

SUSTAINABLE INTERVENTION OF FOOD WASTE TREATMENT PROCESSES AND PRODUCTS

Submitted by

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Declaration

I certify that the work in this thesis entitled “Sustainable Intervention of Waste Treatment Processes and Products” has not previously been submitted for a degree nor has it been submitted as part of requirement for a degree to any other university or institution other than Macquarie University.

I also certify that the thesis is an original piece of research and it has been written by me. All help and assistance that I have received in my research work and the preparation of the thesis itself have been appropriately acknowledged.

In addition, I certify that all information sources and literature used are indicated in the thesis.

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Date: 10 August 2016

“Jabir (May Allah Subhanahu wa ta'ala be pleased with him) reported: I heard Allah's Apostle (May Peace, blessings and mercy of Allah Subhanahu wa ta'ala be on him) as saying that the inmates of Paradise would eat and drink but would neither spit, nor pass water, nor void excrement, nor suffer catarrh. It was said: Then, what would happen with food? Thereupon he said: **They would belch and sweat** (and it would be over with their food), and their sweat would be that of musk and they would glorify and praise Allah as easily as you breathe”

- Sahih Muslim: Book 040, Number 6798 -

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Dedication

To my beloved family and all environmentalist

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Abstract

Due to resource scarcity and impacts amelioration, efforts are ongoing to widen recycling capacity of organic waste and smartly appropriate its products to ensure optimization and a zero waste system. In this work, food waste is treated with full consideration of two treatment streams (anaerobic digestion and pyrolysis) using the energy, environment, agronomic and socio-economy as indicators to evaluate the sustainability extent of these treatment processes and their products.

Review of the organic waste treatment processes and their products was explored to identify treatment gaps and its effects on the products vis-à-vis sustainability. Fresh food wastes were collected from Macquarie and Eastwood shopping centres and sampled compositely for both biochemical (anaerobic digestion) and thermochemical (pyrolysis) treatments. Characterization results of fresh food wastes were compared with food wastes in other part of the world through a review to reflect properties parity. Meanwhile, to reduce experimental cost and save biochemical digestion time, digestate was collected from EarthPower Technologies Sydney Pty Limited (a commercial food waste to green energy company). This was equally characterized analytically to evaluate its organic, inorganic and elemental constituents. The raw food wastes and the digestate were then pyrolysed separately at different temperatures (300, 400, 500 and 700°C) to evaluate temperature effect on the products' (biogas, bio-oil and the biochar) quantity and properties.

The energy proficiency of these treatment processes using food waste and its digestate were evaluated through a novel energy harvesting system (EHS) after discrete assessment of the two processes (anaerobic digestion and pyrolysis). The hybrid EHS wherein anaerobic digestion was sequenced with pyrolysis provided the highest transitional energy base products. This was accomplished using industrial pyrolysis temperature (500°C).

The biochar produced through pyrolysis from the raw food waste were activated using CO₂ (a major constituent of the biogas generated) to drastically reduce greenhouse gas (GHG) emission. This activated and oxidised chars were compared with commercial activated carbon. The produced activated chars (with surface area range of 797.2 to 1024.7m²/g) were evaluated as a component of pressure swing adsorption (PSI) for refinery off gases (ROG) treatment and or purification. Raw food waste oriented chars adsorbed 330 to 380mg/g of benzene gas and 4.1 to 4.4mmol/g of CO₂. The abolition of CO₂ flaring and scrubbing of C₆H₆ gas are significant environmental impact amelioration.

Similarly, the digestate (DFW) and digestate derived chars (PyD500) potential for soil enhancement and or fertilizer were evaluated. Sand to substrate rate, germination index, water retention capacity and plant available water were used to assess agronomic capacity of these products (DFW and PyD500). DFW provided the best reaction to plant available water with increasing application rate in the sandy soil considered. However, PyD500 delineated better phytotoxicity, water holding capacity and nutrient sorption rates compared to DFW.

Finally, life cycle analysis (LCA) of the three processes (commercial one stage anaerobic digestion, pyrolysis and the integration or sequence of AD and pyrolysis) and their products are considered to gauge the likely environmental impacts putting all in perspective. The sustainability stance of variables (input and outputs) and treatment processes are determining with energy, environment, agronomic and socio-economy as indicators for a life cycle analysis. This is expected to widen and broaden treatment of food wastes and ensure the fitness and robustness of the model developed in most part of the globe.

List of Publications

The following is a list of publications derived from this thesis with declaration of authorship contributions outlined in Appendix A.

Journal Articles

Opatokun, S. A., Strezov, V., & Kan, T. (2015). Product based evaluation of pyrolysis of food waste and its digestate. *Energy*, 92, Part 3, 349-354.

Opatokun, S. A., Kan, T., Al Shoaibi, A. S., Srinivasakannan, C., & Strezov, V. (2015). Characterisation of food waste and its digestate as feedstock for thermo-chemical processing. *Energy & Fuels*. DOI: 10.1021/acs.energyfuels.5b02183.

Opatokun, S. A., Azhagapillai, P., Al Shoaibi, A. S., Srinivasakannan, C., & Strezov, V. (2016). Food Waste Derived Adsorbents for Benzene Gas Sorption. Submitted to the *Journal of Hazardous Materials*.

Opatokun, S. A., Lina, F. Yousef., & Strezov, V. (2016). Agronomic Assessment of Pyrolysed Food Waste Digestate for Sandy Soil Management. Submitted to the *Journal of Environmental Management*.

Opatokun, S. A., Ana M. Lopez-Sabiron., German. Ferreira, & Strezov, V. (2016). Environmental Burdens and Benefits of Food Waste Treatments Scenarios: A Life Cycle Analysis Perspective. To be submitted to *Environment International*

Opatokun, S. A., & Strezov, V. (2016). A Review of Properties, Application and Prospects of Carbonaceous Biomass Post-processing Residues. To be submitted.

Peer-reviewed Conferences

Opatokun, S. A., Strezov, V., & Kan, T. (2014). Product based evaluation of pyrolysis of food waste and its digestate. 9th Conference on Sustainable Development of Energy, Water and Environment Systems (SDEWES 2014), The MSC Preziosa Cruiser from Venice, Italy to Istanbul, Turkey.

Opatokun, S. A., Kan, T., Al Shoaibi, A. S., Srinivasakannan, C., & Strezov, V. (2015). Characterisation of food waste and its digestate as feedstock for thermochemical processing. 5th Sino-Australian Symposium on Advanced Coal and Biomass Utilisation Technologies. Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan, Hubei 430074, People's Republic of China.

Introduction

1.1 Problem Statement

There is an increased concern for the growing rate of food wastes globally despite the undernourished 870 million people [1] and industrial demand for food oriented value added resources. The world 1.3 billion tonnes of food losses and waste per annum was estimated to cost more than USD 900 billion [2] with potential of 53% increase by 2025 [3]. Food waste mostly consists of uneaten food and leftover food wastes from residences, commercial establishments, such as restaurants, institutional waste sources like school cafeterias, industrial sources like the food and beverages companies (leftover of edible raw materials), departmental or retail stores and factory lunchrooms. The general C/N ratio of food waste ranges from 14 to 80, while garbage and refuse are 14 -16 and 34 – 80 C/N ratio respectively [4]. The major sources of food waste are from production through retailing while consumer oriented food wastes are mostly generated in North America and Oceania followed by the United Kingdom [2]. About 39% of the total 200 million tonnes of MSW generated in Europe in 2000 was food scraps or food waste [3], while in Australia 15% of every 20Mt of waste landfilled is food wastes [5]. Food wastes are also driven by consumer behaviour, lack of co-ordination and quality standards in medium to high income countries, whereas harvesting technique limitation, storage constraints, lack of infrastructure and packaging account for the waste in low income countries [1]. Beside the preventive and recycling management measures, food waste treatment is inevitable. Food wastes generally contain high moisture content and are very susceptible to odour production (ammonia). They also produce large amounts of leachates with high concentration of COD as a result of their richness in organics [6]. This latter feature invariably limits the choice of treatment process if not pre-treated. In the USA, composting facilities are

provided for residential source separated food wastes [7] while, a mesophilic anaerobic digestion was reported to be deployed in Sydney for commercial food waste management [8]. Managing this stream of waste becomes inevitable to ensure proper utilization and appropriateness of this 'resource out of place' called food wastes.

1.2 Objectives of the study

The aims of this thesis are:

- (i) To evaluate the sustainability extent of selected treatment processes (anaerobic digestion and pyrolysis) for food waste management
- (ii) To determine a hybrid treatment process for the food waste and
- (iii) To provide value added products through these interventional treatment processes.

1.3 Structure of the thesis

The thesis is structured as thesis by publication consisting of six chapters excluding the introduction, conclusion and recommendations chapters.

Chapter 2 aims to review the biomass treatment processes for organically rich wastes post-processing residues. Emphasis of the review was on biochemical and thermochemical treatment techniques after a holistic schematic presentation of available biomass treatment processes. The principle and degradation pathways of biomass through which these residues are generated were highlighted. The physicochemical properties of the residues were indicated with the view to reflect the environmental impact implication and provide insight into treatment process selection. The efficiency and effectiveness of both laboratory and pilot scale treatment processes were also indicated as reported in literatures. Limitations and strengths of the processes under review were provided. The contemporary application and uses ranging from energy, carbon sequestration, agriculture and metallurgy of the products

including the residues (where applicable) were expressed. Finally, life cycle analysis of waste management processes was reviewed before a conclusion to the chapter.

Chapter 3 chronicles experimental characterisation of raw food wastes and the digestate, which were the major feedstocks. The physicochemical characteristics of the resultant products after slow pyrolysis were extensively considered. The biochar, bio-oil and the biogas were produced at different temperatures. Properties of biochars at 300, 400, 500 and 700°C and details of bio-oil and biogas produced at 500°C were presented. This chapter represents the published article Opatokun, S.A., Tao kan, Ahmed Al Shoaibi, C. Srinivasakannan & Vladimir Strezov (2015) *Characterisation of food waste and its digestate as feedstock for thermochemical processing*. Energy & Fuels, DOI: 10.1021/acs.energyfuels.5b02183.

Chapter 4 related the effect of treatment process on the feedstocks (raw food wastes and food waste digestate) especially as related to energy outputs. The commercial one stage anaerobic digestion (AD) and pyrolysis were separately considered as biochemical and thermochemical treatment processes for food waste. The study then proposed the energy-harvesting system (EHS) wherein AD was sequenced by pyrolysis. These three scenarios were compared using energy output as indicator. This work was published as Opatokun, S.A. V. Strezov & T. Kan, 2015. *Product based evaluation of pyrolysis of food waste and its digestate*. Energy 92 (2015) 349 - 354.

Chapter 5 considered the agronomic relevance of the biochar generated after optimal energy extraction through the proposed EHS. Indicators such germination index, water holding capacity, nutrient dynamics and carbon thermostability of the pyrolysed digestate at different temperatures were evaluated and compared to using the digestate as bio-fertilizer. The phosphate sorption, plant available water and

biochar-sand soil application rate were equally assessed using pyrolysed digestate produced at 500°C (PyD500) only.

Chapter 6 represents an experimental evaluation of the potential of the functionalised raw food waste oriented biochars (PyF) as commercial adsorbents. The efficacy of these adsorbent on benzene and CO₂ adsorption were determined using analytical techniques. The most significant transformation on the biochar was accomplished using CO₂ as a means of activation. Thus, recycling CO₂ which is a major GHG gas produced during either anaerobic digestion or pyrolysis. The thermodynamics of C₆H₆ adsorption isotherm were determined while CO₂ adsorption isotherms (appendix) were considered on doped and un-doped matrix.

Chapter 7 synthesized the life cycle inventory (LCI) using real time data from three scenarios (commercial one stage anaerobic digestion - AD , laboratory scale pyrolysis and the integration of AD and pyrolysis) to determine and compare the environmental performance of the treatment stream. Impact categories, such as climate change (CC), ozone depletion (OD), terrestrial acidification (TA), fresh water eutrophication (FE), marine eutrophication (ME), human toxicity (HTox), photochemical oxidant formation (POF), particulate matter formation (PMF), terrestrial ecotoxicity (TEcox), fresh water ecotoxicity (FEcox) marine ecotoxicity (MEcox), water depletion (WD), minerals depletion (MD) and fossil fuel depletion (FD) of the processes were determined and discussed.

Chapter 8 provides the conclusion and recommendations as indicated in the study outcomes.

1.4 References

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A Review of Properties, Applications and Prospects of Carbonaceous Biomass Post-processing Residues

2.1 Introduction

Substantial quantities of biomass and organic wastes are redirected from landfills and other 'end of pipe' treatments to usher in integrated solid waste management (ISWM) system primarily for environmental protection and recycling. Through ISWM system, waste avoidance and minimisation are given priority, followed by 3Rs (reduce, reuse and recycle) to ensure efficiency in the appropriation of these outplaced resources, termed waste. This widely adopted strategy provides tangible throughput across the sustainability scorecards (ecology, economy and social). This initiative thus, attracts not only standards and regulations but evident the role of process assessment and optimization in biomass management. Organically rich wastes are now considered resources for the production of renewable energy, biogas, biofertilizers, compost / soil amendment and recently considered as liquid and solid fuel sources [1]. This quantum leap provides insight into smart utilization of scarce resources while environmental impacts are significantly ameliorated. For instant, the globe annual 11.2 billion tonnes of solid wastes require attention to avert approximately 5% of the planet greenhouse gas (GHG) emissions [2] which are generated due to unstructured decay of the waste organic constituents.

Sources of these wastes include sectors, such as agriculture [3] (animal dumps, plant and animal remains), municipal solid waste (food waste, yard trimmings) and commercial and industrial sectors (food and pharmaceutical industries, wholesale and retail food distribution, sales outfits and hospitality and catering industries) [4, 5]. The nascent biochemical conversion processes (fermentation, aerobic and anaerobic digestion,); thermochemical conversion processes (biochar, charcoal, bio-oil) and physicochemical (esterification, extraction and or separation) treatment processes [6] offer varying advantages and disadvantages with waste composition and treatment goals as pre-requisite for process adoption. These treatment processes equally produce residues most of which pose greater or equivalent challenges for management [6, 7].

Thus, the environmental issues, constraints and risks of these residues are associated with their environmental safety; lack of standards and assessment framework for their management, such as treatment (if further treatments are necessary) and disposal procedures or policies; and the application directions, including their sustainable use as fertilizer substitutes.

Although biomass related energy makes more than 14% of world's final energy consumption [8] the choice and effect of biomass treatment processes are critical to unlock about 470 KJ (112kcal) of energy captured through every gram mole carbon fixed during photosynthesis [9, 10]. Biomass related energy, unlike solar, wind and geothermal, remains the most patronised form of renewable energy partly due its abundance and provision of material feedstock alongside energy. Thus, harnessing the cyclic and biospheric carbon from these organic wastes requires adequate characterisation and careful selection of treatment technique to ensure equilibrium in socioeconomic and environmental stance of the waste system [11]. Treatment process design is pivoted often on the quantity of biomass, the desired form of product (such as energy, chemicals), environmental standards and economic viability especially at commercial scale [12].

This chapter aims to review the properties and uses of the carbonaceous solid products of biomass processing (digestates, compost, fermentation residue and biochar) from various organic oriented treatment processes with the view to: i) expose or reflect the potential resourcefulness of biomass post-processing products beyond their current deployment as fertilizers or soil amendments, ii) present the implication or effects of treatment processes on the resultant product characteristics and applications.

2.2 Properties and uses of the biomass post-processing residues

Organic waste substrate's degradation path can broadly be classified into three categories, as indicated in Figure 1. The physicochemical processes explore extraction techniques to stir reactions for target products; thermochemical processes reflect temperature treatment on substrates in the absence or presence of oxygen [13]; while biochemical process express microbial processing of substrates [14]. The latter process is often characterized by solubilization of substrates through a hydrolytic stage

wherein substrate's macromolecules are mineralized through enzymatic activities into monomers and consequently gases and other products (Figure 2).

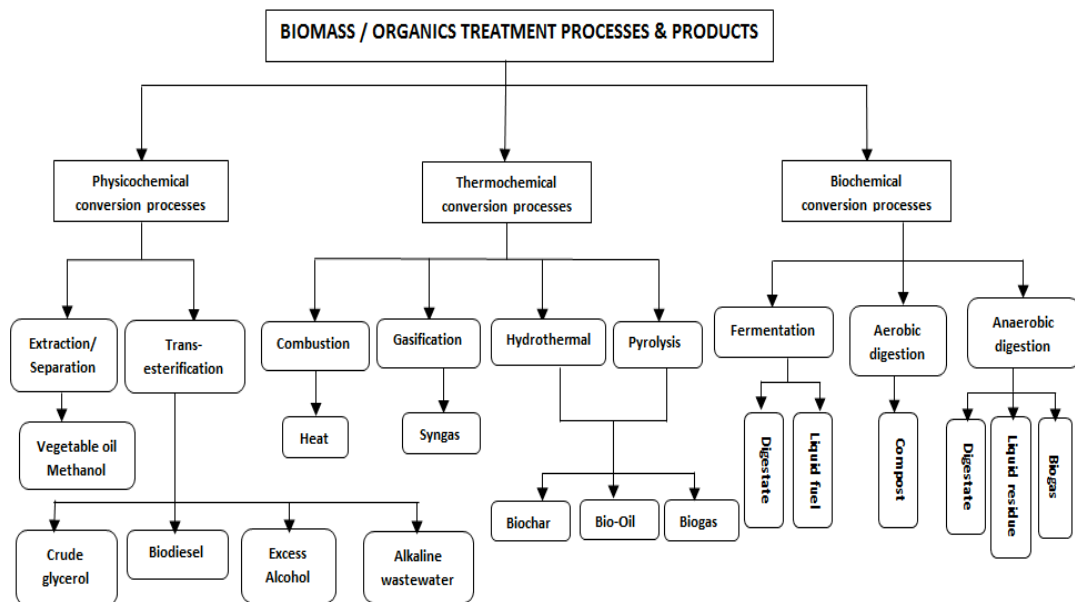


Figure 2.1: Substrates Degradation Processes & Products (Adapted and modified from [6, 15, 16])

Biodegradation of substrates is mostly deployed due to its environmental and cost benefits, as indicated in [17] wherein operations and cost effectiveness of implementing various invessel anaerobic digestions in UK and USA are reviewed.

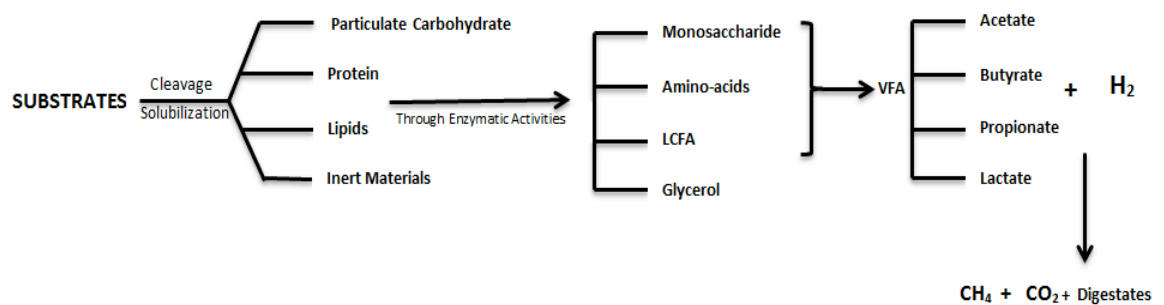


Figure 2.2: Substrates digestion sequence (adapted from [18, 19])

Waste treatment residues as solids (digestates with TS > 15%), liquids (digestates with TS range of 0.5 to 15%) [14] and gaseous products, as shown in Figure 1, is a function of the inputs and processing technique coupled with other key factors. Subsequent

products of the digestion process are vested in either aerobic or anaerobic pathways, which equally determine the microbial constituents, performance and output features.

2.2.1 Residues of the biochemical treatments of food wastes

2.2.1.1 Fermentation Residues

Fermentation residues are produced during microbial conversion of simple sugars to ethanol, enzymes and CO₂ especially in pharmaceutical, food, brewery, waste treatment and other related industries. The residues consist of incomplete fermented fibres, water, microbial cells, organic constituents (glycols) and other components useful as fertilizer, animal feeds and other purposes [20, 21]. Although fermentation has a long history associated with ethanol and its related products (wine, beer, drugs), the demand for ethanol as substitute of gasoline strengthens the industrial relevance of the process. In this process, sugar or starch oriented feeds and, in more advanced processes, lignocellulosic biomass are subjected to four serial but complex biochemical pathways (pre-treatment, hydrolysis and saccharification, fermentation of monomers and purification) with adequate consideration of substrate component and structure [22]. Generally, the major challenges associated with fermentation techniques are the formation of waste streams (acid pre-treatment materials and toxic compounds), high cost of enzymes and economic subsidies [23].

Interestingly, fermentation process yield are often high (> 90%) however, residues quantity cannot be underestimated due to disposal conditions, cost and the associated environmental impacts. For instance, Juang et al. [24] reported 75 – 80% conversion efficiency for the production of ethanol, thus about 20 – 25% organic waste residues (pH of 4.0) with 1481 mg/l volatile solids, 22600 mg/l carbohydrate, 4400 mg/l organic nitrogen, organic acids and other forms of alcohols. Enzyme compatibility, inhibitory consequences of pre-treatment and different temperature demands are other disadvantages of simultaneous saccharification and fermentation despite the yield height and low enzyme requirement [25]. Nutrients and mineral richness of selected biomass residues after fermentation are illustrated in Table 2.1.

Valorisation pathways and information related to nutrients, minerals and other complex constituents of fermentation residues are nowadays facilitated through characterisation using analytical tools [26]. Brewery malt residue was reported to

contain 28.4% hemicellulose, 27.8% lignin, 16.8% cellulose, 15.25% protein and small quantity of extractives and ashes [25]. The fermentation residues are now considered for gas production, fertilizer and animal feed inputs. Lignin rich wet residues (77.3 wt% moisture content) were gasified in the presence of catalyst to produce synthesis gas (H_2S and COS) [27] required for some industrial operations. Compared to unfermented slurry (animal faeces, urine and slaughterhouse liquid), fermented slurries are richer in nutrients, thus considered more suitable for agricultural use except for higher NH_4-N and pH which necessitate hygiene during application [28].

Table 2.1: Elemental and nutrients constituents of fermentation residues from selected biomass

	HHV	C	H	N	O	P*	K*	Protein
	(MJ/kg)	(wt%)	(wt%)	(wt%)	(wt%)	(%)	(%)	(wt%)
Red maple	24.2	56.8	5.6	1	35	0.14	1.5	6.1
Switchgrass	20.8	50.1	5.5	1.5	36.5	0.14	2	9.6
Miscanthus	19	45.6	4.7	1.4	34.1	0.11	1.1	8.5

Source: Sannigrahi, P., et al., *Journal of Biobased Materials and Bioenergy*, 5(4), 514-519. *Approximated and converted from histogram values.

2.2.1.2 Digestate

Anaerobically digested organic wastes produce renewable energy (methane) and nutrient rich residues [3, 29] called digestate. Anaerobic digestion (AD) is widely deployed relatively effective treatment method for processing of organic wastes. Biogas and other by-products are produced using single or two stage digestion of agricultural wastes, such as animal manure; sewage sludge and or industrial effluent; food and vegetable solid wastes and organic fraction of municipal solid waste (OFMSW). Anaerobic digestion produces high quantity of digestate residues due to varying posits on its process parameters [30-33] which are a function of the process aims and objectives. Moreover, the heterogeneity of the co-digestated wastes attracts facultative and anoxic microbial diversity which equally limit its efficiency, especially in the absence of a proper trade off process conditions [24]. Studies indicate methane

yield range of 40 to 70% of entire biogas while CO₂ ranges between 32 to 38% [14]. However, about 15 to 40% of the organic inputs are often utilised for biogas production, especially on large scales (Table 2.2) while the remaining liquid and or solid digestates constitute the effluent [34-36]. Consequently, biogas, slurry and solid residues (digestate) are produced and invariably quest for management, mostly due to its toxicity.

Several studies provide significant information on the performance patterns of anaerobic digestion with respect to substrate utilisation and biogas yield while emphasis are laid on scale, substrates type and digestion process adopted [37-39] as illustrated in Table 2.2. The isolated high percentage substrate utilization expressed by [40] can be accredited to the process scale, especially the extremely low working volume of substrates. Furthermore, most laboratory scale digestion processes reported significantly effective yields while single stage anaerobic digestion ensures efficient utilization of substrate and cost benefit and commercialization improvements relative to the two stage anaerobic digestion system. However, this may not be unconnected to several other factors previously highlighted. Although degradation process evaluation cannot be isolated from the loading rate and the system hydraulic retention time [41, 42] adequate optimisation of process conditions is basic requirement for bioconversion system setup.

Generally, the large-scale organic digestion significantly increases the net farm income and reduces odour, while substantially reducing the greenhouse gases (CO₂ and CH₄ produced through uncontrolled disposal). However, there are no significant reductions in ammonia emission and water quality potentials in the system outputs. Digestates often comprise of a partially degraded organic matter coupled with microbial biomass and other inorganic constituents [7]. Unlike compost, digestate is un-mature product of anaerobic processes [36] which may require post-treatment measures and management. The physicochemical constituents of digestates, as summarised in Table 2.2, are greatly influenced by substrate source, microbial composition, pre-treatment measures and process techniques and parameters [41, 43, 44].

Table 2.2: Selected Process Performance/ Efficiency

Digestates Sources	Digestion Process	Energy/Biogas Yield	Substrate* utilization Percentage (%)	Process scale	Ref.
Beet leave & potato	Two stage AD	3.9 kWh/kg VS	-	Pilot	[45]
Pharmaceutical industry sludge	Mesophilic AD	0.36 l/g	72.84	Laboratory	[40]
Primary sludge & OFMSW	Thermophilic AD	0.67 l/g	53.40	Laboratory	[40]
Cattle manure	Mesophilic AD	0.14 l/g	53.40	Laboratory	[40]
Pig manure, Industrial waste & Biowaste	Two Stage & Aerobic system	19 GWh/yr	13.11	Large Scale	[36]
§Cattle Dairy & Pig slurry	AD	-	38.96	Large Scale	[46]
§Pig Slurry	AD	-	40.88	Large Scale	[46]
§Dairy Cattle slurry (in Kent & Scotland)	AD	-	33.33 & 17.18	Pilot scales	[47]
§Cow slurry	Plug flow AD	93,501ft ³ /day	38.50	Large Scale	[48]

*Values are calculated from the data reported, NB: [40] values determination was based on the VS as a function of the organic constituents, while §studies utilization strength are determine using the chemical oxygen demand of input and output respectively.

The distribution and mineralisation dynamics of nutrients in digestates are dearthly discussed in the literature, [45]. Phosphorus in the digestate is repositied in the solid fraction while the liquid residue hosts most of the mineralised nitrogen, especially in a two-stage anaerobic digestion system. These digestion residues are mainly characterised (Table 2.3) by a slightly neutral pH, except for few substrates, such as sugarcane, which indicates an acid state due to its homogeneity [49].

Similarly, the pH of digestates were reported to be equally influenced by the substrate composition, microbial constituents and the other process parameters adopted for the system [45, 46, 50]. Although, volatile solid (VS) and total solid (TS) constituents of most digestates are proportional, volatile solids are often used to estimate the organic concentration of the substrate [45]. This parameter is considered as a vital degradation measure and thus an indicator for microbial activities within the system. Nevertheless, critical evaluation of the VS percentage on TS basis, as presented in Table 2.3, shows VS content at an average of above 70%, is a characteristic of higher biodegradability resulting in more digestate yields [51].

Table 2.3: Physical Properties of Digestates

Digestates Sources	Digestion Process	pH	*Total Solid (%)	*Volatile Solid (%)	Ref.
Dairy manure & Biowaste	Two stage AD	7.4	4.1	3.0	[52]
Pharmaceutical industry sludge	Mesophilic AD	7.8	22.5	15.7	[40]
Primary sludge & OFMSW	Thermophilic AD	7.5	23.6	16.5	[40]
Cattle manure	Two stage AD	7.6	122.6	105.4	[40]
Food waste	Thermophilic AD	7.87	3.9	2.7	[53]
Wastewater Sludge	Mesophilic AD	7.9	3.9	2.66	[53]

*Original values of these data are converted to percentage for coherence

Organic constituents and their degradation pattern are also reflected with parameters such as neutral detergent fiber (NDF), volatile fatty acid (VFA) and both

the chemical and biological oxygen demand [54-57]. Most of these parameters are considered to evaluate not just the microbial metabolic strength and pattern on residues produced but also to determine the effectiveness of the process and, consequently, the quality of the yield and other products.

Table 2.4: *Nutrients & Macro-elements Constituents of Digestates

Digestates Sources	Digestion Process	TN (%)	pH	TP (%)	TK (%)	C (%)	C/N	Ref.
Pig manure & rape residue	AD	0.36	7.82	0.11	0.31	1.47	4.083	[7]
Pig manure & Sunflower residue	AD	0.35	7.92	0.11	0.31	1.22	3.486	[7]
Cattle manure & maize oat silage	Mesophilic AD	0.397	7.50	0.08	0.31	3.38	8.5	[59]
Slaughter house waste water & Biodiesel wastewater	Mesophilic AD	0.396	8.20	0.02	0.2	0.59	1.5	[59]
Pig slurry + Slaughterhouse sludge + Biodiesel Wastewater	Mesophilic Industrial AD	0.38	8.3	0.05**	0.24***	0.47	1.2	[7]
Pig Slurry	Industrial Thermophilic AD	2.67	6.54	3.1	1.14	35.2	13.18	[60]

*Values are calculated from the data reported. **As P₂O₅, *** As K₂O

Similarly, the organic fraction behavior in the system provides information on the relationship between the substrates, microbial performance and inhibitory features. For instance, volatile fatty acid (VFA) accumulation in the system results in low pH and consequently increases the concentration of ammonium, especially at the methanogenesis stage of the system [30, 51, 58]. Although increased retention time (RT), air stripping and chemical precipitation are possible solutions to these accumulations, further initiatives, such as immobilization of organisms using inert materials, ion exchangers or adsorbants, may be necessary for an effective output.

The fate of micro and macro-elements are crucial in the residue formation and equally determine the post treatment nature and eventually the use of these products. Nutrients in Table 2.4 have significance in the use of residues as soil amendment and fertilizer. The main constraint of the anaerobic digestion product is the abundance of readily available $\text{NH}_4\text{-N}$ which can easily be converted into $\text{NO}_3\text{-N}$ and N_2O through nitrification and denitrification processes by soil organisms. Although, $\text{NH}_4\text{-N}$ could be readily available for plants absorption, its excess as reflected in the C/N ratio (Table 2.4) may result into emissions of N_2O and NH_3 . Moreover, residues with low C/N ratios (< 25) provide significant quantities of nitrogen, which mineralise in the soil.

Elemental constituents, such as heavy metals and other metallic elements reported in Table 2.5, are significantly low perhaps due to substrate sources which are largely food crops, animals' dumps and source separated organic fraction of municipal solid wastes. Comingled wastes are reported to contain higher concentration of nutrients when compared to sorted or source separated wastes. Study of Parawira et al. [45] shows the significance of co-digestion as compared to single substrate digestion wherein co-digestion yield is 60% higher. Synergetic performance of heterogeneous substrates are equally reported for organic fraction of municipal solid waste (OFMSW) and wastewater [64], industrial products of potato and pig manure [65] and energy crops and animal manure [7].

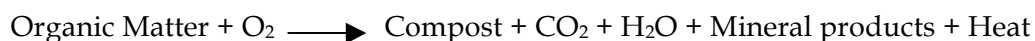
Table 2.5: *Heavy Metals & Micro-elements Constituents of Digestates

Digestate Sources	Digestion Process		Ca (%)	Mg (%)	Na (%)	Ni (%)	Zn (%)	Cu (%)	Ref.
Food waste	Fermentation		7.74	0.23	2.36	-	-	-	[61]
Willow	Two stage AD		-	-	-	-	0.018	0.002	[62]
Sugar Beet	Two stage AD		-	-	-	0.004	0.019	0.010	[62]
Pig manure & rape	AD		0.20	0.06	0.07	-	-	-	[7]
Grass	Two stage AD		-	-	-	0.001	0.011	0.006	[62]
Maize	Two stage AD		-	-	-	0.001	0.0034	0.003	[63]
Horse Manure	Two stage AD		-	-	-	0.0004	0.004	0.0014	[63]

*Values are calculated from the data reported

2.2.1.3 Compost

Composting process transforms and practically stabilises organics or biomass into nutrients and minerals rich materials. This technique not only recycles substantial segment of wastes but safely and beneficially conditions and amends soil structures. Moreover, degradation of large organic molecules by composting also ensures energy management [66], influence disinfection of the organic matter through the heat produced while CO₂, leachate and other products are equally produced as indicated in the equation below.



Meanwhile, recent large awareness about health, bioavailability, metal constituents and organic loads of compost and residues challenges direct application of the latter and thus demands for stringent standards [52].

Compost, unlike organic degradation residues, is considered matured and fit for agronomical use with no lagging physicochemical characteristics. Its relatively stable biodegradable organic matter is measured as the process evolution index [67]. The greenhouse gas (GHG) effect, free radicals intrusion and leachate concentration from composting could have environmental impacts significant enough for assessment and review of the process. Hao et al. [68] posited the effect of composting methods on GHG emissions. The study showed that active treatment (turning for aeration) of cattle feedlot manure accounts for more than 200% and 100% carbon lost in the form of CO_2 and CH_4 respectively when compared to passive treatment (no turning). Similarly, nitrogen lost in the form of N_2O is equally more than 150% higher for the active method even though compost produced through passive system results in unstable manure [68]. In-vessel composting was also reported to be 68% cheaper operationally compared to sanitary landfill system but the latter provides greater energy yield [69].

Unstable compost or digestion residue is characterised by high proportion of biodegradable matter which further sustain an elevated microbial activity in the soil [70]. The application of immature organic constituents to soil also increases nutrients immobilization, especially nitrogen, and may spread animal and plant pathogens [71]. Physicochemical and microbiological properties are often considered when setting up standards and regulations for typical processes and products, such as composting across various countries [72, 73], a situation currently dearth in the use of digestates for similar purpose. The institutionalisation of biomass or organic digestion product standards should be broadened and widened to accommodate entire life cycle rather than only focusing on the application points, as currently experienced by the sector. Established indicators, shown in Table 2.6, such as C/N ratio, microbial activity, germination index, cation exchange capacity (CEC), humic substances, water soluble carbon (WSC), dissolved organic matter, NH_4^+ -N and NO_3^- -N; ratios of NO_3^- -N/ NO_4^+ -N, WSC/TN and WSC/organic-N [74-78] are possible inventory data sources to be considered. However, due to differences in feedstock coupled with the wide variety of

process conditions (e.g. facility scale, aeration, temperature, pH and moisture content), no single maturity indicator can be applied [79].

Table 2.6: Properties of Compost from Organic Wastes

Sources of Wastes	pH	DM (%)	TN (%)	TOC (%)	C/N	Germination index	Ref.
Rice husk	4.51 -8.91	-	1.13	40.62	36	85	[84]
Sawdust	6.09- 8.6	-	0.87	44.98	51.5	45.2	[84]
Rice Bran	Initial 4.18	-	1.59	49.33	31	-	[84]
Food waste & Straw	4.47	-	3.4	34.8	10.24	-	[85]
Pig slurry + Slaughterhouse sludge + Biodiesel Wastewater	-	1.9	0.38	0.47	1.2	-	[7]
Digestate + Wheat straw + Almond Shell	-	-	3.93	49.06	12.5	98	[60]

Another major constraint associated with the recycling system is the loss of minerals during composting which includes ammonia volatilisation, nutrients leached through runoff or rainwater (in a large scale windrow system) and methane or nitrous oxide emissions. Peigne & Girardin [80] reported negligible nitrogen loss of 0.5% to leachate water, while 19 - 42 % of initial manure nitrogen was forfeited by gas emissions during feedlot beef manure composting. However, the environmental and sustainability quotient of these impacts should be considered to establish impact assessment in all spheres. Generally, the equilibria and rates of nutrient dynamics are influenced mostly by interaction of the process conditions and substrate

physicochemical properties [81]. The environmental and health importance of heavy metals makes the dynamic in composts and behaviour in soil significant. Smith [82] revealed increased heavy metals complexation when organic waste residues are applied directly to soil. This invariably limits metals solubility and bioavailability in soil because of its strong interaction with compost matrix. Although the metal sorption properties of compost from municipal solid waste (MSW) and sewage sludge can be of advantage in the remediation of metals contaminated soils [83], the application of compost to agricultural soil with relatively stable metals distribution may equally contribute to bioaccumulation degree of metals in crops.

2.2.2 Thermochemical treatment: pyrolysis and products

2.2.2.1 Charcoal (biochar)

Charcoal is the primary product of thermochemical conversion and is one of the earliest forms of synthetic fuel produced by man. The properties of charcoal depend on the thermochemical process conditions. High temperatures typically reduce the volatile matter and enhance the carbon content of charcoal, as shown in Figure 2.3. Charcoal with high carbon concentrations may be theoretically desired, however, higher heating temperatures would seriously reduce the production levels and mechanical strength of the charcoal. Lower heating temperatures would leave larger amounts of volatile matter still remaining in the charcoal. The recommended maximum heating temperature to achieve maximized charcoal yields is 400°C [86]. Charcoal transformation is almost complete at this temperature and it typically contains 20-25% of volatile matter, 3-4% ash, with the remaining 75-80% being fixed carbon. The maximum heating temperature has strong impact on the charcoal heat of combustion [87]. The heat of combustion is almost constant at 23 MJ/kg for charcoals produced at temperatures below 250°C, while the charcoals produced at temperatures above 300°C the heat of charcoal combustion increases by 45% [88]. Cordero et al., 2001 proposed a correlation for the higher heating value (HHV) of charcoal based on the percentage of fixed carbon (FC) and volatile matter (VM):

$$\text{HHV} = 0.3543 \times \text{FC\%} + 0.1708 \times \text{VM\%} \quad (\text{MJ})$$

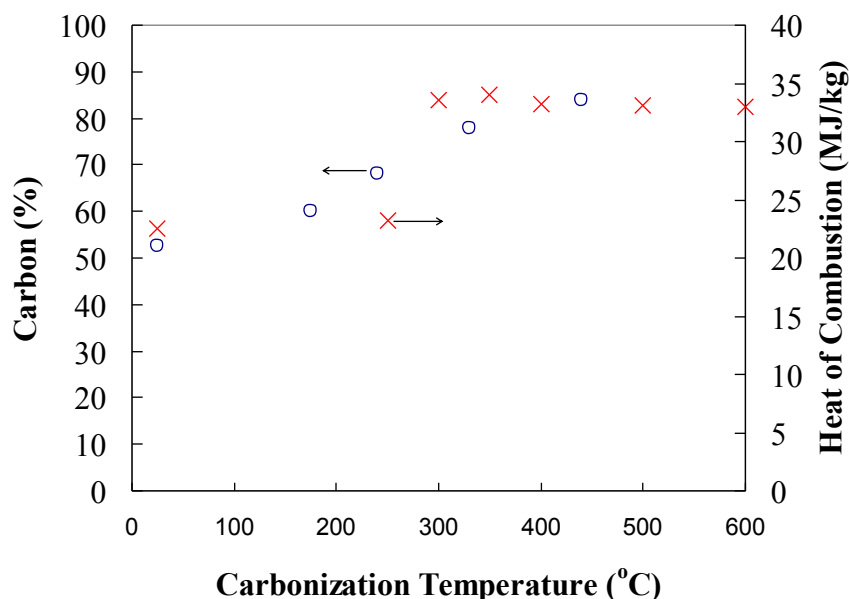


Figure 2.3: Effect of carbonization temperature on (o) charcoal carbon content (based on [89]) and (x) heat of charcoal combustion (based on the results of [87]).

Due to the loss of large amounts of mass from liberation of volatiles and liquids, the charcoal contains dangling carbon bonds making it a highly reactive material ([86]. Particle size was found to affect the carbon macromolecular structure increasing the homogeneity of the porous carbon material and reducing the intra-particle pore size [90]. The specific surface area of charcoal increases at temperatures above 450°C and can reach high surface areas of over 250 m²/g at 700°C, making it very suitable material for filtration as an activated carbon. Char porosity and surface area depend on the heating conditions and higher heating rates generate chars with more open pore structures and larger macropore surface areas [91]. Mochidzuki et al., [92] determined the physical and electrical properties of charcoal materials produced in laboratory conditions. They found predominantly alkyl aromatic structure with oxygen enriched C-O-H, C=O and C-O-C functional groups. Upon thermal treatment at 650°C these groups decompose forming condensed aromatic C-H structures, which further break down at 750°C and, consequently, evolve hydrogen at elevated temperature range.

Heating rate has a profound effect on the final char yields. Figure 2.4 illustrates the char yields from fixed bed carbonization of pine wood for five different heating rates and final carbonization temperature of 800°C. The char yields ranged between 22% for the heating rate of 10°C/min and 13% for heating rates close to 1000°C/min.

The decreasing trend of cellulose char yields with increased heating rates was reported previously [93]. Rapid heating rates enhance transfer of volatiles through the biomass particle, reducing the time available for the primary gases and oils to undergo secondary reactions, cracking and re-polymerization.

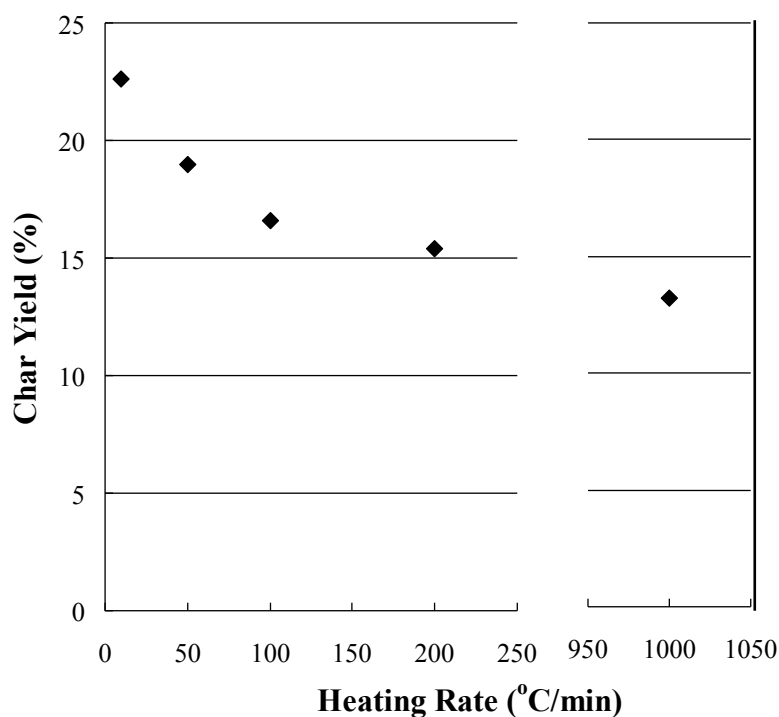


Figure 2.4: Effect of heating rate on the char yield of pine wood [94].

Biochar exhibit varying properties based on feedstock and pyrolysis conditions, as indicated in Table 2.7. Physicochemical features of most biochars vary, therefore reacting distinctively due to differences in stability and morphological architecture [95-97].

Table 2.7: Physicochemical properties of biochar

Sources	Physical Properties				Chemical Properties				Ref.
	pH	EC mS/m	Temp (°C)	Ash	C/N	TP	TK	TC	
Corn residue			350	-	72.6	-	1.04	67.5	[98]
			600	-	85.9		6.7	790	
Wood	7.0		350	-	144	0.6	-	824	[99]
Poultry litter	9.9		450	-	19	25	22	380	[100]
Algae <i>Ulva flexuosa</i>	8.0	53	450	-	8.4	7078 ^d	167 ^e	22.6%	[101]
Sesame			550	36.80	12.50	3.45%	3.38%	86.64	[102]
Mustard				28.10	13.85	2.87%	4%	85.43	
Neem				24.50	14.30	0.35%	2.38%	82.34	
Wastewater	5.32	4.12	300	52.8	7.71	492.5*	< 1%	25.6	[103]
Sludge	4.87	4.15	400	63.3	8.42	740*		20.2	
	7.27	4.7	500	68.2	9.53	567.5*		20.3	
	12	2.5	700	72.5	17	527.5*		20.4	
Algae <i>Tetraselmis chui</i>	12	39 ^a	500	30.3	8.70	10 ^b	2.1 ^c	40	[104]
	8.39		300	12.6	8.47	2.92	0.87	45.4	
Food waste	9.69		400	49.2	8.27	4.13	1.24	37.3	[105]
digestate	10.1		500	55.1	8.80	4.54	1.39	35.3	
	10.7		700	60.2	17.9	4.78	1.53	34	

*Plant available phosphorus (Colwell Phosphorus). ^aDs/m. ^bPhosphorus as P₂O₅. ^cPotassium as K₂O.

^dmg/kg. ^emol/kg

For instance Steibeiss et. al., [96] reported the adaptation of soil indigenous microbes and the stability of varying biochar condensation grade and chemical composition as the main drivers for the various production treatments considered. Like most other residues or treatment products, the quality of biochar produce is pivoted on the type of

substrate and process conditions, such as temperature and holding time used during production [106]. Biochar structure and morphology are thus influenced by production temperature. Extreme heat increases the proportion of aromatic carbon, its turbostratic arrangement and graphitic structure which are responsible for its porosity and surface area [107]. However, the structural complexities of biochar are observed to be lost during pyrolysis, as posited by Amonette and Joseph [108] and Haas et. al., [109] studies respectively.

2.2.2.2 Bio-oil

Bio-oils are dark brown pyrolysis liquids generated when biomass is subjected to heat in the absence of oxygen. This complex mixture of free-flowing organic liquids and water are physically multiphase with char particles, waxy materials, droplets of different nature and micelles [110]. Bio-oils are highly oxygenated compounds formed through depolymerisation and fragmentation of rapidly heated biomass especially at fast heating and cooling rates [111]. Biomass pyrolysis oil reflects elemental composition of the parent feedstock and contains multifunctional compounds, such as aldehydes, ketones, esters and others which are prone to further reactions (depending on temperature) at storage to form macro-molecules [112]. Bio-oil yields are reported to be largely influenced by heating rates, reaction temperatures, vapour residence time and, most importantly, feedstock composition [113]. For instance, wood bio-oil yields range of 72 – 80wt% was reported by Mohan et. al., [112] while Isahak et. al., [114] expressed 60 - 70 wt% as average bio-oil yield of fast pyrolysed biomass. Biomass often contains active catalysts (potassium and sodium) which promotes secondary cracking and consequently impairs bio-oil yield and quality [111]. Sawdust and sugarcane bagasse were reported to produce similar bio-oil yields (about 70%) while banana rachis yielded below 30% despite being subjected to the same conditions indicating substrates effects on bio-oil output [115].

Moisture content and oxygen concentration of pyrolysis liquids are attributed to their low heating values when compared to hydrocarbon products (See Table 2.8). The lower heating values of 16 – 19 MJ/kg in wood oriented bio-crude compared to 40 MJ/kg in conventional heavy fuel were attributed to 15 – 30 wt% moisture and 35 – 40 wt% of oxygen in the wood against 0.1 wt% moisture and 1 wt% oxygen in the heavy fuel [116].

Table 2.8: Yields, heating values, pH and elemental composition of bio-oils from different biomass

Feedstock	Treatment process	Yield	HHV	pH	C	H	O	Ref.
Macro-alga	Fast pyrolysis	26.7	28.3	6.1	64.3	7.7	25.3	[117]
Food waste	Slow pyrolysis	60.3	11.2a	-	-	-	-	[105]
Corn stover (multi-pass and Single-pass)	Fast pyrolysis	48.7	19.2	-	44.9	14.3	40.1	[118]
		and 45.0	and 23.0		and 53.3	and 17.0	and 29.0	
Paulownia wood	Slow pyrolysis	-	28.6	-	66.1	8.7	25.2	[119]
Hardwood shavings	Fast pyrolysis	63.3	22.6	2.7	55.3	6.5	37.6	[120]
Corn cobs	Fast pyrolysis	61.0	26.2	-	55.1	7.6	36.9	[121]
Soybean	Fast pyrolysis	24.19	33.6	-	67.9	7.8	13.5	[122]

Bio-oil potential as combustion fuel and source of heat in boilers are considered [113] despite its low heating values and pH. The organic and inorganic constituents of the liquid oil are viable source of platform chemicals. Although, wood flavor is commercially extracted from bio-oil, however, essential pharmaceutical and industrial

chemicals locked up in the oil are expected to be annexed through various upgrading techniques [111].

2.2.2.3 Biogas

Biogas or syngas are mixtures of gases produced through biochemical or thermochemical degradation of organic matter (biomass). Gas production from biomass offers renewable and sustainable energy production with a significant potential to contribute to the key economic sectors, such as transportation, electricity and manufacturing industries. Biogas is produced during anaerobic degradation of organics in various established systems, such as sewage treatment plants, landfills and digesters. The latter predominately consists of CH_4 (55 – 75%) and CO_2 (> 40%) with trace components of H_2S , CO , N_2 and volatile organic compounds (VOC). Meanwhile, syngas mainly comprises of H_2 , CO , hydrocarbons (CH_4 , C_2H_2 , C_2H_4 and C_2H_6) water and CO_2 , as indicated in Table 2.9. Several endothermic reactions produce H_2 in syngas through cracking of the hydrocarbon at high temperature while intermediate products are responsible for the light hydrocarbon formation [123]. CO and CO_2 traceable to oxygenated organics decrease with increased temperature, whereas H_2 and CO are posited to increase with the charring temperature. Quantity and constituents of the produced biogas depends on treatment techniques (anaerobic digestion, pyrolysis or gasification) adopted and feedstock involved [124, 125]. Temperature, retention time, feed type, stream flow rate and pre-treatment conditions are generally considered critical parameters for gas yield and quality [126, 127] substrate efficient and optimal utilization are hinged mostly on process configurations [128, 129]. For instance, $\text{H}_2:\text{CO}$ ratio of syngas varies with respect to production technology and feedstock [130]. Generally all types of organic wastes, such as putrescible components of municipal solid wastes, agricultural waste, sewage sludge and industrial effluents, are suitable for biogas production.

Table 2.9: Composition of selected biogas and syngas and heating values

	CH ₄ (%)	CO ₂ (%)	O ₂ (%)	N ₂ (%)	H ₂ S (ppm)	Benzene (mg/m ³)	Toluene (mg/m ³)	HV	Ref.
Landfill	47-57	37-41	< 1	< 1- 17	36-115	0.6-2.3	1.7-5.1	-	[131]
Anaerobic sewage digester	61-65	36-38	< 1	< 2	< 0.1	0.1-0.3	2.8-11.8	-	[131]
Landfill	59-68	30-37	-	-	15-428	22-36	83-172	-	[132]
Farm biogas plant	55-58	37-38	< 1	<1-2	32-169	0.7-1.3	0.2-0.7	-	[131]
	H ₂	CO	CO ₂	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	HV	Ref.
Gasified biomass char [□]	52.4	14	27.6	1.7	0.2	4	0	8.3*	[127]
Pyrolysed Food waste	5.2	2.2	7	2.6	-	0.14	0.32	15.7	[105]
Pyrolysed food waste digestate	9.1	0.7	2.03	1.3	-	0.12	0.3	17.2	[105]

[□] Measured in v%/dry basis while others are in wt%/min. *lower heating value in MJ/Nm³ while, others are in higher heating values

Biogas is currently a valuable renewable source for electricity production and heating systems with potential for engine combustion [3]. Similarly, biomass oriented syngas is considered as a fuel and feedstock for production of tailored chemicals [133].

2.3 Applications of biomass post-processing residues and products

2.3.1 Energy applications

The focus on biomass for energy cannot be dissociated from its industrial demand as renewable sources. Although, the globe requires additional one-third of its current energy demand [134], the renewed interest on indigenous energy sources, such as biomass, is driven by its environmental qualities. For instance, about 2.73×10^{10} MJ

of energy was generated in rural China through the spread of approximately 35 million anaerobic digesters [135]. Considerable achievement has been recorded in conversion or treatment often targeted at waste biomass as sustainable means of primary and secondary energy sources. Recently, 42% increase in electricity was reported by coupling AD with pyrolysis using agricultural wastes instead of the initial 9896KWh_{el} generated on a stand-alone AD plant [136]. Constrains related to biomass initial moisture content and lignocellulose configuration are appropriated through integrated treatment systems, while the environmental challenges of digestate are equally ensured [128]. The latter study reported 96% and 77.3% theoretical efficiency for pyrolysed food waste and its digestate respectively and subsequently produced nutrient rich biochar with potential for soil applications [105].

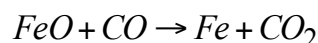
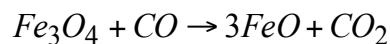
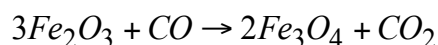
Notwithstanding, AD effluents are equally used as co-substrate or bio-fertilizer provided the regulatory standards are fulfilled. The blend of AD liquid effluent (yard and food wastes at 20 – 30 C/N ratio) were used to increase biogas yield and ensure optimal microbial performance [137] through the blend. Similarly, 60% food wastes were combined with dairy manure to improve throughput [138] ensuring zero waste. Co-digestion of feedstock does not only increase biogas yield but also balances nutrient distribution and dilutes toxic compounds [137]. Dry digestates, like biochar, are also considered as solid fuel with 85% efficiency achieved when two digestate pellets with combustion power of 44KW and net calorific values of 15.8 and 15.0 MJ/kg respectively were used [139].

2.3.2 Metallurgical Applications

The metallurgical application of charcoal has traditionally been associated with the reduction of iron oxides in the process of producing metallic iron, although this practice has declined over time, specifically since the progress of the coke making technology. More recently, charcoal is considered a reductant in the processes of reduction of silica to silicon and other metallic oxides (nickel, lead etc.) to their corresponding metals. In metallurgy, charcoal supplies the heat and carbon required to maintain the oxide reduction process. Renewed interest in reintroduction of biomass based metal smelting technology is based on the attempt to improve the sustainability of the metallurgical operations through inclusion of renewable energy sources. The annual energy consumption of the iron and steel industries is equivalent to 5% of the

world's total energy consumption and also account for 3 – 4% of the global greenhouse gas emissions [140]. According to Birat, [141], the CO₂ emissions from different ironmaking routes range from 2 tCO₂ per tonne of liquid iron for blast furnace ironmaking, to 0.7 tCO₂/t liquid iron for metal smelting with an electric arc furnace. One alternative approach in reducing the greenhouse gas emissions, while maintaining desired iron and steel production levels is by transforming the existing industries in more sustainable operations with biomass as renewable energy and reductant source.

Blast furnace operations require separate coke-making and sintering plants to feed the furnace. Charcoal exhibits high reactivity with CO₂ ($C + CO_2 \rightarrow 2CO$) producing the reductant CO gas which maintains the iron ore reduction process in a stepwise mechanism:



Some reports suggest that the iron ore reduction with charcoal is occurring at higher rates when compared to coal and coke [142]. The reduction with charcoal in blast furnaces occurs at temperatures up to 250°C lower than coke blast furnaces, mainly due to differences in carbon reactivity [89]. The volatile matter content in the charcoal is expected to additionally contribute to the reduction process, considering charcoal consists 25% by weight of volatile matter, which is mainly hydrogen and carbon monoxide.

Charcoal as an additive to coal blends for coke making was considered in a report published by the NSW SERDF, 2001, however the results showed anti-fissuring effects and decrease in coke strength due to the non-softening properties of charcoal. It appears that unprocessed biomass may have the potential to serve as a blending material in coke production. Das et al., [143] found that some blends of coal and biomass, in particular molasses, may produce reasonably high swelling ratios, which are required for metallurgical production of coke. Blast furnace technologies can incorporate fuel injection where charcoal and biomass have been considered as potential injectants. NSW SERDF, 2001 conducted trials to assess the performance of charcoal as slag foaming injectant, while Takekawa et al., [144] studied the gasification

reactions of waste wood as a blast furnace injectant. The electric arc furnace technology for ironmaking is based on re-melting and recycling of scrap steel. This technology produces lower amounts of CO₂ per liquid iron comparing to the blast furnace, however the production capacity is limited to the availability of scrap steel. Since this technology is essentially an electric based steelmaking, the potential for inclusion of charcoal in the process is in relation to the electricity generation as a front end of steel production.

The most recent emerging generation of smelting operations consist of direct reduction of iron ores with coal. Direct Reduced Ironmaking (DRI) processes have several advantages over the conventional blast furnace operations with low pollution effects, low capital intensive operation and they can provide successful smelting with low grade thermal coal. The DRI process consists of carbo-thermic reduction of iron oxides directly with the volatiles liberated during coal devolatilisation, carbon monoxide regenerated from coal char as well as dissolved carbon in iron bath. The DRI technologies offer viable potential for substitute of coal with biomass as a carbon-bearing reductant material. Strezov, [145] has recently found that iron ore can be successfully reduced to predominantly metallic iron using 30wt% of biomass in a biomass-ore pellet. The shortcomings in potential development of biomass based metal smelting technology is related to the low density of biomass requiring larger volumes, hence potentially can reduce the metal production rates. More realistically charcoal can potentially provide substitution for coal in the direct reduced ironmaking technologies. Further research will be required to ensure the metallurgical operations maintain the desired levels of energy efficiency, productivity and process quality.

2.3.3 Agricultural and carbon sequestration applications

The application of post-processing residues such as digestate, compost and biochar as fertilizers or soil enhancements explores the soil-microbe-nutrients interaction to make the available micro and macronutrients in residue to biotic constituent of the system. Anaerobically degraded biomass provides an alternative source of energy and offers an alternative route to synthetic fertilizer due to mineral richness [146] instead of untreated biomass. This mixture of partially degraded organic matter (OM), microbial biomass and inorganic compounds are considered inexpensive disposal means and suitable recovery approach to minerals and organic constituents

for agricultural use [147]. Digestate's ability to eliminate weed seed and impairing pathogen loads provides justification for digestate's use as fertilizer or soil enhancement [148]. Meanwhile, heavy metal concentrations, organic loads, odour and workers health and safety associated with digestate remains a challenge [149]. Expectedly, quality standards, national guidelines and protocols instituted by governments is changing the disposal impression to a recovery process [7, 150]. Compost remains the most applied means of slow mineralization of stabilized and humified organic materials in soil [151]. Young and mature composts are reported to be influenced by the material of origin, maturity extent and storage conditions [152]. Similarly, plant- soil disease suppression potential of compost is pivotal to maturity and degree of phytotoxicity. The mineral fertilizer substitution extent of compost depends on its quality and consequently nitrogen immobilization.

Unlike digestate and compost, biochar is widely considered as a stable carbon with potential for soil improvement and fertilization. There are several reports on the benefits of biochar in the soil from major effect, such as soil structure enhancement (water retention, mitigation of nutrients leach), increasing soil biological activities, soil remediation and specific effect on plant and crop growth [153]. Different animal manures stabilized through pyrolysis indicated nutrients recycling and management ability of biochar when applied to soil [154]. The persistence of char in soil for years due to its recalcitrant nature accounts for the carbon sequestration capacity. The O_2 or H_2 to C ratios of biochar are indicators for the stability and carbonization which equally depends on the parent feedstock elemental constituents [155]. Half-life of less than 100 years are predicted for chars with atomic O/C ratio of greater than 0.6 while at least 1000 years are attributed to O/C molar ratios lower than 0.2 [153]. For instance, Opatokun et al. [105] posited the carbon sequestration potential of food waste which indicates molar O/C ratio lower than 0.2 despite the difference in charring temperature as against pyrolysed food waste digestate with O/C molar ratio ranges of 0.2 to 0.6. Therefore, biochar process parameters are fundamental factors that shape char properties, agronomic values and the large and long term C sink or sequestration [155].

2.4 Life cycle analysis of waste processes and products

Life cycle assessment or analysis (LCA) is a management approach to quantify the amount of substrates, energy and other form of inputs used over a complete

process or product production to identify or evaluate energy cost, social and or environmental performance of the process or product at all stages. Fundamentally, LCA derives standards from the International Standards Organisation (ISO) 14040 (Principle and framework) and ISO 14044 (Requirement and guidelines) using primary (direct information from facilities or systems) and secondary (public database, published reports etc) data sources. Processes and products design are benchmarked and compare to environmental standards through LCA to continuously identify emission and waste during the life cycle of the system or product while enabling identification of more sustainable options [156].

The major cardinal structures of LCA proposed by the ISO 14040 comprises of four main phases namely, the goal and scope definition, inventory analysis, impact evaluation and interpretation [157] as annotated in Figure 2.5. These iterative phases constitute a framework for holistic assessment of inputs and emissions associated with the stages of a process or product life cycle from cradle to grave [158] leading to a more sustainable evaluation. The applicability and uses of the study or assessment are expected to be articulated in the goal and scope which determines selection of the life cycle inventory (LCI) framework. Meanwhile, LCI is predicated on functional unit which is considered the central hub of the entire assessment since other data in the assessment are referenced and normalized by this unit [159]. Functional unit therefore, quantitatively provides comparability to study or assessment for instance, 1 kg of food waste indicates the unitary measure of the system. The impact assessment aggregate the inventory wastes data through midpoints to endpoints categories depending on the characterisation model used. Impacts categories such as ozone depletion, climate change, terrestrial acidification or ecotoxicity, etc are environmental indicators through which environmental burdens are reflected or interpreted depending on the tool or software (SimaPro, GaBi, EASEWASTE, ORWARE, e.t.c.) and methods (ReCiPe, CML, EDIP, EcoIndicator 99, etc) deploy. The choice of impact category, normalization and weighting needs to be consistent with the study goals. The intended applications of the LCA are related in the interpretation wherein conclusions of the study are derived followed by recommendations.

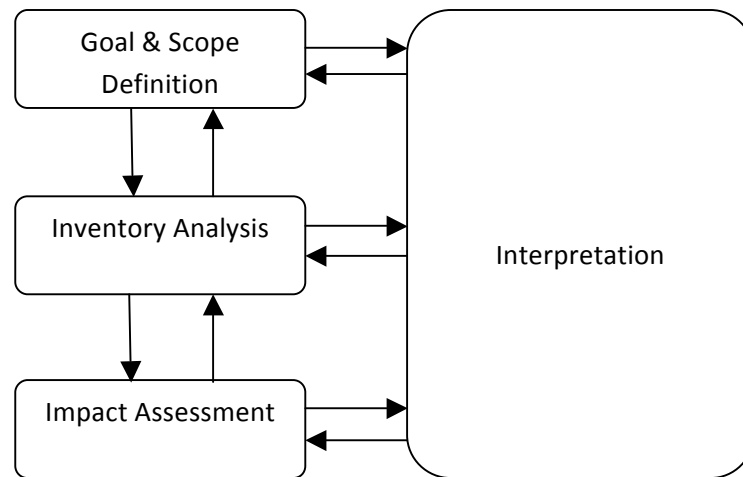


Figure 2.5: Structural components of a life cycle assessment study

A handful of studies have evaluated waste treatment processes while some focus on energy and emission related to the products. For instance, life cycle of biogas and digestate utilization was considered to evaluate the emission mitigation, agricultural benefits and rural energy needs (heating, illumination and fuel) of China [135]. Similarly, the energy, economic and climate change potential of biochar was estimated using life cycle assessment of the product [160], while a comprehensive cradle to grave assessment of anaerobic digestion in term of energy output was benchmarked with landfill and incineration during waste treatment scenarios [156, 161]. Similar to conventional waste treatment, wherein single treatment technique are deployed, most LCA studies so far focus on comparing different treatment processes mainly to evaluate the energy and emission impacts. Moreover, very few studies narrow assessment to specific waste type through which complexity associated with modelling heterogeneity and waste composition of such system [162]. Conversely, overburden assumptions and widening uncertainty threshold which impair the quality of the report despite the specificities of such LCI [162, 163].

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Characterisation of Food Waste and its Digestate as Feedstock for Thermochemical Processing

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Abstract

The products of a commercial one stage anaerobic digestion and a laboratory scale pyrolysis of raw food waste (RFW) and digestated food waste (DFW) were characterized to evaluate treatment effect, products yield and physicochemical properties. The pyrolysis of the RFW and DFW resulted in generation of 7.4 and 5.3 wt% of gas and 60.3 and 52.2 wt% of bio-oil while biochar yields decreased with increase in pyrolysis temperature. Differential thermogravimetric (DTG) tests of RFW and DFW shows 20% in both solid residues produced at a temperature of 550°C, indicating relatively low impact of the digestion process on the raw food waste. The mineral matter content was found to be lower for RFW compare to DFW. The variation in the content of fixed carbon and volatile matter reflected the effect of anaerobic degradation of the food waste. The bio-oils showed low concentration of phenols, esters and derivatives of hydrocarbons for DFW compared to RFW. The specific heat capacities were determined for RFW and DFW while their morphological properties at different temperatures were equally considered using SEM and FTIR. The results of this study provides indicator for treatment process assessment and measures to increase value added products from food wastes.

Keywords: Anaerobic digestion, Pyrolysis, Digestate, Biogas, Bio-oil and Biochar.

3.1 Introduction

Food waste prevention, reduction, reuse and recycling are significant environmental considerations by FAO, UNEP, WRAP and others, who have developed various tools, including 'Think. Eat. Save', 'Love Food Hate Waste', 'Reduce Your Footprint' and other initiatives. Despite these initiatives, about 1.3 billion tons/yr of food wastes are generated worldwide from households, industries and supply chains¹,

which demand sustainable treatment and management options. Most food wastes are largely hosted by landfills, which continuously produce greenhouse gases, leachates and pose significant health and environmental threats² in spite of its low levels of toxic contents.

There are various treatment and beneficiation options for food waste reuse or waste to energy. Table 3.1 provides a summary of the physico-chemical properties of this organically rich biomass. The high carbon and hydrogen content suggests potential for energy recovery through either biochemical or thermochemical means. The widely deployed biochemical treatment, anaerobic digestion (AD) significantly favour high moisture biomass such as food waste by reducing transportation and pre-treatment cost especially when treated insitu ³. However, biological processes are operationally constrained by the formation of inhibitors, on-line monitoring of temperature, pH, mixing and organic load concentration. These parameters affect the methane production and process stability especially at commercial scales. Moreover, studies show that only about 40% of feed inputs in AD process are utilised for biogas production while the remaining is considered digestate⁴. The thermochemical options include combustion, gasification and pyrolysis. However, high moisture content makes some substrates (food wastes) unattractive to thermochemical process⁵ especially when not pre-treated or preceded by digestion.

Multiple treatment and management options are rarely deployed in waste treatment despite potential for optimal resource recovery and improved overall economy of waste processing. Multiple treatments may provide the opportunity to integrate the advantages of individual techniques to promote the sustainability of the processes and the products generation. The aims of this study are to: i) characterise raw food waste and its digestate as potential substrates for thermochemical (pyrolysis) process, and ii) determine the products distribution pattern with emphasis on the effect of temperature and heating rate. The results are expected to provide information on optimal resource recovery in respect to energy, fuels, bio-fertilizer production and chemical sources for industries from food wastes.

Table 3.1: Characteristics of food waste across countries and regions*

Country	TN	Total Carbo- hydrate	VS/TS	TC	S	H	C/N	Ref.
Canada	2.4-16.7	n.a	n.a	n.a	n.a	n.a	2.8-20.5	6
Japan	3.4- 4.2	6 – 7.2	0.89-0.92	42.3	n.a	6.1	13.2	7, 8
South Korea	2.8-5.2	2.55	0.89- 0.94	47.8-51.2	0.7	6.1- 7.7	18.3	9,10
South Korea	3.5	n.a	0.95	51.4	0.1	6.1	14.7	11
USA	2.8- 2.95	2.5	0.86-0.94	51.2	0.8- 0.7	7.2	18.3	12,13
Spain	1.5	n.a	0.86	55.5	n.a	n.a	37	14
Taiwan region	3-4	n.a	n.a	50-52	n.a	n.a	15	15
China	2.56	n.a	0.91	48.30	n.a	6.91	18.9	16
UK	3.44	45.3	0.92	47.6	0.15	7.04	13.9	17

* All parameters are in Percentage. n.a = Not provided/ available. TN = Total nitrogen, VS = Volatile Solids, TS = Total solids, TC = Total carbon

3.2 Materials and methods

3.2.1 Sample preparation

Fresh raw food waste (RFW) was sourced from the Macquarie shopping mall and a local food market in the Sydney region. RFW was weighed, oven dried at a temperature of 105°C for 24hrs and then milled into smaller sizes using a power cutting miller (pulverisette 25). Digested food waste (DFW) in the form of pellets after an industrial mesophilic anaerobic treatment was collected from Earthpower Technologies, an urban food waste treatment plant in the same suburb. The samples were stored in airtight food grade plastic containers until further testing. Pellets of

DFW samples were dried in a vacuum oven dryer (Extech Equipment) at 60 – 70°C for 4hrs prior to analysis.

3.2.2 Pyrolysis and analysis

Pyrolysis of the sample was carried out by heating an aliquot of dry raw food waste (RFW) and the digested food waste (DFW) in a fixed bed horizontal tubular reactor at heating rate of 10°C /min to four final temperatures (300°C, 400°C, 500°C and 700°C). The quantity of the sample involved during biochar production was in the range of 150 – 300 g. Inert nitrogen at a rate of 100 L/min was maintained while the off gas was channeled through an ice cooling chamber to condense the heavy tars. Biochar yield (wt%) was predicated on the percentage of produced char after pyrolysis divided by the mass of feedstock. The calorific values of both the biochars and bio-oils were experimentally determined according to AS 1038.5. Pyrolysis of food waste and its digestate at selected temperatures is expected to provide better understanding of the treatment process (thermochemical) and the resultant products or outputs (biogas, bio-oil and biochar) of the system.

3.2.2.1 *Bio-oil production and analysis*

The bio-oils produced from the pyrolysis of RFW and DFW were condensed in a sealed container covered by ice cubes. Typical industrial pyrolysis temperature of 500°C was considered for RFW and DFW bio-oils production⁴. These were produced separately at 10 and 60°C/min heating rates with about 1g of substrate in a fixed bed reactor to the temperature of 500°C. The bio-oils condensed at room temperature in a wool stopper were then dissolved in dichloromethane and subjected to analysis using gas chromatography- mass spectrometry (GC-MS).

3.2.2.2 *Gas chromatographic analysis of volatiles*

The volatiles evolved during pyrolysis of RFW and DFW were analysed separately using a M200 Micro gas chromatograph from MTI Analytical Instruments. Helium was used as the carrier gas flowing at 25mL/min, channeled through about 50mg of the substrate heated under constant heating rate of 10 and 60°C/min to the maximum temperature of 1000°C. CO and H₂ were determined with molecular sieve 5A column kept at 50°C (10m in length and 0.32mm in diameter), while CO₂, CH₄, C₂H₄ and C₂H₆ were determined through polymer Poraplot U column (8m in length and

0.32mm in diameter) kept at 55°C. Chromatograms were collected every 90s through the gas thermal conductivity detector. The volatiles evolved during pyrolysis were calculated as a weight percent of the initial mass to the total sample used as described in previous studies^{18, 19}.

3.2.2.3 SEM-EDS of samples

Scanning electron microscope (SEM) images of the samples were determined using air-dried substrates and the produced biochars were ground and sieved to a size range of 0.18 to 0.45mm for carbon and gold coat respectively. The gold coating or masking of the samples was to avoid charging during observations. Scanning Electron Microscope (SEM) micrographs of biomass and biochars were taken using a JEOL model JSM operated at 5kV and similar magnification and magnitude (X400, 50µm).

3.2.2.4 Fourier transform infrared spectroscopy (FTIR)

The FT-IR spectra of substrates and biochars after pyrolysis were recorded through a Nicolet 6700 FT-IR spectrometer using an attenuated total reflectance (ATR) method with a diamond crystal. This was accomplished through a 32 total number of scans along with spectral resolution of 4cm⁻¹.

3.2.2.5 Textural properties of biochars

The specific surface area and pore size distribution of the chars were determined by nitrogen adsorption, on Micrometrics TriStar 3000 using BET model. Samples were conditioned to a dynamic vacuum system at temperature of 150°C for 3hrs. Data were recorded at $P/P_0 = 0.07 - 0.27$. The true density and total pore volume of substrate and biochars were determined by measuring the pressure change through an automated gas (helium) displacement Pycnometer to determine the volume of samples' irregular and regular shape or powdered in one piece within calibrated volumes. This experiment was carried out using a Micrometrics AccuPyc II 1340 machine interfaced with AccuPyc II 1340 V1.05 software.

3.2.2.6 Thermogravimetric analysis

Mettler Toledo thermogravimetric analyser (TGA/DSC 1 STARe system) interfaced on the STARe software was deployed to analyse the change in weight of

RFW and DFW with temperature at different heating rates. Approximately, 35 mg of each sample was used in each TGA measurement. Two heating rates (10 and 60°C/min) were evaluated with nitrogen flowing at 20mL/min as the carrier gas.

3.2.3 Chemical analysis

Proximate analysis was conducted using Australian Standard (AS) 1038.3 and USEPA 6010. The ultimate analysis was conducted using AS 1038.6 (for carbon, hydrogen and nitrogen) and USEPA 6010/6020A ICP for sulfur while oxygen was determined by difference.

3.2.4 Lignocellulose analysis

The sequential fractionation of hemicellulose, cellulose and lignin content according to Datta²⁰ was adopted with slight modifications. 1g of each substrate was suspended in 100 ml distilled water, kept at 100°C for 2hrs and filtered through glass microfiber. The residue was thereafter dried to constant weight. The loss components were considered as water-soluble. The dried residue was then suspended in 100 ml of 0.5 M H₂SO₄ for 2hrs at 100°C in a water bath. This mixture was again filtered, dried and weighed as described and loss in weight was measured as hemicellulose content. For cellulose and lignin estimations, 10 ml of 72% (v/v) H₂SO₄ was added to the latter residue and kept at room temperature for 1hr on a rotary shaker at 200 rpm. After incubation the mixture was diluted up to 4% (v/v) of H₂SO₄ and autoclaved at 1.06 kg/cm² for 40 mins. The contents were filtered, dried and weighed. The loss in weight was treated as cellulose, and the left over residue was considered as the lignin content in the food wastes and digestates.

3.3 Results and discussion

3.3.1 Physicochemical properties of RFW, DFW, and their biochars

3.3.1.1 Lignocellulose components of RFW and DFW

The lignocellulose properties of food wastes (RFW) and its digestate (DFW) are shown in Table 3.2. Cellulose (36.9w/v%) constitutes the highest component in food wastes while hemicellulose with 33.5w/v% is highest in the digestate (DFW). The percentage of lignin in RFW (12.6w/v%) and DFW (13.4w/v%) as indicated by Datta²⁰ maybe significant due to recalcitrant polymers that influence biochemical degradation,

such as anaerobic digestion, if not pre-treated. Moreover, the similarity in the lignin content of raw food waste and its digestate justify the inability of biochemical treatment in extracting the lock-up energy content in the component²¹. Similarly, the water-soluble constituents of the digestate (20.8w/v%) provide an estimate of possible poly and/or oligosaccharides to be leached when applied to soil as bio-fertilizers²².

Table 3.2: *Lignocellulose components of food waste and digestate

Components	RFW (w/v %)	DFW (w/v %)
Hot water-soluble	23.9	20.8
Hemicellulose	26.6	33.5
Cellulose	36.9	32.3
Lignin	12.6	13.4

*All analysis were based on dry basis and single measurement analysis only

3.3.1.2 Elemental composition of RFW, DFW and chars

The elemental composition of the raw food (RFW), its digestate (DFW) and their chars produced at different temperatures are shown in Table 3.3. Although, 500°C was reported⁴ as the industrial temperature especially for slow pyrolysis with heating rate such as 10°C/min, lower and higher pyrolysis temperatures considered reflect the significance of pyrolysis temperature in the distribution of nutrients and properties of the products particularly on the substrates. The raw food waste contains significantly low ash content (5.5%) with relatively fixed carbon concentration of 21.1%. Meanwhile, food digestate shows substantial difference with much higher ash content at 25.6% and lower fixed carbon content at 12.6% due to the prior biochemical treatment of the waste. The volatile matter, hydrogen, nitrogen and oxygen contents in both samples decreased with increase in temperature while their ash and fixed carbon contents increased in concentrations. The low ash and volatile matter in chars from food waste compared to its digestate suggests the former economic stance for long-term carbon sequestration in soil²³. However, the low fixed carbon in the digestate and its chars indicates low recalcitrant carbon susceptible to biological decomposition. Substrate (RFW and DFW) chars with O/C ratio below 0.2 indicated in Table 3.3 equally signify

a half-life of at least 1000 years²⁴. The ratio of volatile matter and fixed carbon (VM/FC) of chars produced are less than 1.0 (similar to coal) except for DFW 300.

Table 3.3: Physicochemical properties (wt%, on dry basis) of raw food wastes, food digestate and their respective biochars at different temperatures

	Ash	FC	VM	C	H	N	O	S	H/C	O/C	(O+N)/C	Æ
RFW	5.5	21.1	73.4	46.1	5.7	1.7	41.0	0.2	1.49	0.67	0.70	0.95
RFW300	12.6	50.2	37.2	66.7	4.8	3.7	12.2	0.18	0.86	0.14	0.18	0.74
RFW400	15.2	62.7	22.1	69.6	3.3	3.6	8.3	0.18	0.57	0.09	0.13	0.67
RFW500	17.4	69.3	13.3	71.3	2.1	2.6	6.6	0.11	0.35	0.07	0.10	0.69
RFW700	18.1	74.5	7.4	74.6	0.8	2.1	4.4	0.14	0.13	0.04	0.07	0.65
DFW	25.6	12.6	61.8	42.1	5.2	5.8	21.3	0.91	1.48	0.38	0.50	0.76
DFW300	35.7	20.3	44	45.4	4.4	5.4	9.1	0.44	1.16	0.15	0.25	0.60
DFW400	49.2	30.8	20	37.3	2.3	4.5	6.7	0.51	0.74	0.13	0.24	0.56
DFW500	55.1	32.3	12.6	35.3	1.2	4.0	4.4	0.53	0.41	0.09	0.19	0.49
DFW700	60.2	34.6	5.2	36.7	0.9	1.9	0.3	0.63	0.29	0.01	0.05	0.12

FC= Fixed carbon, VM= Volatile Matter, percentage of oxygen was calculated by difference.

Æ = O/C:(O+N)/C

The carbon-carbon bonds formation in RFW with increase pyrolysis temperature can be established with the equivalent decrease in O₂ content. Meanwhile, C-C bonds have been posited to contain greater energy than C-O and C-H bonds³. Interestingly, DFW oriented biochars retained its relatively high nitrogen and Sulphur content (compared with RFW) to suggest its fitness as soil amendment instead of fuel source since N and S content of substrate determines the environmental quality of the fuels³. In addition to the proximate and ultimate analysis, H/C and (O + N)/C are often used as indicator of the biochar – water interaction²³. This study atomic ratio decreases with increase charring temperature to indicate biomass to biochar carbon enrichment and equally reflect the degree of hydrophobicity of carbonized raw food waste and its digestate.

3.3.2 Thermogravimetric results of RFW and DFW

The thermogravimetric (TG) and its differential (DTG) analyses for RFW and DFW using two heating rates (10 and 60°C /min) are shown in Figure 3.1. As expected, higher heating rate delays the reactions for both samples. The DTG analysis clearly shows three discrete stages of decomposition to indicate thermal behavioral pattern of

the substrates. The initial negative DTG peaks centering at 80 – 100°C and 85 – 120°C can be attributed to loss of inherent moisture peculiar to most biomass^{25, 26}. The second short peak in the DTG curves of RFW indicates removal of strongly bonded water and decomposition of the weaker hydroxyl bonds. This peak is absent for the digested DFW sample indicating these bonds are removed during the digestion process.

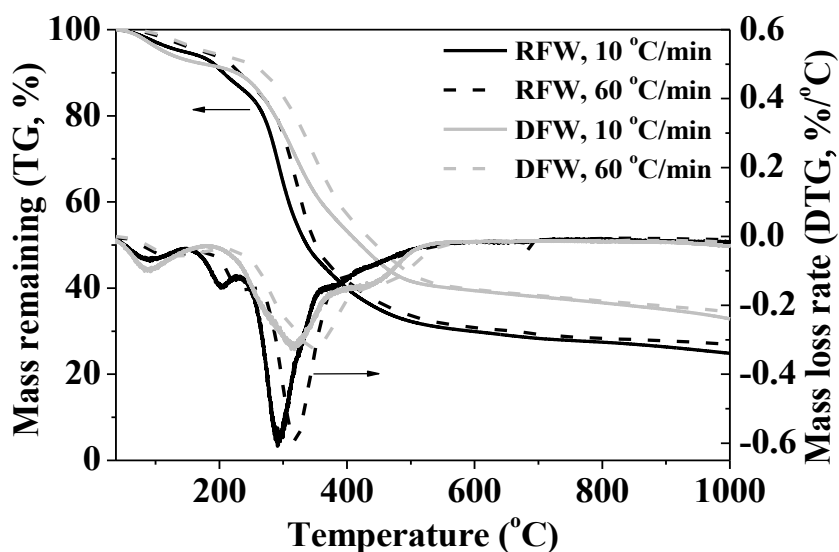


Figure 3.1: TG and DTG curves of RFW and DFW at heating rates of 10 and 60°C /min

The most significant weight loss in the food waste is shown with a sharp trough between around 250 and 400°C with maximum mass loss rate of 0.6 wt%/°C for both heating rates under consideration while DFW indicated a wider trough between 200 and 500°C with a maximum mass loss rate of 0.32 wt%/°C and an approximately 35% solid residue left at 1000°C. These reactions account for the primary decomposition and release of a wide variety of volatiles^{18, 27}.

3.3.3 Pyrolysis & its products

3.3.3.1 Analytical properties of biochars

3.3.3.1.1 Morphological features of substrates

The effect of temperature on the variability and morphological characteristics of food wastes and its digestate were determined with scanning electron microscopy (SEM) and results are presented in Figure 3.3. The compositional Figures 3.3A to 3.3E expressed the SEM micrographs of substrates taken at 400 magnifications to reflect the physical alteration due to temperature change. There are distinct differences in the morphology between the RFW and DFW. The chars of RFW showed significant increase in large open pores when increasing the temperature, while the chars of the DFW were less porous, with cracks in the structure.

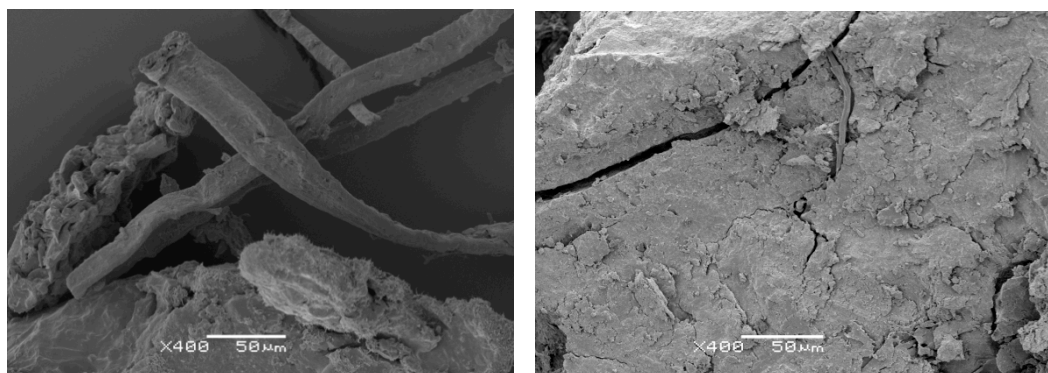


Figure 3.3A: Micrographs of Raw food waste (RFW, left) and digestate (DFW, right)

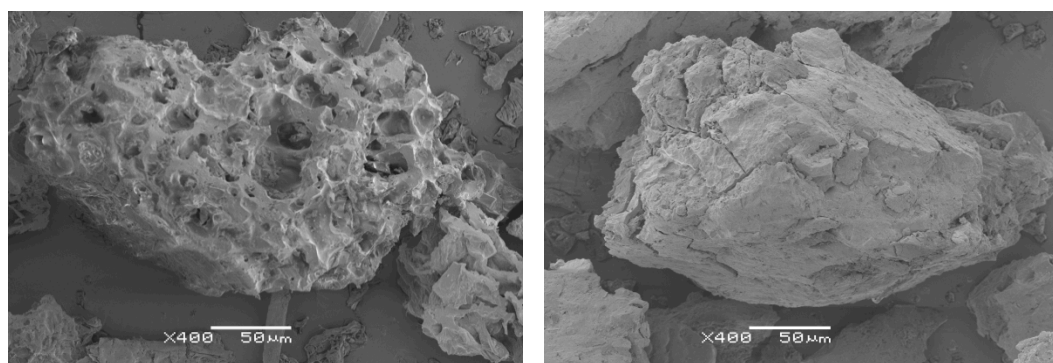


Figure 3.3B: Micrographs of RFW 300 (left) and DFW 300 (right)

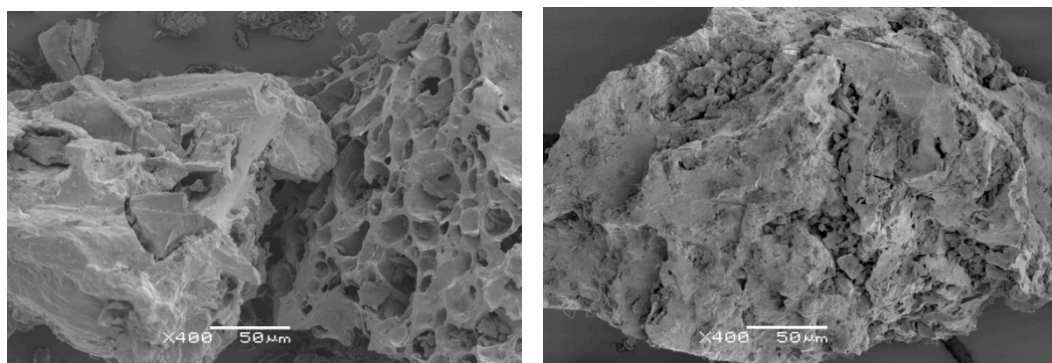


Figure 3.3C: Micrographs of RFW 400 (left) and DFW 400 (right)

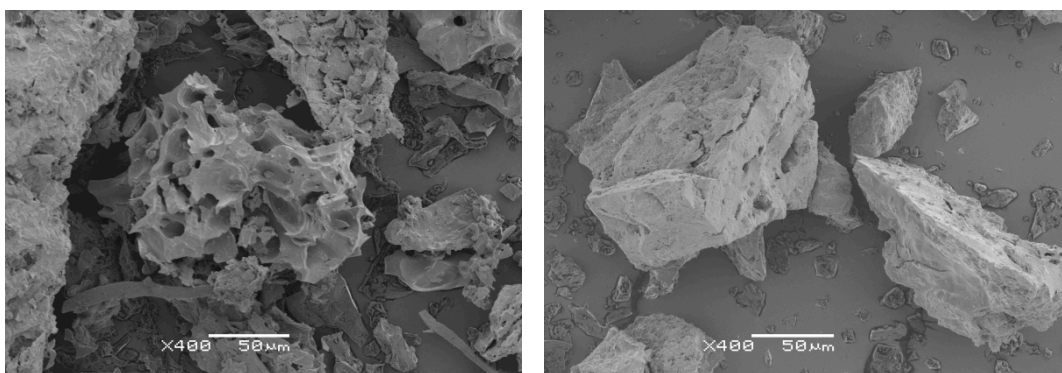


Figure 3.3D: Micrographs of RFW 500 (left) and DFW 500 (right)

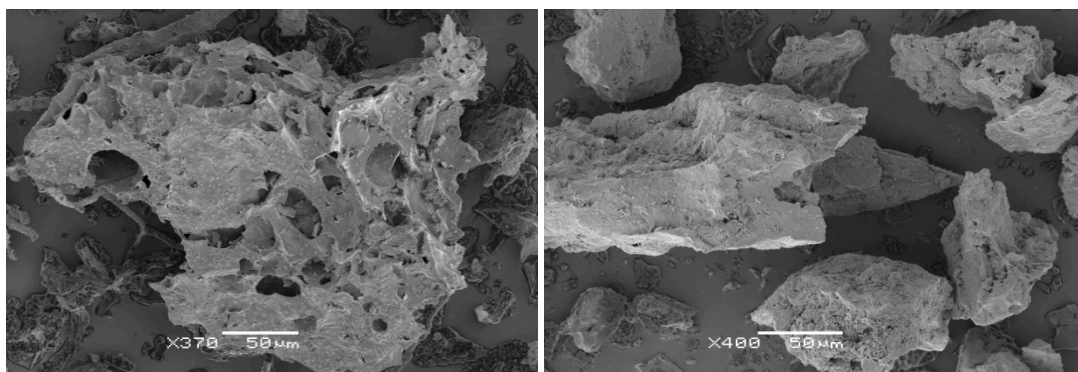


Figure 3.3E: Micrographs of RFW 700 (left) and DFW 700 (right)

3.3.3.1.2 Chars textural distribution

The data in Table 3.4 indicates textural and pore distribution properties of the chars. The specific surface area (BET) of RFW chars are generally higher compared to DFW chars. Significant increase in the BET values at higher temperature (700°C) may be attributed to severe reaction, resulting into mesoporous pores distribution in the

chars²⁸. The transport and storage cost implications of pre-treated food waste and its digestate are reflected by the substrates density and volume values²¹. Both samples (RFW and DFW) exhibited similar intrinsic densities and pore volumes, as presented in Table 3.4. DFW chars exhibited higher density and proportional rise in total pore volume with the change in pyrolysis temperature, which may be due to equivalent increase in ash content as shown in the proximate analysis profile (Table 3.3). The density and pore volume results of DFW chars are considerably higher across all temperatures considered compared to RFW results. Surface area 63.8 and 26.9 m²/g for RFW and DFW produced at 700°C respectively provides significantly higher pore distribution compare to date palm (1.99 m²/g) and rhode grass (16.78 m²/g)²³ but similar to hemp pyrolysed at 650°C and 750°C²⁹.

Table 3.4: Raw food wastes (RFW) and digested food waste (DFW) and their biochars BET, density and total pore volumes

		Raw	300°C	400°C	500°C	700°C
RFW	Surface area (m ² /g)	-	1.91	0.79	1.90	63.83
	Density (g/cm ³)	1.48	1.40	1.51	1.63	1.81
	Pore Volume (cm ³ /g)	0.32	0.29	0.34	0.39	0.45
DFW	Surface area (m ² /g)	-	0.66	1.57	0.93	26.95
	Density (g/cm ³)	1.46	1.54	1.83	2.02	2.22
	Pore Volume (cm ³ /g)	0.32	0.35	0.45	0.50	0.55

3.3.3.1.3 *Spectra dynamics of food waste, digestate and its chars*

Fourier transform infrared spectroscopy (FTIR) analysis was employed to investigate the functional groups in RFW and DFW as well as their chars produced at different temperatures (300, 400, 500 and 700°C). The spectra are shown in Figure 3.4. For RFW (Figure 3.4a), the absorption bands between 3749 to 2993 cm⁻¹ (peak position: 3276 cm⁻¹) were attributed to the O-H stretching vibrations, indicating the existence of phenols, alcohols or carboxylic acids. The sharp peak at 2920 cm⁻¹ and the side weaker peak at 2850 cm⁻¹ corresponded to the asymmetric and symmetric CH₂ bonds¹⁹. The peak at 1413 cm⁻¹ also confirmed the C-H groups in alkanes. The absorption band between 1600 to 1800 cm⁻¹ (peak at 1740 and 1623 cm⁻¹) indicates the presence of C=O

in either carboxylic acid/ester or aldehydes/ketone groups^{20, 21}. The peak at 1413 and 1238 cm^{-1} are likely due to the aromatic-O, O-O-C and C-N bonds. The most intensive peak at 1030 cm^{-1} is an indicator of C-O and /or C-C stretching³⁰. The small side peak at 873 cm^{-1} was assigned to C-O group in carbonate. Comparing the spectra of the chars to the raw RFW, nearly all bands are greatly reduced. For the char produced at 300°C, a certain amount of CH_2 bonds remained, which disappeared when the temperature was further increased.

For the raw DFW, a similar FTIR spectrum was obtained as raw RFW. The most obvious difference was the much higher contents of C=O or O-H bending of water (1634 cm^{-1}) and the N-H in plane bending of amides and amines (1540 cm^{-1}). Most groups disappeared or greatly reduced in produced chars.

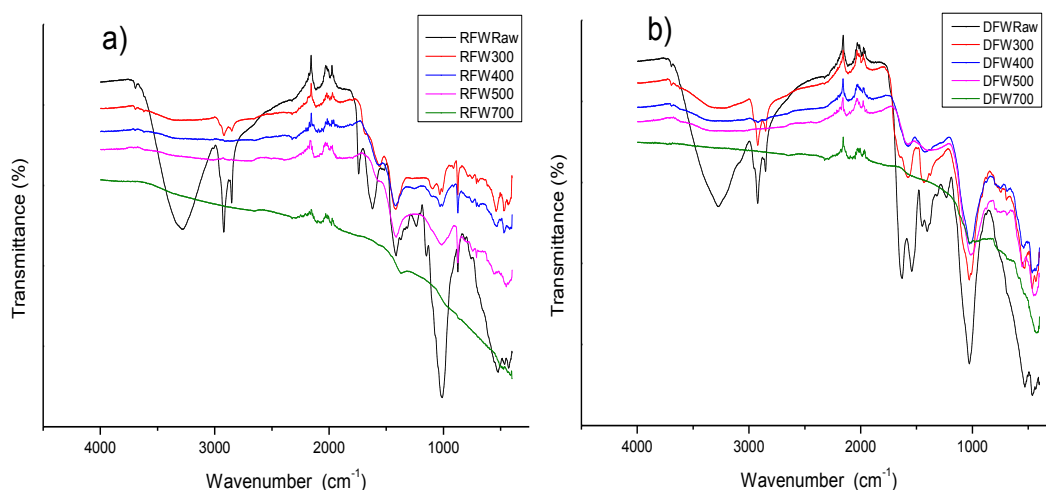


Figure 3.4: FTIR spectra of (a) food waste (RFW) and their chars at different temperatures, and (b) digestate (DFW) and their chars at different temperatures

3.3.3.2 Gases evolution rate at different heating rates (10 & 60°C/min)

Figure 3.5 illustrates the evolution of volatile gases from the RFW and DFW at different heating rates (10 and 60°C/min). All the gases eluded at temperature >200°C. CO_2 (maximum values of 0.5 and 0.3 wt%/min respectively for RFW and DFW) was substantially released between 250 and 500°C during the lower heating rate (10°C/min) followed by CO (~0.18wt%/min) in RFW and H_2 (0.08wt%/min) in DFW. Decarboxylation and decarbonylation transformation of biomass are responsible for the generation of primary products such as CO_2 and CO¹⁸. The emergence of hydrocarbon gases (C_2H_4 and C_2H_6) in the later region of the gas profiles are widely

reported to be products of secondary thermal fracture of high temperature oil vapor³¹. The obvious differences in the CO₂, CO and H₂ evolutions between RFW and DFW may be attributed to the biological treatment producing the latter.

Gases evolutions at 60°C /min were delayed beyond 300°C to produce CO₂ as the highest, followed by H₂ with dual peaks in RFW. Meanwhile, DFW eluded gases after 500°C with H₂ (~9wt%/min) as the most abundant followed by CO₂ and CH₄ respectively at 2.05 and 1.5wt%/min. Major depolymerization of food waste (RFW) resulted in increase in CH₄ and decrease in CO₂ at ~600°C especially at 10°C/min. The evolution of CO₂ after 700°C may be due to secondary reactions, which are more pronounced at the lower heating rates.

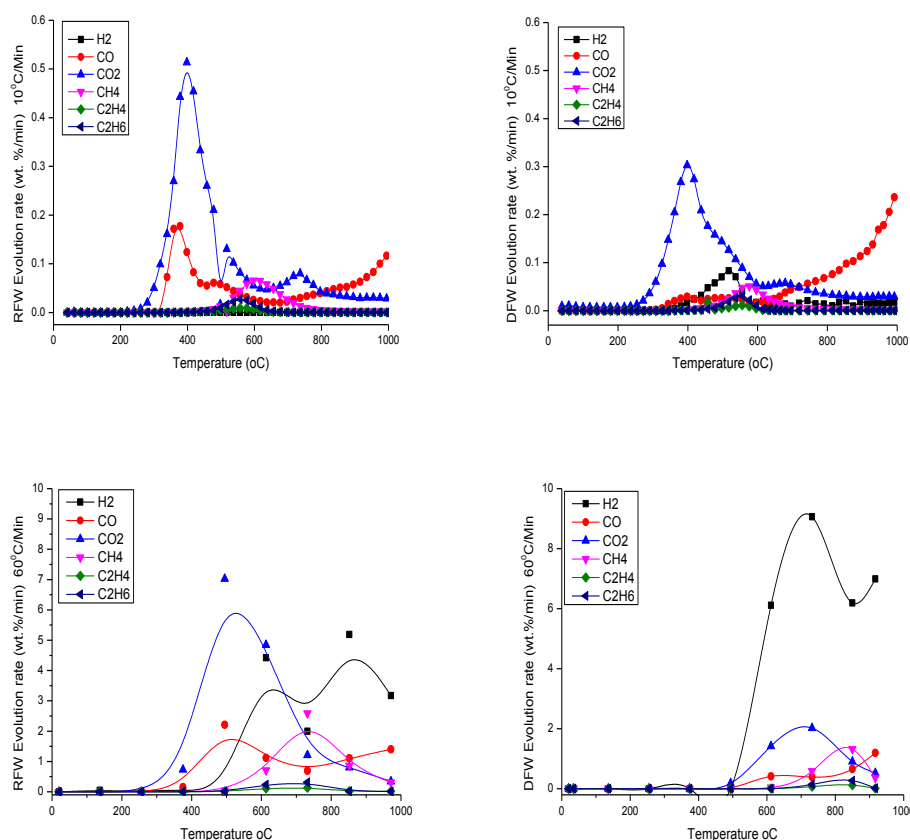


Figure 3.5: Evolution of volatile gases from RFW and DFW at 10 and 60°C/min

respectively

3.3.3.3 *Bio-oil constituents at different heating rates*

The liquids obtained at 500°C and 10 and 60°C /min were complex mixtures of organics, reaction water and condensed water from original samples. The major compounds corresponding to the chromatograph peaks were identified and listed in Tables 3.5 and 3.6 for RFW and DFW bio-oils respectively. The compounds were reported in the derivatised form to provide the initial addition of N, O-bis (trimethylsilyl) trifluoroacetamide for GC-MS analysis.

Phenols, esters, saturated and unsaturated hydrocarbons and their derivatives were identified despite the difference in the heating rates however, varying concentrations of these compounds were produced. Generally, compounds concentrations are higher in the oils produced from the raw food wastes compared to the digestates, regardless of the heating rates. At heating rate of 10°C /min esters formations were apparently the most favored in both samples (RFW and DFW). Compared to 60°C /min rate, for RFW the low heating rate (10°C/min) forms higher silane, 1,2-phenylenebis(oxy)]bis[trimethyl with 3.53% content, silane, 2-furanylmethoxy trimethyl with 2.69% content and 2-Isopropyl-3-ketobutyrate, bis(O-trimethylsilyl) with 2.18% content with carbon of C₈ to C₁₃. Despite the varying retention time similar compounds, such as hexanoic acid and 4-methylcatechol, are produced at different heating rates with significant concentration difference due to change in heating rates (Table 3.5). Irrespective of the heating rate carboxylic acid such as pentanoic acid (1361s) produced similar concentration while, hexanoic acid concentration is higher at 60°C/min heating rate. Compound concentrations are generally lower in bio-oil of digestate (DFW) origin but show more distributive spread although with equivalent lower retention time when compared to RFW. Moreover, 10°C /min heating rate provided higher outputs amidst the considered rates.

Table 3.5: GC-MS results of bio-oil from pyrolysis of food wastes (RFW)* produced at 10 & 60°C /min

Retention Time (s)	Name of compound	Relative Content (%)	
		10°C /min	60°C /min
1034.7	Silane, (2-furanylmethoxy) trimethyl-	2.69	1.22
1170.9	Silane, trimethylphenoxy-	1.15	1.23
1352.2	Silane, trimethyl(2-methylphenoxy)-	0.50	0.53
1361	Pentanoic acid, 4-oxo-, trimethylsilyl ester	1.21	1.12
1508.4	2,4-Hexadienoic acid, tert-butyldimethylsilyl ester, (E,E)-	0.94	0.52
1754.4	Silane, [1,2-phenylenebis(oxy)]bis[trimethyl-	3.53	0.33
1689.7	Hexanoic acid, trimethylsilyl ester	0.83	1.74
1699.3	Cyclohexene, 3-butyl-3-methyl-1-trimethylsilyloxy-	1.14	1.82
1713.9	Hexanoic acid, trimethylsilyl ester	0.85	1.18
1822.9	Uridine, 5-chloro-2'-desoxytris-O-(trimethylsilyl)-	0.97	1.99
1900.8	4-Methylcatechol, bis(trimethylsilyl) ether	0.58	1.06
1921.9	4-Methylcatechol, bis(trimethylsilyl) ether	0.54	0.79
1927.7	Silane, [1,4-phenylenebis(oxy)]bis[trimethyl-	0.33	0.91
2013	2-Isopropyl-3-ketobutyrate, bis(O-trimethylsilyl)-	2.18	0.66
2026.5	2,2-Dimethyl-5-[2-(2-trimethylsilylethoxymethoxy)-propyl]-[1,3]dioxolane-4-carboxaldehyde	0.49	1.01
2471.9	α-D-Galactopyranoside, methyl 2,4,6-tris-O-(trimethylsilyl)-, acetate	0.31	0.19

*Single measurement analysis only

Unlike the raw food waste, esters' dominance in the digestate bio-oil content is apparent. The high molecular weights of bio-oils may also be attributed to the lignin content of the original feedstock (RFW and DFW)³².

Table 3.6: GC-MS results of bio-oil from pyrolysis of digestate (DFW)* produced at 10 & 60°C /min

Retention Time (s)	Name of compound	Relative content (%)	
		10°C /min	60°C /min
940.5	2-(4-(2-Hydroxy-3-(isopropylamino) propoxy) phenyl) acetamide tetraatms	0.27	0.10
1002.7	N-(Trimethylsilyl)acetamide	0.53	0.19
1033.1	Silane, (2-furanylmethoxy) trimethyl-	0.55	0.22
1119	2-Pentenoic acid, trimethylsilyl ester	0.43	0.16
1127.5	Pyridine, 3-trimethylsiloxy-	0.31	0.11
1137.7	4-Methylvaleric acid, trimethylsilyl ester	0.24	0.08
1172.5	Silane, trimethylphenoxy-	1.11	0.48
1216.6	Hexanoic acid, trimethylsilyl ester	0.28	0.12
1366.9	Pyridine, 3-trimethylsiloxy-	0.73	0.26
1404.2	Silane, trimethyl (4-methylphenoxy)-	1.25	0.51
1432.1	Silane, trimethyl[1-methyl-2-oxo-2-(trimethylsilyl) ethoxy]-, (R)-	0.40	0.13
1553.7	N-Ethyl-3-methyl-3-nonanamine	0.88	0.22
1595.6	3-Ethylphenol, trimethylsilyl ether	0.47	0.17
1755.3	Silane, [1,2-phenylenebis(oxy)] bis[trimethyl-	0.61	0.25
1823.2	Uridine, 5-chloro-2'-desoxytris-O-(trimethylsilyl)-	0.32	0.11
1931.9	Parabanic acid, bis-O-(trimethylsilyl)-	0.69	0.13
2095.4	Parabanic acid, bis-O-(trimethylsilyl)-	0.39	0.11
2230.9	Cyclopropane, 2-methylene-1-phenyl-1-[1-(trimethylsilyloxy) ethenyl]-	0.37	0.14
2318.6	Silane, trimethyl (1-phenylethoxy)-	0.18	0.06
2392	Dodecanoic acid, trimethylsilyl ester	0.63	0.25
2711.8	Tetradecanoic acid, trimethylsilyl ester	0.50	0.22
2805.9	n-Pentadecanoic acid, trimethylsilyl ester	0.38	0.16

2818.7	n-Pentadecanoic acid, trimethylsilyl ester	0.53	0.23
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*Single measurement analysis only

3.3.3.4 Substrates yields and products distribution

The mass and energy distribution of char, bio-oil and gases produced during the pyrolysis of RFW and DFW at 10°C /min are given in Table 3.7. The proximate energy distribution patterns of substrates are equally presented in Table 3.7 wherein liquid yields (including condensed water) of 60.3 and 52.2 wt% were obtained for RFW and DFW respectively. The latent energy potential of pyrolysis products (biogas, bio-oil and biochars) is also indicated. The heat of combustion, which expressed the energy content, shows the chars provides the highest energy content followed by the gas. The DFW inherent energy content further illustrates its impending use beyond bio-fertilizer.

Table 3.7: Mass and energy spectrum of pyrolysis products at 500°C

	RFW	DFW
Gas (wt%)	7.4	5.3
Char (wt%)	32.3	42.5
Liquid (wt%)	60.3	52.2
^a Heat of combustion of biogas (MJ/kg)	15.7	17.2
^a Heat of combustion of biochar (MJ/kg)	24.8	13.0
^a Heat of combustion of bio-oil (MJ/kg)	11.2	13.5

a= Moisture inclusive.

3.4 Conclusions

Physico-chemical properties of food waste showed its high nutrients concentration. The potentials (such as degradation of high moisture substrate and feedstock reduction) and limitations (lignin decomposition constrain and efficient substrate utilisation) of the commercial one stage anaerobic digestions for biogas production are expressed. The total carbon transition with temperature change shows

the suitability of RFW for carbon sequestration while DFW demonstrated low recalcitrant carbon thus, making the latter suitable as bio-fertilizer. However, digestate high water-soluble concentration (20.8%) and its relatively high energy content (17.2 MJ/kg) indicated its resourcefulness beyond fertilizer use. The BET surface area 63.8 m²/g of RFW shows possibility of higher textural properties compared to DFW (26.95 m²/g) produced at 700°C. The economic stance of substrates management are reflected through its ease of handling, transportation and storage cost mirrored through the pore volume (0.39 and 0.5 cm³/g) and density (1.6 and 2.0 g/cm³) respectively for RFW and DFW when pyrolysed at industrial temperature (500°C).

Meanwhile, TGA reflected substrates mass losing rate smoothen after 500°C despite change in the heating rate. Also, the DTG of RFW and DFW shows ~20% solid residue, an insignificant parity in their thermographs express relatively low impact of the digestion process on the raw food waste. Moreover, the spread of phenol, esters and other hydrocarbons in the bio-oil can provide for chemicals demand despite the biogas quantity. The morphological features of the chars at different temperature coupled with elemental distribution shows pyrolysis temperature effects on the food waste and its digestate.

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Product Based Evaluation of Pyrolysis of Food Waste and its Digestate

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Abstract

The aim of this work was to assess the energy potential of food waste energy harvesting system (digestion followed by pyrolysis of digestate). Digestate (DFW) with increased calorific content of 17.2MJ/kg was produced after a commercial one stage anaerobic digestion of the raw food waste (RFW). Separate pyrolysis of RFW and DFW (digested food waste) distributed 15.7MJ/kg and 17.2MJ/kg respectively, among the gas, char and bio-oil while energy of pyrolysis equals 0.72 MJ/kg for RFW and 0.87MJ/kg for DFW at the heating rate of 10°C/min to 500°C. Increase in digestate specific heat to 2.5MJ/m³ and its significant ash difference reflects the substrate (RFW) transformation due to biochemical treatment. The thermogravimetric analysis indicated the substrates mass dynamics and stability extent of the treatment products (DFW, RFW₅₀₀ and DFW₅₀₀). Generally, transitional energy base products (biogas and bio-oil) are generated through the energy harvesting system (EHS) of food waste, while energy rich solid fuels can be produced through pyrolysis at 500°C. Thus, the sustainable potential of EHS to widen and broaden recycling capacity of biomass and smartly appropriate its resources are demonstrated to be dependent and pivoted on the adopted treatment method.

4.1 Introduction

Biomass derived energy evinced its potential to replace fossil fuel despite the challenges with the various treatment processes currently deployed. Presently 8.5% of global energy is derived from biogenic (traditional biomass) sources [1]. This indicates the tremendous growth potential of the world's 73.9 Tg and 1549.4 Tg wasted crops and lignocelluloses when sustainably annexed [2]. Although biomass is a lower energy density source, environmental impacts and fast depleting global resources necessitate action, especially on the continuous growing volume of food wastes [3]. Moreover, the daily growing demand for cheap energy source makes imperative the adequate use of materials through efficient treatment systems

Studies show that only about 15 to 40% of the organically rich inputs are utilised for biogas production especially during large-scale digestion while the remaining liquid and / or solid digestate constitute the effluent [4-6]. The equilibria and rates of this immature product from anaerobic and / or aerobic processes (digestate) are influenced mostly by interaction of the process conditions and substrate properties. Thus, sustainable assessment measures and improvement of these processes are essential to optimise the energy and mineral constituents of this waste. In the same context, pyrolysis of biomass to produce pyrogenic carbon (biochar), bio-oil and biogas is recently patronised due to its significant environmental management and strategic capabilities [7,8]. The individual strength of these treatment techniques, especially anaerobic digestion (biochemical) and pyrolysis (thermochemical), have not been integrated to fully explore substrates inherent energy and other potentials.

This study considers the sustainability extent of biomass (food waste) undergoing biochemical and thermochemical treatment process with focus on energy derivatives. The main objectives of this study are: (1) to determine the energy potential of biomass food waste using individual biochemical and thermochemical conversion processes and (2) to determine the equivalent energy strength of a proposed energy harvesting system (EHS) comprising of integrated biomass digestion followed by pyrolysis process which has not been studied in the past.

4.2 Materials and methods

4.2.1 Materials

Fresh raw food waste (RFW) was sourced from the Macquarie shopping mall and a local food market in the Sydney region in Australia. The anaerobically digested food waste (DFW) in a dried pellet form was collected from an Australian pioneer commercial food waste-to-energy treatment plant in the same Sydney region.

Nomenclature

RFW	Raw food waste,
EHS	Energy harvesting system,
OAD	One-stage anaerobic digestion
RFW ₅₀₀	Pyrolysed raw food waste at 500°C
DFW	Digested food waste
DFW ₅₀₀	Pyrolysed digestate at 500°C.

The collected digestate is commercial source of bio-fertilizer after a single or one-stage mesophilic anaerobic digestion (OAD) of food waste. Composite sampling of digestate was ensured and stored in airtight plastic containers and maintained throughout the course of this study. The samples were dried in a vacuum oven dryer at 70°C for 4 h before used.

4.2.2 Methods**4.2.2.1 Proximate and ultimate analysis of substrate and chars**

Proximate analysis results were acquired using Australian Standard (AS) methods 1038.3 and United States Environmental Protection Agency (USEPA) standards. The ultimate analysis methods were conducted using AS 1038.6 (for carbon, hydrogen and nitrogen), modified USEPA 6010/6020A ICP for the trace elements (Ca, Cu, Fe, Mg, P, K, Zn, Pb and Ni); modified APHA 4500 for ammonia nitrogen and water soluble nitrate; modified APHA 4130/4500 for total nitrogen and modified USEPA 9060A for both the organic and inorganic carbon while oxygen was determined by subtraction. These analyses were undertaken at the National Measurement Institute of Australia except for the AS 1038 methods, which were conducted in-house.

4.2.2.2 Treatment processes flow

Figure 4.1 illustrates waste treatment processes adopted in this study. The transformation, transport, and storage of materials are also indicated by the materials' and substances' flow charts. This is necessary to identify the system functional units and the flow across the system units. Figure 4.1a annotates the flow of raw food wastes (RFW) through an industrial mesophilic one-stage anaerobic digestion process to

produce food waste digestate. Pyrolytic chars (RFW₅₀₀ and DFW₅₀₀) were thermochemically produced in a fixed bed reactor heated in a horizontal tube furnace (Figure 4.1b). An average of 150 and 270 g of dry RFW and DFW were packed into the reactor and then heated in an inert argon atmosphere with the flow rate of 100 ml/min and heating rate of 10°C/min to 500°C. The sample was then held for 4 h at this temperature to ensure temperature equilibration across the heated sample. The energy harvesting system (EHS) represented by Figure 4.1c combined both the anaerobic digestion (OAD) and pyrolysis processes respectively with RFW as the input material.

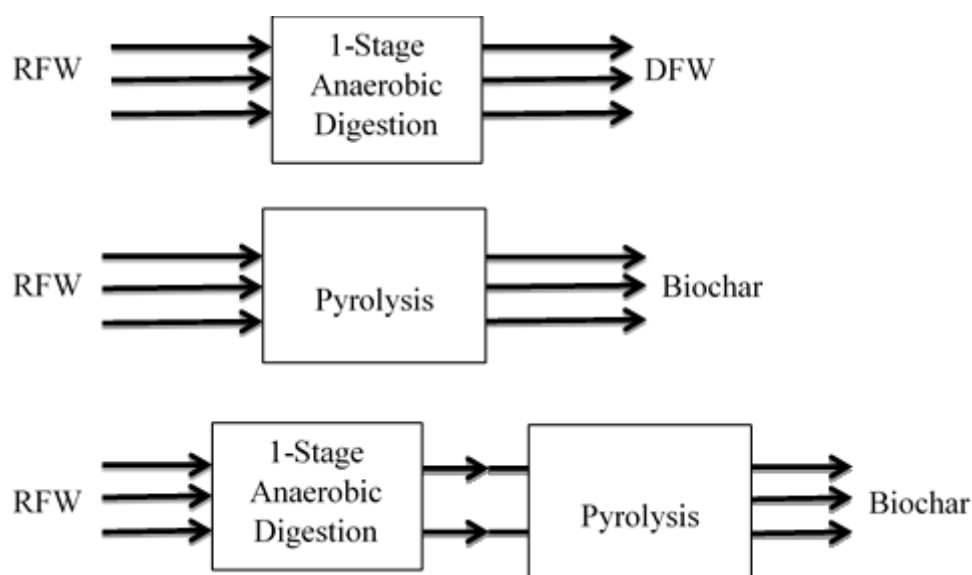


Fig. 4.1: Flow diagram of the treatment processes: 1a- Commercial-stage anaerobic digestion (OAD) system of food waste; 1b- Pyrolysis (PB) of food waste using a fixed bed horizontal tubular reactor; 1c- Energy harvesting system (EHS) using treatment process) AD followed by PB.

4.2.2.3 Higher heating value determination

The calorific values of both the biochars and bio-oils were experimentally determined according to AS 1038.5.

4.2.2.4 Thermo-gravimetric and Computer Aided Thermal Analyses

Mettler Toledo thermogravimetric analyser (TGA/DSC 1 STARE system) operated with STARE software was used to analyse the weight changes of RFW, DFW,

RFW₅₀₀ and DFW₅₀₀ with temperature during heating. Approximately 35 mg of each sample was used in each TGA measurement. Nitrogen was used as the carrier gas with a flow rate of 20mL/min and a heating rate of 10°C/min to the maximum temperature of 1000°C.

The Computer Aided Thermal Analysis (CATA) was employed to determine samples' specific heats. The experiment was carried out in a modified infra-red image furnace [9]. Around 1.5 cm³ of each sample was packed in a silica tube and then heated through radiation by a surrounding graphite cylinder at 10°C/min in inert argon gas flowing at 5 mL/min through the sample tube. The surface and centre temperatures and data of sample were continuously acquired at a frequency of 1 Hz through the surface and centered thermocouples.

4.2.2.5 Gas chromatography (GC) analysis of volatiles

The samples' volatiles evolved during pyrolysis were analysed separately using gas chromatograph. Carrier gas of helium flowing at 50 mL/min was channeled through about 50mg of the substrate heated at a constant heating rate of 10°C/min to the maximum temperature of 1000°C. An M200 Micro gas chromatograph from (MTI Analytical Instruments) equipped with thermal conductivity detectors was connected to the gas outlet of the sample heating tube. CO and H₂ were determined with molecular sieve 5A column kept at 50°C (10m in length and 0.32 mm in diameter), while CO₂, CH₄, C₂H₄ and C₂H₆ were determined through polymer Poraplot U column (8 m in length and 0.32 mm in diameter) kept at 55°C. The GC spectrum was obtained at every 90s.

4.2.2.6 Gas chromatography-mass spectrometry analysis (GC-MS)

The bio-oil produced during pyrolysis were separated by heating 1g of the sample to the temperature reached 500 at heating rate of 10 °C /min. These heavy organics (bio-oil) entrained through the gas were condensed and absorbed using quartz wool at ambient temperature. The absorbed bio-oil were dissolved using dichloromethane (DCM) solvent. The bio-oil - DCM solutions were dried using N₂ gas to a known concentration. The dried samples were dissolved by 0.5ml of DCM and 8 drops of N,O-bis (trimethylsilyl) trifluoroacetamide added to derivatised the labile

groups (such as hydroxyl functions) in the oil. These were then analysed by Agilent 7890A gas chromatograph with a 60m DB5_MS column coupled to a Pegasus 4D time-of-flight mass spectrometer.

4.3 Results and discussion

4.3.1 Characterization of RFW and DFW

As shown in Table 4.1, the digested food waste (DFW) had volatile matter of 61.8% and fixed carbon of 12.6% compared with corresponding value of 13.3% and 69.3% for pyrolysed food wastes (RFW₅₀₀). At 21.1%, the fixed carbon content of raw food waste (RFW) is considerably higher compared to sawdust and microalgae [13, 14], while 12.6% of the digestate (DFW) is similar to pine, holm oak and sunflower [11]. The volatile matter of both samples (73.4% and 61.8% respectively for RFW and DFW) indicates their potential for fast degradation and/or destruction using appropriate treatment methods. Although, the average proximate analysis of 80 - 88% of volatile matter, 15% of fixed carbon and 5% of ash are reported for food waste [12, 13], the relative properties of RFW used in the current work explain its' heterogeneity and suitability for a biochemical treatment product (DFW). Meanwhile, the high ash content in DFW (25.6%) and low inorganic carbon (12.4%) suggested that most of the carbon and hydrogen elements in the digestate (DFW) are slightly higher hydrocarbons (12.4%).

4.3.2 Pyrolysis behaviour of RFW and DFW

The mass loss during pyrolysis of RFW and DFW is presented in Figure 4.2. TGA and DTG behaviour of RFW and DFW are used as fundamental prerequisite for treatment process assessment [14, 15]. The substrates thermogravimetric data and their derivatives (DTG) revealed the presence of residual water as evidenced by the slight decrease within the temperature range of 85 to 180°C which is similar to posited dehydration temperature range [16].

Table 4.1: Proximate and ultimate analysis results of food waste (RFW) and its digestate (DFW)

Substrates	Gross dry CV (MJ/kg)	Proximate analysis (%) db			Ultimate analysis (%) db				
		VM%	FC%	Ash%	C%	H%	N%	O%	S%
RFW	15.7	73.4	21.1	5.5	46.1	5.7	1.74	40.79	0.17
DFW	17.15	61.8	12.6	25.6	42.1	5.2	5.81	20.38	0.91
RFW ₅₀₀	24.81	13.3	69.3	17.4	71.3	2.1	2.64	6.44	0.12
DFW ₅₀₀	12.97	12.6	32.3	55.1	35.3	1.2	4.01	3.86	0.53
RFW _{Bio-oil}	11.15	97.78	2.15	0.07	60.4	0.5	7.45	31.5	0.08
DFW _{Bio-oil}	13.52	99.97	0	0.03	26	8.67	8.84	56.24	0.22

CV= Calorific values (samples are reported on as analysed basis for single analysis). VM= Volatile matter, FC= Fixed carbon, C= Total carbon, H= Hydrogen, N= Total nitrogen, O= Oxygen, S= Sulfur. Oxygen was derived by difference, db = dry basis.

Figure 4.2 illustrates two phases of behaviour in RFW and DFW beside the dehydration phase. From 200 to 250°C respective steeper and steady decrease in mass of RFW and DFW was observed until 550°C then, stabilized through to 900°C. RFW exhibited a significant mass loss of 74.9% up to 600°C, while only 66.2% of DFW mass was reduced for the same temperature range. This difference is likely due to the low ash concentration of RFW (5.5%) compared to 25.6% of DFW, as indicated in Table 4.1. The DTG curves equally identified the distinct effect of anaerobic digestion with the obvious second trough for RFW (190 to 235°C) just after the dehydration range (Figure 4.2). Loss of the main organic matter due to the digestion process was displayed by the difference between the third and second peak (240 to 370°C) of RFW and DFW respectively (see

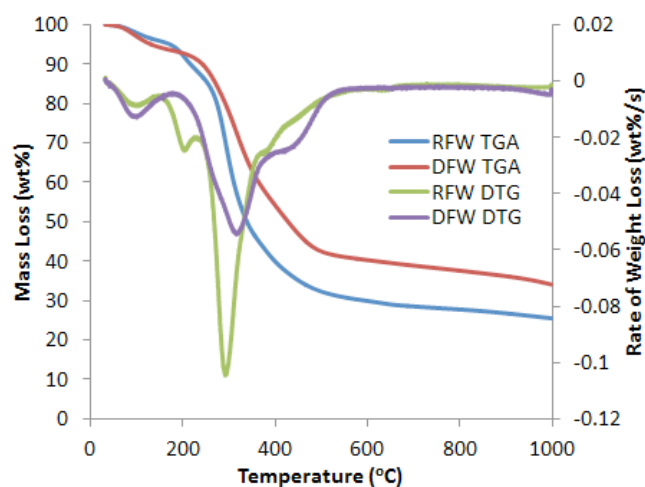


Fig. 4.2: The last trough in the DTG curves within 380 and 540°C represents the degradation of the higher organic molecules.

Figure 4.3 shows the change in the apparent volumetric specific heats of RFW and DFW used in this study. The intrinsic specific heat of RFW, measured at 1.2 MJ/m³K was higher than DFW (0.9 MJ/m³K) however, for the elevated temperatures the specific heat in DFW was greater than RFW. This is because DFW exhibited more significant endothermic reaction at the temperature range between 100 and 200°C due to the loss of the bound water in the substrates.

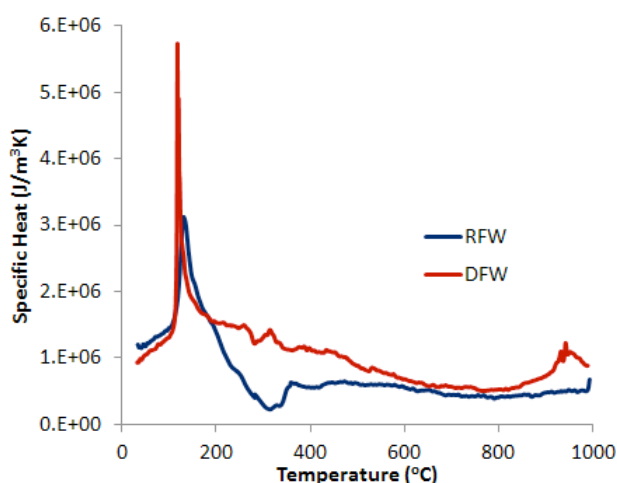


Fig. 4.3: Specific heat of RFW and DFW as obtained by Computer Aided Thermal Analysis (CATA)

The peak for DFW was higher than RFW, indicating the difference in the organic load and the thus the degradation with temperature change. Additionally,

RFW exhibited an exothermic trough (until 360°C), which is associated to the chemically bound water and the degradation of short chain hydrocarbons, whereas DFW showed both lower endothermic and exothermic troughs across this temperature range (Figure 4.3). These characteristics were equally displayed in the TG and DTG thermograms of substrates with RFW maximum mass loss at around 290°C and DFW slower mass loss at 320°C.

4.3.3 Pyrolytic bio-oils

Bio-oils are essential products of pyrolysis with the potential for energy or chemical source. The calorific value of the bio-oil produced during the pyrolysis of food waste was measured as 11.2 MJ/kg, while for bio-oil obtained through pyrolysis of the digestate it was 13.5 MJ/kg. The bio-oils formed during the pyrolysis of food waste and its digestate are complex mixtures of condensed water and other groups of compounds. Adequate understanding of this mixture, especially the liquid fuel component, may increase its efficiency when combusted for energy instead of burning the biomass directly [17]. The raw food waste and its digestate were heated respectively at 500°C to obtain the bio-oils, which were analysed for constituents identification, and quantification using GC-MS. Compounds are reported in the derivatised form. Detail concentrations of the main organic constituents of bio-oil from the raw food waste (RFW) are listed in Table 4.2.

Table 4.2: GC-MS results of bio-oil from pyrolysis of raw food waste (RFW)

Peak number	Compound name	Retention Time (s)	Formula	Compound content (%)
1	2-Furancarboxaldehyde, 5-methyl-	967.8	C ₇ H ₇ F	0.20
2	Cyclohexane, 1-ethenyl-2-methyl-, trans-	977.7	C ₆ H ₈ O	0.29
3	Pentanoic acid, trimethylsilyl ester	996.9	C ₈ H ₁₈ O ₂ Si	0.26
4	Carbamic acid, phenyl ester	1010.3	C ₇ H ₇ NO ₂	0.06
5	Silane, (2-furanylmethoxy)trimethyl-	1036.3	C ₈ H ₁₄ O ₂ Si	1.46

6	2-Cyclopenten-1-one, 3,4-dimethyl-	1041.2	C ₉ H ₁₂	0.10
7	4-Hexen-2-one, 3-methyl-	1049.5	C ₇ H ₁₂ O	0.24
8	Benzene, 1,2,3-trimethyl-	1107.9	C ₉ H ₁₂	0.06
9	Hexanoic acid, trimethylsilyl ester	1124.2	C ₉ H ₂₀ O ₂ Si	0.18
10	4-Methylvaleric acid, trimethylsilyl ester	1138.8	C ₉ H ₂₀ O ₂ Si	0.44
11	2-Cyclopenten-1-one, 2,3-dimethyl-	1143.1	C ₇ H ₁₄ O ₂	0.36
12	Silane, trimethylphenoxy-	1171.2	C ₉ H ₁₄ OSi	1.29
13	Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester	1180.1	C ₁₅ H ₃₂ OSi ₂	0.14
14	Benzene, butyl-	1191	C ₁₀ H ₁₄	0.20
15	2-Cyclopenten-1-one, 2,3,4-trimethyl-	1197.6	C ₈ H ₁₂ O	0.07
16	Ethanone, 1-(1H-pyrrol-2-yl)-	1211.6	C ₁₀ H ₁₄	0.11
17	Hexanoic acid, trimethylsilyl ester	1217.3	C ₉ H ₂₀ O ₂ Si	0.30
18	2-Cyclopenten-1-one, 3-ethyl-	1235.8	C ₁₀ H ₁₈ O	0.14
19	2-Cyclohexen-1-one, 3,4-dimethyl-	1262.8	C ₇ H ₈ O ₂	0.17
20	Undecane	1287.3	C ₁₁ H ₂₂ O	0.22
21	Benzofuran, 2-methyl-	1318.5	C ₉ H ₈ O	0.33
22	Silane, trimethyl(2-methylphenoxy)-	1353.8	C ₁₀ H ₁₆ OSi	1.43
23	Silane, trimethyl(3-methylphenoxy)-	1378.1	C ₁₀ H ₁₆ OSi	1.29
24	4-Trimethylsilyloxyaniline	1401.8	C ₁₀ H ₁₆ OSi	0.64
25	Benzene, (3-methylbutyl)-	1426.9	C ₁₀ H ₁₂ O	0.13
26	Tetracyclo[5.3.0.0<2,6>.0<3,10>]deca-4,8-diene	1430.7	C ₁₀ H ₁₀	0.11

27	Heptanoic acid, trimethylsilyl ester	1438.2	C ₁₀ H ₂₂ O ₂ Si	0.21
28	2-Ethylphenol, trimethylsilyl ether	1498.7	C ₁₁ H ₁₈ OSi	0.27
29	2,4-Hexadienoic acid, tert-butyl dimethylsilyl ester, (E,E)-	1511	C ₉ H ₁₄ O ₂ Si	1.34
30	1-Allyldimethylsilyloxy-3,5-dimethylbenzene	1533.5	C ₁₁ H ₁₈ OSi	0.63
31	Silane, trimethyl (3,5-xylyloxy)-	1563.4	C ₁₁ H ₁₈ OSi	1.70
32	1,2-Ethanediamine,N,N,N',N'-tetraethyl-1,2-bis(4-fluorophenyl)	1593.7	C ₁₁ H ₁₈ OSi	0.70
33	Silane, trimethyl(3,5-xylyloxy)-	1642.4	C ₁₁ H ₁₈ OSi	0.35
34	Octanoic acid, trimethylsilyl ester	1648.4	C ₁₁ H ₂₄ O ₂ Si	0.20
35	Cyclohexene, 3,3-dimethyl-1-(trimethylsilyloxy)-	1666.5	C ₂₁ H ₂₀ Cl ₂ O ₃	0.42

Phenols are the most abundant compounds in the RFW bio-oil with silane trimethyl (3, 5-xylyloxy) of 1.7% (peak 31), trimethyl (2-methylphenoxy) of 1.4% (peak 12), and trimethylphenoxy of 1.2% (peak 12) however, it should be noted that the presence of silicon in some of the compounds originated from the derivatisation of sample which preceded the analysis.

Silane (2-furanylmethoxy) trimethyl (1.4%, peak 5), 2,4-Hexadienoic acid (1.3%, peak 29) and silane, trimethyl(3-methylphenoxy) 1.2% peak 23 are the most predominant esters in the RFW bio-oil. Other significant compounds present in the bio-oil are 2-Furancarboxaldehyde (peak 1), carbamic acid (peak 4), and cyclohexane as fluorine, nitrogen and chlorine containing organics respectively.

As indicated in Table 4.3, phenols, esters, ketones and mostly nitrogen-containing organics are predominant in the bio-oil obtained during the pyrolysis of food waste digestate (DFW). Trimethylphenoxy (peak 2), and trimethyl (3-methylphenoxy) peak 12 followed by trimethyl (2-methylphenoxy) were the most abundant phenols with 4.9%, 3.9% and 2.2% contents respectively, which are

significantly higher than the phenol contents of RFW. Aside 2-methyl-1-tetradecene (0.5%, peak 24) with chlorine constituent, nitrogen-containing compounds majorly includes: 2,5-pyrrolidinedione (peak 4), 3-ethyl-1,3-dimethyl- (0.4%, peak 4), nonanenitrile (0.4%, peak 12), benzenepropanenitrile (1.5%, peak 22) and Acetophenone, 2'-(trimethylsiloxy (0.7%, peak 31).

Table 4.3: GC-MS results of bio-oil from pyrolysis of food digestate (DFW)

Peak number	Compound name	Retention Time (s)	Formula	Compound content (%)
1	2-Furancarboxaldehyde, 5-methyl-	967.8	C ₇ H ₇ F	0.20
2	Cyclohexane, 1-ethenyl-2-methyl-, trans-	977.7	C ₆ H ₈ O	0.29
3	Pentanoic acid, trimethylsilyl ester	996.9	C ₈ H ₁₈ O ₂ Si	0.26
4	Carbamic acid, phenyl ester	1010.3	C ₇ H ₇ NO ₂	0.06
5	Silane, (2-furanylmethoxy)trimethyl-	1036.3	C ₈ H ₁₄ O ₂ Si	1.46
6	2-Cyclopenten-1-one, 3,4-dimethyl-	1041.2	C ₉ H ₁₂	0.10
7	4-Hexen-2-one, 3-methyl-	1049.5	C ₇ H ₁₂ O	0.24
8	Benzene, 1,2,3-trimethyl-	1107.9	C ₉ H ₁₂	0.06
9	Hexanoic acid, trimethylsilyl ester	1124.2	C ₉ H ₂₀ O ₂ Si	0.18
10	4-Methylvaleric acid, trimethylsilyl ester	1138.8	C ₉ H ₂₀ O ₂ Si	0.44
11	2-Cyclopenten-1-one, 2,3-dimethyl-	1143.1	C ₇ H ₁₄ O ₂	0.36
12	Silane, trimethylphenoxy-	1171.2	C ₉ H ₁₄ OSi	1.29
13	Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester	1180.1	C ₁₅ H ₃₂ OSi ₂	0.14
14	Benzene, butyl-	1191	C ₁₀ H ₁₄	0.20
15	2-Cyclopenten-1-one, 2,3,4-trimethyl-	1197.6	C ₈ H ₁₂ O	0.07

16	Ethanone, 1-(1H-pyrrol-2-yl)-	1211.6	C ₁₀ H ₁₄	0.11
17	Hexanoic acid, trimethylsilyl ester	1217.3	C ₉ H ₂₀ O ₂ Si	0.30
18	2-Cyclopenten-1-one, 3-ethyl-	1235.8	C ₁₀ H ₁₈ O	0.14
19	2-Cyclohexen-1-one, 3,4-dimethyl-	1262.8	C ₇ H ₈ O ₂	0.17
20	Undecane	1287.3	C ₁₁ H ₂₂ O	0.22
21	Benzofuran, 2-methyl-	1318.5	C ₉ H ₈ O	0.33
22	Silane, trimethyl(2-methylphenoxy)-	1353.8	C ₁₀ H ₁₆ OSi	1.43
23	Silane, trimethyl(3-methylphenoxy)-	1378.1	C ₁₀ H ₁₆ OSi	1.29
24	4-Trimethylsilyloxyaniline	1401.8	C ₁₀ H ₁₆ OSi	0.64
25	Benzene, (3-methylbutyl)-	1426.9	C ₁₀ H ₁₂ O	0.13
26	Tetracyclo[5.3.0.0<2,6>.0<3,10>]deca-4,8-diene	1430.7	C ₁₀ H ₁₀	0.11
27	Heptanoic acid, trimethylsilyl ester	1438.2	C ₁₀ H ₂₂ O ₂ Si	0.21
28	2-Ethylphenol, trimethylsilyl ether	1498.7	C ₁₁ H ₁₈ OSi	0.27
29	2,4-Hexadienoic acid, tert-butyl dimethylsilyl ester, (E,E)-	1511	C ₉ H ₁₄ O ₂ Si	1.34
30	1-Allyldimethylsilyloxy-3,5-dimethylbenzene	1533.5	C ₁₁ H ₁₈ OSi	0.63
31	Silane, trimethyl (3,5-xylyloxy)-	1563.4	C ₁₁ H ₁₈ OSi	1.70
32	1,2-Ethanediamine,N,N,N',N'-tetraethyl-1,2-bis(4-fluorophenyl)	1593.7	C ₁₁ H ₁₈ OSi	0.70
33	Silane, trimethyl(3,5-xylyloxy)-	1642.4	C ₁₁ H ₁₈ OSi	0.35
34	Octanoic acid, trimethylsilyl ester	1648.4	C ₁₁ H ₂₄ O ₂ Si	0.20
35	Cyclohexene, 3,3-dimethyl-1-(trimethylsilyloxy)-	1666.5	C ₂₁ H ₂₀ Cl ₂ O ₃	0.42

4.3.4 Substrates (RFW and DFW) gas constituents and evolution

The evolutions of volatile gases from both substrates are noticeable between 200°C and 800°C (except for CO) after completion of dehydration as shown in Figure 4.4. The primary volatiles predominant in food wastes (RFW) are CO₂, CH₄ and CO while the digestate (DFW) were dominated by CO₂, CH₄, CO and H₂ with trace components of C₂H₄ and C₂H₆. DFW indicated the lowest cumulative CH₄ of 0.82 wt%/min compared to RFW with 1.064 wt %/ min. Redistribution of initial carbon across digestion products (gases and digestate) may be responsible. 8.31 and 6.88 wt% of CO₂ eluded from RFW and DFW respectively at temperature range of 230 to ~ 800°C. The occurrence of CO₂ after 600°C and subsequent increase in CO may be due to further decarboxylation as posited in previous studies [18, 19]. H₂ was with the lowest concentration and evolved at temperature above 500 °C as a product of secondary reactions

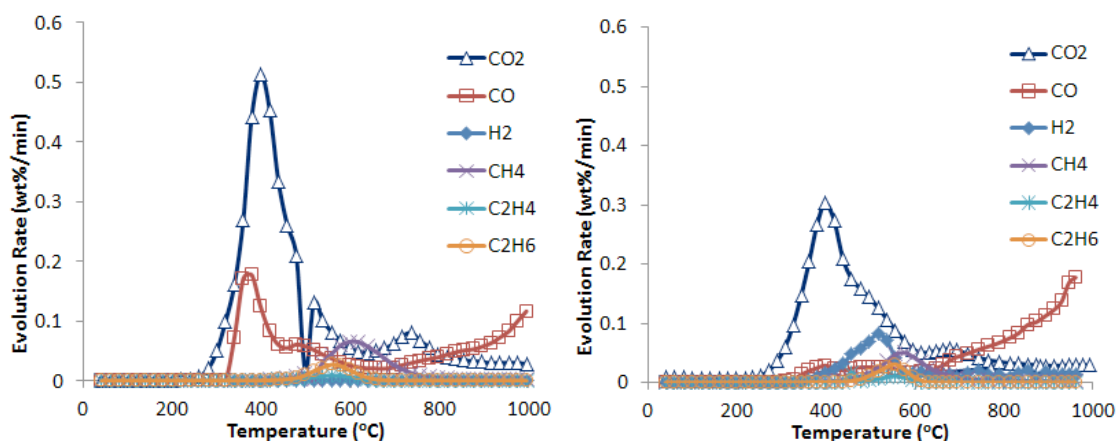


Fig. 4.4: Evolution of volatile gases from raw food waste (RFW) and food waste digestate

4.3.5 Mass and energy balance of the substrates and their products

The proportional estimate of char, bio-oil and gases produced during the pyrolysis of RFW and DFW at 10°C/min heating rate are given in Table 4.4. The energy distribution pattern of these products are equally estimated in Table 4.4 wherein bio-oil mass are calculated by difference to include water. The percentages of gases produced were 7.41 and 5.32 wt% for RFW and DFW respectively. The raw food waste (RFW) indicated an experimental gross calorific value of 15.7 MJ/kg wherein the calorific

values of digested food waste was 17.15 MJ/kg. Lower oxygen content in the DFW may be responsible for its higher calorific value, comparing of the raw food waste.

The pyrolysed raw food waste (RFW₅₀₀) on the other hand (Figure 4.1b) depicted as biochar produced at 500°C provided the highest calorific content at 24.8 MJ/kg. This is due to significant reduction in the oxygen content and increase in the fixed carbon content in the RFW₅₀₀ while the mineral matter content exhibited significantly lower increase, comparing to DFW₅₀₀ in which case decrease in calorific value at 13 MJ/kg was registered. The carbon sequestration potential of pyrolysis coupled with the models dependent on substrate carbon concentration maybe responsible for the inherent energy content, as posited in previous studies [10, 20]. The increase in biochar carbon percentage, especially when pyrolysed at higher temperatures, could also be due to the removal of the volatile compounds [21, 22] which in turns lowered the hydrogen and oxygen fractions.

Generally, the substrates demonstrated considerably higher calorific value when compared to waste water sludge [23] and similar calorific values as macro and microalgae stated in previous studies [18].

Table 4.4: Mass and Energy distribution of Pyrolysis Products at 500°C

	RFW		DFW	
	Mass %	Energy (MJ/kg)	Mass%	Energy (MJ/kg)
Gas	7.41	0.22	5.32	0.83
Char	32.29	8.01	42.48	5.51
Liquid	60.3	7.55	52.2	7.78

The total energy required to pyrolyse the sample to 500°C were acquired by integration of the specific heat curve in Figure 4.3 and these energies for RFW and DFW were 0.72 and 0.87 MJ/kg respectively. Moreover, sequential treatment of food waste described in Figure 4.1c as energy harvesting system -EHS (wherein the one-stage anaerobic digestion is followed with pyrolysis) indicates its potential as the most efficient method of energy extraction from food waste. EHS provided not just an

energy rich DFW but equally optimised the heat of combustion in the biogas, bio-oil and the biochar as illustrated both theoretically and experimentally in this study.

4.4 Conclusions

The biochemical and thermochemical treatment of food wastes to value added products (gases, bio-oil and biochars) is a potential source of energy or industrial raw material and significantly minimizes waste management cost. The energy and products proficiency of these treatment processes using food wastes and its digestate were investigated through their thermal behaviour, calorific values, gases evolution and products compositions. Both substrates (food waste and digestate) demonstrated potential for fast degradation due to relatively high volatile matter content. The difference in the DTG troughs of RFW and DFW expressed the biochemical treatment effect meanwhile approximately 65- 75% mass loss was shown before 600°C. Pyrolysis of RFW spreads energy almost evenly on the chars and bio-oil whereas bio-oil conserved the highest energy in DFW followed by the char while, gases provided significantly low energy in both cases. The theoretical maximum efficiency of pyrolysed food wastes heated at 500°C was calculated at 96% while digestate indicated 77.3% efficiency.

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4.5 References

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Food Wastes Derived Adsorbents For Benzene Gas Sorption

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Abstract

Food wastes are produced worldwide in large quantities that could have potential to produce higher value products, including industrial adsorbents. The present work attempts valorization of food waste followed by CO₂ activation and functionalization through nitric acid treatment. The prepared porous materials were subjected to gas phase adsorption of benzene. Highly porous carbon materials with surface area range from 797 to 1025 m²/g were synthesized with a maximum benzene uptake capacities of 381 mg/g for the food waste activated at 700°C, for 2 hours duration (PyF720). Differential thermogravimetric (DTG) analysis showed the thermostability of the precursors to validate selected initial pyrolysis temperatures (500 and 700°C). C₆H₆ sorption lies mainly in the physisorption region for all adsorbents ensuring regeneration potential. PyF720 and PyF520 recorded the highest isosteric enthalpy of 64.4 KJ/mol and 48.7 KJ/mol respectively, despite the low degree of coverage of the latter. Thus, at ambient temperature PyF720 demonstrated the potential for use as sustainable and cost effective adsorbents for benzene gas containment suitable for swing adsorption system.

Keywords: Adsorption, Isotherm, Isosteric enthalpy and thermostability

5.1 Introduction

Capturing or adsorption of gases, such as C₆H₆, is not only synonymous to environmental amelioration, rather a beneficial technique for gas purification, treatment or management, especially for the refinery off gas (ROG). Array of different adsorbents in pressure swing adsorption (PSA) units are typical of such containment

systems [1]. Besides, the stringent regulatory policies on carcinogenic emissions, the economic stances of gas management to the upstream and downstream oil sectors are also significant. For instance, removing plasticizing components from crude natural gas (sweetening of gas), such as BTEX, improves the product market value [2]. Similarly, previous studies have associate C_6H_6 in landfill gas or biogas plant with the health or mutagenic implication on the workers and nearby inhabitants [3]. Even at low concentration, environmental impacts (such as photochemical oxidation, acid rain formation and climate change) are equally traceable to major VOC components like benzene from industrial pollutants[4]. To comply with pipeline specification during natural gas delivery, extensive treatment is required [2]. This substantially and continually adds to the quest for sustainable adsorbents and techniques to ameliorate 60 - 80% of the overall cost incurred during gas capture and separation [5]. The preferences on solid adsorbents are hinged on ease of handling, lower regeneration energy due to less heat capacity and cheap sources [6, 7]. Moreover, lack of corrosion constraints during the circulation of basic solutions further endorses solid over liquid sorbents [8, 9]. Biomass oriented chars are widely researched as sources of porous carbon due to their feasible and favorable properties [7]. Unlike the seasonal or regional sources of homogeneous biomass or wastes (such as sugarcane bagasse, wood chips, palm front and EFB), the heterogeneity of food waste and its relative global availability makes its use imperative. Therefore, pyrolysed food wastes may be an effective source of carbonaceous adsorbents instead of landfilling. Pyrolysis has recently been deployed as an effective management process for the valorization of putrescible wastes [10, 11], such as food wastes., wherein the resultant products are functionalized for uses as adsorbents, mineral adsorbent in soil [12] and gas purification or sequestration [7].

However, surface oxides (acidic or basic surfaces) on adsorbents are critical to the sorption capabilities [13, 14]. The formations of these oxides largely depend on the nature, quantity and structural architecture of carbon with H and O elements [15]. Thus, choice of surface functionalization of precursors (biochar) after activation augments significantly the textural dynamics of this material, particularly after oxidation. Unlike benzene gas, modifications tailored towards CO_2 gas selection uses nitrogen containing functional groups (amines, urea or melamine), which react with O_2 group on the carbon surface to immobilize amines. Therefore, development of cost effective solid sorbent with relatively high adsorption potential for gases, such as C_6H_6

and CO₂, remains a relevant industrial challenge for sectors, such as the petroleum industry, coal power generators and natural gas management.

The objectives of this study are to: i) produce, functionalize and assess the adsorbent surface transition and commercial suitability of food waste oriented adsorbents. ii) determine the adsorption - desorption strength of these precursors (functionalised PyF) as cost effective adsorbents for C₆H₆ gas.

5.2 Material and methods

5.2.1 Sample synthesis and functionalization: Locally sourced fresh food waste was oven dried at 105°C and milled into smaller sizes. The dry food waste was then pyrolysed at two different temperature of 500 and 700°C using a fixed bed horizontal tubular reactor set at a heating rate of 10°C min⁻¹, under N₂ flow, as previously described [16]. The latter pyrolysis temperature (700°C) was considered to evaluate the effect of initial temperature on the adsorption properties, while 500°C was selected due to its industrial acceptance. The chars produced were washed and subsequently activated using CO₂ which is a significant constituent of the gas eluded during the commercial anaerobic digestion or pyrolysis of the raw food waste [16]. About 10 to 15 g of the chars were activated in a tubular quartz reactor at 900°C with 236 cm³/min flow of CO₂ gas for either 1.5 or 2 hrs. The activated chars were oxidized by stirring the mixture of activated char and 69% HNO₃ at 1:10 ratio for 1 hr on the hot plate at 60°C after which the adsorbents were washed and dried at 110°C. These adsorbents were thus referred to as PyF515, PyF520, PyF715 and PyF720 for the pyrolysed, activated and oxidized food waste respectively, wherein the suffix indicates the original pyrolysis temperature and activation time.

5.2.2 Adsorbent characterization: Fourier transform infrared (FT-IR) chromatographs of the samples before and after each transformation stage were measured with Nicolet 6700 FT-IR spectrometer using an attenuated total reflectance (ATR) method with a diamond crystal. The transitional patterns of C, H and N in the adsorbents through the modification stages were determined using EuroEA elemental analyser (model EA3000). This featured the dynamic flash combustion (DFC) principle interfaced with Callidus software. About 0.7 – 1.3 mg of samples were crushed in the collapsible crucible and loaded for auto selection into the dual furnace embedded with

CHNS standard protocols of the analyzer. The temperature-based mass profile of the food waste (FW) was determined using Mettler Toledo thermogravimetric analyser (TGA/DSC 1 STARe system) interfaced on STARe software. About 30 mg of sample was placed in the alumina crucible and measured at 5°C/min with N₂ flow rate of 20 mL/min as a carrier gas.

Brunauer-Emmett-Teller (BET) model was used to determine the adsorbents' surface area and pore distributions. Nitrogen adsorption on Micrometrics TriStar 3000 was used wherein samples were dynamically vacuumed at 150°C for 3 hrs while data were recorded covering a P/P_0 from 0.07 to 0.27. Density and total pore volume of the adsorbents were measured through an automated gas carrier (helium) displacement pycnometer. Both the regular and irregular configuration of the substrates within the calibrated volumes were determined using Micrometrics AccuPyc II 1340 machine interfaced with AccuPyc II 1340 V1.05 software. The C₆H₆ gas adsorption was carried out using gravimetric sorption analyzer (IsoSORP STATIC 3xV-MP) from Rubotherm, Germany. The magnetic suspension balance (MSB) accurately measures sample weight and gas dosing to determine adsorption equilibrium. Samples were first pre-treated in a vacuum at 150°C for 3 hrs then cooled to 25°C, aiming at degassing and ensuring constant mass. The MSB three positions allow measuring the zero point (position one), the sample weight plus the sample holder (position two), and in position three a titanium sinker, with a known volume, is added to the weight. By means of the weight change of the sinker, the density of the gas can be measured in situ. With this density, and the known volume of the sample, a buoyancy correction was applied to the sample weight. The sample in the stainless steel holder was pressurized for 4 hrs. Thus, a continuous measure of sample mass gain during adsorption of C₆H₆ was determined through IsoSorp automated magnetic suspension balance (MSB) system. Adsorption equilibrium was reached within 2 to 3 hrs for PyF at 25, 35 and 45°C starting at maximum pressure of 90, 150 and 240 mbar.

5.3. Results and discussion

5.3.1 Textural modification effects on PyF

The increases in char porosity after activation are shown in Table 5.1. This can be accredited to the removal of deposited tar or opening of blocked pores, as posited by Chang et al. [17]. In our previous study [18], pyrolysed food wastes indicated carbon richness and high-pitched volatile evolution at 400°C and gradual stabilization in mass loss rate after 500°C to suggest fundamental porous structure formation. The C - CO₂ reactions initiated through the activation agent (CO₂) also accounts for the depletion of carbon atoms as carbon monoxide [19], this is evident in the chars carbon transition indicated in Table 5.1. PyF515 and PyF715 shows 43.6 and 55.9% yield respectively after activation while 2hrs activation yields are similar for PyF520 (33.96%) and PyF720 (33.78%). Low burn-off at high activation temperature may be attributed to the effects of original charring temperatures of 500 and 700°C. PyF520 and PyF720 carbon concentration reduced by 25% and 14% respectively. This may be related to the modification in the reactivity and surface properties of carbon. The degree of primary crystalline organization in carbon black was earlier reported to influence structure and reactivity of carbons [20]. This phenomenon may be responsible for the significant transformation of PyF5XX and PyF7XX as compared to the original PyF sample shown in the FT-IR spectra.

Table 5.1: Characteristics of chars before and after functionalisation

Samples		Burn-off (wt%)	Activatio n time (mins)	Surface	Pore volume (cm ³ /g)	Density (g/cm ³)	Elemental			
				area			Constituents (%)			
				(m ² /g)			C	H	N	S
				BET						
A	PyF500	---	---	1.9	0.4	1.6	71.3	2.1	2.6	6.4
	PyF700	---	---	63.8	0.5	1.8	74.6	0.8	2.1	0.1
B	PyF515	56.4	90	830.3	0.49	1.98	63.8	1.9	2.7	nd
	PyF520	66	120	1024.7	0.52	2.11	53.3	1.8	2.9	nd
	PyF715	44.1	90	797.2	0.59	2.5	68.7	1.3	3.1	nd
	PyF720	66.2	120	901	0.49	1.98	63.6	1.2	3.1	nd

A = Before activation, B = After activation, nd= not detected.

Figure 5.1 shows thermogravimetric (TG) transition of mass loss of dried food waste (RFW) with temperature increase from ambient to 1000°C. The differential (DTG) thermographs of the substrate at 5°C/min indicated low trough for primary devolatilisation at a temperature of 193°C to initiate evolution of primary volatiles. The subsequent sharp trough between 221°C and 524°C may be attributed to secondary decomposition of heavier chemical components [21]. RFW mass loss rate of 0.015 wt%/°C at the maximum temperature (1000°C) represents about 24.1% of the solid residue (see Figure 5.1). This reflects the maximum depletion potential of the pyrolysis, despite the difference in flowing gases involved [19]. The 32.8% and 29.02% mass of the solid residues at 500 and 700°C respectively determined with the TG indicated a linear relationship when correlated with the substrate yields after pyrolysis. Although, the adsorbent yields at 90 mins indicated a reverse (negative) correlation, the adsorbent yields of PyF activated at 2hrs were positively inclined.

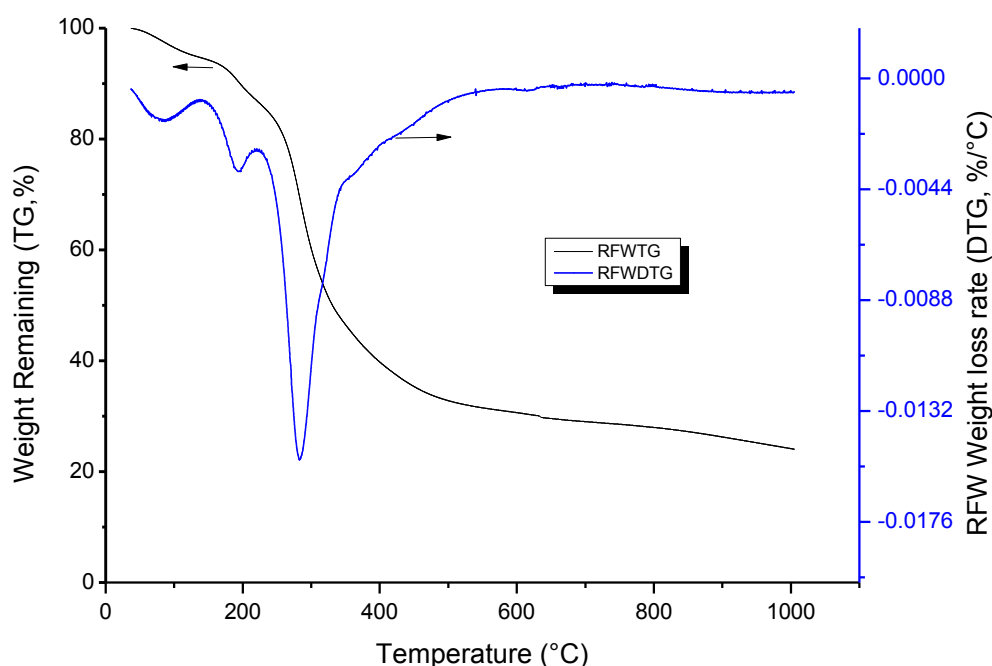


Figure 5.1: TG and DTG curves of raw food wastes (RFW) at heating rates of 5°C /min

CO₂ is the second largest gas after methane produced during commercial anaerobic digestion and pyrolysis of food wastes [16, 18]. This gas (CO₂) was thus recycled as an activation agent to reduce GHG emission and the formation of inorganic

pollutants attributed to chemical activation [17] ensuring cleaner production. Reaction with CO₂ further degrades the hydrocarbon skeleton of the chars generated by pyrolysis (PyF), while oxidation using HNO₃ appropriately enhanced the carbon-oxygen surface group that characterised activated carbonaceous material without damage to its physical morphology [23]. Although longer activation time provided larger surface area, as shown by PyF520 and PyF720, the burn-off is equally higher, which could be detrimental for commercial consideration. Notwithstanding, the surface area of these modified chars are considerably higher than the commercial Darco activated carbon from Aldrich with 564 m²/g and granulated activated carbon (GAC) from Merck-Albus with 886 m²/g. PyF715 provided the highest adsorbent yield (55.91 wt%) and pore volume (0.59 cm³/g) at a relatively stable elemental distribution, but exhibited the least surface area (797.2 m²/g) compared to others. This suggests the inevitable need for trade-off in chars' textural properties, especially when activated with CO₂.

FTIR chromatographs of the samples' transition due to textural transformation are shown in Figure 5.2. The infra-red spectra at 1417, 1043 and 875 cm⁻¹ were considerably impacted to reflected activation effect on PyF500 series while the spectra at 1410 (aliphatic CH₂) and 874 cm⁻¹ of PyF 700 series disappeared. The abrupt absence of bands between 4000 cm⁻¹ and approximately 2000 cm⁻¹ may be accredited to the effect of the initial pyrolysis temperature wherein significant polar groups, such as -OH and C-O, are eliminated along with the side weaker asymmetric and symmetric CH₂ bonds [18, 24]. The distinction in PyF520 bands within 1600 to 850 cm⁻¹ further evinced carbon depletion during activation. The skewedness of O₂ containing functional groups below 1900 cm⁻¹ expectedly increases both the polarity and selectivity of the carbon surfaces [25]. Carbon oxidation using HNO₃ enhanced absorption bands within the ranges of 1520 – 1000 cm⁻¹ when compared to the non-oxidised precursors irrespective of the activation time, as equally posited in [15]. Broader band shapes distinguished oxidised substrates from merely activated feedstocks, especially at fingerprint regions lower than 1700 cm⁻¹.

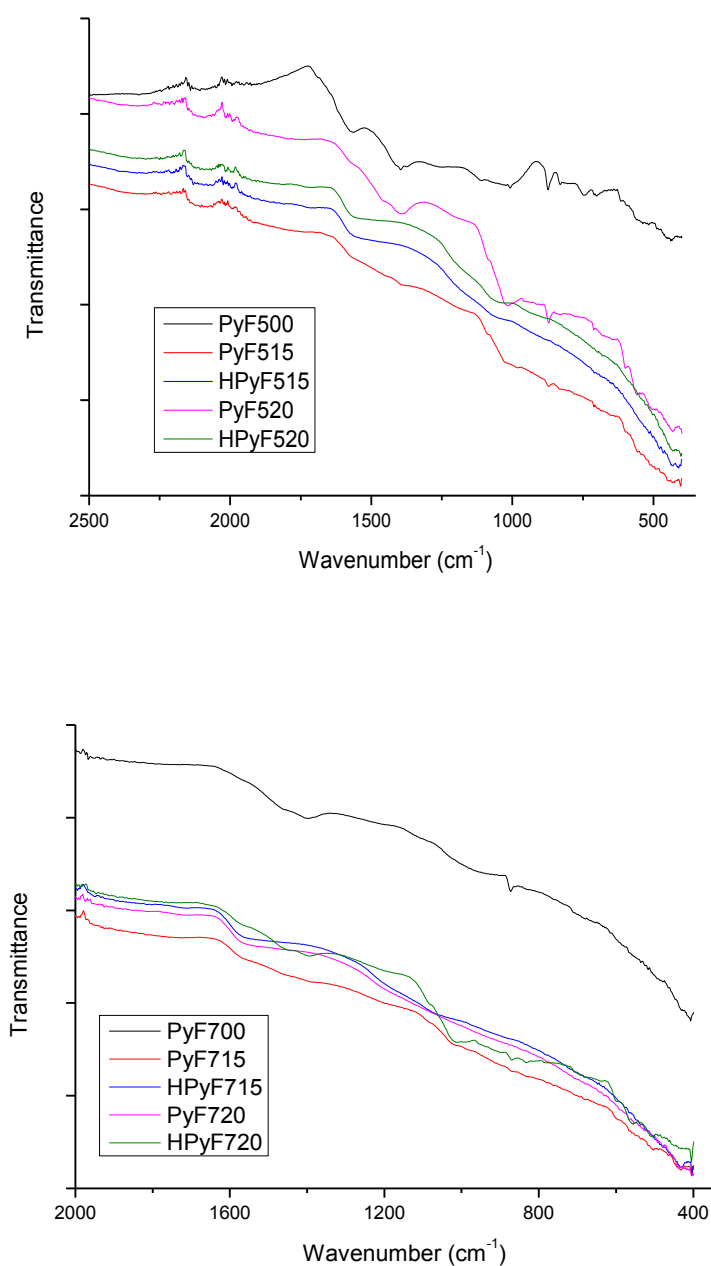


Figure 5.2: FTIR spectra of original pyrolysed food waste (PyF) at 500 and 700°C, activated PyF 500°C and PyF 700°C and their subsequent oxidation (HPyF series)

5.3.2 Adsorption isotherm of C_6H_6 gases

C_6H_6 temperature dependent uptake performances of the modified PyF are shown in Figure 5.5 and Figure 5.6 for PyF 515, PyF 520, PyF 715 and PyF 720. The surface hydrophobicity or hydrophilicity of these adsorbents are reflected through the amount of adsorbed benzene, which is in accordance to the adsorbents produced from

other carbon materials [26]. Since adsorption processes are exothermic, the gas uptake increases with decreasing temperature [27, 28]. Therefore, C_6H_6 uptake by activated PyF expectedly decreases with increase in temperature. In this work, C_6H_6 adsorption was found to be high at low temperature (25°C) for PyF 515 and PyF 720 with uptake concentration of 345.6 and 380.7 mg/g respectively and at relatively low pressure (100 mbar). At higher temperature (35°C) and pressure (150 mbar) the highest C_6H_6 sorption isotherm (360.5 mg/g) was exhibited by PyF 520 indicating dominance of hydrophobic surface compared to the other samples. The significance of adsorption isotherms vis-à-vis temperature, especially for industrial adsorption system, cannot be underestimated since this relates to the isosteric heat of adsorption [29]. Irrespective of the temperature considered, PyF 520 illustrated the IUPAC type I model with gradual steep increase at low pressure and subsequent plateau at higher pressures [30]. The adsorption equilibrium spread across PyF 5XX and PyF 7XX series entrenches the significance of buoyancy correction as a function of C_6H_6 uptake. The dependence of C_6H_6 uptake on adsorbents' properties and pressure further entrenched the significance of buoyancy correction to ensure adsorption equilibrium across all samples [31]. Although the selectivity gradients of these materials were not evaluated, this study reveals low cost and regeneration energy potential due to no hysteresis in the desorption curve, coupled with fast adsorption kinetics [28, 32] of the food waste activated carbons.

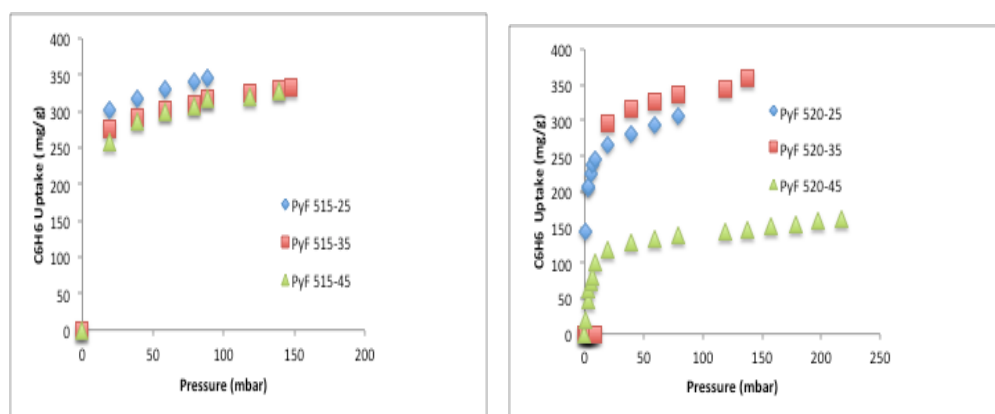


Figure 5.5: C_6H_6 adsorption isotherm of activated, oxidized and pyrolysed food waste (PyFXX) at 500°C for 1.5 and 2hrs performed at temperature range of 25, 35 and 45°C

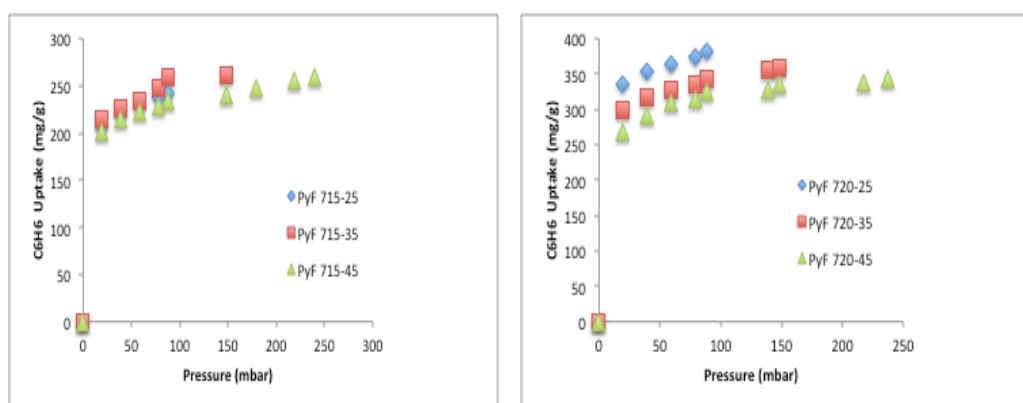


Figure 5.6: C_6H_6 adsorption isotherm of activated, oxidized and pyrolysed food waste (PyF) at 700°C for 1.5 and 2hrs performed at temperature range of 25, 35 and 45°C

The significance and effect of activation time on the precursors were demonstrated by the apparent difference in the adsorption isotherms of PyF515 and PyF520. This may be attributed to the pore structure configuration (slitness or roundness) of PyF515 which is responsible for its high performance as an adsorbent. The latter 1.7 degree of coverage equally suggests its higher sorption potential against PyF520 with greater enthalpy (49 kJ/mole), as shown in Table 5.2.

5.3.3 Thermodynamics of gas adsorption

The maximum isosteric heats of adsorption and degree of coverage of benzene on PyF5XX and PyF7XX determined through the family of experimental isotherms obtained on individual sample at 298K, 308K and 318K respectively at equilibrium pressure range of 19 to 250 mbar are shown in Table 5.2. C_6H_6 adsorption isobars of PyF5XX and PyF7XX were calculated using the Clausius–Clapeyron equation (detailed in the supplementary data). This provides insight into the temperature dependency of adsorption isotherms indicating the interaction between the adsorbent and adsorbate [29]. PyF720 indicated the highest isosteric enthalpy of 64 kJ/mol at 1.8 degree of coverage, followed by PyF520 with 49 kJ/mol isosteric heat of adsorption. These are expected since the energies are function of the degree of surface coverage that also depend on the solid surface area and monolayer volume [33].

Table 5.2: Summary and maximum values of thermodynamic parameters for benzene adsorption on food waste oriented adsorbents

Adsorbents	Degree of coverage	Isosteric Enthalpy (kJ/mol)
PyF515	1.7	23
PyF520	1.2	49
PyF715	1.4	11
PyF720	1.8	64

The benzene enthalpies of adsorption are in the physisorption range < 80 kJ/mol [34], which are typical for un-doped carbonaceous sorbents. Yu-Chun and co-workers reported an adsorption enthalpy range of 33 – 68 kJ/mol for benzene gas adsorption at lower temperature and 38 – 76 kJ/mol for the same adsorption at high temperatures [35] using three different types of activated carbon. The varying fractional coverage of benzene gas adsorbed for each sample material suggests surface heterogeneity [33]. For instance, the degree of coverage of PyF515 were extractable at the intersections range of 1.5 – 1.7 similar to 1.5 – 1.8 of PyF720 however, their sorption behaviour are in contrast with each other (see supplementary data). Therefore, the most energetic sites for benzene adsorption are repositied in PyF720 followed by PyF520 while PyF715 indicated the least heat of sorption (11 kJ/mol).

5.4 Conclusion

Food waste transformation into an efficiently porous adsorbent capable of C_6H_6 gas uptake through char formation and activated using a greenhouse gas (CO_2) for activation is a clear indication of sustainable means of recycling food waste and disengaging landfill. The produced adsorbents showed considerable stance and properties to match commercial activated carbon despite the trade-off in yield during activation. The physical activation using CO_2 proves to be an effective means of surface enhancement. Thermostability of the precursors indicated stability at temperature of $500^\circ C$ authenticating the pyrolysis temperatures as reflected through the differential thermograph (DTG).

At low temperature ($25^\circ C$) PyF720 and PyF515 provided the highest C_6H_6 uptake whereas PyF520 exceeded the latter during adsorption at higher temperature. Interestingly, all the samples indicated physisorption relationship with the adsorbent which imply ease of re-generation. Therefore, food waste oriented porous carbon materials are potential cheap sources of adsorbent for gas management.

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Agronomic Assessment of Pyrolysed Food Waste Digestate for Sandy Soil Management

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Abstract

The digestate (DFW) of an industrial food waste treatment plant was pyrolysed for production of value added products (biochar) in addition to its direct application as bio-fertilizer or soil enhancer. Nutrient dynamics and agronomic viability of the pyrolysed food waste digestate (PyD) produced at different temperatures were evaluated using germination index (GI), water retention/availability and mineral sorption as indicators when applied on arid soil. The pyrolysis enriched P, K and other micronutrients in the biochar at an average enrichment factor of 0.87. All PyD produced indicated significantly low phytotoxicity with GI range of 106 – 168% and an average water retention capacity of 40.2%. Differential thermogravimetric (DTG) thermographs delineated the stability of the food waste digestate pyrolysed at 500°C (PyD500) against the degradation of DFW despite the latter poor nutrient sorption potential. Plant available water in soil is 40% when treated with 100g of DFW per kg soil, whereas PyD500 treated soil indicated minimal effect on plant available water, even with high application rates. However, the germination index, nutrient enrichments and sorption suggest additional benefits of the pyrolysis process, considering the additional energy extracted.

Keywords: Agronomy, Pyrolysis, Relative enrichment, Thermogravimetric, Germination and Nutrient sorption

6.1 Introduction

Pyrolysis of waste biomass to biochar (a carbon rich material resembling charcoal) and its subsequent application to soil as a mechanism to enhance water and nutrient retention is becoming a widely accepted practice (Hossain et al., 2011; Sohi et al., 2010). The 30 - 50% organic carbon loss in soil due to intensive tillage (Khalifa and Yousef, 2015; Lee et al., 2013) may be ameliorated

through organic rich digestate or organic oriented biochars. Generally, reduction in soil aggregate capacity, lack of water and nutrient retention properties lead to soil erosion and fertility losses (Novak and Busscher, 2013) and consequently low crop production. Biochar application to soil appears to offer ancillary environmental benefits. For example, biochar produced from cattle manure were reported to lower CO₂ emission and stabilised N₂O gas emissions when compared to raw cattle manure and anaerobically treated digestate (Schouten et al., 2012). The potential of carbonaceous bio-solid sludge for the remediation of acidic or alkaline soil was reported with delinquent tendency of heavy metal bioaccumulation and bioavailability (Hossain et al., 2011). Successful cases of soil improvement and other prospective use of biogas plant digestate were also reported. The emerging use of food waste digestate as sources of inoculum while, the fibers are recycled for fuels and or materials are typical instance posited (Sheets et al., 2015). Jacob and co-workers outlined the water retention, herbicides/biocides reduction and erosion reduction ability of digestate beside its carbon binding and saving inorganic fertilizers (Møller et al., 2009). The practice of using biochar or digestate for soil improvement particularly vital to agricultural Mediterranean soils and other arid regions known to exhibit a progressive depletion in soil organic matter due to warm climate that cause high rates of mineralization (Montemurro et al., 2010). However, the use of digestate as bio-fertilizer could be problematic if not monitored or produced properly. This is because digestates may contain substantial concentrations of heavy metals and organic pollutants (Brändli et al., 2007; Wu et al., 2016), physical impurities, pathogens (Al Seadi and Lukehurst, 2012), viscosity and odour (Arthurson, 2009), and quality management (Albuquerque et al., 2012). Thus, further treatment may be essential to ease utilization.

Characteristics and use of different biomass oriented chars are reported in a number of studies (Albuquerque et al., 2014; Keiluweit et al., 2010; Opatokun et al., 2016) however, feedstock availability, seasonal or regional

peculiarity and cost benefit analysis have limited the commercial realization of these findings. Targeting food wastes for biochar production maybe a sustainable pathway to solving environmental impacts related to its disposal while recycling soil nutrients and minerals. Global food wastes are currently estimated at 1.3 billion tons per year and are also expected to increase by 53% by 2025 (Adhikari et al., 2006; FAO. 2011). The rate of generation and investment implication of this food waste are extensively described in Girotto study (Girotto et al., 2015). Anaerobic digestion of food or organic wastes for energy and digestate are established measures to alleviate loads on landfills while simultaneously producing fertilizer for soil. There is also an option to pyrolyse digestates produced from anaerobic digestion for biogas and biochar with the objective of maximizing the recovery of energy and the potential utility of biochar in agriculture (Monlau et al., 2016; Yuan et. al., 2016).

The objective of this work is to study the properties of biochars produced at different temperatures from food waste digestate, and assess their suitability for agronomic applications. Elemental enrichment, water holding capacity and the seed germination index effect of biochars produced from food waste digestate at different charring temperatures (300, 400, 500 and 700°C) were evaluated. Furthermore, the phosphate sorption capacity and plant available water in sandy soil treated with biochar produced at 500°C (PyD500) was further evaluated.

6.2 Material and methods

6.2.1 Materials (Soil, food waste digestate and biochar production)

Pelleted food waste digestate (9.8% dry matter) was collected from EarthPower Pty Ltd located in Sydney, after an industrial mesophilic anaerobic treatment process. The sample was oven dried (60 – 70°C) and converted to biochar using a fixed bed horizontal tubular reactor with 10°Cmin⁻¹ heating rate considering four peak temperatures of 300, 400, 500 and 700°C at holding time of 4 hrs. Production details of the chars can be found in (Opatokun et al., 2016).

The chars were washed using distilled water to reduce the dust accrue during production, subsequently milled and sieved through 0.45 mm aperture before oven dried and kept in sealed container for use. These are subsequently referred to as PyD with suffix number representing the production temperature.

Sandy textured soil was collected from a farm located in Al-Rahba in Abu Dhabi (United Arab Emirates). The properties of the soil are shown in Table 6.1 and were determined as described in (Khalifa and Yousef, 2015). Subsequently, the biochar was added to soil at application rates of 10, 50, 100 and 150 g biochar per kg of oven-dried soil. The mixture was mixed manually to homogeneous consistency, oven-dried at 70°C for 24hrs and stored in glass mason jars at room temperature until analysis.

Table 6-1: Properties of the sandy soil used

Texture	Sand (%)	Silt (%)	Clay (%)	pH	EC (μS /cm)	TOC (%)
Sandy	96.12	3	0.88	7.9	752	1.12

6.2.2 Biochar characterisation and analysis

Elemental and physicochemical analyses of the biochars were obtained using Australian Standard (AS) 1038.3, 1038.6 and USEPA 6010/ 6020A ICP. The relative enrichment (RE) of the chars were determined as reported (Hossain et al., 2011) to express the substrate elemental and nutrients diversity and equally show the degree of volatility expressed by these elements. Larger enrichment is expressed by RE factor greater than 1 while elements depletion is exhibited for RE lower than 1. RE factors are calculated according to equation 1:

$$\text{Relative enrichment (RE)} = \frac{\text{Elemental Concentration in Biochar}}{\text{Elemental Concentration in Substrate}} \times \frac{\text{Char}}{100} \dots\dots\dots \text{eq. 1}$$

The pH and EC were measured using water to sample ratio of 1 : 1 (w/w) for slurry of mixture through the pH probe, after having sieved the homogenized soil-char mixture as indicated in (Khalifa and Yousef, 2015). The water holding

capacity (WHC) of biochar was determined by saturating about 8g of dried sample (contained in hilgard cup) with water. The latter was allowed to drain in humid enclosure after which the differences in mass were calculated. The phytotoxicity was evaluated based on germination index (Thipkhunthod et al. 2006) using tomato seed (*Lycopersicum esculantum*) on water-soluble extracts from specific biochar. One gram (dry weight) of each substrate was mixed with 10 ml of distilled water through an electric rotator at 125 rpm for 1 h. The extracts were then filtered while the filtrate obtained was centrifuged at 9,000 rpm for 15 minutes. For the germination test, 2 ml of the supernatant was diluted with 1 ml of distilled (DI) water and sprayed over a petri dish with double layered filter papers. Ten seeds of tomato were seeded per plate at room temperature in a dark cupboard and allowed to germinate after five days of incubation. All plates were incubated at ambient temperature (25°C) in a dark cupboard. Control treatment was maintained with equivalent amount of DI water only. The number of germinated seeds (G) and root length (L) were recorded while the seed germination index calculation was related as percentage of the control as expressed through equations 2 – 4, as described by Tiquia (Tiquia, 2003).

$$\text{Relative seed germination (\%)} = \frac{\text{Number of germination seeds in extract}}{\text{Number of tested seeds in control}} \times 100 \dots \text{eq. 2}$$

$$\text{Relative root growth (\%)} = \frac{\text{Mean Root Length in Extract}}{\text{Mean Root Length in Control}} \times 100 \dots \text{eq. 3}$$

$$\text{Germination Index (\%)} = \frac{(\% \text{ Seed Germination}) \times (\% \text{ Root Growth})}{100} \dots \text{eq. 4}$$

The differential thermogravimetric (DTG) analysis of DFW and PyD500 were determined using Mettler Toledo thermogravimetric analyser (TGA/ DSC 1 STARE system) interfaced on STARE software. About, 30 mg of each sample was used in each measurement. Heating rate of 5°C/min with nitrogen flowing at 20 mL/min as a carrier gas was selected to evaluate the substrate stability and thermal degradation pattern. Phosphate batch sorption experiments were

carried out at room temperature as indicated in (Yao et al., 2012) with slight modifications. Briefly, 0.1 g of biochar was added to a known concentration of phosphate solutions, and the mixture (0.1 g of each biochar with 50 mL of 30 ppm phosphate solutions sourced from KH_2PO_4) was shaken for 24 hrs at 60 rpm. Thereafter, the mixture was filtered through nylon membrane. PO_4^{3-} concentrations were determined using HACH reagent (high range total phosphate, 0 – 100mg/l PO_4^{3-}) and DR 4000 spectrophotometer. The difference between initial and final aqueous concentration of phosphate was considered to be the amount of phosphorus concentration in the biochar. Plant available water was determined in wetted (clay like consistence) untreated and biochar treated soil using a pressure plate extractor. Soil cores (19 cm^3) were saturated in water overnight and subsequently transferred to the pressure plate extractor at 0.3 bar (soil water at field capacity) and 15 bar (soil water at wilting point). The difference in soil water between 0.3 and 15 bar is defined as plant available water. Volumetric water content is calculated from gravimetric water content in soil using the following equations.

$$\text{Gravimetric water content } (\sigma_g) = M_w / M_s \dots\dots\dots \text{eq. 5}$$

Where M_w is mass of water (g) and M_s is mass of dry soil (g)

$$\text{Volumetric water content } (\sigma_v) = \sigma_g \times \rho_{bs} / \rho_w \dots\dots\dots \text{eq. 6}$$

Where ρ_{bs} is dry soil bulk density and ρ_w is water density (g.cm^3)

6.3 Results and discussions

The physicochemical characteristics of digestate from food waste (DFW) and the biochars (PyD) produced at different temperatures are given in Table 6.2. Carbon composition of pyrolysed food waste digestate was in the range from 34 – 42.1% with relatively high ash contents (35.7 – 60.2%). As oppose to the digestate (DFW) the recalcitrant nature of the biochars' carbon, as established in a previous study (Opatokun et al., 2016), further shows suitability of PyD as soil organic carbon substitute. P and K increases in the chars as

charring temperature rises while N shows slight decrease (4.01 – 5.36%) until 500°C and substantial loss (1.9%) at 700°C. The depletion of the latter due to volatilization (Gaskin et al., 2008; Hossain et al., 2011) may also account for the non-detectable concentration of ammonia-N in the carbonized digestate at temperature above 400°C. Although, significant amount of N was retained at 500°C, its availability for plant uptake remains questionable. This is due to its gradual transformation into pyridine like structure which are bonded organically (Hossain et al., 2011) as recalcitrant component. However, P and K, as other major nutrients essential for the plants, increase with charring temperature. This is a similar trend to P and K enrichment in the biochar with temperature for pyrolysed sewage sludge (Chan and Xu, 2009; Hossain et al., 2011). Unlike most wood and nut oriented biochars with extremely high C/N and C/P ratios (Kookana et al., 2011), biochar from food wastes are characterised with nutrient and ash enrichment, therefore lacking stability attributed to carbon enriched and aromatically condensed wood based chars (Singh et al., 2010).

The metals and metalloids, such as Ca (4.55 – 7.76%), Fe (1.37 – 2.22%) and Mg (0.37 – 0.55%), concentration in the chars were higher compared to those in the feedstock (3.17, 0.93 and 0.27% respectively). This indicates the influence of pyrolysis temperature and raw feed composition on the concentration and fate of elements in the pyrolysis products, as reported in previous studies (Hossain et al., 2011; Kookana et al., 2011). Cu appears to be sensitive to pyrolysis temperatures, because it showed the lowest enrichment value (0.22) at 400°C when compared to micronutrients Ca, Fe, P, K and Zn, which appear to be stable and have similar enrichment values throughout the considered pyrolysis temperatures (Table 6.3).

Table 6.2: Characterization of food wastes digestate (DFW) and its biochar (PyD) produced at different temperatures^a

	SUBSTRATES	PYROLYSED DIGESTATE (%)			
	DFW	PyD300	PyD400	PyD500	PyD700
Yield	-	60.55	42.61	38.05	35.03
pH	8.02	8.39	9.69	10.08	10.70
Ash Contents	25.6	35.7	49.2	55.1	60.2
Total Solids	89.7	99.6	100	99.8	100
Total Carbon	42.1	45.4	37.3	35.3	34.0
Ammonia-N	0.15	0.004	nd	nd	nd
Total Nitrogen	5.81	5.36	4.51	4.01	1.9
Potassium	0.62	0.87	1.24	1.39	1.53
Phosphorus	1.97	2.92	4.13	4.54	4.78
Calcium	3.17	4.55	6.53	7.26	7.76
Magnesium	0.27	0.37	0.50	0.53	0.55
Iron	0.93	1.37	1.97	2.18	2.22
Zinc	0.03	0.04	0.06	0.07	0.06
Copper	0.008	0.007	0.004	0.01	0.011
Chromium	0.004	0.004	0.004	0.004	0.002
Nickel	0.002	0.002	0.003	0.005	0.004
Lead	0.001	0.001	0.002	0.002	0.002
Arsenic	9.8×10^{-5}	9.1×10^{-5}	1.1×10^{-4}	9.8×10^{-5}	nd
Cadmium	nd	5.7×10^{-5}	8.2×10^{-5}	9.3×10^{-5}	nd

^aAll parameters are in percentage. nd, below detectable limit.

Relative enrichment (RE) of the biochar nutrients reflects the prevalence of lignin residue with less heat resistant constituent in sequence with increasing pyrolysis temperature and consequent decrease in C-matrix of the feedstock (Keiluweit et al., 2010). The peak of volatilization was exhibited at 400°C in most

of the elements considered with average RE of 0.87, excluding Cu. Marginal differences are shown between the stability of these nutrients at higher temperatures (500 and 700°C), and shown in Table 6.3.

Table 6.3: Relative enrichment factors of nutrient concentrations in biochars produced at different temperatures

Elements	PyD300	PyD400	PyD500	PyD700
Ca	0.85	0.88	0.86	0.86
Cu	0.57	0.22	0.46	0.47
Fe	0.88	0.90	0.88	0.84
Mg	0.81	0.80	0.74	0.72
P	0.88	0.89	0.86	0.85
K	0.83	0.86	0.85	0.87
Zn	0.85	0.88	0.84	0.70
Pb	0.64	0.71	0.69	0.55
Cd	0.75	0.78	0.77	0.35
Cr	0.59	0.52	0.46	0.21
Ni	0.69	0.63	0.95	0.72
As	0.55	0.48	0.38	0.28

The toxic trace metals demonstrated relatively lower stability during the pyrolysis process, except for Ni (ranging from 0.63 – 0.95) which appears to have similar degrees of volatility across the charring temperatures, as shown in Table 6.3. Previous studies had equally attributed high volatility and or thermal removal of heavy hydrocarbon to biomass and sludge oriented biochars (Evangelou et al., 2014; Hossain et al., 2011). For instance Luo and co-workers (Luo et al., 2014) reported an increase in the heavy metal concentrations in maize and sludge derived chars with the charring temperature when compared

to raw materials. Imperatively, the distribution of these nutritive elements and their enrichment characteristics account for the acidity or alkalinity of the biochar and consequently determine its suitability for soil application (Luo et al., 2014; Singh et al., 2010).

Figure 6.1 provides the thermal analysis results of DFW and pyrolysed food waste digestate at 500°C (PyD500). The degradation of DFW and stability of PyD500 were reflected through the thermograph profiles determined at low heating rate ($5^{\circ}\text{C min}^{-1}$) to avoid right inclination of peaks due to increment of initial devolatilisation (Gómez et al., 2007). The stability of the selected biochar (that is PyD500 partly due to industrial acceptance of pyrolysis at 500°C) was analysed further by the DTG (Figure 6.1). There is an early dehydration of inherent moisture or surface oxygenated oxides at 66°C, followed by a broadly stable peak which appear to slightly decline at about 550°C and stabilized at 657°C.

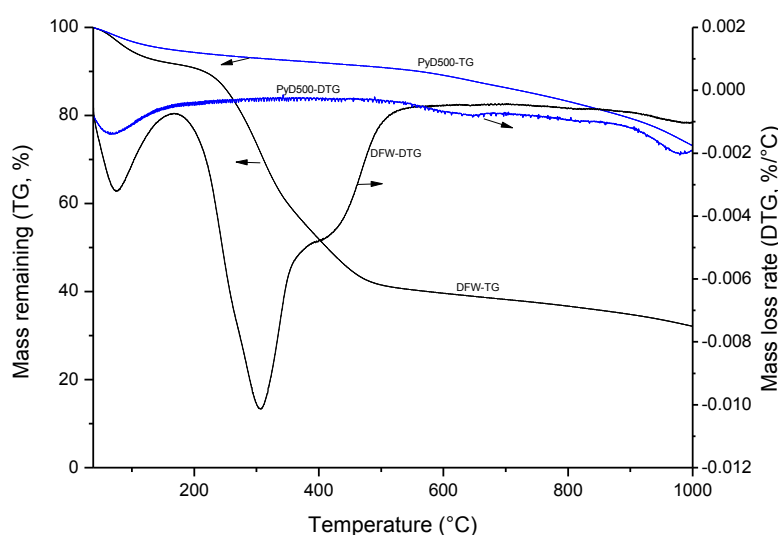


Figure 6.1: Thermogravimetric analysis (TGA) and its differential (DTG) showing the stability potential of raw food digestate (DFW) and pyrolysed food waste digestate at 500°C (PyD500) at 5°C/min

The degradation of water-soluble components such as hemicellulose, cellulose and microbial constituents (Wu et al., 2011) of the DFW at 273°C

(approximately 21%) was preceded by the usual dehydration of residual water (Figure 6.1). Furthermore, the decomposition of lignin and organic polymers (higher molecular weight compounds) present or generated during the penultimate process may be attributed to the temperature increase from 359°C through 407°C before stabilizing at approximately 540°C. The DFW profile shows similar trend to alkali lignin, digested cattle manure and organic fraction of municipal solid waste (OFMSW) during thermal analysis (Gómez et al., 2007; Yang et al., 2007). These thermographs also provide insight into the direct and long term effect of temperature on substrates (DFW or PyD500) when applied on hyper arid sandy soil located in solar belt region, such as Abu Dhabi, with daily mean solar radiation of 730 W/m² (Islam et al., 2010). The stability of DFW shortly after 500°C suggests the temperature is suitable for industrial pyrolysis of digested food waste.

Seed germination index bioassay of digestate and its derived chars produced at different temperatures are shown in Figure 6.3. Digested food waste (DFW) expressed the smallest seed germination index (GI) of 48.1% (Figure 6.3) indicating it is phytotoxic because its below the 70% seed GI threshold used to indicate non-phytotoxicity (Abdullahi et al., 2008). The GI of digestate oriented biochars increases with charring temperatures showing a negative correlation with carbon degradation and partial correlation (0.75) with carbon to nitrogen ratio (Figure 6.3). All biochars indicated GI above 105% illustrating a decrease in phytotoxic precursors and also reflect gradual degradation of feedstock primary and secondary intermediate compounds (phenolic, polyalcohols and volatile fatty acids) as charring temperature changes (Vassilev et al., 2013). PyD700 provided the highest GI (166.8%) while PyD300 expressed the least GI value (106%). Biochars PyD400 and PyD500 have a similar GI of 123.6 and 130% respectively. Beside the extractable energy constituent of food waste digestate (Opatokun et al., 2015), its phytotoxicity quotient maybe another substantial factor impeding digestate valorisation as a suitable product for agricultural soils use. Although negative impacts, such as

the release of toxicants and inhibition of seed germination, maybe attributed to some biochars (Kookana et al., 2011) the behaviour of food waste derived biochars produced at temperatures above 300°C appear to be beneficial for plant germination. Sorghum based biochar was equally reported to increase germination and seedling growth despite being enriched with tar and produced through fast pyrolysis (Keller et al., 2008).

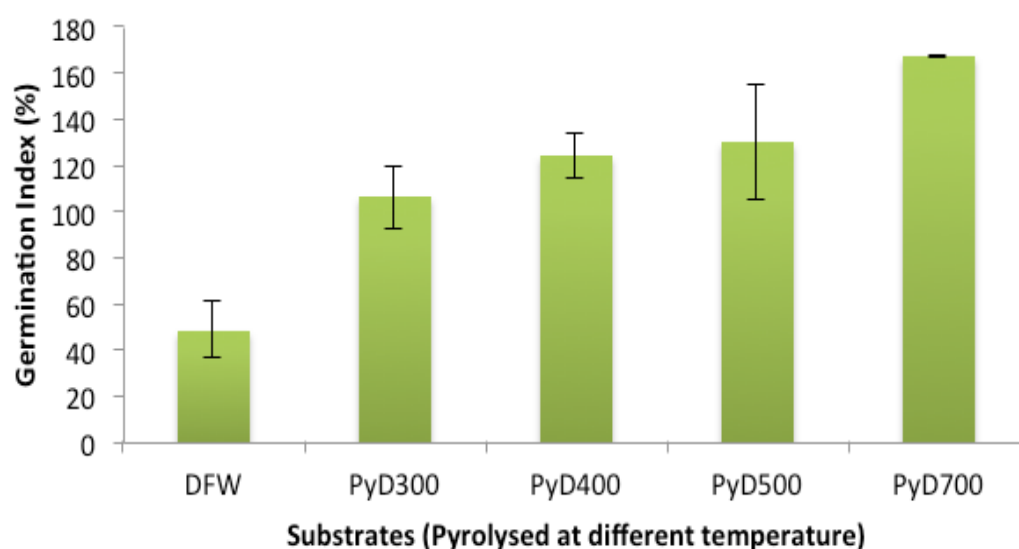


Figure 6 - 3: Germination index (GI) of leachate collected from raw digested food waste (DFW) and pyrolysed food waste digestate (PyD) at temperatures ranging from 300 - 700°C.

The water holding capacities (WHC) of the biochars produced at different temperatures were compared to the digestate, as shown in Figure 6.4. Pyrolysed food waste digestate (PyD) at 300°C indicated higher capacity to store water with 42.3%, when compared to the chars produced at higher temperatures. This retention capacity may be attributed to carboxylate and ionisable functional group characteristic for biochars produced at lower temperatures (Basso et al., 2013; Mukherjee et al., 2011) as detailed in the Fourier Transform infrared of the same biochars reported earlier (Opatokun et al., 2016). It is important to note that water holding mitigation and nutrient leaching potentials of biochar are related to the amount of recalcitrant carbon constituents in the biochar (Woolf et al., 2010) which might have been impaired

during the commercial one stage anaerobic digestion that preceded the pyrolysis process. The distinct WHC of DFW (64.9%) may be attributed to the dominance of hemicellulose and water-soluble (poly and/or oligosaccharides) constituents of the substrate (Opatokun et al., 2016). Incomplete degradation of labile organic content of the parent feed (due partly to limited residence time) during digestion may account for unstable organic matter (Albuquerque et al., 2012) which influences WHC increase. However, the latter's regime is temporary when compared to biochar composed of stable carbon (Sohi et al., 2010). Therefore, porous structured PyD is targeted towards direct and long-term modification of soil water holding capacity, especially when applied at appropriate biochar application rates, instead of DFW with 21% leachable constituent (water soluble). Biochar surface oxidation during contact with air or water may be responsible for the hydrophilic features of PyD500 and PyD700 with 40.9 and 40.8% WHC respectively. This equally correlates with the marginal difference in their carbon content despite the large variation in the charring temperature.

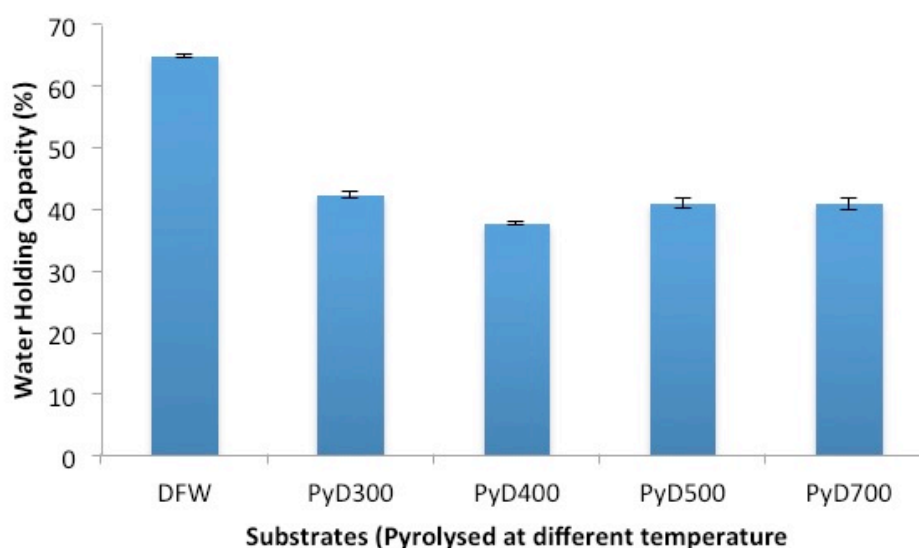


Figure 6 - 4: Water holding capacity of raw digestated food waste (DFW) and pyrolysed food waste digestate (PyD) at temperatures ranging from 300 - 700°C. The degrees of variability between parameters considered in this study are shown in Table 6.5 using the linear correlation coefficient (R^2). This overview

summarised the relationship between essential plant nutrients (N, P and K) in PyD (pyrolysed food waste digestate), production variable (temperature and yield) and their combined influence on agronomic indicators, such as germination index and water holding capacity. About 73 and 91% of the variations in GI are accounted for by the variations in the WHC and biochar yield respectively. However, pH, GI and yield (invariably temperature) are highly related to the N, P and K with variation range higher than 80%, except for N in relation to yield (56%). Xu et al. (Xu et al., 2012) equally reported the strong correlation of soil pH buffering capacity and cation exchange capacity due to the latter presence in the biochar.

Table 6 - 5: Linear correlation coefficients (R²) of essential nutrients in pyrolysed food waste digestate, biochar production variables (Temperature and Yield) and agronomic indicators (germination index and water holding capacity)

	GI	WHC	pH	Yield	Temp	N	P	K
GI	1							
WHC	0.731	1						
pH	0.846	0.484	1					
Yield	0.906	0.895	0.778	1				
Temp	0.988	0.658	0.889	0.881	1			
N	0.805	0.295	0.857	0.560	0.853	1		
P	0.892	0.677	0.953	0.920	0.911	0.728	1	
K	0.899	0.605	0.982	0.876	0.930	0.803	0.991	1

Pyrolysis temperature of 500°C is most frequently used for commercial biochar productions (Opatokun et al., 2015). For this reason, biochar produced at 500°C (PyD500) was further analyzed and compared to DFW for phosphate mineral sorption and its effect on plant available water when applied to soil at various application rates. DFW released phosphate into the solution (4.3%)

while PyD500 adsorbed 42.2% of the nutrient in the solution. Phosphate sorption ability of PyD500 may be attributed to its pore distribution which provides more adsorption sites through which nutrients and water retained are made available to plants (Peng et al., 2011). Biochar is reported to be very efficient adsorbers for nitrate, phosphate and hydrophobic organic compounds (Lehmann et al., 2006) which may slowly be released into soil with time. DFW available PO_4^{3-} further indicates the digestate nutrients richness as bio-fertilizer.

The liming potential of biochar and the resultant effects of its pH on soil when applied at different rates are indicated in Table 6.6. Soil initial pH (8.3) rises with an increase in biochar application rates. The effect of biochar on soil pH is dependent on soil properties (Hossain et al., 2010; Nelson et al., 2011) and the observed effect depends on both soil and biochar characteristics. Application rate of 150 g/kg indicated the highest pH unit of 9.18 while at 10 g/kg the unit was 8.65. Hossain et al. (Hossain et al., 2010) reported pH unit change of 4.5 from the initial soil unit of 4.6 and biochar value of 8.2 whereas PyD500 amended sandy soil behaved contrary to reflect the complex interaction involved and the effect of soil properties and parent feed characteristics. The impact of biochar on soil pH should be monitored to determine the short or longevity of the trend. Although the EC is increasing, the apparent lowering pH of DFW on soil can be attributed to the presence of volatile fatty acids that becomes transient in alkaline soil (Joseph et al., 2010). The DFW may have increased significantly the conductivity of the precursor mostly due to the presence of the lignocellulose and water-soluble compounds (as earlier reported by Opatokun et al., 2016) and shown in the DTG thermograph of DFW and its WHC. Also the decrease in EC of soil after treatment with pyD500 could be due to the sequestration of salts by Cation Exchange Sites (CEC) present in the biochar at low levels of application. The soil might have reached a 'biochar saturation' point at which higher rates of application would result in biochar (and salts present in the biochar) to become soluble in soil solution thereby reducing the effect of salt sequestration. Generally, Biochar has higher CEC

than the raw material used to derive it. CEC tends to increase in biochar with an increase in pyrolysis temperature reaching (Nelissen et al., 2014). Conversely, PyD500 reduced drastically the initial 430 $\mu\text{S}/\text{cm}$ of the untreated soil before increasing with the rise in soil – biochar application rate.

Table 6 - 6: pH and electrical conductivity (EC) of soil solution (1:1 soil: water) for food waste digestate (DFW) and pyrolysed digestate at 500°C. Untreated soil has a pH of 8.3 and EC of 430 $\mu\text{S}/\text{cm}$

		Biochar application rate (g/Kg)			
		10	50	100	150
DFW	pH	8.08	7.73	7.59	7.6
	EC ($\mu\text{S} / \text{cm}$)	848	1607	2042	3970
PyD500	pH	8.65	8.75	8.94	9.18
	EC ($\mu\text{S} / \text{cm}$)	251	327	387	466

The difference between soil moisture at field capacity (0.3 bar) and permanent wilting point (15 bar) for PyD500 and DFW were presented in 6. 5. Interestingly, DFW not only provided nutrients quickly but equally responded positively with continuous increase in plant available water (at negligible error internal) along application rate. PyD500 clearly decreases the plant available water of the mixture when compared to untreated soil and subsequently indicated no change, despite the increase in application rates. Lowering of available water by PyD500 treated soil may be specific to this soil or due to complex interaction of the interstitial biochar-sand space and the pores within the biochar grains, which influence porosity of the mixture as, reported by Barnes and co-workers (Barnes et al., 2014). The digestate (DFW) provided 40% (0.4 g/cm^3) available water at application rate of 100 g/kg , which is almost double of the PyD500 performance at the same application rate (see Figure 6.5). This transient effect of PyD500 on this soil should transcend physical (WHC, thermal properties and aggregation effect) benefits rather than alter the chemical (disintegration of leachable ash, soil pH alteration) and biological (improvement of microbial activities) (Shackley et al., 2010) components of the soil. Therefore, observing the short and long term effects of organic load content of DFW and the surface

chemistry of PyD500 are imperative for proper understanding of their application on this and other soils.

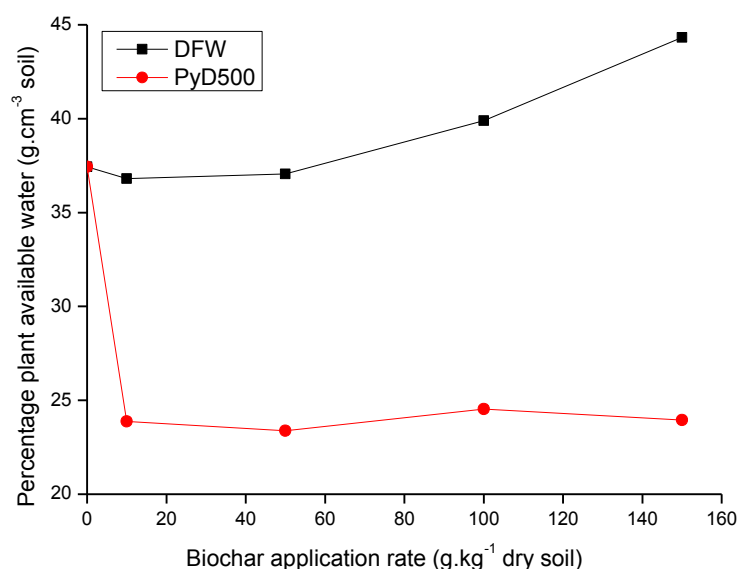


Figure 6 - 5: Volumetric available water for (a) digestate (DFW) and (b) pyrolysed food waste digestate at 500°C (PyD500) at application rate of 10, 50, 100 and 150 g/kg

Crop yields performance of DFW incorporated soil is expected to improve significantly compared to PyD500-treated soil since yields are enhanced by plant available water, which consequently influences nutrient accessibility (Karhu et al., 2011). DFW potential to attenuate loss organic matter suffered by the sandy soil may be attributed to the performance. Meanwhile, determining the proper concentration or application rate of the digestate is crucial to avoid terrestrial eco-toxicity inflation (Pivato et al., 2015). It is also important to note that 20% plant available water and 40.9% WHC entrenched through PyD500 on sandy soil are equally substantial to arid regions, not only because irrigation rates may reduce, but also provide a source of stable carbon to the soil after extraction of the energy in the digestate.

6.4 Conclusions

In this study, digestate from food waste (DFW) and biochars produced from DFW at various pyrolysis temperatures (300, 400, 500 and 700°C) were characterized and evaluated for their potential use in agronomic applications. Specifically, DFW and biochars were evaluated for plant macronutrients (N, P, K), micronutrients (e.g. Fe), water holding capacity (WHC), and plant germination index (GI) using tomato seeds. The increase in pyrolysis temperature used in the conversion of DFW to biochars decreased total nitrogen, but increased the concentration of macronutrients (P, K) as well as most of the other micronutrients. The WHC of biochars were similar (~40%) but lower than DFW (~60%). However, DFW showed phytotoxicity in tomatoes as indicated with a low GI (~40%) when compared to biochars, all of which had GI above 100%. The biochar produced at 500°C (PyD500) was also evaluated for its thermal resistance and its potential application to soil. The TG and DTG profile of PyD500 suggested higher thermal stability because it only showed 9.1% mass loss compared to 58.5% for DFW. Treatment of a sandy textured soil with PyD500 (application rates up to 150 g per kg soil) increased soil pH and resulted in less plant available water (~23%) when compared to untreated soil control (~37%). This observation suggests PyD500 is not useful for soil application if it is intended to increase the water holding capacity of soil. However, it is potentially useful as a liming agent. It is important to note that the interaction of biochar with soil is a complex process that depends on the physicochemical properties of both biochar and soil. Therefore, the evaluation of PyD500 for its applications as a soil product requires further investigation using different soils. Collectively, the enrichment of DFW derived biochars with plant macro and micronutrients combined with the observed positive effect on seed germination suggests their potential utility in agronomic applications. Valorisation of food waste digestate to biochar is an opportunity to further extract energy from the material while maintaining its original intended use in agriculture.

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Environmental Burdens and Benefits of Food Waste Treatments Scenarios: A Life Cycle Analysis Perspective

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Abstract

The life cycle assessment (LCA) of industrial anaerobic digestion (AD), pyrolysis and Integrated system (AD sequence with pyrolysis) end of life (EOL) scenario for the treatment of food waste were presented aiming at evaluating the environmental performance associated with these treatment options. The scenarios are modelled using SimaPro V.8 and results are primarily based on ReCiPe characterisation method. The results shows that all the case studies are environmentally viable and better options than the conventional landfilling of the food wastes based on the considered impact categories. The integrated treatment system indicated similar environmental benefits with AD despite the increased energy harvested and valuable products (biochar and bio-oil) provided. Pyrolysis illustrated the highest burdens across the categories such as water depletion, fossil fuel depletion and mineral depletion however, remains more eco-friendlier than conventional landfilling of food waste. Dewatering phase in the AD process accounted for 70% of the treatment impact while substrate pre-treatment is responsible for the overall burdens in the pyrolysis process. The study shows the effect of waste treatment choice on the sustainability of the process and the products. Thus, provides decision-makers insight into environmental impacts related to sustainable industrial food waste treatment or planning.

Keywords

Life cycle assessment (LCA), environment, end-of-life (EOL), food, management scenarios

NOMENCLATURE

EOL: End of Life

LCA: Life Cycle Assessment

LCI: Life Cycle Inventory

CC: Climate Change

OD: Ozone Depletion

TA: Terrestrial Acidification

FE: Fresh water Eutrophication

ME: Marine Eutrophication

HTox: Human Toxicity

POF: Photochemical Oxidant Formation

PMF: Particulate Matter Formation

TEcox: Terrestrial Ecotoxicity

FEcox: Fresh water Ecotoxicity

MEcox: Marine Ecotoxicity

WD: Water Depletion

MD: Minerals Depletion

FD: Fossil fuel Depletion

AD: Anaerobic Digestion

MSW: Municipal Solid Waste

CHP: Combine Heat and Power

7.1 Introduction

Food waste management has rapidly been influenced by local and regional policies to ensure recycling, resource optimisation and mitigation of environmental impacts. Waste management, food and energy security, climate change and resource recovery are the primary concerns [1] shaping waste treatment and process adoption across the globe. The renewed acceptance of anaerobic digestion (AD) in some countries, such as Australia and the European union (EU) member states, is closely associated with the Renewable Directives and the Waste Framework Directives for renewable energy target against 2020 [2], while organic waste management in developing countries are hinged on international initiatives, such as sustainable development and resource conservation [3]. The ease at which wet biomass is treated without pre-treatment to harvest energy and digestate may fundamentally be responsible for AD acceptance.

About 14 Million functional small-scale digesters were developed in China and 50,000 estimated in Nepal [3], while Germany leading role in EU is expected if her 30% increase projection of the current 7000 small and large scale on farm AD system are fulfilled by 2020 [2]. However, constraints associated with digestate utilisation or disposal include physical and chemical (heavy metals and organic pollutants) impurities, pathogens and biological matter concentrations [4], distribution and mineralisation dynamics of digestate nutrients in soil [5], and quality management [6], . Many studies delineated the merits of liquid (digestates with total solid (TS) range of 0.5 to 15%) and solid (digestates with TS > 15%) residues [7] as bio-fertilizers [6, 8-10]. Recently, energy extraction from digestate using pyrolysis is reported as another sustainable management measure [11, 12] to extract energy from this bio-resistant or non-biodegradable organic product of the AD system. The soil enhancement and other environmental potential [13-15] of the biochar (black carbonaceous residue) from the thermochemical process are thus exploited.

Monitoring and quantifying the inputs and outputs of these treatment processes (anaerobic digestion and pyrolysis) and their resultant products through a life cycle pattern expectedly enables identification of emissions, wastes and more environmentally sustainable options in the system [2] which consequently ensures sustainability of policy and its implementation. Life cycle assessment (LCA) is an established technique for environmental and socio-economic analysis wherein system

inputs (materials, energy and others) are adequately correlated with the outputs (product, waste and emissions) using standard methodologies with the aim of improving the system environmentally and economically. However, LCA of waste treatment are often based on single treatment technique coupled with daunting uncertainties which make them extremely case specific with data unconnected to specific plant or functional scenarios [16, 17].

Multiple or isolated treatment options mirrored through environmental metrics for food wastes management may be a potential measure to utilise the increase in global food waste production. This strategy is imperative as waste management industries transit from mere waste treatment and disposal to being active suppliers of energy and recovered materials [18].

This study evaluates and compares the environmental performance of three end of life (EOL) management scenarios for food waste treatment processes and their resultant products with focus on the environmental benefits and burdens using selected impact categories as characterised by the LCA methodology.

7.2 Methodology

The LCA is an established methodology, both technically and scientifically [19], and proposed by the standard ISO 14040 [20]. This methodology was synthesised in four interrelated phases: goal and scope definition, inventory analysis, impact evaluation and interpretation, where the old data will be replaced with new, leading to a more realistic evaluation [21] and [22].

The inputs and outputs of each end of life (EOL) management scenario were defined, and the inventory developed were calculated using SimaPro v.8 [23]. In this study, the midpoint approach is used to evaluate the environmental impact using the ReCiPe method [24, 25], since it is one of the most recent and harmonised indicator approaches. Although the method is able to calculate eighteen midpoint indicators, this study was focused on: climate change (CC), ozone depletion (OD), terrestrial acidification (TA), fresh water eutrophication (FE), marine eutrophication (ME), human toxicity (HTox), photochemical oxidant formation (POF), particulate matter formation (PMF), terrestrial

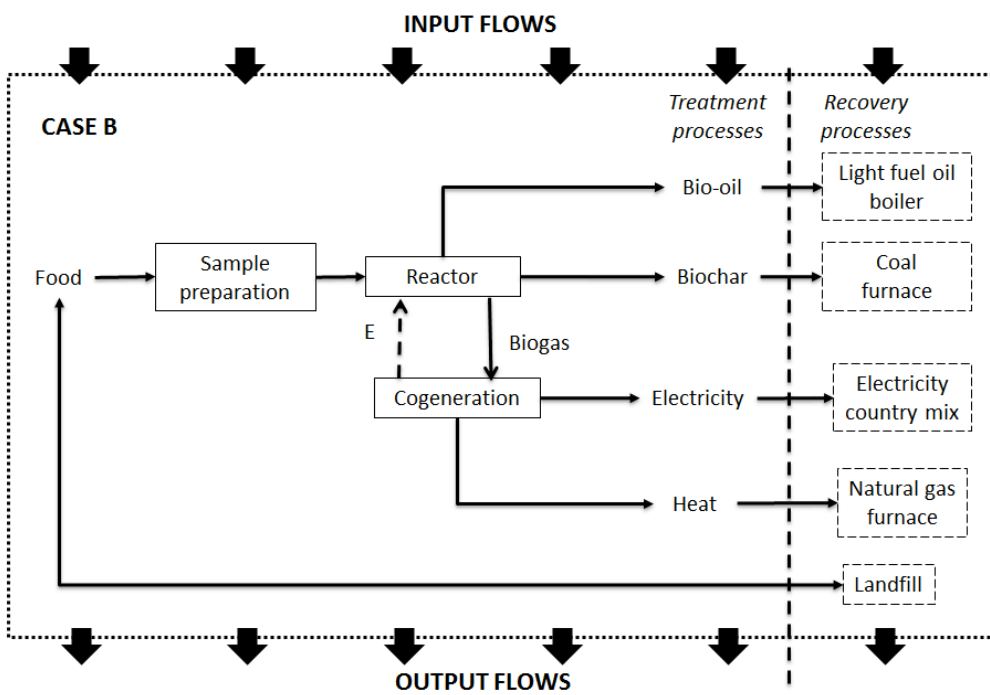
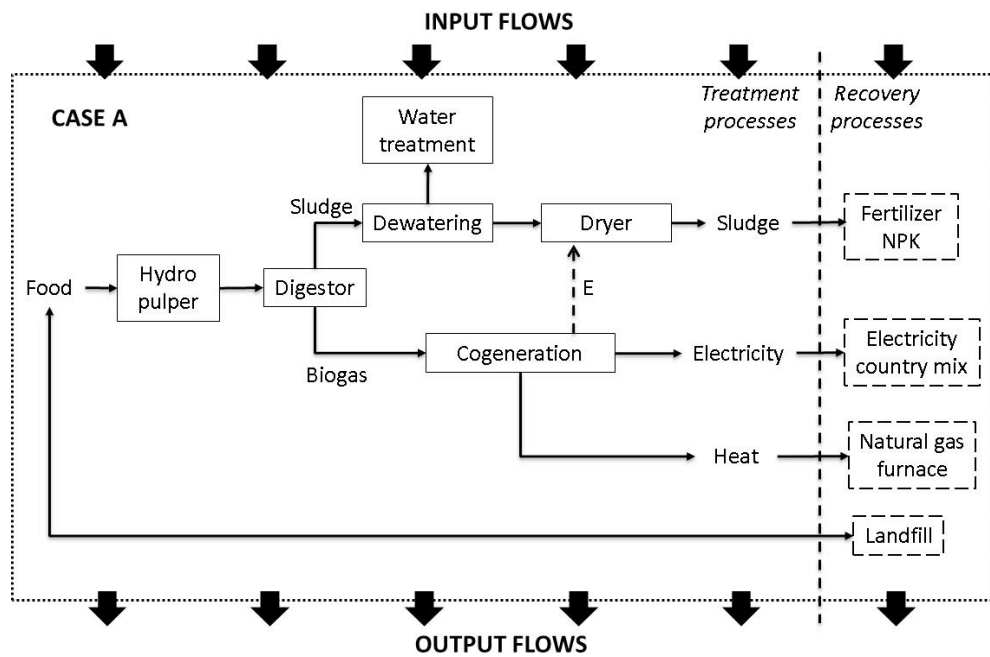
ecotoxicity (TEco_x), fresh water ecotoxicity (FEco_x) marine ecotoxicity (MEco_x), water depletion (WD), minerals depletion (MD) and fossil fuel depletion (FD).

7.2.1 Scope of the analysis and functional unit

This study proposes an environmental analysis based on the LCA methodology to identify impact preventive measures and system improvement strategies necessary to improve the environmental performance of an existing industrial food waste treatment process. Alternative end-of-life (EOL) management scenarios, such as anaerobic digestion, pyrolysis or integrated system (sequence or integration of anaerobic digestion and pyrolysis) are promoted to reduce the amount of food landfilled while obtaining valuable by-products (bio-fertilizer, biochar, bio-oil and biogas) for other uses or applications. Therefore, it is necessary to provide a reference through which the process inputs and outputs are correlated. In this study, 1 kg of food waste was established as the functional unit.

7.2.2 System description and boundaries

As seen in Figure 7- 1, the assessment focused on three different EOL scenarios to manage food waste. Considering this approach, previous stages related to the food production and use phase are not included in this analysis, since they can be considered as independent of the scenario evaluated. Only the material and energy inputs and outputs associated with the different EOL treatment processes and the strategies for application of the generated by-product are inside the system boundaries, excluding the existing infrastructure. Moreover, in view of the goal of the assessment, disposal in a landfill was considered as the conventional management option.



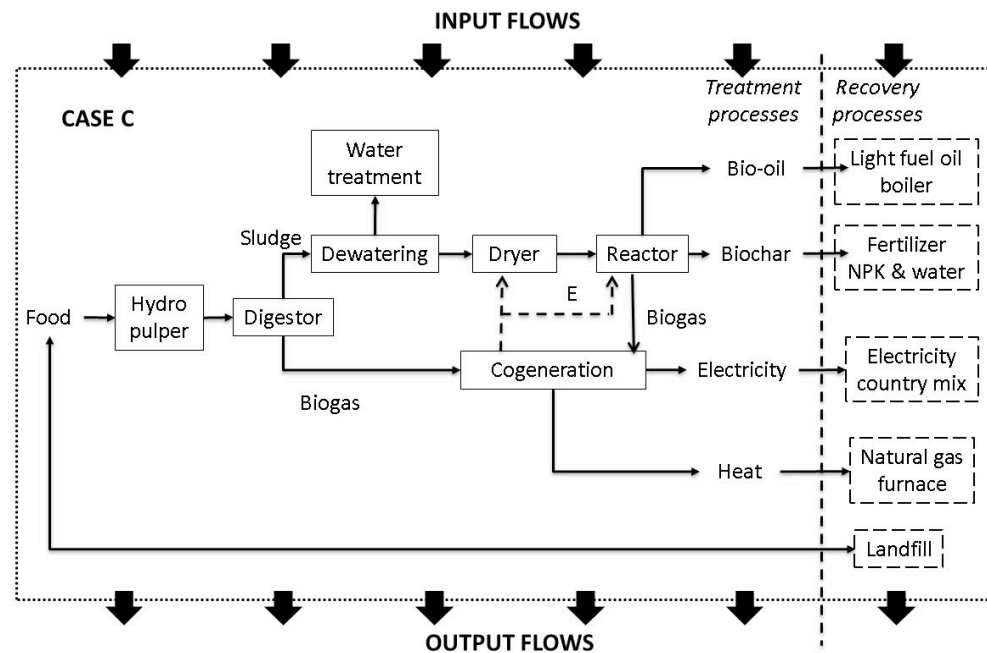


Figure 7- 1: System boundaries of the three EOL management scenarios including the definition of the treatment and recovery processes: Case A: Anaerobic digestion; Case B: Pyrolysis; and Case C: Integrated or sequenced anaerobic digestion and pyrolysis system

Since the electricity consumption is an important parameter, relevant consideration to take into account is the local energy supply mix [17]. In this case, the assessment was developed considering the Australian country mix as at 2013. Figure 7- 2 shows the distribution per sources of the electricity generation across the country, which accounts for a high ratio of fossil fuels (86%), especially of coal (73%) and natural gas (13%) [26]. As a final assumption, the evaluation was carried out excluding the infrastructure impact associated to the three scenarios studied.

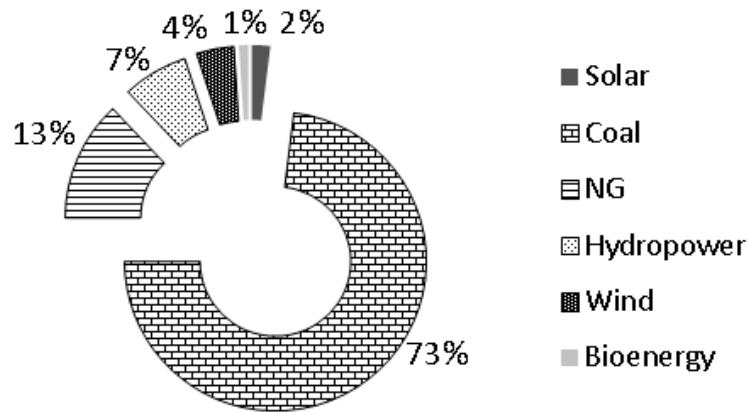


Figure 7- 2: Australian electricity mix in 2013 (Origin [26])

7.2.3 EOL management scenarios description

The current policy driven stance of AD for energy extraction in most EU countries and Australia makes imperative an evaluation of the process and other related processes in the management of food waste. An industrial one-stage anaerobic digestion (henceforth refer to as AD) plant designated predominantly for food waste treatment and provision of electricity to the Australia national grid was compared with a parallel pyrolysis treatment and an integrated treatment process (wherein AD was sequenced with pyrolysis) for optimal energy extraction. These three food waste treatment pathways were analysed and compared as sustainable means of further valorising the generated food wastes.

7.2.3.1 Anaerobic digestion process

Anaerobic digestion (AD) is the microbial degradation of food waste or organics in the absence of molecular oxygen to produce bio-methane gas, liquid and solid residues as annotated in Case A of Figure 1. The one-stage AD treatment plant (1000 tonnes per week capacity) typically collects suitable solid and liquid organic food waste material from the industrial, commercial and residential sectors and converts it to energy and nutrient-rich fertiliser. The mesophilic AD system generates methane, which is converted to electricity (supplied to the national grid for distribution) and heat through the combined heat and power (CHP) system. Some of the operational data of the AD process may be obtained in the authors previous studies [12, 27], as summarised in Table 1 to Table 3 respectively. Part of the heat generated is used for the de-watering of

digestate, control AD process and feedstock sterilisation when necessary. Process parameters, such as temperature and retention time (RT), are important to AD performance [28], especially at industrial scale. Operational cost of maintaining sludge heat for microbial activities and mixing in the reactor accounts for RT trade-off which results in residues with potential for energy recovery, such as those targeted in the proposed integrated system (Case C).

7.2.3.2 Pyrolysis treatment process

Pyrolysis is an endothermic process through which pre-treated (dried) food waste or bio-resistant digestate is thermally degraded for production of biogas, biochar and bio-oil. Details of energy distribution, yield and characterisation results of these products produced at industrial pyrolysis temperature (500°C) were present in previous studies [12, 27]. Heating rate may be leveraged on to influence of the choice of products during pyrolysis. Slow heating rate ensures higher biochar yields while fast rate (100°C/min) is dominated by bio-oil or biogas. The gas produced is expected to be co-generated (CHP) to electricity while the resultant heat is budgeted for the food waste pre-treatment, as indicated in the schematic diagram (see Case B in Figure 1). Other related input and output data of this scenario are presented in Table 1.

7.2.3.3 Integrated treatment process

The integrated treatment process implied sequence or combining both anaerobic digestion and pyrolysis processes, as shown in Case C of Figure 1. The summary of the inputs and outputs are also provided in Table 1.

7.2.4 Life Cycle Inventory

The Life Cycle Inventory (LCI) includes the energy and material involved in the analysis of the EOL scenarios. These data were obtained by the combination of different sources; mainly from a functional industrial one-stage anaerobic digestion food waste treatment plant in Sydney, in-house laboratory tests and analysis of samples carried out at Macquarie University using the data published previously by the authors [12, 27] and standardized Eco-invent 3.1 database [29]. Material and energy consumption associated with the waste treatment processes involved in the pyrolysis and the proposed integrated management scenarios were obtained from the in-house experimental trials. Since the industrial scale pyrolysis provides the inert condition

simulated by N₂ in the laboratory scale, nitrogen was therefore excluded in the evaluation while maintaining other data obtained through the lab-scale pyrolysis trials. On the other hand, data supported by Eco-invent database [29] after validation was selected to characterize the modelling and use on the valuable by-products and the conventional landfill scenario. Table 7.1 show the most relevant data included in the LCI considering the case studies and system boundaries defined in Figure 1. Additionally, it is necessary to take into account the materials and energies saved or conserved through the recovery or recycling of useful products generated by the treatment processes as included in the description of the EOL management scenarios (Figure 7- 1). For instance, in case A (digestion), the material saved by using digestate as a conventional fertilizer and the grid electricity saved were included in the evaluation. In case B (pyrolysis), besides the grid energy saved, fossil fuel consumption was treated as potential saving, since bio-oil was considered as substitute for light fuel oil in boilers and biochar was characterized as substitute for coal in industrial furnaces for heat production. This assumption was predicated on the physicochemical properties of the pyrolysed raw food waste as detailed in previous study [27]. In case C (integrated digestion and pyrolysis system), similar recovery actions for electricity generated from bio-oil alongside the cogeneration while biochar produced in this scenario was considered as a conventional fertilizer due its nutrient richness and water retention potential (consequently, saving irrigation water) and equally replace digestate function as bio-fertilizer were assumed. Finally, it's important to note that the heat generated in the CHP (indicated in the Figure with dotted arrow lines) are not considered as inputs since they are within the boundaries under consideration as shown in the illustrated system boundaries (see Figure 7.1).

Table 7-1: Main inputs and outputs related to anaerobic digestion (Case A), Pyrolysis (Case B) and Integration of AD and pyrolysis (Case C)

MAIN INPUTS			MAIN OUTPUTS	
CASE A	Food waste	1 kg	Electricity from biogas (CHP)	0.240 kWh
	Water	0.569 kg	Heat*	0.369 kWh
	Electricity	0.008 kWh	Organic fertilizer	0.030 kg
	Caustic soda	0.005 kg		
CASE B	Food waste	1 kg	Electricity from biogas (CHP)	0.026 kWh
			Heat*	0.020 kWh
			Biochar	0.097 kg
			Bio-oil	0.181 kg
CASE C	Food waste	1 kg	Electricity from biogas (CHP)	0.242 kWh
	Water	0.569 kg	Heat*	0.365 kWh
	Electricity	0.136 kWh	Biochar	0.013 kg
	Caustic soda	0.005 kg	Bio-oil	0.016 kg

*Heat remained after covering the energy require along the process

7.2.5 Cut-off criteria

All relevant environmental impacts were incorporated in the study through the following cut-off criteria:

(i) Materials: Flows < 1% of the cumulative mass of the inputs and outputs are excluded due to their environmental irrelevance which predicates on the type of flow of the LCI. However, this sum of the neglected material flows does not exceed 5% of the mass, energy or environmental relevance.

(ii) Energy: Flows < 1% of the cumulative energy of all the inputs and outputs (depending on the type of flow) of the LCI model, are excluded from this analysis. Their environmental relevance is equally not a concern.

These criteria were established based on a thorough analysis of the system with adequate evaluation of energy and mass balances of the processes involved.

7.3 RESULTS AND DISCUSSION

7.3.1 Case A: Anaerobic digestion (AD)

The environmental impact results of industrial one stage anaerobic digestion treatment as EOL management scenario are summarised in Table 7.2, considering the midpoint categories analysed by the ReCiPe method.

Table 7-2: Environmental impact for Case A

Impact category	Unit	Treatment processes	By-products use and landfill avoided	Total
Climate change	g CO ₂ eq	144.22	-901.38	-757.16
Ozone depletion	µg CFC-11 eq	4.79	-5.24	-0.45
Terrestrial acidification	g SO ₂ eq	0.57	-1.90	-1.33
Fresh water eutrophication	g P eq	0.22	-0.42	-0.21
Marine eutrophication	g N eq	0.06	-2.94	-2.88
Human toxicity	g 1,4-DB eq	2.33	-12.85	-10.52
Photochemical oxidant formation	g NMVOC	0.34	-1.10	-0.75
Particle matter formation	g PM10 eq	0.17	-0.56	-0.39
Terrestrial ecotoxicity	g 1,4-DB eq	0.01	-0.03	-0.02
Fresh water ecotoxicity	g 1,4-DB eq	0.01	-0.18	-0.17
Marine ecotoxicity	g 1,4-DB eq	0.02	-0.22	-0.20
Water depletion	l	327.29	-918.85	-591.56
Minerals depletion	g Fe eq	0.50	-0.99	-0.49
Fossil fuel depletion	g oil eq	37.55	-125.48	-87.94

The negative values observed in the results represent environmental benefits in the analysed impact categories, while positive values refers to environmental impacts. The results demonstrate that the case A achieved the highest environmental benefits along the whole value chain of this EOL management scenario. This means that, although the food refuse treatment process carried out entailed environmental impacts for all the indicators, these impacts were compensated through the energies generated by the biogas and the digestate substituting for synthetic fertilizer, thus, enabling large enough conventional EOL disposal to balance the rest of the contributed impacts.

The environmental burdens and benefits associated with specific phases and stages of AD treatment process are shown in Figure 7- 3. The most impacting stage for all the indicators is the dewatering process, which accounts for more than 70% of the total impact associated to the AD treatment processes. Specifically, OD rose to about 84% to indicate the highest impact category. The inclusion of wastewater treatment in the dewatering stage may have accounted for the burdens and consequently increased the overall impact. On a broader perspective, the electricity consumption associated with the wastewater treatment related the most relevant impact, while OD indicator was specifically influenced by the sodium hydroxide used. High quantities of tetrachloromethane (CFC-10) emissions are involved during NaOH productions, which are factored for its use in the wastewater treatment. In addition, although the dryer energy demand was sourced from the heat generated by the CHP, this equally includes impacts associated with wastewater treatment, which consequently accounted for an average of 11% of the impacts. Similarly, the hydropulper stage impacts were indicated to be driven by electricity and water used during the phase. Interestingly, the microbial digestion phase delineated the least impact due low electricity demand of this treatment phase.

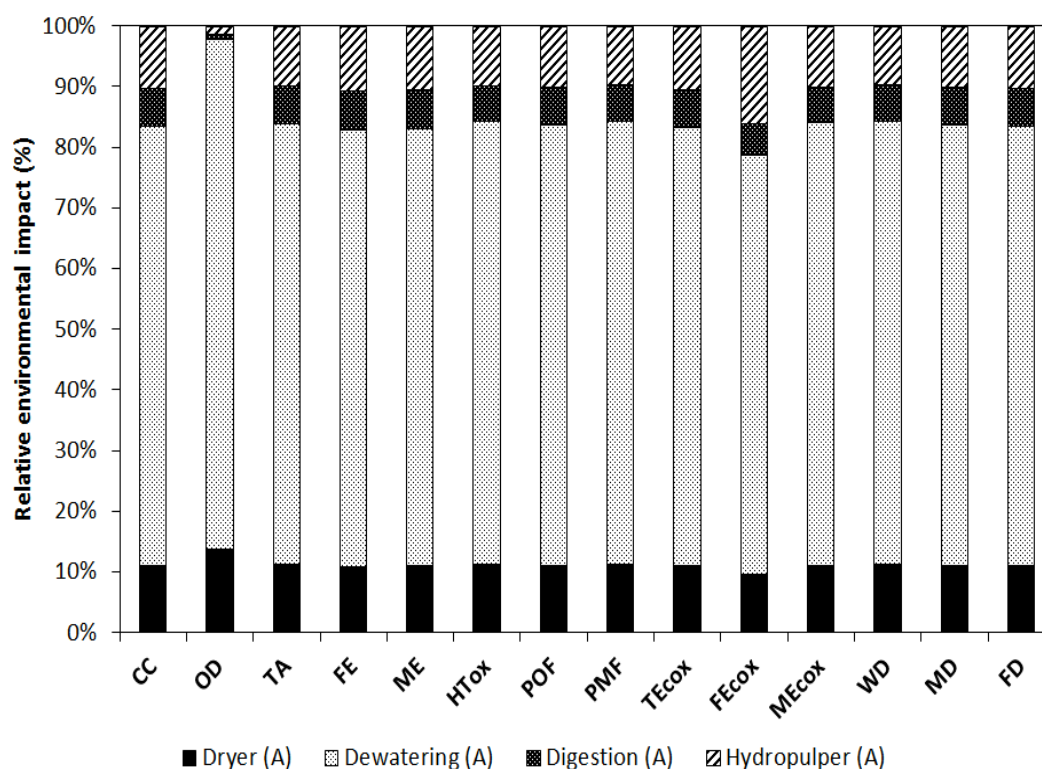


Figure 7- 3: Environmental impacts for the industrial one stage anaerobic digestion treatment process

On the other hand, Figure 7- 4 shows the environmental benefits obtained by the application of the AD by-products and the avoided landfilling implications. In this case, recovery process performance was predicated on the indicator choice. Some indicators, such as TA, FE, POF, PMF, TEcox, WD and FD, were specially affected by the Australian electricity production that would be avoided considering the electricity production by biogas cogeneration. Nevertheless, other indicators reflected the fertilizer role of digestate, for example OD, HTox, MEcox, and MD were more sensible to the fact that synthetic fertilizer production can be avoided by the use of digestate produced during the AD treatment system. Particularly averted is the high burden associated to urea and phosphate production, which is one of the main material inputs during the manufacturing of synthetic NPK fertilizers. Additionally, the conventional EOL scenario (landfill avoidance) had a significant relevance for the environmental categories CC, ME and FEcox. The excess heat generated during the cogeneration stage is another benefit when recycled into the system or deployed in industrial

furnaces, thus avoiding natural gas consumption. Nevertheless, no relevant contribution was provided by the intervention to any of the environmental categories.

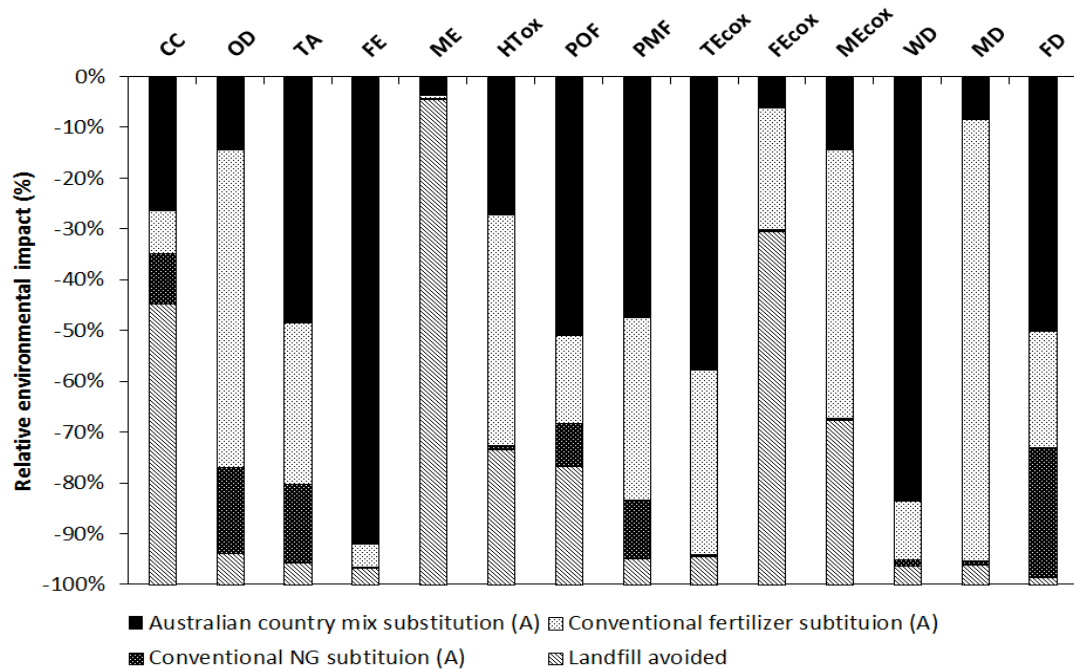


Figure 7- 4: Environmental impacts for the recovery processes included in Case A

7.3.2 Case B: Pyrolysis

The environmental impact results obtained in the midpoint analysis using ReCiPe method for pyrolysis treatment process are summarised in Table 7.3

In this scenario, the results showed different behaviour depending on the indicator analysed. Prominent environmental burdens were indicated especially on FE and FD followed by PMF and TEcox while, CC, OD, ME, HTox, FEcox and MEcox of this EOL management scenario delineated environmental benefits along the whole value chain. The neutralising effect of the energies and materials produced during the thermochemical treatment may be attributed to the afore-mentioned impact categories.

Table 7-3: Environmental impact for Case B

Impact category	Unit	Treatment processes	By-products use and landfill avoided	Total
Climate change	g CO ₂ eq	683.11	-809.08	-125.97
Ozone depletion	µg CFC-11 eq	2.82	-14.63	-11.82
Terrestrial acidification	g SO ₂ eq	2.61	-1.19	1.43
Fresh water eutrophication	g P eq	1.07	-0.10	0.96
Marine eutrophication	g N eq	0.29	-2.84	-2.56
Human toxicity	g 1,4-DB eq	10.27	-12.59	-2.32
Photochemical oxidant formation	g NMVOC	1.59	-1.39	0.20
Particle matter formation	g PM10 eq	0.76	-0.45	0.31
Terrestrial ecotoxicity	g 1,4-DB eq	0.04	-0.01	0.03
Fresh water ecotoxicity	g 1,4-DB eq	0.03	-0.14	-0.11
Marine ecotoxicity	g 1,4-DB eq	0.10	-0.12	-0.02
Water depletion	l	1457.88	-164.09	1293.79
Minerals depletion	g Fe eq	2.32	-0.14	2.18
Fossil fuel depletion	g oil eq	178.34	-81.38	96.97

Food waste preparation or pre-treatment and its carbonisation (pyrolysis) stages relative impacts are depicted in Figure 7- 5. The feedstock pre-treatment (moisture removal) accounts for impact in all the indicators analysed, particularly, due to the associated electricity consumption. Recycling the heat generated during electricity production equally compensated for some of the system energy demand.

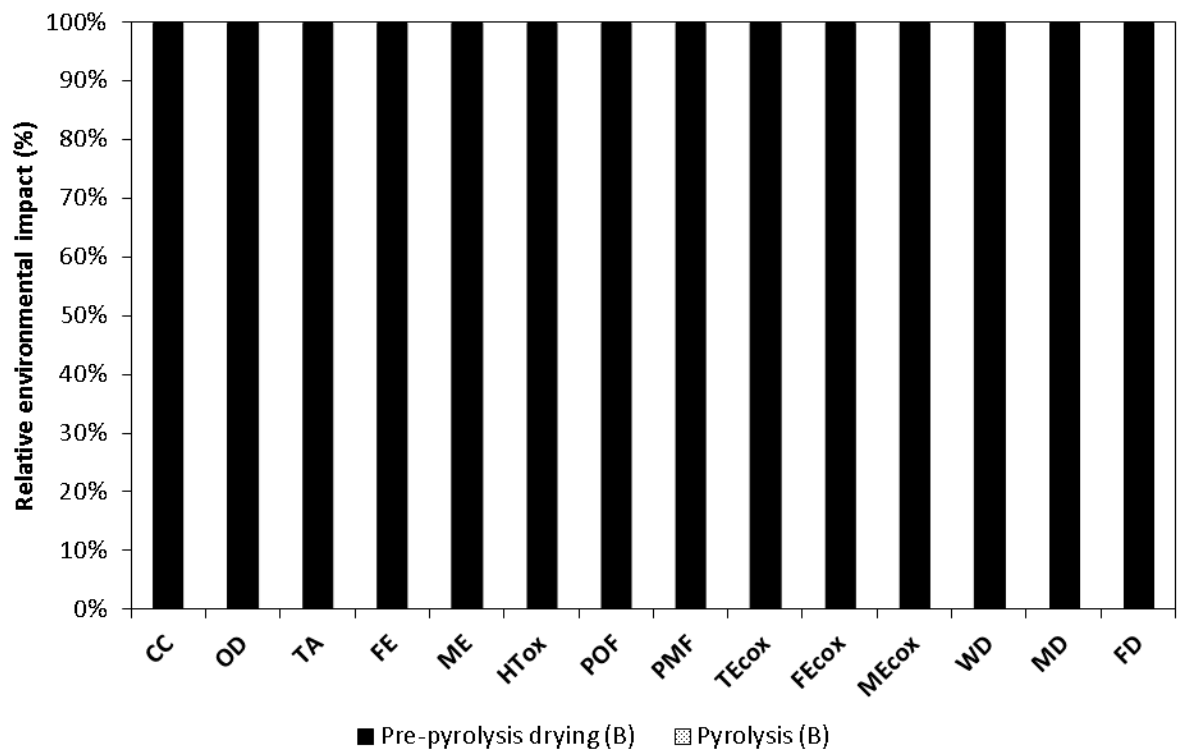


Figure 7- 5: Environmental impacts for the treatment processes included in Case B

On the other hand, Figure 7- 6 shows the environmental benefits obtained by the use of the by-products (biogas, bio-oil and biochar) generated in this scenario and the avoided landfilling implications. Similar to the Case A, it was found that variation in the performance of the indicator is a function of the considered product utilisation choice. The benefits obtained by the use of the biochar obtained to substitute coal in industrial furnaces and the avoided conventional landfill disposal had the highest impact in most of the indicators. For example, coal replacement with biochar influenced specifically TA, FE, HTox, POF, PMF, TECox and MD categories accounting for relative benefits from 43% (TEcox) to 72% (PMF) while the averted landfill disposal had a high relevance in CC, ME, FEcox and MEcox with relative benefits from 61% to 99%. The other options considered for the utilisation of the obtained by-products only show the predominant relevance in three of the categories analysed that is the WD in case of electricity generation from biogas through the CHP which prevents grid electricity consumption. Similarly, the OD and FD in case of bio-oil used to substitute

light fuel oil in boilers due to the impacts avoided and associated to the fossil fuel production.

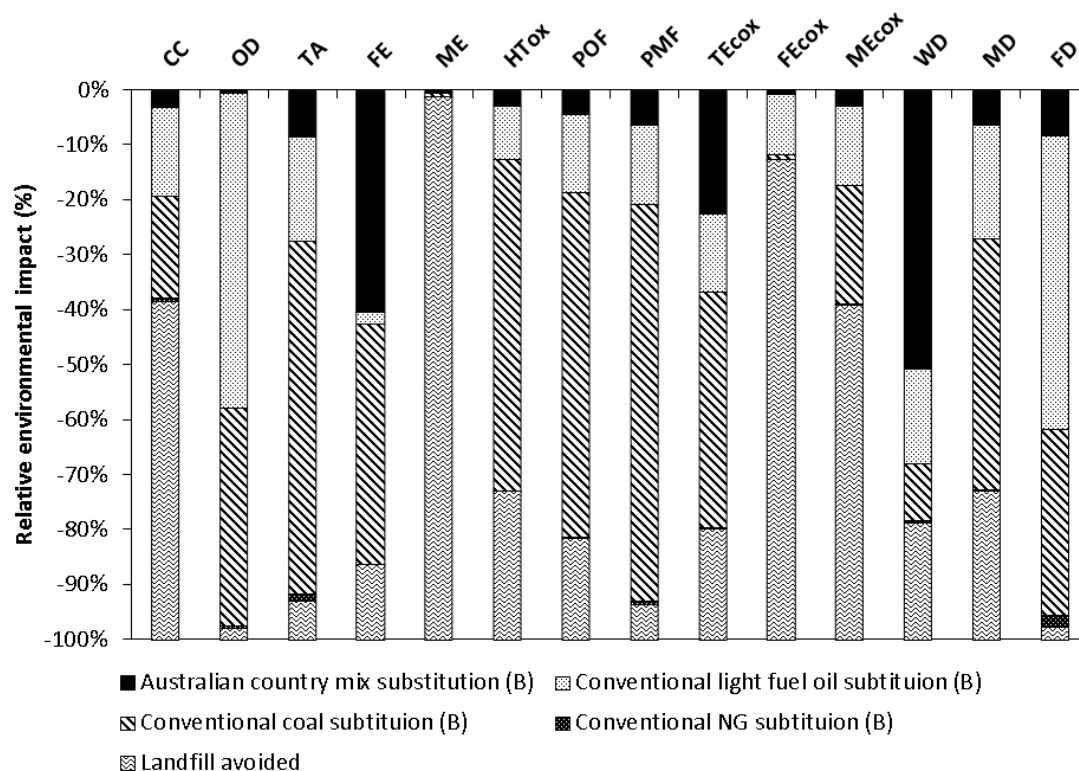


Figure 7- 6 Environmental impacts for the recovery processes included in Case B

7.3.3 Case C: Integrated system

The environmental burdens related to the integrated food waste EOL management scenario wherein AD treatment is sequenced by pyrolysis are summarised in Table , considering the midpoint categories analysed by the ReCiPe method. This EOL management scenario revealed the environmental benefits throughout the considered environmental categories, except for OD with a burden along the entire value chain. Expectedly, material and energies (since more combustible biogas is produced) substitution through by-products coupled with conventional EOL disposal are robust enough to compensate for the impacts associated with this food waste treatment process.

Table 7-4: Environmental impact for Case C

Impact category	Unit	Treatment processes	By-products use and landfill avoided	Total
Climate change	g CO ₂ eq	144.22	-865.66	-721.44
Ozone depletion	µg CFC-11 eq	4.79	-3.88	0.91
Terrestrial acidification	g SO ₂ eq	0.57	-1.57	-1.00
Fresh water eutrophication	g P eq	0.22	-0.42	-0.21
Marine eutrophication	g N eq	0.06	-2.92	-2.87
Human toxicity	g 1,4-DB eq	2.33	-9.74	-7.41
Photochemical oxidant formation	g NMVOC	0.34	-1.01	-0.67
Particle matter formation	g PM10 eq	0.17	-0.46	-0.29
Terrestrial ecotoxicity	g 1,4-DB eq	0.01	-0.02	-0.01
Fresh water ecotoxicity	g 1,4-DB eq	0.01	-0.17	-0.16
Marine ecotoxicity	g 1,4-DB eq	0.02	-0.16	-0.14
Water depletion	l	327.29	-882.02	-554.73
Minerals depletion	g Fe eq	0.50	-0.64	-0.14
Fossil fuel depletion	g oil eq	37.55	-110.17	-72.63

In the integration scenario C pyrolysis assumes processing of the dried digestate. Moreover, the biochar produced is expected to replace the agronomic role of digestate due to the char NPK nominal properties and its water holding capacity. Therefore, the relative global impact contribution of the system stages were analysed as depicted in Figure 7- 7. Again the dewatering process constitutes more than 65% of the impacts in all the indicators included in this study. The main reason is the wastewater treatment included in the dewatering stage. However, the rest of the processes had a distributed impact to the environmental categories. Hydro-pulper and drying component of the integrated system provided impacts around 10-16% respectively, while the environmental burdens of the digestion process are less than 6% of the impacts across different indicators.

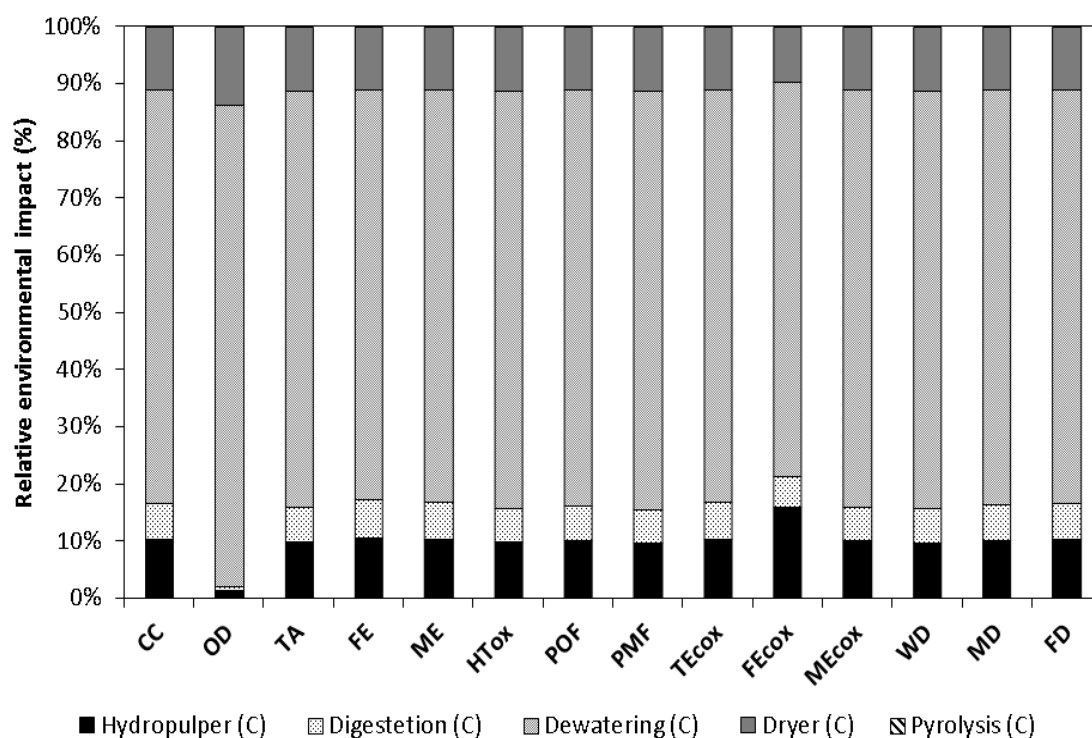


Figure 7- 7: Environmental impacts for the treatment processes included in Case C

The environmental benefits obtained by virtue of utilising the by-product generated in this scenario and the avoided landfill are shown in Figure 7- 8. The two main relevant factors that accrue this treatment option the highest environmental gains are electricity generation (through the CHP from the biogas produced consequently through which mix electricity consumption are avoided) and the avoided landfill use. The Australian electricity production had an important impact from the hard coal activities involved indicators such as TA, FE, HTox, POF, PMF, TEcox, WD and FD, which were avoided to imply benefits for the process. Additionally, the benefits from the avoided landfill use were profound for ME, FEcox CC, and MEcox due to the associated treatments. The avoided conventional fertilizer production by using the biochar equally accounts for about 80% and 30% of the total impacts for MD and OD respectively in these categories. Since NPK type of fertilizer was considered, the MD was particularly affected by the potassium chloride and the urea production had an important influence in the OD indicator.

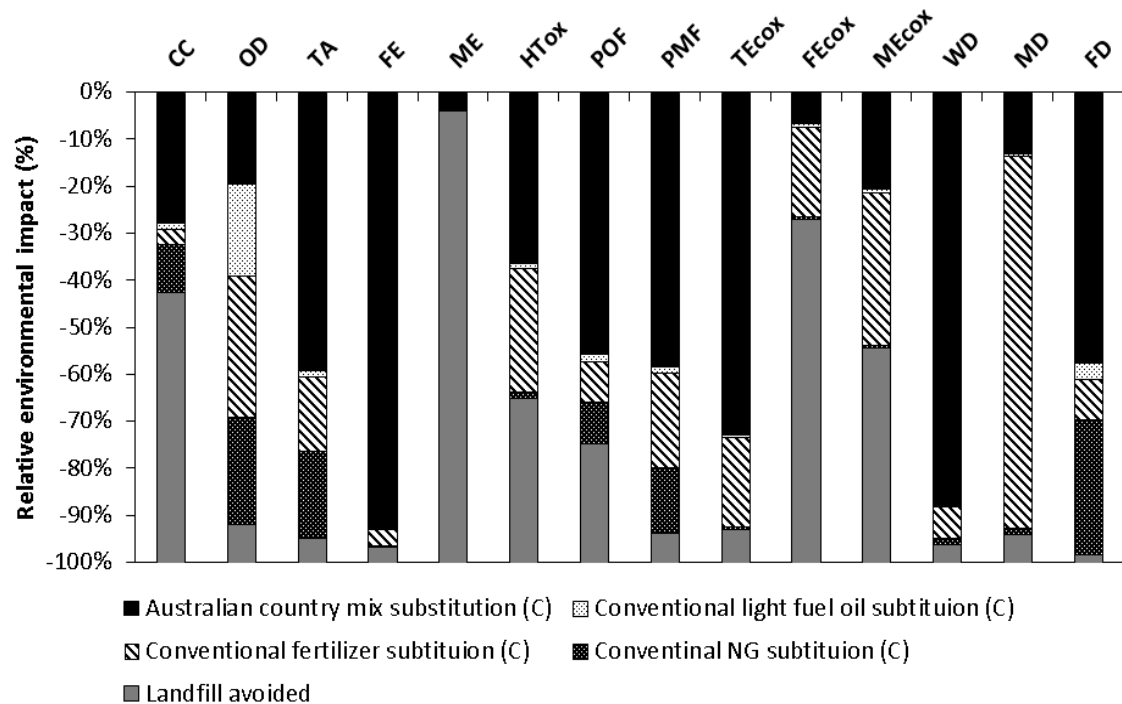


Figure 7- 8: Environmental impacts for the recovery processes included in Case C

7.3.4 Comparison of the EOL management scenarios analysed

The overall environmental performance of the scenarios as related to environmental burdens entrenched were compared and equally related to the conventional landfill option as shown in Table . Although some indicators showed impacts in cases B and C, the results evinced that all the case studies were environmentally viable and better options than the conventional landfilling of the food wastes as indicated by all impact categories. Despite, the degree of burdens in some of the EOL management scenario such as pyrolysis, when compared to conventional landfilling, the latter impacts are significant with 4000% higher FE and FD against the former. Meanwhile, the overall impacts reduction of the EOL management scenarios considered in this study are more than 100%.

Comparatively out of the three scenarios, Case B was the least environmentally favoured with overall environmental impacts for FD, FE, PMF, TEcox, MD, POF, TA and WD categories (see Table). The integrated scenario C only exhibited an overall environmental impact for ozone depletion (OD) while the AD treatment process

indicated environmental benefits in all the impact categories. Case C and Case A indicated similar environmental performance in all the categories even though the latter expressed slightly higher environmental gains. However, the feasibility and environmental viability of the two are reflected in the results.

Table 7-5: Comparison of the three EOL management scenarios and the conventional

Impact category	Unit				Conventional
		Case A	Case B	Case C	landfill
Climate change	g CO ₂ eq	-757.16	-125.97	-721.44	498.27
Ozone depletion	µg CFC-11 eq	-0.45	-11.82	0.91	0.32
Terrestrial acidification	g SO ₂ eq	-1.33	1.43	-1.00	0.08
Fresh water eutrophication	g P eq	-0.21	0.96	-0.21	0.01
Marine eutrophication	g N eq	-2.88	-2.56	-2.87	2.81
Human toxicity	g 1,4-DB eq	-10.52	-2.32	-7.41	3.41
Photochemical oxidant formation	g NMVOC	-0.75	0.20	-0.67	0.26
Particle matter formation	g PM10 eq	-0.39	0.31	-0.29	0.03
Terrestrial ecotoxicity	g 1,4-DB eq	-0.02	0.03	-0.01	0.00
Fresh water ecotoxicity	g 1,4-DB eq	-0.17	-0.11	-0.16	0.12
Marine ecotoxicity	g 1,4-DB eq	-0.20	-0.02	-0.14	0.07
Water depletion	l	-591.56	1293.79	-554.73	34.98
Minerals depletion	g Fe eq	-0.49	2.18	-0.14	0.04
Fossil fuel depletion	g oil eq	-87.94	96.97	-72.63	1.86

The results obtained in this study were further related to previous studies. For example, similar trends were reported by [30] during evaluation of different municipal solid waste management scenarios using a comparative LCA approach in Iran. The latter study included anaerobic digestion, landfilling combined with composting, incineration, incineration combined with composting and anaerobic digestion combined with incineration. The results obtained in for climate change varied from 800 kg CO₂ eq per tonne in case of landfilling to -250 kg CO₂ eq per tonne in case of digestion combined with incineration posited as the most eco-friendly scenario. Similarly, higher environmental benefits (above 1000 kg CO₂ eq per tonne) were

achieved by [31] considering also the digestion and incineration treatments options. In the extended study by [18] wherein ten different integrated EOL scenarios were evaluated through four impact categories, around -30 to -1100 kg CO₂ eq per tonne was reported for CC, which was a similar emission trend to this study. The latter study equally reiterated that not a single management system performed best in all impact categories. The relevance of recycling and recovery of energy and materials included in the EOL management scenarios were also addressed by [32] focusing on biogas from food wastes. Similar to those depicted in Table 2, Table 3 and Table 4 of this study, the results presented by [32] equally indicated that environmental benefits achieved in the overall treatment processes are pivoted on the utilisation and recovery of the generated energy.

7.4 CONCLUSIONS

This study investigated the environmental burdens and benefits of three different food waste treatment options using life cycle assessment. Despite the variation in the magnitude and use of energy and other valuable products from the scenarios, integrated system provided similar overall benefit and impacts with AD. The hard coal based Australia electricity mix impact was significantly avoided in the AD and integrated treatment processes whereas, accounted for the burdens associated to pyrolysis especially the feedstock pre-treatment. Despite the specific impacts of the EOL scenarios, these treatment options are considerably more environmentally friendly than the conventional landfilling of food wastes.

The use of NaOH in the dewatering phase needs to be substituted with a better approach to further enhance the performance of the AD and the integrated treatment processes. The use of biogas generated by the pyrolysis as replacement or substitutes as against the electricity considered in this study maybe a more sustainable pathway to mitigate burdens related to pyrolysis. Meanwhile, the quality of this model is predicated on the use of real time industrial AD data through which uncertainties are minimised. This is particularly important for food wastes management owing to its universality and recent growing rate.

ACKNOWLEDGMENT

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Conclusions and Recommendations

8.1 Conclusions

The aim of this thesis was to manifest the effect of waste treatment choice on the valorisation and sustainability of industrial scale food waste management. Waste treatment process transcends conventional mere disposal to become active sources of energy and material input for industries, this precludes selection of treatment processes adopted in this study. The study provides understanding and reasons for the need of a robust and flexible design of waste treatment plants to accommodate the economics of zero waste or emissions with a focus on sustainability as related to waste management industries. Comprehensive assessment of biomass treatment techniques indicated the edge of anaerobic digestion and pyrolysis for food waste management. The sustainability extent of the currently deployed processes for food waste management needs to be better understood. Meanwhile, the dearth of treatment integration and industrial treatment data was equally identified despite the entrenched prospects.

The key research outcomes and outputs achieved through this PhD research program are summarised as below.

- 1) The literature review (Chapter 2) on post-processing residues indicated that anaerobic digestion with different configuration was the most deployed biochemical treatment process on wet substrates while pyrolysis recently wide acceptance are due to its strength on dry biomass despite the duo environmental friendliness. However, extracting beyond 40% of feed inputs during anaerobic digestion (AD) process is the latter challenge while moisture concentrated substrates, such as food waste, makes pyrolysis unattractive especially when not pre-treated. The abundance and physico-chemical similarities of generated food waste across the globe make it a perfect substrate to indicate the necessity of this project and the importance of its reproducibility.

- 2) A thorough understanding of food waste processing through anaerobic digestion and pyrolysis were sorted through analytical analysis of the process input and outputs. The proximate and ultimate analysis of food waste indicated the nutrient richness of the waste, which overrules any justification for landfilling option, especially

when source separated. The industrial one stage anaerobic digestion process showed strength in the degradation of high moisture substrate (food waste), reduction of feedstock and energy production. Meanwhile, slow pyrolysis of the waste (food waste) after drying provided biogas, bio-oil and biochar. The latter was a carbon sequestration product (biochars) with higher carbon concentration range of 68 – 75% compared to pyrolysed digestate with carbon range of 35 – 45% at different charring temperatures. Lignocellulose analysis of the digestate indicated that about 20% of the digestate is susceptible to leaching or erosion being soluble in hot water, thus raising environmental issues, such as surface and groundwater contamination due to its current use as bio-fertilizers. Both AD and pyrolysis produced CO₂ (greenhouse gas) as major constituent of the biogas which needs to be appropriated to enhance the sustainability of these processes.

3) The integration of AD and pyrolysis processes offers the best treatment pathway for optimal energy extraction from food wastes. The integrated system not only indicated sustainability in energy output, it equally provided value added products such as the bio-oil and biochar. The difference between the inherent energy of food waste (15.8 MJ/kg) is insignificant when compared to digestate (14.1 MJ/kg), which shows the ineffectiveness of only AD treatment, especially when energy is the hallmark. The laboratory scale pyrolysis evaluated indicated a theoretical efficiency of 96% and 77.3% for the food waste and the digested respectively when pyrolysed at 500°C, indicating potential high-energy conversion.

4) The highly carbonaceous biochar produced through slow pyrolysis of raw food was activated with CO₂ to provided highly porous adsorbents thereby recycling CO₂ and consequently reducing the emission of greenhouse gas. The produced adsorbents did not only compete with available commercial activated carbon but equally indicated significant adsorption of CO₂ and C₆H₆. Therefore, volatile aromatic constituent of non-combustible fraction of the biogas can be scrubbed using the functionalised biochar. Aside harmful gas-scrubbing interventions provided by the produced activated carbon to the plant, its stands to reduce drastically the overall operation cost of the treatment process. The average open market cost of gas adsorbent is between USD \$1000 – \$2000 per metric ton thus, economically viable in industrialised countries and offers additional carbon offset claim at the carbon trade market for developing states.

5) Additionally, the nominal NPK values of the digestate (5:1:2) and the biochar equivalent values of 4:1:5 (when the digested was pyrolysed at 500°C) provided justification for the integrated treatment process and use as a bio-fertiliser. Similarly, the agronomic indicators, such as germination index, water holding capacity coupled with the nutrient enrichment factors, indicated the appropriateness of the biochar when considered as soil enhancer or bio-fertilizer. However, the digestate behaved better when applied on sandy soils, especially at application rate of 100 g/kg with plant available water twice greater than biochar amended sandy soil.

6) Integrated treatment process and AD indicated similar environmental performance in all the categories even though the latter expressed slightly higher environmental gains. The associated environmental burdens are related to the dewatering stage (accounting for >70% of the impact) while the benefits are predicated on the process product utilisation. Pyrolysis provided the least performance environmentally, mostly due to the use of electricity. Thus, the environmental relevance of recycling and recovery of energy and materials included in the EOL management scenarios are significant pathways for the sustainability of food wastes.

8.2 Recommendations

This thesis performed exhaustive study on the needs for flexible design of waste treatment plants. However, several gaps emerged with multidisciplinary inputs demand to achieve or ensure sustainability of food waste. The followings are thus recommended to further enrich the study:

1. Trade – off of process parameters in the one stage AD system to improve the outputs using treatment product, such as the heat from the CHP instead of releasing it into the atmosphere.
2. The lignocellulose analysis of the chars should also be determined to evaluate thermochemical effects on the lignocellulose constituents. This is expected to provide better understanding of food waste transformation with changing charring temperatures.
3. The purity and standardization capacity of the functionalised biochar needs to be determined to ascertain its use beyond gas purification and equally improve the market value of the activated chars.

4. The short and long time effects of the biochars and the digestate should be investigated to identify the fate of water soluble component of the digestate and further evaluate interaction rate of the char with sandy soil at varying application rates.
5. The life cycle cost implication needs to be considered alongside environmental benefits and burden assessment to help attract investors for the integrated treatment process. Few more product utilisation options can be considered especially on the use of the biochar produced during the pyrolysis of raw food wastes.
6. Water treatment using NaOH could be reviewed or replaced with functionalised biochar to mitigate the accrued impacts through the use of this chemical.

Appendix A: Declaration of authorship contributions

Journal Articles

1. Characterization of Food Waste and its Digestate as Feedstock for Thermochemical Processing

Contributions to the paper were as follows:

(87%) Suraj Opatokun collected the raw food waste from Macquarie shopping center and Eastwood vegetable market. He also collected pellet of digested food waste from EarthPower Technologies Sydney Pty Limited. The feedstocks were oven dried at the soil laboratory while the thermal conversion and other most analytical tests were carried out in the laboratory at Macquarie University. Few analyses were done at The Petroleum Institute during the offsite research stay while other outsourced analyses were equally managed. Suraj was the first author for the manuscript.

(5%) Vladimir Strezov acted in his capacity as the main supervisor with insight into analytical work and acted as a major reviewer of the manuscript.

(3.5%) C. Srinivasakannan contributed as the adjunct supervisor during my offsite research trip to The Petroleum Institute at Abu Dhabi in the United Arab Emirate. He also provided inputs to the manuscript in form of review.

(2.5%) Tao Kan supported this work by providing training and interpretation of analytical results. He was also involved in the review of the article.

(2%) Ahmed Al Shoaibi contributed by making available the fund for the offsite trip and stay in The Petroleum Institute. He was also involved in the manuscript review.

2. Product Based Evaluation of Pyrolysis of Food Waste and its Digestate

Contributions to the paper were as follows:

(91%) Suraj Opatokun undertook the thermochemical conversion and analytical work at Macquarie University laboratories and managed outsourced analysis that was necessary. Suraj is the primary author for the manuscript.

(5%) Vladimir Strezov acted in his capacity as the main r with insight into analytical work and acted as a major reviewer of the manuscript.

(4%) Tao Kan provided support on the GC-MS and CATA analysis and a limited reviewer of the manuscript.

3. Food Waste Derived Adsorbents for Benzene Gas Sorption (*Under Review*)

Contributions to the paper were as follows:

(88%) Suraj Opatokun produced the carbonaceous material and functionalised the materials. Suraj characterised the material all through to a highly porous adsorbent using analytical tools in Macquarie University and ThZe Petroleum Institute laboratories respectively. Suraj was the first and corresponding author for this manuscript.

(5%) Vladimir Strezov acted in his capacity as the main supervisor with insight into analytical work and acted as a major reviewer of the manuscript.

(2.5%) C. Srinivasakannan contributed as the adjunct supervisor during my offsite research trip to The Petroleum Institute at Abu Dhabi in the United Arab Emirate. He also provided inputs to the manuscript in form of review.

(2.5%) Ahmed Al Shoaibi contributed by making available the fund for the offsite trip and stay in The Petroleum Institute. He was also involved in the manuscript review.

(2%) Prabhu Azhagapillai acted in his capacity as a post-doctoral researcher with support on the Rubotherm use and analysis. He was also involved in the review of the article.

4. Agronomic Assessment of Pyrolysed Food Waste Digestate for Sandy Soil Management (*Under Review*)

Contributions to the paper were as follows:

(91%) Suraj Opatokun undertook the thermochemical conversion and analytical work at Macquarie University laboratories and managed outsourced analysis that was necessary. Suraj is the primary and corresponding author for the manuscript.

(5%) Vladimir Strezov acted in his capacity as the main supervisor with insight into analytical work and acted as a major reviewer of the manuscript.

(4%) Lina F. Yousef provided support on the gravimetric and volumetric analysis of the biochar on soil and was a limited reviewer of the manuscript.

5. Environmental Burdens and Benefits of Food waste Treatments Scenarios: A Life Cycle Analysis Perspective (To be submitted)

Contributions to the paper were as follows:

(82.5%) Suraj Opatokun collected the data and undertook the modelling and was the primary author and correspondent of the manuscript.

(5%) Vladimir Strezov acted in his capacity as the main supervisor with insight into analytical work and acted as a major reviewer of the manuscript.

(10%) Ana Maria Lopez- Sabiron contributed as Suraj trainer during my trip to the Research Centre for Energy Resources and Consumption (CIRCE) in Spain. Ana-Maria acted recognized expert in the field of LCA, she assisted with refinements of the model and was a major reviewer of the manuscripts.

(2.5%) German Ferreira supported as an expert in the LCA and was a limited reviewer of the manuscript.

6. A Review of Properties, Application and Prospects of Carbonaceous Biomass Post-processing Residues (to be submitted)

Contributions to the paper were as follows:

(90%) Suraj Opatokun undertook the literature search and review for this work and was the primary author for the manuscript.

(10%) Vladimir Strezov was a contributor and major reviewer of the manuscript.

Appendix B: Supplementary Information

The following represent supplementary information relevant to CO₂ gas adsorption a part of Chapter 5.

B1: CO₂ sorption performance

Carbon dioxide uptake isotherms measured at low-pressure region are shown in Figure B1.1 and Figure B1.2. All the adsorbents show excellent adsorption of CO₂ especially at low pressures. APyF515 (aminated material) with 4.36mmol/g indicated no significant sorption difference to PyF515 (un-aminated material) 4.41mmol/g uptake capacity of CO₂. Similar initial trend was observed for PyF715 (4.18mmol/g) and APyF715 (3.86mmol/g) until a spilt at about 40KPa. These adsorption capacities are significantly higher when compare to other carbonaceous material oriented adsorbent recently reported [1, 2] especially at low pressure. The 2hrs activated and oxidised PyF equally provided substantial adsorption capacities of 4.07 and 4.36mmol/g for PyF520 and PyF720 respectively while amination shows no effect on CO₂ sorption for APyF520 with 4.30mmol/g. Meanwhile, ammonia modified substrates CO₂ uptake capacities (see Figure B1.1 and B1.2) might not be justifiable for pyrolysed food wastes intended as PSA component especially at industrial level, which is the intent of this study. The distinct sorption behaviour of APyF720 (1.75mmol/g) further justifies the irrelevance of amination process during functionalization of the precursor. Lu and co-workers reported 25.1 mg/g and 26.3 mg/g marginal increase of CO₂ adsorption with mono-ethanolamine (MEA) and NH₃ modified granulated activated carbon (GAC) compare to 24.9mg/g CO₂ sorption of the raw GAC [3]. Although, the selectivity gradients of these materials were not evaluated in this study however, low cost and regeneration energy potential (due to no hysteresis in desorption curve), coupled with fast adsorption kinetics [1, 4] that characterise these activated carbons like others shows the importance of the study.

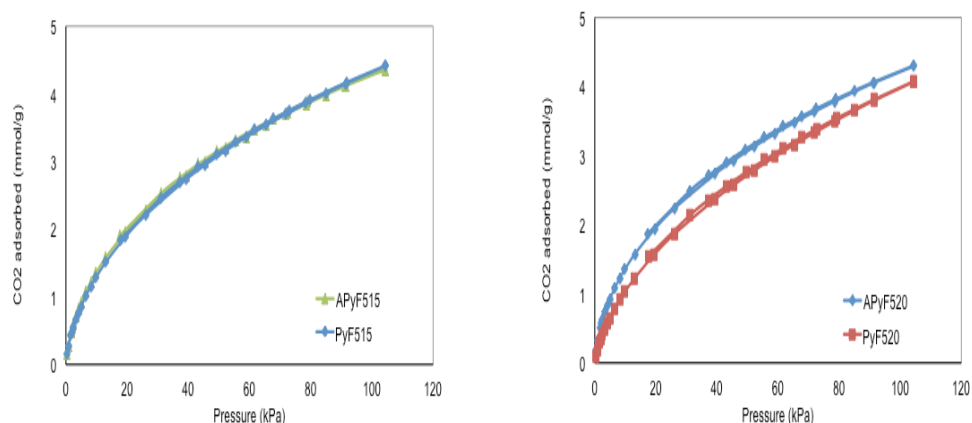


Figure B1.1: CO₂ adsorption isotherm of activated, oxidized and pyrolysed food waste (PyF5XX) at 500°C for 1.5 and 2hrs performed at temperature range of 25, 35 and 45°C

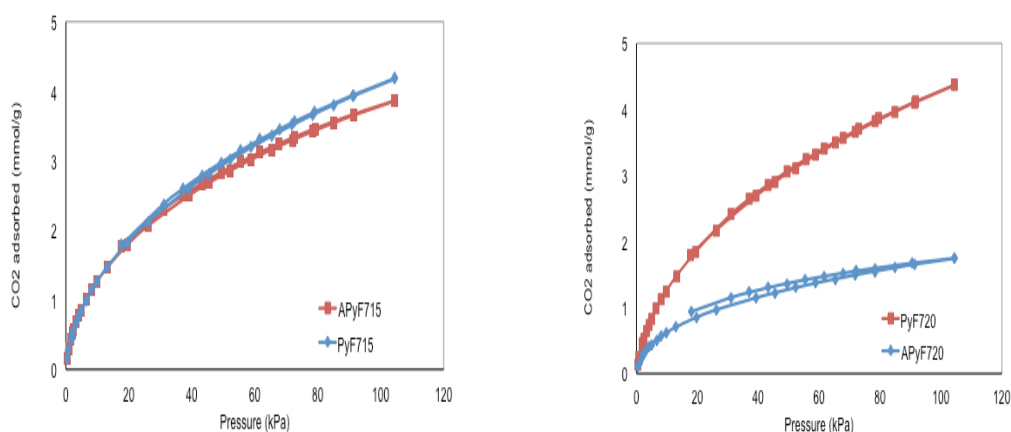


Figure B1.2: CO₂ adsorption isotherm of activated, oxidized and pyrolysed food waste (PyF7XX) at 700°C for 1.5 and 2hrs performed at temperature range of 25, 35 and 45°C

B1.1 References

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Appendix C: Supplementary Information

The following represent supplementary information relevant to C_6H_6 gas adsorption a part of Chapter 5.

C1: Determination of isosteric heat of adsorption

1. The family of experimental isotherms obtained on individual sample at 298K, 308K and 318K respectively at equilibrium pressure range of 19 to 250mbar (in torr).

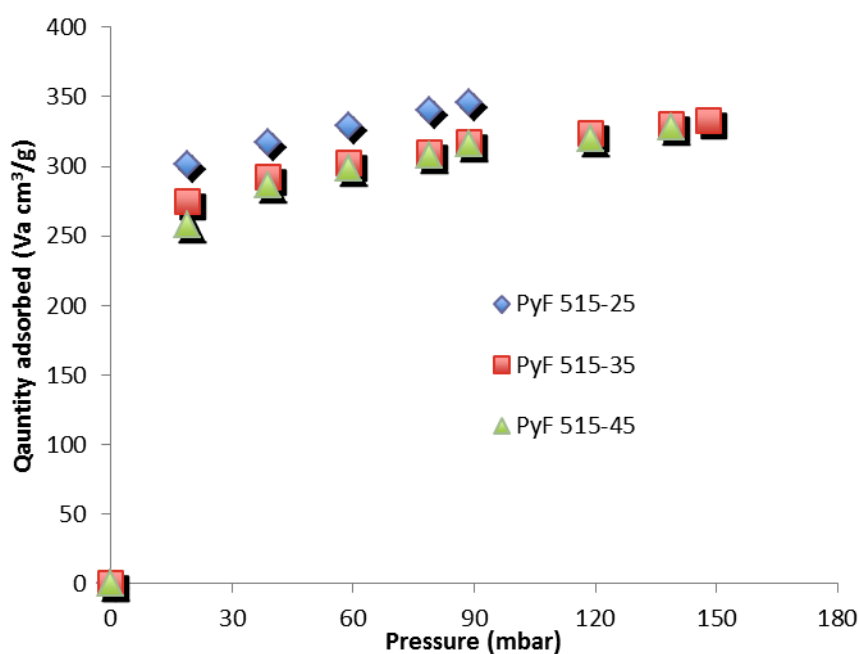


Figure C1: C_6H_6 adsorption isotherms of PyF515 at 298, 308 and 318K

2. Degrees of coverage at respective points on the isotherm were calculated using the monolayer capacity values from the BET analysis of the sample using equation I as shown in Table A1.

Table C1: Surface area, pore volumes and monolayers values obtained from BET analysis

	Pressure (torr)	Surface Area	Pore Volume	Monolayer volume (Q _m)
PyF515		830.3	0.49	190.72
PyF520		1024.7	0.52	235.39
PyF715		797.2	0.59	183.13
PyF720		901	0.49	206.98

Degree of coverage = V_a/V_m Where V_a is the quantity adsorbed at pressure (P) while V_m is the value of monolayer capacity.

- The degrees of coverage obtained were plotted against the temperature in Kelvin as indicated in Figure S1.

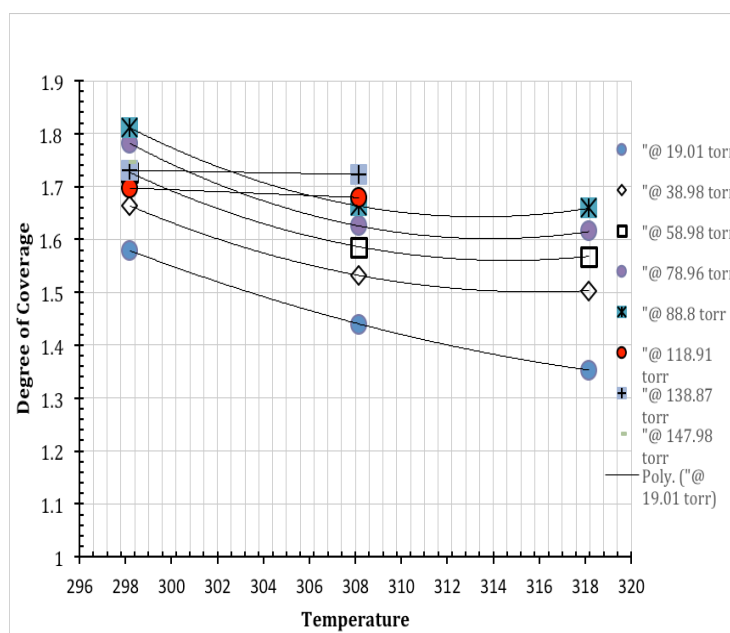


Figure C2: Isobar plots derived from experimental isotherms for PyF515

Table C2 – Table A4 are extracted at the intersections of the isobar plot with various values of degree of coverage.

Table C2: Values derived from the isobar when the degree of coverage is 1.5
for PyF515

Pressure	Ln(P)	Temp (K)	1/T
19.01	2.95	303.5	0.0033
38.98	3.66	313.5	0.0032
58.98	4.08		
78.96	4.37		
88.8	4.49		
118.9	4.78		
138.9	4.93		
148.0	5.01		

Table C3: Values derived from the isobar when the degree of coverage is 1.6
for PyF515

Pressure	Ln(P)	Temp (K)	1/T
19.01	2.95		
38.98	3.66	302	0.0033
58.98	4.08	306.5	0.0033
78.96	4.37	313	0.0032
88.8	4.49		
118.91	4.78		
138.87	4.93		
147.98	5.01		

Table C4: Values derived from the isobar when the degree of coverage is 1.7 for PyF515

Pressure	Ln(P)	Temp (K)	1/T
19.01	2.95		
38.98	3.66		
58.98	4.08	300	0.0033
78.96	4.37	302.2	0.0033
88.8	4.49	304.5	0.0033
118.91	4.78	298	
138.87	4.93		
147.98	5.01		

4. Consequently, the plot of Ln (P) against 1/T to determine the slope of each plot (see Figure C3).

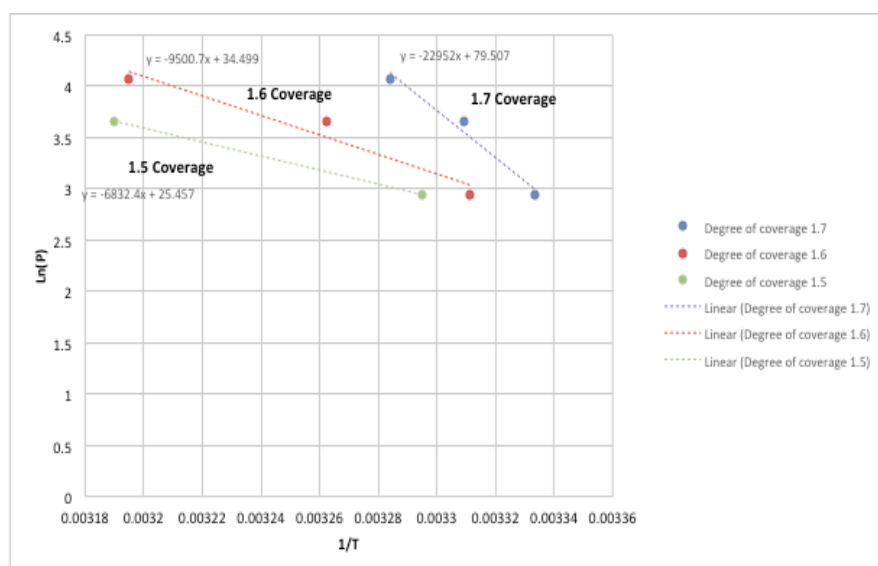


Figure C3: Linear plots of the extracted coverage and their slopes, coefficients and intercepts values

The heat of adsorption at a particular load of benzene was then calculated from the derivative of the polynomial following the Clapeyron-Clausius equation. Meanwhile, these derivatives are linearly dependent on the temperature.

Table C5: Variation of isosteric heat of adsorption (qst) vs. degree of coverage for the PyF515.

qst	Degree of coverage
6832.4	1.5
9500.7	1.6
22952	1.7

Note: the steps above were repeated for PyF520, PyF715 and PyF720.