have been categorised based on additional synergies between the technologies; from AD operations to a broader range of applications to provide additional functionality of the solid and liquid products. The research topics include the use of hydrochar in; biogas production; agricultural bioremediation and amelioration; energy and storage, and the use of HTC process waters in the generation of bio-hydrogen, bio-alcohols and other fine chemicals (carboxylate platform). Additionally, implementing a large-scale facility will also need to consider reactor design and scalability, material availability and pre-treatment, current and future policies, incentives and regulations, including markets and associated economics for the sale and use of hydrochar and HTC process waters.

9.5.1. Hydrochar application within AD for biogas production and upgrading

The application of hydrochar within the digestion process itself has been recently investigated. Hydrochar has been applied as a substrate for anaerobic digestion, as a microbial catalyst to support archaea growth and mitigate inhibition and as a material for CO_2 scrubbing for the purpose of upgrading biogas to bio-methane.

Studies have shown the performance of hydrochar when used as a substrate for biogas generation. Hydrochar, when added as a substrate to AD increased methane yields by 32 percent [241] and also increased HTC-AD systems methane generation efficiency by up to 32 percent [242]. Whilst this increase of methane generation can be attributed to methanisation of labile carbon there is also evidence to suggest that hydrochar can also be used as a microbial catalyst. Hydrochar could be used as a support medium for archaea growth and to mitigate inhibition via adsorption of ammonia. A study showed that hydrochar reduced mild ammonia inhibition and increased methanogenic microflora, aiding the digestion process itself [241]. The addition of hydrochar within HTC process water (HTC slurry) also increased the performance of biogas generation, most likely due to the increased availability of water extractable carbon [112]. Hydrochar has also been recognised as a material to upgrade biogas, highlighting its physical properties suitable for CO_2 sorption. Chemically activated hydrochar from digestate material has been enabled as a CO_2 adsorbent above CH_4 due to its high porosity and large surface areas [121]. Whilst studies in this area are limited, it is important that further research be conducted in the area of integrating hydrochar obtained from the HTC of digestate within the anaerobic digestion process itself for increased synergy between HTC and AD.

9.5.2. Hydrochar for remediating digestate and soils

Continuous spreading of digestate to land as a fertiliser product has caused concerns of eutrophication of nearby ground water, due to phosphorous and nitrogen overload [243,244]. As a result, application for hydrochar from the conversion of digestate and green waste as an ammonia and phosphorous sorbent should be investigated further.

The post processing of hydrochar could also be a potential method for improving agronomical and environmental properties for soil amendment purposes. Secondary thermochemical treatment, involving the pyrolysis of digestate hydrochar has shown a reduction of polycyclic aromatic compounds (PAH) and the complete removal of phenolic compounds with increasing temperatures, including an increase in Brunauer-Emmett-Teller (BET) surface area [120]. Hydrochar also has the potential of reducing the risk of pesticide accumulation [117]. Additionally, the washing of hydrochar should be investigated for its potential to remove residual process water, eco-toxic compounds and labile carbon to improve stability. As discussed in Chapter 7, hydrochar co-composting with organic wastes should also be investigated as a post-processing method to improve phytotoxicity to plant growth. Furthermore, the long term biogeochemistry effects of hydrochar application to land are still unknown and should be investigated to influence future quality standards.

9.5.3. Hydrochar as other energy and storage applications

A potential route of hydrochar application lies in the generation of heat and electricity, including its ability for electrical storage. Generation of electrical and heat energy from the combustion of digestate hydrochar remains a challenge due to its inherently high levels of inorganic materials, as reported in this study. However, since hydrochar is easily friable, there is potential for energy generation through plasma gasification for the conversion into syngas. However, this technology is relatively new and it is not known how high ash content hydrochar would perform. High ash hydrochar may still be useful in some industries that require furnaces to be continually under combustion, such as glass, cement and incineration factories. In addition, hydrochar has also been investigated for its use as an activated carbon material for supercapacitors, which opens up the possibility of an alternative sustainable capacitive material for storing electrical energy [245]. Furthermore, there is potential to produce carbon spheres from the water soluble fraction of process waters via secondary HTC and followed by activation methods [246]. HTC slurries (process water and hydrochar) have also been investigated for their use as an alternative to diesel in developing countries for making electricity with engine generators, with promising results.

9.5.4. Generation of other energy vectors from HTC process waters

Anaerobic digestion technology can be employed in different ways for energy generation other than mesophilic digestion as described in this study. Thermophilic and dark fermentation techniques are utilised by changing key process variables and microbial communities for the production of carboxylic acids, including bio-alcohols and bio-hydrogen.

One of the outputs of this study has led to a joint collaboration with the University of Akureyri, Iceland. In this collaboration, selected HTC process waters generated in this study have been examined for the ability of *Thermoanaerobacter pseudoethanolicus* (thermophilic bacteria) to convert short-chain fatty acids present in the process water to their corresponding alcohols in the presence of a source of reducing potential [247].

Further investigation on how different feedstock and HTC process waters affect alcohol production should be conducted for the generation of alternative aviation fuel, such as bio-butanol. Dark fermentation of HTC process waters, where the methanogenesis stage of AD is inhibited to facilitate hydrogen accumulation with methane (biohythane), is now also of research interest. Only a few studies explore the integration of HTC with dark fermentation, where soluble carbohydrate concentrations is found to have a significant positive correction with hydrogen yields [248,249].

The author of this thesis proposes a three-stage AD integration with HTC; the first digester would operate at thermophilic conditions and produce acids, alcohols and fine chemicals; the second digester would operate at mesophilic conditions to produce hydrogen and the third digester also operating at mesophilic conditions would receive regular AD feedstock and produce methane; lastly a hydrothermal carboniser would treat the digestate and pre-treat other recalcitrant biomass wastes for the subsequent digestion stages.

9.5.5. Modelling and large scale implementation

Assessing the application of products is vital in order to develop a business case for large-scale implementation. Process modelling should be employed to further this integration approach by way of understanding the whole energy and carbon balance, including a cost-benefit analysis for successful business operations. Additionally, an understanding of competitive markets offering similar products, such as large scale composting facilities, will also develop the feasibility to whether this approach is predominantly a cost saving, or income generating concept from the production of functional materials and valuable chemicals. Furthermore, assessing future material resource and availability, technological interventions, land use and climate change will give an understanding of the viability and necessity of such an integration approach. Lastly, a grasp on the changes and opportunities from local and national strategies and policies can help the realisation of an integrated waste management system and bio-refinery, including its part in shaping the circular economy.

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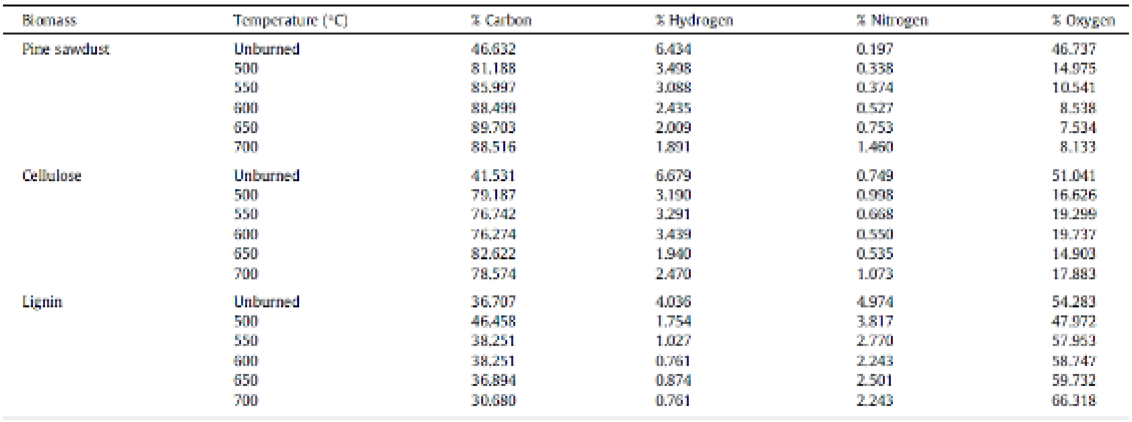
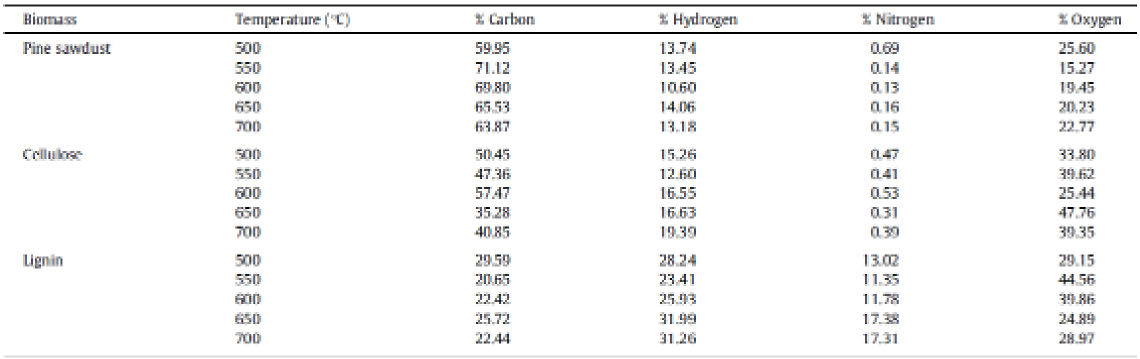
APPENDICES

Appendix Table 1. Elemental analysis of the solid fraction from pyrolysis of pine sawdust, cellulose and lignin compared to their respective biomasses [62].



Biomass	Temperature (°C)	% Carbon	% Hydrogen	% Nitrogen	% Oxygen
Pine sawdust	Unburned	46.632	6.434	0.197	46.737
	500	81.188	3.498	0.338	14.975
	550	85.997	3.088	0.374	10.541
	600	88.499	2.435	0.527	8.538
	650	89.703	2.009	0.753	7.534
	700	88.516	1.891	1.460	8.133
Cellulose	Unburned	41.531	6.679	0.749	51.041
	500	79.187	3.190	0.998	16.626
	550	76.742	3.291	0.668	19.299
	600	76.274	3.439	0.550	19.737
	650	82.622	1.940	0.535	14.903
	700	78.574	2.470	1.073	17.883
Lignin	Unburned	36.707	4.036	4.974	54.283
	500	46.458	1.754	3.817	47.972
	550	38.251	1.027	2.770	57.953
	600	38.251	0.761	2.243	58.747
	650	36.894	0.874	2.501	59.732
	700	30.680	0.761	2.243	66.318

Appendix Table 2. Elemental analysis of the liquid fraction from pyrolysis of pine sawdust, cellulose and lignin [62].



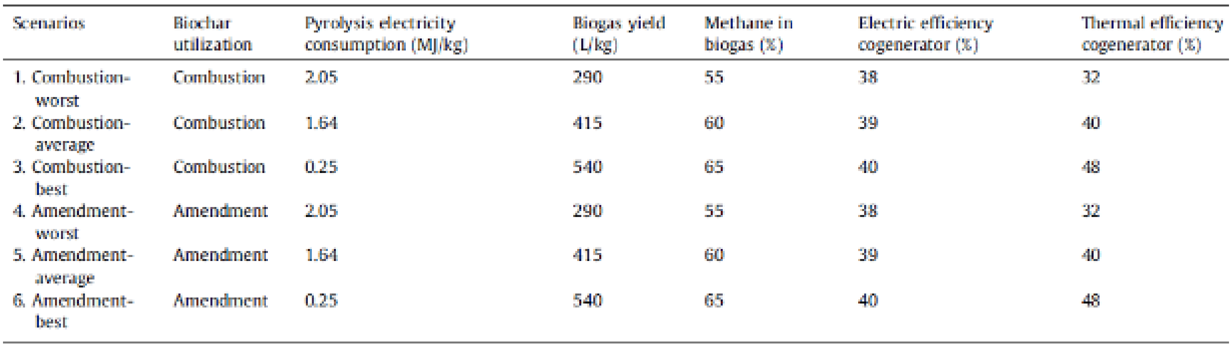
Biomass	Temperature (°C)	% Carbon	% Hydrogen	% Nitrogen	% Oxygen
Pine sawdust	500	59.95	13.74	0.69	25.60
	550	71.12	13.45	0.14	15.27
	600	69.80	10.60	0.13	19.45
	650	65.53	14.06	0.16	20.23
	700	63.87	13.18	0.15	22.77
Cellulose	500	50.45	15.26	0.47	33.80
	550	47.36	12.60	0.41	39.62
	600	57.47	16.55	0.53	25.44
	650	35.28	16.63	0.31	47.76
	700	40.85	19.39	0.39	39.35
Lignin	500	29.59	28.24	13.02	29.15
	550	20.65	23.41	11.35	44.56
	600	22.42	25.93	11.78	39.86
	650	25.72	31.99	17.38	24.89
	700	22.44	31.26	17.31	28.97

Appendix Table 3. Proximate and elemental analysis of the solid fraction from hydrothermal carbonisation of wood meal, lignin, cellulose and D-xylose compared to their respective biomasses [80].

Material	Proximate analysis (%) db			Ultimate analysis (%) db				
	VM	FC	Ash	C	H	N	O*	S
Wood meal	87.31	12.40	1.24	45.02	6.70	0.47	46.24	0.33
WM H 225°C	51.31	47.38	1.31	67.55	5.60	0.35	24.94	0.25
WM H 245°C	48.59	49.71	1.40	69.86	5.41	0.39	22.69	0.26
WM H 265°C	47.15	51.12	1.73	74.22	5.54	0.37	17.91	0.23
Lignin	59.75	38.80	1.45	45.36	5.07	0.57	42.94	4.61
L H 225°C	44.42	54.11	1.47	63.95	5.21	0.57	27.30	1.51
L H 245°C	41.66	56.86	1.48	66.15	5.01	0.50	25.55	1.30
L H 265°C	36.24	62.22	1.54	68.43	4.65	0.54	23.59	1.25
Cellulose	93.77	6.23	-	42.37	6.54	-	51.09	-
C H 225°C	54.28	45.72	-	66.40	5.11	-	28.49	-
C H 245°C	45.88	54.12	-	69.70	4.99	-	25.31	-
C H 265°C	43.36	56.64	-	72.10	5.05	-	22.85	-
D-xylose	94.23	5.77	-	39.88	6.88	-	53.24	-
D H 225°C	45.82	54.18	-	68.65	4.66	-	26.69	-
D H 245°C	43.93	56.07	-	69.78	4.69	-	25.53	-
D H 265°C	42.19	57.81	-	72.80	4.93	-	22.27	-

* Oxygen by difference

Appendix Table 4. Technical performances of the six analysed scenarios of AD with pyrolysis [85].



Scenarios	Biochar utilization	Pyrolysis electricity consumption (MJ/kg)	Biogas yield (L/kg)	Methane in biogas (%)	Electric efficiency cogenerator (%)	Thermal efficiency cogenerator (%)
1. Combustion-worst	Combustion	2.05	290	55	38	32
2. Combustion-average	Combustion	1.64	415	60	39	40
3. Combustion-best	Combustion	0.25	540	65	40	48
4. Amendment-worst	Amendment	2.05	290	55	38	32
5. Amendment-average	Amendment	1.64	415	60	39	40
6. Amendment-best	Amendment	0.25	540	65	40	48

Appendix Table 5. Ultimate analysis and heating analysis of the digestate and green waste feedstock on a dry ash free basis.

	Digestate				Green waste		
	AGR	**MSW**	**SS**	**VGF**	**Grass**	**Hedge**	**Woodchip**
Ultimate analysis							
C (wt%, daf)	52.5	54.3	53.8	52.5	52.0	50.3	53.2
H (wt%, daf)	6.1	3.8	5.9	5.4	6.0	6.0	6.9
N (wt%, daf)	3.8	3.5	6.4	3.6	4.0	1.2	0.4
S (wt%, daf)	0.3	0.4	2.9	0.6	0.1	0.0	0.0
O[a] (wt%, daf)	37.3	38.0	31.0	38.0	37.9	42.4	39.5
Energy density							
HHV (MJ/kg, daf)[b]	21.5	21.0	22.3	21.2	21.3	20.2	21.7

daf, dry ash free basis; [a], calculated by difference; [b], calculated according to Eq (1)

Appendix Table 6. Concentration of macro and micro nutrients, including heavy metals for SS digestate and green waste hydrochar, including blends (dry basis).

Feedstock and hydrochar	Macro nutrients (g/100 g, db)						Micro nutrients (mg/kg, db)					Heavy metals (mg/kg, db)		
	N	P	K	Ca	Mg	Na	Fe	Cu	Mn	Zn	Mo	Cr	Ni	Pb
SS digestate	3.41	2.48	0.98	3.46	1.00	0.49	28203	328.6	1446	902	n.d	307.1	92.5	192.9
150 °C	3.70	1.95	0.70	2.78	0.83	0.31	23747	272.5	1251	766	n.d	n.d	90.7	140.2
200 °C	2.62	2.23	0.75	3.38	0.98	0.42	26979	350.9	1454	890	n.d	265.8	84.7	147.6
250 °C	2.42	2.58	0.93	3.78	1.09	0.47	30317	351.3	1697	977	n.d	302.3	105.7	147.9
Grass clippings	3.50	0.58	1.42	1.93	0.39	0.26	2775	29.4	171	67	n.d	40.3	15.0	n.d
150 °C	3.11	0.55	1.21	1.83	0.25	0.18	581	22.4	112	60	25.2	33.6	16.5	n.d
200 °C	3.24	0.82	1.18	2.35	0.28	0.20	796	45.1	139	90	29.5	n.d	20.5	n.d
250 °C	3.10	0.90	0.65	2.69	0.30	0.21	833	25.1	155	82	28.3	n.d	13.9	n.d
SS + grass 50/50	3.46	1.48	2.06	3.46	0.79	0.47	12262	139.2	664	365	n.d	145.9	47.4	60.5
150 °C	3.61	1.26	1.13	2.23	0.55	0.46	12831	155.2	721	413	n.d	136.1	45.3	88.9
200 °C	2.92	1.50	1.11	2.81	0.64	0.27	14683	178.3	891	517	n.d	149.2	55.5	85.4
250 °C	2.96	1.96	0.90	3.27	0.81	0.26	18943	223.7	1069	659	n.d	166.6	60.8	116.3
Garden hedge	1.10	0.30	1.46	1.65	0.13	0.20	140	18.7	120	85	n.d	n.d	n.d	n.d
150 °C	2.00	0.29	0.77	1.80	0.09	0.14	192	23.1	121	106	n.d	n.d	8.6	n.d
200 °C	1.67	0.40	0.73	1.87	0.07	0.07	232	23.4	130	127	n.d	n.d	9.8	n.d
250 °C	2.23	0.50	0.39	1.92	0.08	0.07	217	18.8	149	129	n.d	n.d	12.5	n.d
SS + hedge 50/50	2.26	1.30	3.14	4.22	0.54	0.54	8354	130.7	650	425	n.d	88.0	26.5	55.3
150 °C	2.71	1.04	1.72	1.95	0.45	0.23	11865	152.3	628	433	n.d	177.5	56.0	0.0
200 °C	2.44	1.29	0.81	2.52	0.53	0.18	13971	192.6	854	552	n.d	181.2	55.1	90.1
250 °C	2.57	1.47	1.20	2.63	0.63	0.21	15952	226.4	895	603	n.d	214.9	66.9	89.5
Woodchip	0.40	0.01	0.02	0.26	0.02	0.05	298	5.5	49	26	n.d	n.d	5.2	n.d
150 °C	0.28	0.01	0.02	0.39	0.03	0.04	490	12.5	71	40	n.d	32.3	14.8	n.d
200 °C	0.29	0.02	0.05	0.63	0.05	0.04	1295	22.3	104	64	n.d	54.1	37.5	n.d
250 °C	0.45	0.02	0.13	0.39	0.04	0.18	858	15.8	81	45	n.d	42.9	17.5	n.d
SS + woodchip 50/50	1.91	0.77	0.46	3.68	0.48	0.63	10440	143.1	900	513	n.d	78.6	79.9	49.4
150 °C	2.00	1.03	0.54	1.57	0.44	0.21	12861	145.1	718	440	n.d	224.7	69.4	n.d
200 °C	1.83	0.98	0.65	1.63	0.46	0.18	12423	164.4	701	447	n.d	172.0	51.1	86.8
250 °C	2.32	1.17	0.68	1.79	0.56	0.34	14298	203.0	747	541	n.d	193.8	54.5	89.8

n.d, not detected

Appendix Table 7. PAS 100 quality criteria matrix for SS digestate and green waste hydrochar at all temperatures.

	PAS 100 criteria (Table 33)													
Feedstock + hydrochar	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13a**	**13b**
SS digestate	▨	▨	▨	🟥	🟥	🟩	▨	🟥	🟥	▨	▨	🟩	🟩	🟩
150 °C	🟩	🟩	▨	🟩	🟥	🟩	▨	🟥	🟥	▨	🟩	🟩	🟩	🟩
200 °C	🟩	🟩	▨	🟥	🟥	🟩	▨	🟥	🟥	▨	🟩	🟩	🟩	🟩
250 °C	🟩	🟩	▨	🟥	🟥	🟩	▨	🟥	🟥	▨	🟩	🟩	🟩	🟩
Grass clippings	▨	▨	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	▨	🟩	🟩	🟩
150 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
200 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
250 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
SS + grass 50/50	▨	▨	▨	🟥	🟩	🟩	▨	🟩	🟩	▨	▨	🟩	🟩	🟩
150 °C	🟩	🟩	▨	🟥	🟩	🟩	▨	🟩	🟩	▨	▨	🟩	🟩	🟩
200 °C	🟩	🟩	▨	🟥	🟩	🟩	▨	🟩	🟥	▨	▨	🟩	🟩	🟩
250 °C	🟩	🟩	▨	🟥	🟩	🟩	▨	🟥	🟥	▨	▨	🟩	🟩	🟩
Garden hedge	▨	▨	▨	🟥	🟥	🟩	▨	🟥	🟥	▨	▨	🟩	🟩	🟩
150 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
200 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
250 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
SS + hedge 50/50	▨	▨	▨	🟩	🟩	🟩	▨	🟩	🟥	▨	▨	🟩	🟩	🟩
150 °C	🟩	🟩	▨	🟥	🟩	🟩	▨	🟥	🟥	▨	▨	🟩	🟩	🟩
200 °C	🟩	🟩	▨	🟥	🟩	🟩	▨	🟥	🟥	▨	▨	🟩	🟩	🟩
250 °C	🟩	🟩	▨	🟥	🟥	🟩	▨	🟥	🟥	▨	▨	🟩	🟩	🟩
Woodchip	▨	▨	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	▨	🟩	🟩	🟩
150 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
200 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
250 °C	🟩	🟩	▨	🟩	🟩	🟩	▨	🟩	🟩	▨	🟩	🟩	🟩	🟩
SS + woodchip 50/50	▨	▨	▨	🟩	🟩	🟩	▨	🟥	🟥	▨	▨	🟩	🟩	🟩
150 °C	🟩	🟩	▨	🟥	🟩	🟩	▨	🟥	🟥	▨	▨	🟩	🟩	🟩
200 °C	🟩	🟩	▨	🟥	🟩	🟩	▨	🟥	🟥	▨	▨	🟩	🟩	🟩
250 °C	🟩	🟩	▨	🟥	🟥	🟩	▨	🟥	🟥	▨	▨	🟩	🟩	🟩
Green = pass, red = fail, grey = not applicable / not analysed														

Appendix Table 8. Solvents, volatile fatty acids and sugars detected in AGR, MSW, SS and VGF digestate HTC process waters.

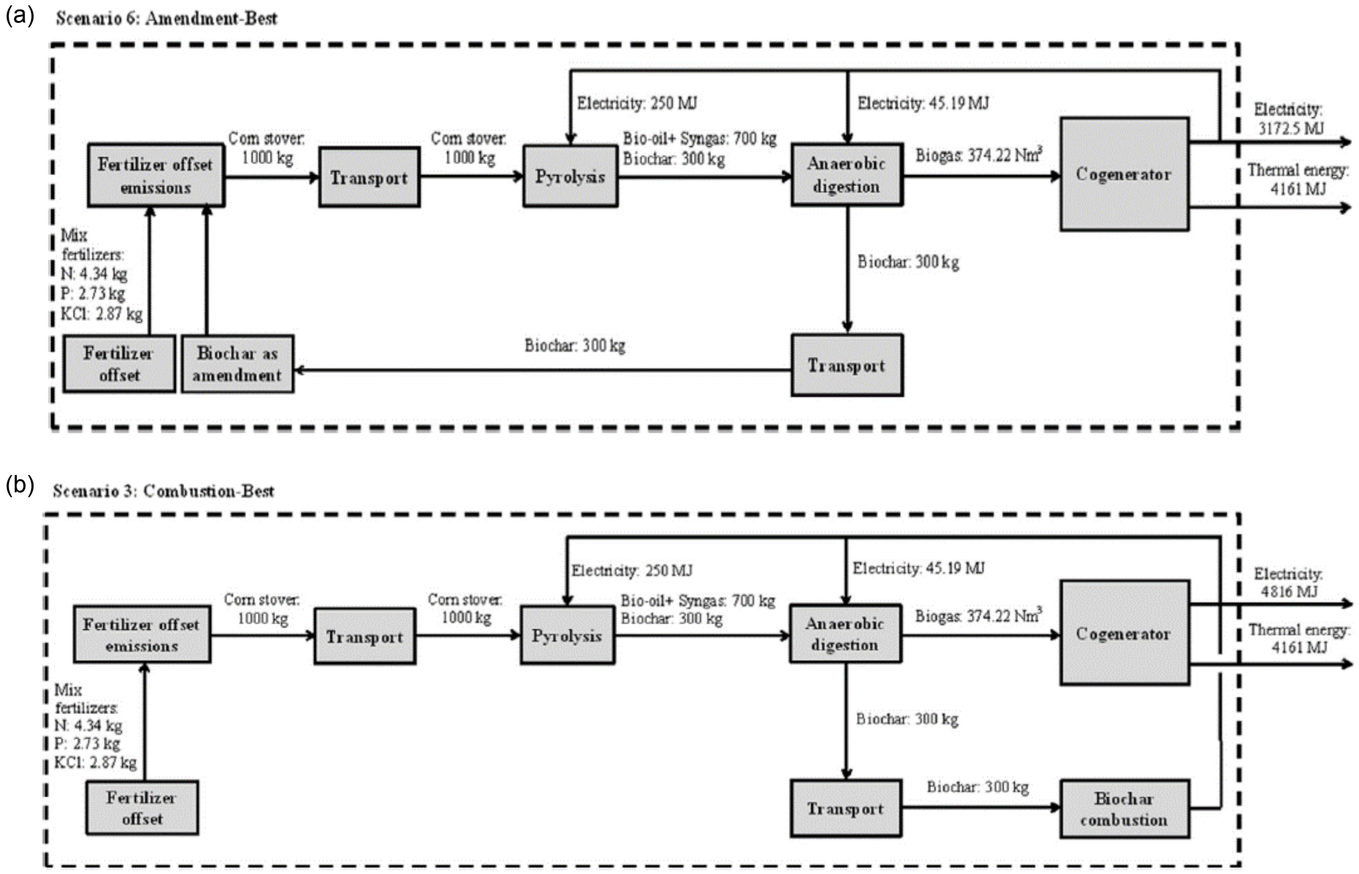
Digestate process waters	Solvents (ppm)				Volatile fatty acids (ppm)									Sugars (ppm)									
	Acetone	Methanol	Ethanol	Butanol	Acetic	Propanoic	Isobutyric	Butyric	Isovaleric	Valeric	Isocaproic	Caproic	Heptanoic	Sucrose	Maltose	Lactose	Glucose	Xylose	Galactose	Arabinose	Mannose	Fructose	Ribose
AGR digestate																							
150 °C at 20%	26	126	-	-	1554	32	6	5	44	1	3	3	6	1803	-	-	361	-	-	-	-	-	-
200 °C at 10%	37	125	66	-	951	46	7	3	19	2	5	9	20	1071	4	8	-	-	-	5	55	-	-
200 °C at 20%	54	320	-	-	1628	79	8	4	21	1	6	7	14	-	-	-	-	-	-	-	-	-	-
200 °C at 30%	83	302	275	-	1328	79	11	9	41	3	9	7	13	75	-	-	24	-	-	522	-	-	-
250 °C at 10%	154	719	179	-	1303	101	18	13	30	2	10	8	8	-	130	-	-	-	-	-	-	-	-
250 °C at 20%	194	1242	296	-	2284	182	25	24	40	4	15	9	12	-	-	-	-	-	-	-	-	-	-
250 °C at 30%	235	1919	794	-	3082	263	33	34	50	4	21	22	7	-	-	0	-	-	-	-	-	-	-
MSW digestate																							
150 °C at 20%	15	-	-	-	622	12	-	2	8	2	1	3	1	72	-	7	-	-	-	528	88	-	-
200 °C at 10%	17	44	46	-	703	41	9	3	25	2	2	5	10	-	-	-	-	-	-	-	-	-	-
200 °C at 20%	18	70	62	-	730	35	9	4	28	2	1	5	9	180	-	-	-	-	-	-	1	-	-
200 °C at 30%	77	312	0	-	972	50	20	6	43	3	3	6	7	136	-	-	-	87	-	-	11	-	-
250 °C at 10%	34	158	13	-	880	104	16	13	29	5	12	13	9	163	-	0	1	-	-	-	-	-	-
250 °C at 20%	61	267	99	-	793	87	15	11	28	5	11	13	9	-	-	-	-	37	-	233	104	110	-
250 °C at 30%	64	346	55	-	1267	81	15	12	29	5	12	14	8	107	1	-	-	94	-	209	12	436	-
SS digestate																			-				-
150 °C at 20%	29	149	60	-	838	32	9	7	24	3	5	9	18	442	-	-	187	-	-	-	-	-	-
200 °C at 10%	48	140	120	-	1021	39	12	5	21	3	3	9	8	-	-	-	-	-	-	-	-	224	--
200 °C at 20%	71	258	277	39	1087	45	12	5	18	3	5	11	13	955	-	-	-	239	-	-	-	-	-
200 °C at 30%	104	390	428	65	1736	68	17	9	23	4	7	16	8	1805	-	-	1684	-	-	-	-	-	-
250 °C at 10%	66	311	567	208	2166	119	24	18	41	8	23	33	20	236	-	-	226	-	-	-	-	70	-
250 °C at 20%	119	573	1182	293	2906	117	25	18	48	7	37	52	35	-	24	-	133	-	-	545	-	-	-
250 °C at 30%	206	893	1123	370	2482	145	32	28	72	9	46	69	35	-	23	-	704	-	-	-	625	495	-
VGF digestate																							
150 °C at 20%	12	-	-	-	786	12	2	2	14	1	1	4	3	1146	-	-	-	-	-	-	37	39	-
200 °C at 10%	27	59	42	-	588	35	9	5	22	2	4	9	13	78	-	-	-	-	-	-	-	-	-
200 °C at 20%	43	209	-	-	739	49	13	6	32	1	2	6	4	6	-	-	4	-	-	779	-	-	-
200 °C at 30%	32	245	-	-	913	58	14	8	40	2	3	5	3	73	-	-	-	-	-	-	-	4	-
250 °C at 10%	53	264	26	-	837	77	23	21	39	4	23	39	30	-	-	-	-	-	-	667	-	-	-
250 °C at 20%	126	831	-	-	1020	96	23	25	38	5	18	25	14	-	-	-	-	53	-	1141	37	-	-
250 °C at 30%	162	885	110	-	1156	119	27	22	59	6	22	32	17	-	-	-	-	-	-	-	-	-	-

-, not detected

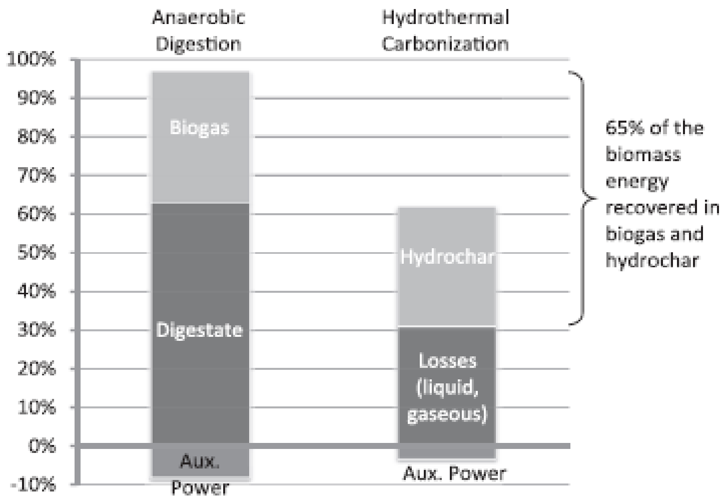
Appendix Table 9. Solvents, volatile fatty acids and sugars detected in SS digestate, green waste and blend HTC process waters (20 percent solid loading).

SS, green waste and blend process waters	Solvents (ppm)				Volatile fatty acids (ppm)									Sugars (ppm)									
	Acetone	Methanol	Ethanol	Butanol	Acetic	Propanoic	Isobutyric	Butyric	Isovaleric	Valeric	Isocaproic	Caproic	Heptanoic	Sucrose	Maltose	Lactose	Glucose	Xylose	Galactose	Arabinose	Mannose	Fructose	Ribose
SS digestate																							
150 °C	5	-	13	-	203	7	1	1	2	-	8	2	2	-	-	-	-	-	-	-	-	-	-
200 °C	46	176	184	-	1,333	40	9	8	9	3	2	12	5	-	-	-	511	-	-	-	-	-	-
250 °C	37	222	540	167	2,836	93	19	12	30	5	23	22	9	-	-	-	-	-	-	-	-	-	-
Grass clippings																							
150 °C	-	136	63	-	1,219	21	2	11	4	1	1	3	3	-	-	-	13,934	-	-	19,493	-	-	-
200 °C	117	225	337	-	2,720	106	6	59	16	2	4	4	10	-	-	-	-	-	-	21,709	-	-	-
250 °C	139	425	326	-	3,472	176	17	94	28	1	14	13	16	-	-	-	-	-	-	-	-	-	-
SS + grass 50/50																							
150 °C	28	159	201	-	1,071	28	3	29	9	1	3	2	8	-	-	-	5,564	-	1,471	13,947	-	-	-
200 °C	112	357	255	-	2,021	59	6	33	9	1	5	8	10	-	-	-	55	-	-	393	-	-	-
250 °C	142	301	374	80	2,858	131	21	47	38	4	23	16	18	-	-	-	-	-	-	6,794			
Garden hedge																							
150 °C	-	832	-	-	1,334	25	3	23	8	1	5	6	6	-	-	-	-	-	1,053	-	-	-	-
200 °C	106	2,507	-	-	4,294	97	2	53	8	3	4	4	9	-	-	-	-	-	-	-	-	-	-
250 °C	123	2,157	-	-	5,564	186	15	103	21	4	11	18	20			-	-	-	-	-	-		
SS + hedge 50/50																							
150 °C	-	238	-	-	934	20	2	23	5	1	1	4	4	-	-	-	-	-	-	-	-	-	-
200 °C	59	946	-	-	2,764	59	4	31	6	1	3	5	4	-	-	-	1,327	-	-	13,585	-	-	-
250 °C	17	531	-	-	913	15	1	14	3	2	1	2	14	-	-	-	22,118	-	1,742		-	-	-
Woodchip																							
150 °C	-	303	-	-	577	12	3	4	5	-	6	10	5	-	-	-	-	-	2,883	9,084	-	-	-
200 °C	56	144	240	-	2,600	35	3	110	4	2	3	5	4	-	-	-	8,410	-	687	-	-	-	-
250 °C	189	413	330	-	3,666	114	7	35	8	1	2	8	8	-	-	-	1,024	-	-	-	-	-	-
SS + woodchip 50/50																							
150 °C	-	76	81	-	664	15	2	9	5	1	1	5	5	-	-	-	-	-	737	-	-	-	-
200 °C	-	-	-	-	1,993	39	5	10	6	2	5	11	8	-	-	-	1,038	-	-	-	-	-	-
250 °C	159	267	-	-	3,065	124	15	33	18	2	8	7	7	-	-	-	-	-	-	-	-	-	-

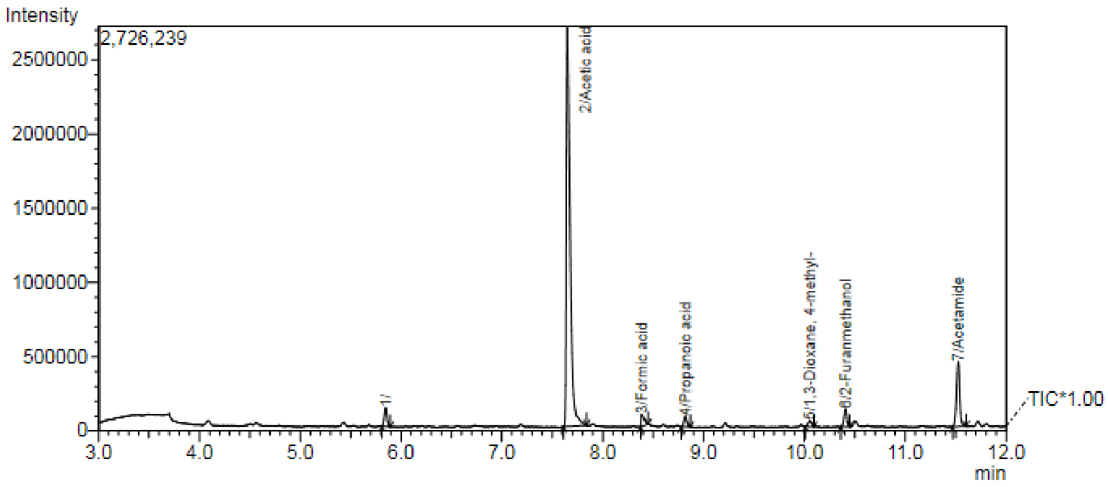
-, not detected



Appendix Figure 1. System boundaries showing mass and energy balance of **a**) best combustion and **b**) best amendment scenarios for the integration of AD and pyrolysis [85].



Appendix Figure 2. Energy balance of combined anaerobic fermentation and HTC of wheat straw [86].

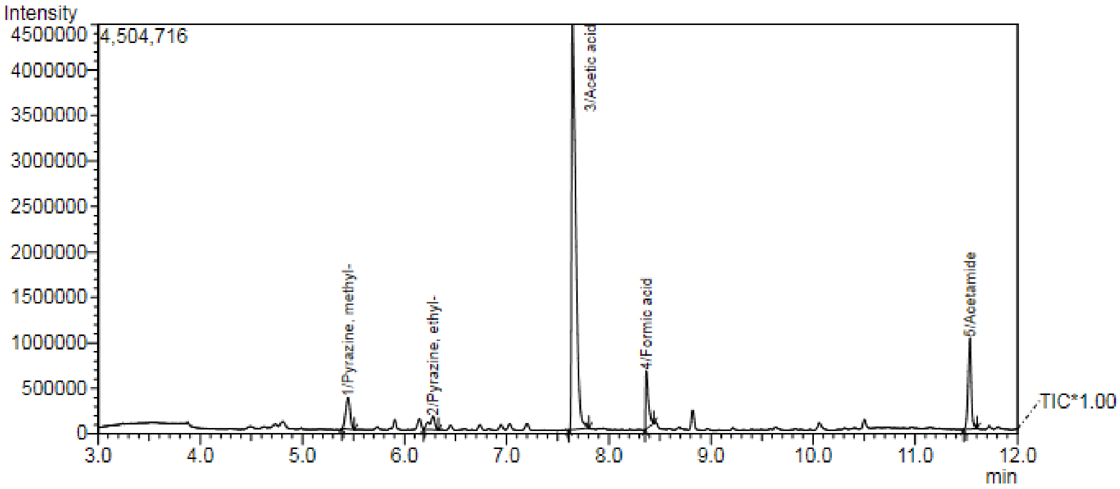


Quantitative Results Table

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.847	5.810	5.895	230364	2.34	126677	3.19	1.82		
2	7.650	7.610	7.840	6972085	70.76	2696098	67.84	2.59		Acetic acid
3	8.387	8.375	8.450	177363	1.80	81152	2.04	2.19		Formic acid
4	8.818	8.780	8.870	136535	1.39	70254	1.77	1.94		Propanoic acid
5	10.054	10.010	10.095	103180	1.05	42857	1.08	2.41		1,3-Dioxane, 4-methyl-
6	10.408	10.360	10.450	265524	2.69	121886	3.07	2.18		2-Furanmethanol
7	11.524	11.470	11.605	1001177	10.16	436842	10.99	2.29		Acetamide
8	16.401	16.360	16.455	139678	1.42	66806	1.68	2.09		4-Hydroxy-3-methylacetoph
9	18.229	18.180	18.310	603822	6.13	248601	6.26	2.43		Benzofuran, 2,3-dihydro-
10	18.443	18.395	18.500	223306	2.27	82993	2.09	2.69		3-Pyridinol
				9853034	100.00	3974166	100.00			

Appendix Figure 3. GCMS injection spectra and identified compounds of AGR 150 °C at 20 percent solid loading.

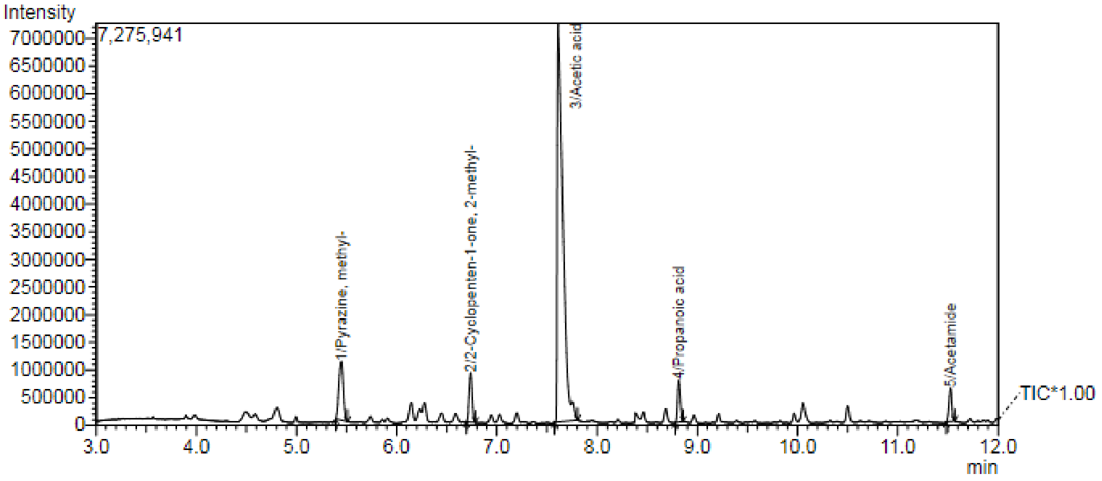


Quantitative Results Table

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.447	5.385	5.510	1055206	4.25	349234	3.88	3.02		Pyrazine, methyl-
2	6.279	6.185	6.330	545594	2.19	148534	1.65	3.67	V	Pyrazine, ethyl-
3	7.645	7.610	7.805	12726816	51.20	4458186	49.57	2.85		Acetic acid
4	8.366	8.355	8.440	1276902	5.14	641076	7.13	1.99		Formic acid
5	11.534	11.475	11.605	2266242	9.12	1003874	11.16	2.26		Acetamide
6	15.321	15.275	15.370	430959	1.73	182485	2.03	2.36		Cyclopropyl carbinol
7	16.128	16.050	16.220	949975	3.82	187072	2.08	5.08		3-Penten-2-ol
8	17.550	17.510	17.635	521039	2.10	173296	1.93	3.01		Pentanoic acid, 4-oxo-
9	18.274	18.190	18.325	683761	2.75	148222	1.65	4.61		3-Pyridinol, 6-methyl-
10	18.446	18.385	18.520	4400166	17.70	1701633	18.92	2.59		3-Pyridinol
				24856660	100.00	8993612	100.00			

Appendix Figure 4. GCMS injection spectra and identified compounds of AGR 200 °C at 20 percent solid loading.

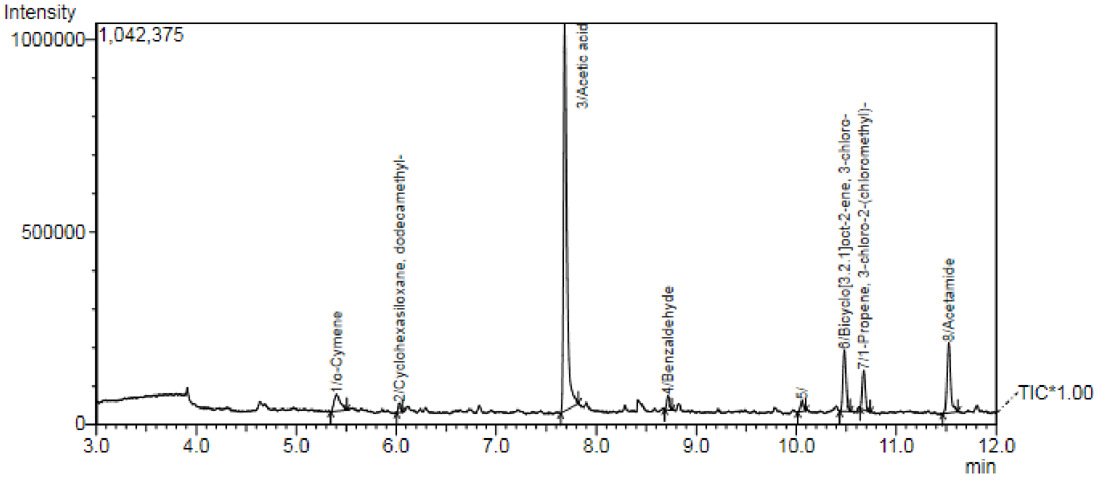


Quantitative Results Table

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.448	5.390	5.510	3251688	6.94	1058295	7.09	3.07		Pyrazine, methyl-
2	6.738	6.695	6.785	1959838	4.18	896233	6.01	2.19		2-Cyclopenten-1-one, 2-me
3	7.609	7.575	7.805	28642117	61.12	7217405	48.37	3.97	S	Acetic acid
4	8.814	8.780	8.860	1426340	3.04	759156	5.09	1.88		Propanoic acid
5	11.527	11.485	11.570	1286617	2.75	601508	4.03	2.14		Acetamide
6	12.812	12.770	12.860	1638905	3.50	830087	5.56	1.97		Phenol, 2-methoxy-
7	14.384	14.345	14.430	1466118	3.13	699280	4.69	2.10		Phenol
8	17.043	17.005	17.090	1284583	2.74	605149	4.06	2.12		Phenol, 2,6-dimethoxy-
9	17.534	17.495	17.610	1690693	3.61	601458	4.03	2.81		Pentanoic acid, 4-oxo-
10	18.445	18.390	18.505	4211971	8.99	1653577	11.08	2.55		3-Pyridinol
				46858870	100.00	14922148	100.00			

Appendix Figure 5. GCMS injection spectra and identified compounds of AGR 250 °C at 20 percent solid loading.

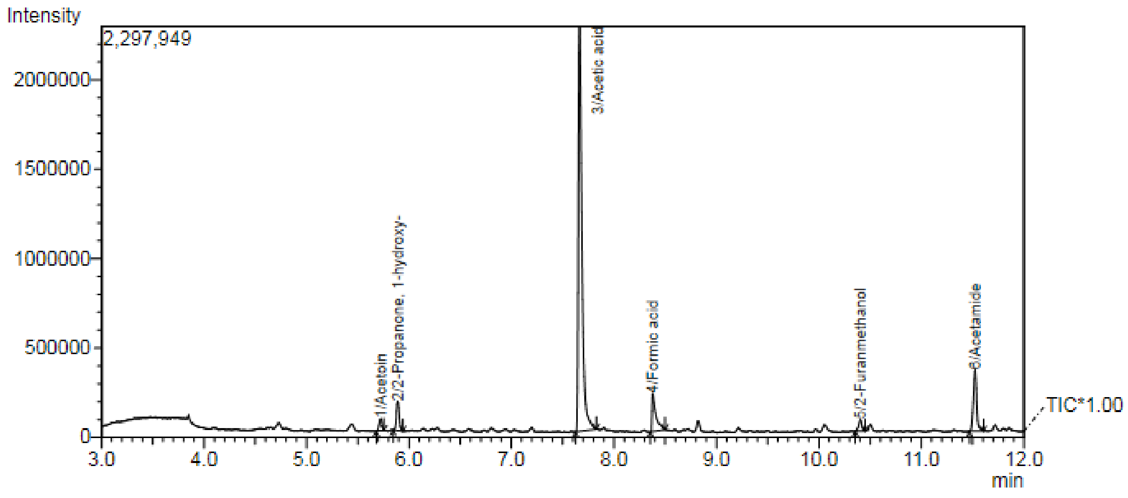


Quantitative Results Table

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.401	5.345	5.505	191494	4.96	43544	2.65	4.40		o-Cymene
2	6.030	6.005	6.060	40177	1.04	24913	1.52	1.61		Cyclohexasiloxane, dodeca
3	7.685	7.645	7.820	2257500	58.44	1006841	61.38	2.24		Acetic acid
4	8.716	8.685	8.755	71602	1.85	36755	2.24	1.95		Benzaldehyde
5	10.060	10.015	10.095	58574	1.52	28310	1.73	2.07		
6	10.482	10.435	10.540	359225	9.30	159053	9.70	2.26		Bicyclo[3.2.1]oct-2-ene, 3-c
7	10.673	10.640	10.740	207275	5.37	101498	6.19	2.04		1-Propene, 3-chloro-2-(chl
8	11.524	11.465	11.615	476383	12.33	182762	11.14	2.61		Acetamide
9	14.381	14.350	14.420	52119	1.35	26186	1.60	1.99		Phenol
10	22.255	22.185	22.320	148565	3.85	30353	1.85	4.89		[1,1'-Biphenyl]-4,4'-diol
				3862914	100.00	1640215	100.00			

Appendix Figure 6. GCMS injection spectra and identified compounds of MSW 150 °C at 20 percent solid loading.

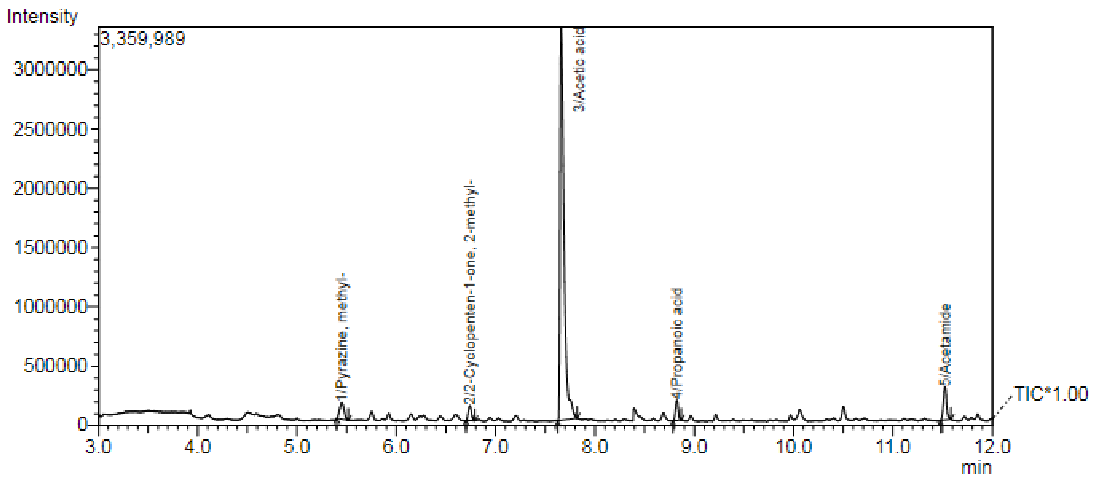


Quantitative Results Table

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.724	5.680	5.755	130883	1.56	67945	1.95	1.93		Acetoin
2	5.891	5.845	5.940	304699	3.63	164400	4.71	1.85		2-Propanone, 1-hydroxy-
3	7.665	7.625	7.830	5419635	64.60	2264062	64.88	2.39		Acetic acid
4	8.377	8.355	8.500	562864	6.71	210667	6.04	2.67		Formic acid
5	10.404	10.355	10.450	150295	1.79	65834	1.89	2.28		2-Furanmethanol
6	11.523	11.470	11.605	781205	9.31	343813	9.85	2.27		Acetamide
7	16.133	16.115	16.205	126268	1.51	42230	1.21	2.99	V	2-Furanmethanol, tetrahydr
8	18.440	18.380	18.505	599648	7.15	224917	6.45	2.67		3-Pyridinol
9	18.650	18.605	18.720	161981	1.93	47802	1.37	3.39		Pyrrolo[1,2-a]pyrazine-1,4-
10	19.779	19.735	19.825	152341	1.82	57965	1.66	2.63		Benzeneacetic acid
				8389819	100.00	3489635	100.00			

Appendix Figure 7. GCMS injection spectra and identified compounds of MSW 200 °C at 20 percent solid loading

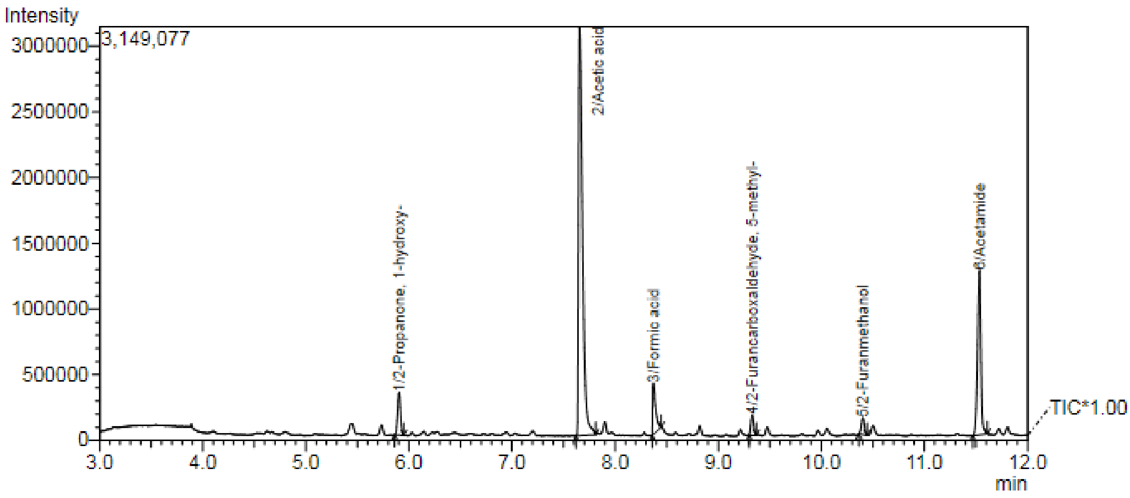


Quantitative Results Table

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.450	5.400	5.515	423267	3.13	140531	2.64	3.01		Pyrazine, methyl-
2	6.740	6.700	6.790	287641	2.13	129711	2.44	2.22		2-Cyclopenten-1-one, 2-me
3	7.661	7.625	7.820	8892047	65.78	3315698	62.37	2.68	S	Acetic acid
4	8.824	8.785	8.870	321305	2.38	170649	3.21	1.88		Propanoic acid
5	11.524	11.480	11.585	623173	4.61	279887	5.26	2.23		Acetamide
6	12.813	12.770	12.860	744790	5.51	376533	7.08	1.98		Phenol, 2-methoxy-
7	14.386	14.345	14.435	318841	2.36	150122	2.82	2.12		Phenol
8	14.709	14.655	14.770	505167	3.74	196720	3.70	2.57		2-Pyrrolidinone
9	17.046	17.005	17.085	349014	2.58	171122	3.22	2.04		Phenol, 2,6-dimethoxy-
10	18.439	18.375	18.510	1052024	7.78	385450	7.25	2.73		3-Pyridinol
				13517269	100.00	5316423	100.00			

Appendix Figure 8. GCMS injection spectra and identified compounds of MSW 250 °C at 20 percent solid loading.

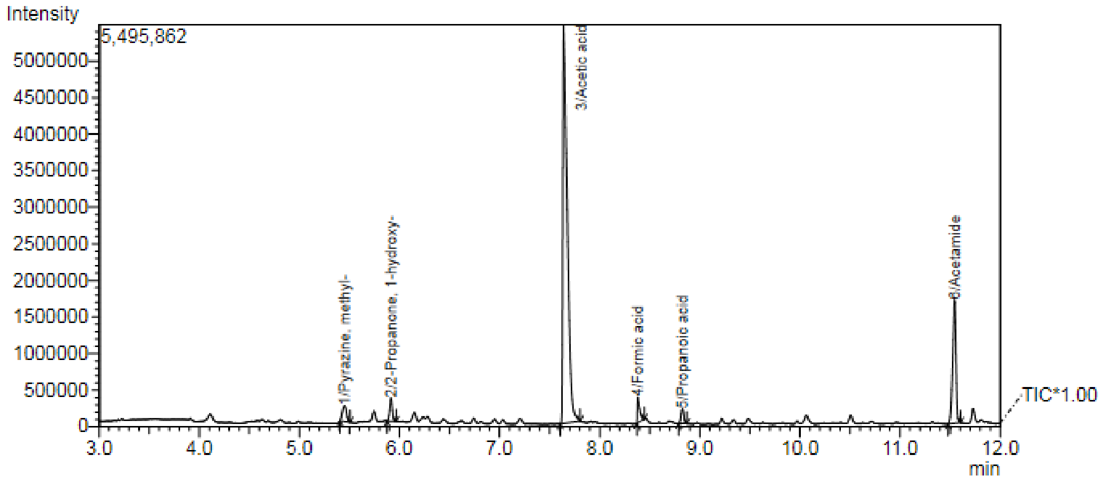


Quantitative Results Table

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.903	5.860	5.950	615896	4.01	324749	5.20	1.90		2-Propanone, 1-hydroxy-
2	7.657	7.620	7.810	8070579	52.61	3112013	49.83	2.59		Acetic acid
3	8.370	8.360	8.445	772687	5.04	389559	6.24	1.98		Formic acid
4	9.331	9.300	9.370	285992	1.86	154230	2.47	1.85	V	2-Furancarboxaldehyde, 5-
5	10.402	10.365	10.445	258046	1.68	126874	2.03	2.03		2-Furanmethanol
6	11.533	11.470	11.610	2889147	18.83	1252874	20.06	2.31		Acetamide
7	14.631	14.585	14.690	348778	2.27	115770	1.85	3.01		1H-Pyrrole-2-carboxaldehy
8	18.272	18.230	18.310	256524	1.67	113430	1.82	2.26		3-Pyridinol, 6-methyl-
9	18.437	18.380	18.500	1436100	9.36	547275	8.76	2.62		3-Pyridinol
10	24.248	24.200	24.335	407128	2.65	108347	1.73	3.76		Acetic acid, phenyl ester
				15340877	100.00	6245121	100.00			

Appendix Figure 9. GCMS injection spectra and identified compounds of SS 150 °C at 20 percent solid loading.

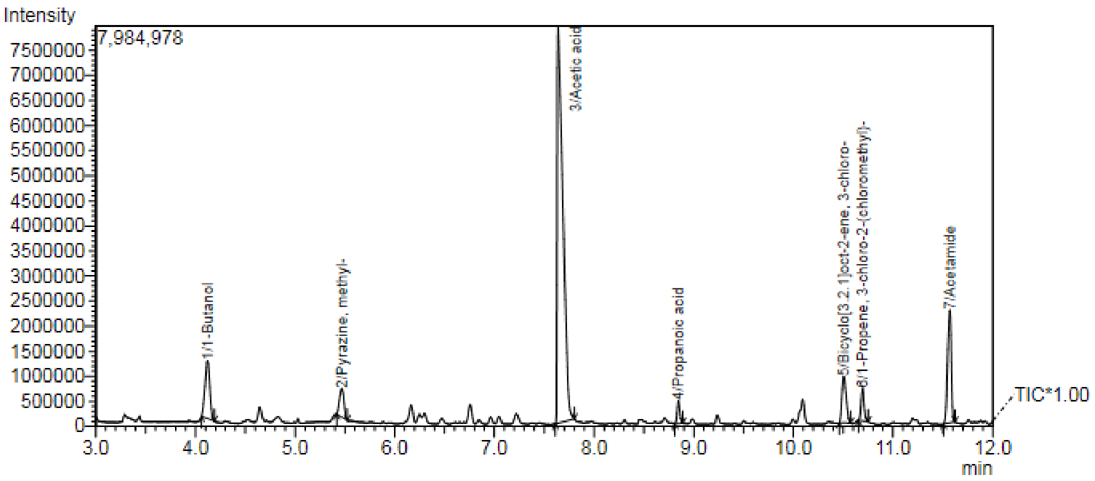


Quantitative Results Table

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.451	5.405	5.505	612426	2.22	217178	2.18	2.82		Pyrazine, methyl-
2	5.915	5.875	5.965	599918	2.18	320342	3.21	1.87		2-Propanone, 1-hydroxy-
3	7.640	7.605	7.805	16992210	61.64	5448362	54.66	3.12		Acetic acid
4	8.380	8.370	8.445	651900	2.36	352865	3.54	1.85		Formic acid
5	8.825	8.790	8.870	368023	1.34	196856	1.97	1.87		Propanoic acid
6	11.546	11.480	11.605	4051400	14.70	1683126	16.88	2.41		Acetamide
7	12.421	12.385	12.465	397088	1.44	205773	2.06	1.93		1,2-Cyclopentanedione, 3-
8	17.546	17.505	17.615	499904	1.81	179629	1.80	2.78		Pentanoic acid, 4-oxo-
9	18.279	18.235	18.325	908044	3.29	378618	3.80	2.40		3-Pyridinol, 6-methyl-
10	18.447	18.390	18.500	2484180	9.01	985832	9.89	2.52		3-Pyridinol
				27565093	100.00	9968581	100.00			

Appendix Figure 10. GCMS injection spectra and identified compounds of SS 200 °C at 20 percent solid loading.

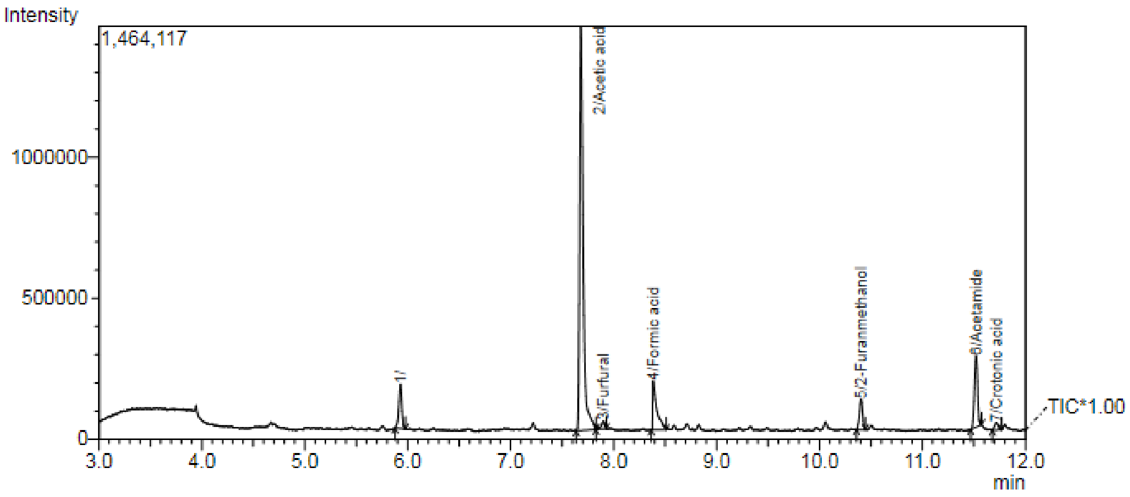


Quantitative Results Table

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	4.121	4.060	4.190	3892084	7.52	1158501	7.52	3.36		1-Butanol
2	5.469	5.420	5.525	1632440	3.15	563382	3.66	2.90		Pyrazine, methyl-
3	7.637	7.610	7.800	31891002	61.59	7919149	51.39	4.03		Acetic acid
4	8.845	8.810	8.890	882620	1.70	456702	2.96	1.93		Propanoic acid
5	10.503	10.460	10.575	2729122	5.27	919078	5.96	2.97		Bicyclo[3.2.1]oct-2-ene, 3-c
6	10.694	10.655	10.750	1371776	2.65	648995	4.21	2.11		1-Propene, 3-chloro-2-(chl
7	11.568	11.505	11.620	5780614	11.16	2249436	14.60	2.57		Acetamide
8	15.716	15.680	15.765	834942	1.61	381160	2.47	2.19		2-Piperidinone
9	18.297	18.260	18.345	921184	1.78	378929	2.46	2.43		3-Pyridinol, 6-methyl-
10	18.468	18.420	18.520	1844341	3.56	735289	4.77	2.51		3-Pyridinol
				51780125	100.00	15410621	100.00			

Appendix Figure 11. GCMS injection spectra and identified compounds of SS 250 °C at 20 percent solid loading.

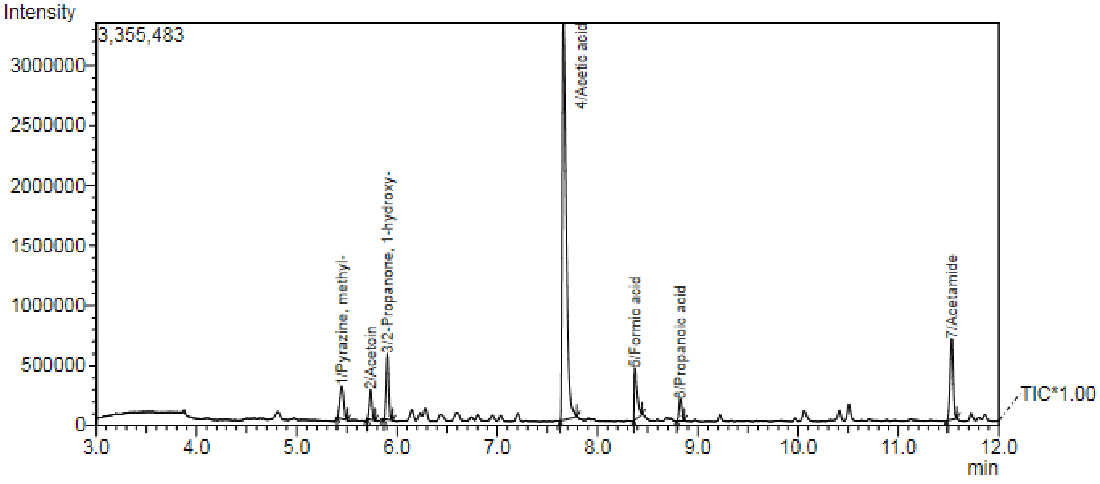


Quantitative Results Table

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.928	5.875	5.980	317578	5.65	157729	6.69	2.01		
2	7.681	7.635	7.830	3372506	59.98	1432361	60.78	2.35		Acetic acid
3	7.899	7.830	7.930	71714	1.28	28136	1.19	2.55	V	Furfural
4	8.385	8.365	8.510	481509	8.56	172804	7.33	2.79		Formic acid
5	10.403	10.360	10.445	228319	4.06	107608	4.57	2.12		2-Furanmethanol
6	11.520	11.470	11.575	553360	9.84	253599	10.76	2.18		Acetamide
7	11.716	11.680	11.770	59303	1.05	25568	1.08	2.32		Crotonic acid
8	18.439	18.385	18.485	262777	4.67	99771	4.23	2.63		3-Pyridinol
9	18.656	18.605	18.740	182653	3.25	43816	1.86	4.17		Pyrrolo[1,2-a]pyrazine-1,4-
10	18.921	18.880	18.960	93318	1.66	35319	1.50	2.64		Succinimide
				5623037	100.00	2356711	100.00			

Appendix Figure 12. GCMS injection spectra and identified compounds of VGF 150 °C at 20 percent solid loading.

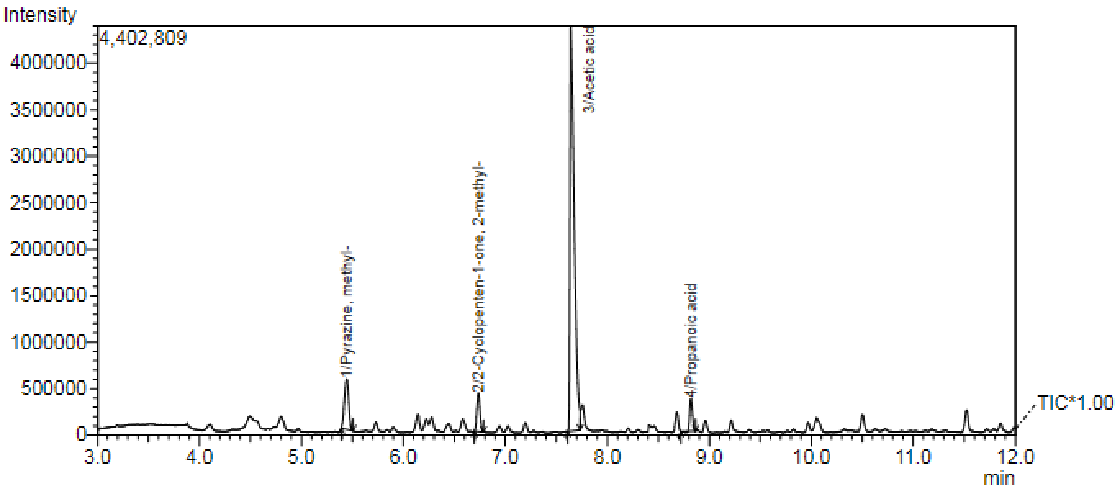


Quantitative Results Table

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.449	5.400	5.505	756744	4.72	271321	4.10	2.79		Pyrazine, methyl-
2	5.736	5.700	5.780	474050	2.96	248043	3.75	1.91		Acetoin
3	5.905	5.865	5.955	1008247	6.29	546752	8.26	1.84		2-Propanone, 1-hydroxy-
4	7.659	7.625	7.795	8756053	54.65	3307520	49.95	2.65		Acetic acid
5	8.372	8.360	8.445	904887	5.65	429902	6.49	2.10		Formic acid
6	8.823	8.790	8.865	324032	2.02	176502	2.67	1.84		Propanoic acid
7	11.532	11.480	11.585	1487369	9.28	669341	10.11	2.22		Acetamide
8	12.819	12.785	12.860	396375	2.47	204908	3.09	1.93		Phenol, 2-methoxy-
9	17.050	17.020	17.090	262780	1.64	136300	2.06	1.93		Phenol, 2,6-dimethoxy-
10	18.444	18.390	18.505	1652214	10.31	630766	9.53	2.62		3-Pyridinol
				16022751	100.00	6621355	100.00			

Appendix Figure 13. GCMS injection spectra and identified compounds of VGF 200 °C at 20 percent solid loading.



Quantitative Results Table

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.443	5.390	5.505	1605518	6.63	543931	5.85	2.95		Pyrazine, methyl-
2	6.735	6.695	6.785	901857	3.72	415679	4.47	2.17		2-Cyclopenten-1-one, 2-me
3	7.643	7.610	7.735	12854158	53.09	4357110	46.86	2.95		Acetic acid
4	8.819	8.720	8.865	615296	2.54	349607	3.76	1.76	V	Propanoic acid
5	12.812	12.765	12.865	2667827	11.02	1313492	14.13	2.03		Phenol, 2-methoxy-
6	14.386	14.345	14.430	763798	3.15	359739	3.87	2.12		Phenol
7	14.708	14.670	14.760	751059	3.10	339916	3.66	2.21		2-Pyrrolidinone
8	16.144	16.110	16.200	742332	3.07	235349	2.53	3.15		Butanoyl chloride
9	17.043	17.000	17.085	1298156	5.36	629752	6.77	2.06		Phenol, 2,6-dimethoxy-
10	18.439	18.385	18.505	2012393	8.31	754106	8.11	2.67		3-Pyridinol
				24212394	100.00	9298681	100.00			

Appendix Figure 14. GCMS injection spectra and identified compounds of VGF 250 °C at 20 percent solid loading.