Hydrothermal Carbonisation of Sewage Sludge: Effect of Process Conditions on Product Characteristics and Methane Production

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Abstract

Hydrothermal carbonisation of primary sewage sludge was carried out using a batch reactor. The effect of temperature and reaction time on the characteristics of solid (hydrochar), liquid and gas products, and the conditions leading to optimal hydrochar characteristics were investigated. The amount of carbon retained in hydrochars decreased as temperature and time increased with carbon retentions of 64–77% at 140 and 160°C, and 50–62% at 180 and 200°C. Increasing temperature and treatment time increased the energy content of the hydrochar from 17–19 MJ/kg but reduced its energy yield from 88–68%. Maillard reaction products were identified in the liquid fractions following carbonisations at 180 and 200°C. Theoretical estimates of the methane yields resulting from the anaerobic digestion of the liquid by-products are also presented and optimal reaction conditions to maximise these identified.

Keywords: Biomass; Carbon storage; Hydrochar; Sludge treatment; Wastewater treatment.

1. Introduction

It is estimated that between 0.6 and 1 billion tons of human faeces are generated each year (Sobsey, 2006), a figure which is set to increase because of the predicted growth in population. In the developing countries, over 90% of sewage is discharged untreated (Langergraber and Muellegger, 2005). Faecal contamination of water sources causes almost 4 billion cases of diarrhoea globally each year, killing nearly 2.2 million children under age five (WHO/UNICEF/WSSCC, 2000). In those regions of the world where sewage treatment is routinely undertaken management of sewage sludge continues to present environmental and health challenges.

The prospects for recovering energy from sewage and waste sludges have recently received renewed interest (Goto et al., 2004; Mumme et al., 2011; Zhao et al., 2014). Hydrothermal carbonisation (HTC) is as an effective method for converting wet biomass at relatively mild reaction temperatures into a coal-like material commonly referred to as 'hydrochar' along with aqueous products and gases -primarily CO₂ (Funke and Ziegler, 2010; Libra et al., 2011). When applied to sewage sludge, HTC results both in sanitisation of the sludge and in its stabilisation (Catallo and Comeaux, 2008). The hydrochar, which is typically the main product, has H/C and O/C ratios comparable to low-grade coal, but a higher calorific value than such coals (Demir et al., 2008) and can therefore serve as a potential fuel source. **Alternatively**, hydrochar is a carbon-rich compound that can be added to soils as a conditioner (Libra et al., 2011) and as it is slow to oxidise provides a means for sequestering carbon that would otherwise be released into the atmosphere as greenhouse gases (Titirici et al., 2007). Other options for the solids produced include biofuel production by transesterification (Levine et al., 2013) and VFA extraction (Wood et al., 2013; Kaushik et al., 2014), and

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5 53 gasification for syngas production (Castello et al., 2014). These options require different
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7 54 ratios of O/C in the hydrochars generated which requires the tailoring of conditions
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9 55 during carbonisation in order to achieve them.
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12 56 The aqueous products from HTC contain organic compounds such as furans,
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14 57 phenols, acetic acid, levulinic acid, and other soluble organic compounds (Goto et al.,
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16 58 2004; Berge et al., 2011; Wang et al., 2012). The discharge of wastewaters rich in such
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18 59 organic compounds would pose serious environmental challenges to receiving water
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20 60 bodies (Arora and Saxena, 2005) and therefore some means of treating such wastes is
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22 61 essential. The formation of difficult to treat coloured organic compounds through the
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24 62 Maillard reaction during hydrothermal treatment (HT) of sludges has been reported
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26 63 (Penaud et al., 1999). However, the conditions leading to the production of Maillard
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28 64 products have not yet been fully understood.
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32 65 The majority of studies into HTC have to date focused on the chemistry and
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34 66 mechanism of the process, and how it can be used to produce various carbonaceous
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36 67 solid products for carbon sequestration when applied to land or as an energy source
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38 68 (Titirici et al., 2007; Funke and Ziegler, 2010; Libra et al., 2011) rather than viewing
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40 69 HTC as an alternative waste treatment process. The application of HTC to achieve
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42 70 volume reduction and sterilisation of animal and municipal wastewater solids has been
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44 71 reported (Catallo and Comeaux, 2008), as well as for evaluating product characteristics
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46 72 (Berge et al., 2011). However, the effects of the operating conditions on product
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48 73 characteristics have not been fully investigated.
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53 74 The potential to produce methane from the liquid products separated from the
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55 75 hydrochar following HTC of biomass has not been previously studied and reported.
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57 76 Hence, a more comprehensive study into methane production from HTC liquid product
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5 77 is required in order to identify the optimum conditions for highest yields. In the work
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7 78 described here, the effects of process temperature and reaction times during the HTC of
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9 79 primary sewage sludge were investigated. Results are presented of hydrochar
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11 80 characteristics in terms of energetics, physical and chemical properties, wastewater
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13 81 quality indicators of the liquid products and of the nature of dissolved organic
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15 82 compounds, composition of gaseous products, and finally of the potential for methane
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17 83 production from the liquid products.
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21 84 22 85 **2. Materials and Methods**

23 24 86 2.1. Primary sewage sludge

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27 87 Primary sewage sludge (PSS), was collected from Wanlip Sewage Treatment Works
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29 88 (Leicestershire, UK) in an enclosed container. PSS primarily comprises faecal matter
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31 89 removed by settlement. The PSS typically contained 4.3% (wt.) solids as received. The
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33 90 PSS was stirred manually before use as the solids had a tendency to settle. The physical
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35 91 and chemical characteristics associated with the PSS feedstock are shown in Table 1.
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39 92 40 93 2.2. Experimental design

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42 94 Response surface methodology (RSM) by means of a central composite rotatable
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44 95 design (CCRD) was used to study the influence of the two variables (reaction
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46 96 temperature, and residence time) and their interaction on hydrochar energetics, carbon
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48 97 distribution, and methane yield. Design Expert 9.0.1 software (Statease, Minneapolis,
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50 98 MN) was used for the CCRD and statistical analysis of variance (ANNOVA), which
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52 99 resulted in 39 tests (16 factorial points, 16 star points, and 7 central points). Each
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55 100 variable was set at 5 levels: $-\alpha$, -1 , 0 , 1 and α (where $\alpha = 1.414$).
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2.3. Hydrothermal carbonisation apparatus and process

HTC experiments were conducted using a 250 mL stainless steel batch reactor (BS1506-845B, UK) immersed in an oil bath (B7 Phoenix II, Thermo Scientific, UK) containing Shell Thermia oil B. HTC of PSS were carried out at reaction temperatures of 140°C for 240 min; 160°C for 60, 120, and 240 min; 180°C for 30, 60, 120 and 240 min; and 200°C for 15, 30, 60, 120 and 240 min. After carbonisation, the reactor was cooled to 25°C and the gas-phase was vented for analysis. The carbonised solids were dewatered from the liquid phase by vacuum filtration using a metal microporous membrane, with 10 µm pores, manufactured by Micropore Technologies Ltd. (Hatton, Derbyshire, UK) to obtain the hydrochar. The dewatered hydrochar was dried in an oven at 55°C for 24 h to remove any residual moisture. Experiments were conducted in triplicate.

2.4. Feedstock and product analysis

2.4.1. Hydrochar and dried feedstock analysis

Feedstock and hydrochar dried in an oven at 55°C for 24 h were analysed for residual moisture, ash and volatile matter using a thermogravimetric analyser (TA Instruments Q5000IR, UK), according to ASTM method D7582-10 (ASTM, 2010). Carbon (C), hydrogen (H) and nitrogen (N) contents were analysed using a CHN Analyser (CE-440 Elemental Analyzer, Exeter Analytical Inc., UK), according to ASTM D5373-08 (ASTM, 2008). Energy content of the PSS feedstock and hydrochars was determined using a bomb calorimeter (CAL2K, Digital Data Systems, South Africa). All tests were conducted in triplicate. Surface elemental composition was analysed using energy dispersed X-ray spectroscopy (EDS) (X-Max 80 mm² Detector, Oxford Instruments, UK) with a microanalysis software (Aztec EDS/EBSD, Oxford

Instruments, UK) having a Truemap capability. The working distance (WD) was 8.5, and target voltage (EHT) of 20 kV, using an aperture of 60 µm with beam current of 2.0 nA.

2.4.2. Liquid product analysis

Total organic carbon (TOC) was analysed using a TOC Analyser (DC-190, Rosemount Dohrmann, USA), in line with Standard Methods 5310 B – High Temperature Combustion Method (APHA, 2005). Liquid samples obtained following filtration with a 10 µm filter medium were further filtered with a Grade 2 Whatman filter paper in order to obtain uniform distribution of suspended and colloidal solids in the liquid samples, and diluted by ratio of 1:10 ml. Chemical oxygen demand (COD) was determined using a COD analyser (Palintest 8000, Palintest Ltd, UK) at a wavelength of 570 nm, in accordance with Standard Methods 5220 D – Closed Reflux Colorimetric Method (APHA, 2005). The samples were diluted by ratio of 1:10. BOD₅ was measured respirometrically using a BOD analyser (BODTrak II, HACH, USA) by the HACH Standard Method procedure. Volatile fatty acids (VFA) in the processed wastewater and feedstock were determined using a spectrophotometer (DR3900, HACH LANGE, Germany) according to the colorimetric ferric hydroxamate method known as the Montgomery method (Montgomery et al., 1962) at a wavelength of 497 nm. Ammonium nitrogen (NH₄-N) was measured by spectrometric technique at a wavelength of 550 nm using a spectrophotometer (DR3900, HACH LANGE, Germany). All measurements were conducted in triplicate.

Liquid samples were filtered and injected into a GC-MS (HP5890, Hewlett Packard, USA) equipped with a mass selective detector (MSD) (HP5973, Hewlett Packard, USA) to identify compounds present in the liquid product. The column used

was a DB-1MS column (25 m x 0.32 mm id, J&W Scientific). Then inlet temperature was set at 150°C, and the septum purge flow was 5.0 ml/min, with helium carrier flow at 1.5 ml/min. The oven temperature was programmed as follows; 60°C for 2 min, followed by a temperature increase at a rate of 15°C/min until 90°C was attained after which the temperature increased at the lower rate of 8°C/min until a final temperature of 300°C was achieved as based on the method of Wang et al. (2012). The compounds were identified using NIST 2008 Library. All analyses were conducted in triplicate.

2.4.3. Analysis of Compounds in Gas-Phase

Compounds in the gaseous products following HTC of PSS were analysed using a mass spectrometer (GeneSys MS 200D, European Spectrometry Systems Ltd, UK). After HTC, the vessel was cooled down to 25°C, and the gas in the head space of the reactor was vented directly through the MS. In order to avoid solid particles and liquid entering the MS, a coalescing gas filter (SS-FCE, GE-15K-FC-03, Swagelok, UK) was connected in between the reactor and the MS to ensure that only the gaseous products are injected. The MS was calibrated using standard CO₂ and N₂ gases (BOC, UK). The compounds present were identified using the Balzers Spectra Library.

Details regarding the results of the elemental composition using EDS, ammonium nitrogen in the liquid products, compounds identified in the process water and gas-phase are available in the Supporting Information

2.5. Data analysis

The hydrochar yield (Y), energy densification (E_d) and energy yield (E_Y) were determined as follows:

$$Y (\%) = \frac{\text{mass of dry hydrochar}}{\text{mass of dry PSS feedstock}} \times 100 \quad (1)$$

$$E_d = \frac{HHV_{char}}{HHV_{feedstock}} \quad (2)$$

$$E_y(\%) = E_d \times Y \quad (3)$$

Carbon recovery in hydrochar (H_{Crec}) and liquid phase (L_{Crec}) were calculated as follows:

$$(\%) H_{Crec} = \frac{\frac{\%C_{char}}{100} \times \text{char mass}}{\frac{\%C_{feedstock}}{100} \times \text{mass of dry PSS feedstock}} \times 100 \quad (4)$$

$$(\%) L_{Crec} = \frac{TOC \times \text{volume of filtrate}}{\frac{\%C_{feedstock}}{100} \times \text{mass of dry PSS feedstock}} \times 100 \quad (5)$$

Carbon storage factor (CSF) was calculated using an equation proposed by Barlaz (1998), as

$$CSF = \frac{\frac{\%C_{char}}{100} \times \left(\frac{\%char\ yield}{100} \times \text{mass of feedstock} \right)}{\text{mass of dry feedstock} - \left(\text{mass of dry feedstock} \times \frac{\%Moisture\ in\ feedstock}{100} \right)} \quad (6)$$

Methane yield was determined using the Buswell equation (Buswell and Neave, 1930), represented as:

where $C_nH_aO_b$ represents, in this case, the chemical formula of the carbonised solids (biodegradable organic waste) subject to the anaerobic degradation. n, a, and b are the mole fractions of C, H, and O respectively in the carbonised slurry. And the percentage yield of CH_4 calculated as,

$$\% CH_4 = \frac{\left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} \right)}{\left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} \right) + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} \right)} \times 100 \quad (8)$$

The second theoretical equation used was a correlation by Franco et al. (2007):

$$\% CH_4 = \left\{ 0.5 - \frac{4 - 1.5 \left(\frac{COD}{TOC} \right)}{8} \right\} \times 100 \quad (9)$$

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5 198 The Design Expert 9.0.1 software was used to analyse the data. The significance of
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7 199 each model term was determined by an F -test with $\alpha = 0.05$ significance level. Test of
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9 200 statistical significance were applied to the difference between the experimental data and
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11 201 the corresponding predictions obtained using RSM by means of t -test using GraphPad
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14 202 software (GraphPad Software, Inc., La Jolla, CA).

203 204 **3. Results and Discussion**

205 Series of randomised HTC runs were carried out to investigate the effects of
206 reaction temperature and reaction time on the physical, chemical and thermal
207 characteristics of the hydrochars produced, as well as those of the liquid- and gas-phase
208 products.

209 210 **3.1. Hydrochar characteristics**

211 *3.1.1. Physical characteristics*

212 Hydrochar yields were significantly affected by the reaction temperature and time,
213 and decreased as the temperature and time of carbonisation increased (Table 1). The
214 highest yield was obtained from carbonisation conducted at 160°C for 60 min (81.13%),
215 and the lowest yield from carbonisation at 200°C for 240 min (60.54%). The yields
216 observed in this study are the within range of values reported in a previous study on the
217 char formation kinetics using PSS feedstock with a different solids loading of 4%
218 (Danso-Boateng et al., 2013). Ash content increased following carbonisation; except
219 that obtained from carbonisation at 140°C for 240 min, and increased as reaction
220 temperature and time were increased. The ash content of the hydrochars were
221 significantly lower than those resulting from carbonisation of anaerobic digested (AD)
222 sludge (55.8% dry basis) as reported by Berge et al. (2011), and slightly higher than

those from activated sewage sludge (18.5–34.68%) reported by Zhao et al. (2014). Volatile matter present in the hydrochar decreased as reaction temperature and time increased. A significantly higher value higher than that of the dried PSS feedstock (68.56% dry basis) was obtained from carbonisation at 140°C for 60 min (75.97% dry basis). The volatile matter content of the hydrochars are within the range of values (57.24–78.49%) reported for carbonisation of activated sewage sludge (Zhao et al., 2014), but lower than (34.50%) reported for AD sludge (Berge et al., 2011).

3.1.2. Energy characteristics

Energy characteristics of the hydrochars from different reaction temperatures and reaction times are illustrated in Fig. 1. As expected, the higher heating value (HHV) of the PSS was improved following carbonisation with the HHV of the hydrochars increasing as the reaction temperature and time were increased (Fig. 1A), which were significantly affected by only the reaction temperature and interactions between temperature and time. The lowest HHV resulted from carbonisation at 140°C for 240 min (16.66 MJ/kg), and those obtained at 160°C and between 60–240 min were in the range of 17.80–18.15 MJ/kg). The HHV of hydrochars resulting from treatment at 180°C for 30–240 min, and 200°C for 15–240 min were between 17.64–18.26 MJ/kg, and 17.52–18.65 MJ/kg respectively. These values are significantly higher than those reported for AD waste (13.7 MJ/kg dry basis) (Berge et al., 2011), but within the range of those reported by Zhao et al. (2014) for hydrochars from activated sewage sludge (18.33–20.18 MJ/kg). Compared with fossil fuels, the HHV of PSS char from carbonisation at 140°C for 240 min was identical to that of lignite coal, and that from carbonisation at 160–200°C were similar to the HHV of sub-bituminous coal (Schnapp, 2012).

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5 248 The energy yield provides a means of relating the energy remaining within the
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7 249 hydrochars to that of the original sewage sludge feedstock, defined as energy
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9 250 densification ratio times mass yield of the hydrochar (Danso-Boateng et al., 2013), and
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11 251 these decreased as the reaction temperature and time increased (Fig. 1B). The energy
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13 252 yield of the hydrochars was significantly affected by both the reaction temperature and
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15 253 time, with values in the range of 76.14% (for 140°C, 240 min carbonisation), 74.57–
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17 254 88.40% (for 160°C, 60–240 min carbonisation), 69.19–76.42% (for 180°C, 30–240 min
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19 255 carbonisation), and 67.11–74.37% (for 200°C, 15–240 min carbonisation). Energy
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21 256 densification occurred as the solid mass decreased as a result of dehydration and
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23 257 decarboxylation reactions (as indicated by the increased **in** carbon contents, and
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25 258 decrease in oxygen and hydrogen contents), and increased as the reaction temperature
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27 259 and time were increased (Fig. 1C). Energy densification associated with the hydrochars
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29 260 ranged from 1.02 (for carbonisation at 140°C), 1.09–1.11 (for carbonisation at 160°C),
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31 261 1.08–1.12 (for carbonisation at 180°C), and 1.07–1.14 (for carbonisation at 200°C); and
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33 262 were significantly influenced by the reaction temperature rather than reaction time.
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42 263 43 264 *3.1.3. Chemical characteristics*

44 265 The elemental composition of the hydrochars was **checked** following carbonisation
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46 266 (Table 1), and showed an increase in carbon content, and decrease in nitrogen and
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48 267 hydrogen contents at all reaction temperatures and treatment times. Atomic H/C and
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50 268 O/C ratios for the initial feedstock and resulting hydrochars (Fig. S1) show that
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52 269 carbonisation at higher temperature (200°C) and shorter reaction times (15–60 min)
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54 270 showed evidence of dehydration (lower H/C). Whilst at 200°C and longer reaction times
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56 271 (120–240 min), dehydration and decarboxylation reactions (lower H/C and O/C)
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58 272 appeared to predominate. These results suggest that carbonisation at lower temperatures
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(140°C) and longer reaction times (240 min) were primarily dehydration reactions, and that at relatively moderate temperatures (160°C) and times (60–120 min) was mainly governed by decarboxylation reactions whilst at longer times (240 min) both dehydration and decarboxylation occurred.

EDS was used to reveal changes to a range of elements before and after carbonisation (Table S1). The elements C, O, N, S, P, Ca, Si, Fe, Mg, Al, K, and Na were detected in the feedstock and hydrochars. The amounts of P, Ca, Mg, Cl and K in the hydrochar decreased significantly following carbonisation; and as expected, the percentage of C in the hydrochars increased as a result of carbonisation. Small amounts of S were observed in the hydrochars and ranged between 0.8% for carbonisation at 140°C, 0.7–0.8% for carbonisations at 160°C, 0.6–1.1% for carbonisations at 180°C, and 0.6–1.0% for carbonisations at 200°C.

3.2. Carbon balance

The relative proportion of carbon in hydrochars was increased compared to that of the PSS following carbonisation, and the proportion was increased as the reaction temperature and time were increased (Table 1). The carbon contents of the hydrochars produced ranged between 37.15–39.24%, which are significantly higher than the carbon content of hydrochar generated from the sludge remaining following anaerobic digestion (27.80% dry basis) reported by Berge et al. (2011), and lower than that from activated sewage sludge (52.19–67.96%) obtained by Zhao et al. (2014). Although these comparisons are broadly indicative, the reaction temperatures, times of treatment, and feedstock characteristics and solid contents were different from that used in this study. The fraction of carbon in the hydrochars as a percentage based on that of the carbon initially present in the feedstock decreased significantly as temperature and

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5 298 reaction time were increased (Fig. 2A). A significant fraction of carbon was retained
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7 299 within the hydrochar resulted from carbonisation at 140°C (77.04%) as compared with
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9 300 64.25–67.36% for carbonisations at 160°C, 52.77–61.87% for carbonisations at 180°C,
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11 301 and 49.92–57.42% for those at 200°C.
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14 302 Smaller proportions of carbon were transferred into the liquid phase for
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16 303 carbonisation at lower temperatures (140°C and 160°C), and this increased as the
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18 304 temperature and reaction time were increased, with a significant carbon **transfer** into the
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20 305 liquid phase at the highest temperature (240°C) and longest reaction time (240 min)
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22 306 used here (Fig. 2B). Fractions of carbon of the total initial carbon present in the
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24 307 feedstock transferred to the liquid phase ranged from 14.82% (for carbonisation at
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26 308 140°C), 13.62–28.52% (for carbonisations at 160°C), 12.86–47.09% (for carbonisations
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28 309 at 180°C), and 31.91–66.39% (for carbonisations at 200°C); indicating that severe
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30 310 reaction conditions caused increased in carbon solubility and resulted in significant
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32 311 **movement** of carbon into the liquid phase. Carbon recovery within the hydrochar and
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34 312 liquid phase were observed to be significantly influenced by both the reaction
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36 313 temperature and time. Previously reported transfers of carbon to the liquid phase range
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38 314 from 20–37% for wastewater solids (Berge et al., 2011).
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44 315 Carbon sequestered in the hydrochars following HTC was significantly affected by
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46 316 both reaction temperature and reaction time, and decreased considerably as the reaction
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48 317 temperature was increased from 140°C to 200°C (Fig. 2C). The carbon storage factor
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50 318 (CSF) is the fraction of carbon which remains unoxidised following biological
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52 319 decomposition, which is defined by Barlaz (1998) as mass of carbon remaining in the
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54 320 solids after biological decomposition in a landfill per unit dry mass of feedstock, and
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56 321 provides a means for comparing the mass of carbon remaining (i.e. sequestered) within
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the solid material following its decomposition in landfills. The CFS of the hydrochars produced ranged from 0.30 (for carbonisation at 140°C), 0.28–0.33 (for carbonisations at 160°C), 0.26–0.29 (for carbonisations at 180°C), and 0.26–0.28 (for carbonisations at 200°C). The results indicate that moderate temperatures and shorter reaction time are required in order to sequester the maximum amounts of carbon in hydrochars following HTC of primary sewage sludge. Previously reported values of CSF for MSW in landfills are of the order of 0.22 (Barlaz, 1998), whilst that in MSW hydrochar is 0.23 (Berge et al., 2011), signifying that more carbon is stored within the hydrochar than if the waste material had been disposed of uncarbonised. The proportions of carbon sequestered during carbonisation in this study are higher than the value of 0.14 previously reported by Berge et al. (2011) for hydrochar from AD waste.

Although the CSFs of hydrochars are greatest at lower reaction temperatures and decrease as the temperature increases, hydrochars from carbonisation at the highest temperature (200°C) and the longest reaction time (240 min) employed here have the lowest O:C molar ratios (1.02) which would suggest that they would be the most stable hydrochars (Fig. S2). However, an exception was found as the hydrochars from carbonisations at 160°C displayed having lower O:C molar ratios than that resulting from carbonisation at 180°C for a longer reaction time (240 min). Spokas (2010) claimed that hydrochars with molar O:C ratios greater than 0.6 could be expected to remain stable for the order of less than 100 years, and that stability increased as the O:C becomes lower. Molar O:C ratios of the hydrochars produced ranged from 1.07 (for carbonisation at 140°C), 1.03–1.04 (for carbonisations at 160°C), 1.04–1.06 (for carbonisations at 180°C), and 1.02–1.07 (for carbonisations at 200°C). Although this study provides information that would be useful for predicting the long term stability of

carbon in the hydrochar from faecal waste, a more extensive investigation into the long-term oxidation or decomposition of hydrochars is required. Factors such as soil type and environmental conditions are reported to affect the stability of the chars in soil (Libra et al., 2011).

3.3. Characteristics of the liquid fraction produced by carbonisation

A number of organic compounds were identified in the liquid fraction following carbonization of the PSS (Table 2). Acetic acid, benzene acetic acid, butanoic acid, pentanoic acid and propanoic acid were present in all samples and are probably products of the decomposition hydrolysis of the PSS. Alkenes, phenolic and aromatic compounds were detected in the liquid fraction at all temperatures and reaction times (Table S2), which indicates that the carbonisation route follows hydrolysis, dehydration, decarboxylation, condensation, polymerisation, and aromatisation as previously reported by Sevilla and Fuertes (2009). Several Maillard products such as aldehydes, furans, pyrroles, pyrazines, and pyridines were identified in liquid samples following carbonisation at 180 and 200°C and reaction times between 30–240 min. 3-methylbenzofurane was only detected following carbonisation at 160°C for 240 min, and 5-methyl-2-furancarboxyaldehyde at 200°C following 15 min treatment. There were no Maillard reaction products when PSS was carbonised at 140°C for 240 min and at 160°C for 60–120 min. Maillard reactions became significant during carbonisations conducted at temperatures starting at 180°C for reaction times longer than 15 min. For comparison, none of the compounds mentioned above were detected in the samples filtered from the untreated feedstock following GC-MS analysis, which confirms that the compounds identified in the carbonised process water had arisen as a result of the thermal degradation of the PSS feedstock.

Typical quality indicators of the liquids produced during carbonisation are shown in Fig. 3. TOC concentrations increased significantly as the reaction temperature and reaction time were increased. This accounted for the largest proportion of carbon recovery in the liquid products at higher temperatures and longer reaction times shown in Fig. 2 (B) (Section 3.2). TOC values ranged from 4.87 g/L (for carbonisation at 140°C), 5.35–9.49 g/L (for carbonisations at 160°C), 4.99–9.99 g/L (for carbonisations at 180°C), and 7.67–13.68 g/L (for carbonisations at 200°C), compared with 2.08 g/L found in the filtrates of the untreated feedstock. COD and BOD values increased marginally as temperature and reaction time were increased, as shown in Fig. 3 (B) and (C) respectively. COD levels of the liquid phase were between 17.53 g/L (for carbonisations at 140°C), 20.09–20.87 g/L (for carbonisations at 160°C), 20.60–21.59 g/L (for carbonisations at 180°C), and 20.60–23.03 g/L (for carbonisations at 200°C), compared with 6.6 g/L for feedstock filtrate. The BOD value of the liquid produced by carbonisation at 140°C was 8.18 g/L, and that for carbonisations at 160, 180 and 200°C ranged from 7.81–8.86 g/L, 9.21–9.29 g/L, and 8.93–9.92 g/L, respectively compared with 4.66 g/L for untreated feedstock filtrate. These results indicating that increasing reaction temperature and reaction time resulted in increased concentrations of TOC, and higher values of COD and BOD which is borne out by the increased concentrations of organic compounds identified in the liquid products at higher reaction severities (Table 2). TOC, COD and BOD values following carbonisations between 140–240°C for reactions from 15–240 min were higher than those of typical domestic wastewater, which are 0.1–0.4 g/L for TOC and BOD, and 0.2–1.0 g/L for COD (Sundstrom and Klei, 1979).

VFA concentrations in the liquid products decreased as the reaction temperature and reaction time were increased from 140–200°C and 15–240 min, respectively (Fig. 3D). This may be as a result of further decomposition of organic acids resulting from decomposition of glucose and fructose into soluble products such as furans (Goto et al., 2004; Sevilla and Fuertes, 2009) as the reaction temperature and time increased (Table 2). Concentrations of VFA ranged between 4.75 g/L (for carbonisation at 140°C), 5.42–6.25 g/L (for carbonisations at 160°C), 5.66–6.58 g/L (for carbonisations at 180°C), and 5.31–6.09 g/L (for carbonisations at 200°C).

The lowest concentration of ammonium-nitrogen was found in liquids produced following carbonisation at 200°C for 15 min; with concentrations between 1.02 g/L (for carbonisation at 140°C), 1.00–1.07 g/L (for carbonisations at 160°C), 0.98–1.21 g/L (for carbonisations at 180°C), and 0.95–1.31 (for carbonisations at 200°C), and increased significantly as reaction temperature and time were increased (Fig. S3). This may be as a result of loss of nitrates in the hydrochar into the liquid phase during HTC, as evident by the decreased N content of hydrochar produced as reaction temperature and time were increased (Table 1). The presence of significant concentration of ammonium-nitrogen will lead to their nitrification if such liquids are discharged into water courses and this may cause toxicity to aquatic life.

3.4. Gas-phase composition

Carbon dioxide was identified at high concentrations in the gas-phase following carbonisation at all temperatures and reaction times, with particularly high concentrations being observed in samples from carbonisations at 160°C for 120 min, and 200°C for 30 min (Table S3) indicating that decarboxylation was taking place during HTC. Of environmental concern was the identification of hydrogen sulphide,

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5 419 nitrogen dioxide, nitric oxide, and ammonia. Hydrogen sulphide was detected in all
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7 420 samples, and was probably produced as a result of Maillard reactions during the thermal
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9 421 decomposition of the PSS, and the concentration did not vary significantly with either
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11 422 the reaction temperature or reaction time. The nitrogen oxides detected resulted from
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13 423 the thermal oxidation of nitrogenous compounds present in the PSS. Nitrogen oxide was
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15 424 identified in varying concentrations, with the exceptions of samples following
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17 425 carbonisations at 160°C for 60 and 240 min, and 180°C for 30 and 60 min, whilst nitric
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19 426 oxide was identified only in the gas-phase of samples following carbonisations at 180°C
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21 427 for 30 and 240 min. Ammonia was also detected in all samples, and the highest intensity
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23 428 was found in samples following carbonisation at lower temperatures (140 and 160°C).
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25 429 Several other volatile hydrocarbons were also identified (Table S3). The results show
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27 430 that gas composition resulting from HTC of PSS varies with reaction temperature and
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29 431 time.

3.5. Methane production potential

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38 434 The liquid phase resulting following HTC was not subjected to anaerobic digestion;
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40 435 instead, the chemical composition of the carbonised material, and the COD and TOC
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42 436 concentrations of the liquid were used to estimate theoretical yields of methane. Fig. 4
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44 437 shows theoretical methane yields estimated using the Buswell equation, which is based
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46 438 on the chemical composition of the feed material (Buswell and Neave, 1930), and a
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48 439 correlation by Franco et al. (2007), which is based on the TOC and COD concentrations
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50 440 of the liquid. Methane yields obtained from both equations were significantly affected
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52 441 by the reaction temperature and time, and decreased as the temperature and time were
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54 442 increased. It must be noted that the Buswell equation (Eq. 8) was based on the
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56 443 compositions of the dried carbonised solids, which was used to mimic that of the liquid
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5 444 products and which gives an indication of the theoretical yields achievable. Theoretical
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7 445 methane yields obtained were 44.65% (for carbonisation at 140°C), 43.16–46.80% (for
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9 446 carbonisations at 160°C), 43.84–45.51% (for carbonisations at 180°C), and 43.73–44.58
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11 447 (for carbonisations at 200°C); compared with 46.72% for the untreated feedstock.
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14 448 The highest theoretical methane yield (77.43%) according to the correlation of
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16 449 Franco et al. (2007), was obtained from liquids generated following carbonisation at
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18 450 180°C for 30 min, with yields ranging from 67.19% (for carbonisations at 140°C),
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20 451 39.61–69.47% (for carbonisations at 160°C), 39.24–77.43% (for carbonisations at
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22 452 180°C), and 31.71–51.61% (for carbonisations at 200°C); compared with 40.19 obtained
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24 453 from feedstock filtrate. These yield were estimated based on the biodegradability
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26 454 characteristics of the liquid phase, and correlated well with the VFA concentrations in
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28 455 the liquid phase ($R^2 = 0.83$) as compared with $R^2 = 0.27$ for the Buswell equation (Fig.
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30 456 S4). The results show that the higher the VFA concentration in the liquid fraction, the
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32 457 higher the methane yield. This is because VFAs are products of hydrolysis by bacteria
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34 458 produced during the first stage of anaerobic digestion, which together with other soluble
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36 459 compounds such as amino acids and sugars are further converted to methane via
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38 460 acetogenic and methanogenic bacteria (Henze and Harremoes, 1983). The decrease in
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40 461 methane yield may also be due to the presence of less digestible higher molecular
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42 462 weight organic compounds in the liquid fraction at these conditions (Table 2). Methane
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44 463 contents of 95.0% and 94.4% have been reported for anaerobic digestion of
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46 464 hydrothermally pretreated, and NaOH pretreated rice straw followed by hydrothermal
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48 465 treatment, respectively (Chandra et al., 2012).
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3.6. Modelling and optimisation

For a comprehensive analysis of the influence of reaction temperature and time on hydrochar energetics, carbon distribution, and methane yield, a multivariable regression analysis was conducted. In order to provide a mathematical framework for future analysis and optimisation of the energetics of hydrochar production, the distribution of carbon and theoretical methane yields, models were developed in order to identify optimal process conditions investigated. The influence of the parameters investigated- reaction temperature, T ($^{\circ}\text{C}$) and reaction time, t_R (min) resulted in the following expressions in terms of actual variables:

$$Y (\%) = 118.49 - 0.26T - 0.04t_R \quad (10)$$

$$\text{HHV (MJ/kg)} = 19.54 - 9.98 \times 10^{-3}T - 0.03t_R + 1.67 \times 10^{-4}Tt_R \quad (11)$$

$$E_y (\%) = 141.21 - 0.34T - 0.19t_R + 8.16 \times 10^{-4}Tt_R \quad (12)$$

$$E_d = 0.89 + 1.03 \times 10^{-3}T + 1.44 \times 10^{-4}t_R \quad (13)$$

$$H_{\text{Crec}} (\%) = 93.95 - 0.18T + 0.17t_R - 1.08 \times 10^{-3}Tt_R \quad (14)$$

$$L_{\text{Crec}} (\%) = -93.07 + 0.61T - 0.07t_R + 1.13 \times 10^{-3}Tt_R \quad (15)$$

$$\text{CSF} = 0.55 - 1.36 \times 10^{-3}T - 6.67 \times 10^{-4}t_R + 2.80 \times 10^{-6}Tt_R \quad (16)$$

$$^*\text{CH}_4 (\%) = 45.40 - 1.38T - 1.12t_R + 0.93Tt_R \quad (17)$$

$$^{**}\text{CH}_4 (\%) = 118.11 - 0.66T - 0.21t_R + 4.55 \times 10^{-4}Tt_R \quad (18)$$

where $^*\text{CH}_4$ and $^{**}\text{CH}_4$ are methane yields according to the Buswell equation and the correlation of Franco et al. (2007), respectively.

In order to validate the accuracy of the model equations generated, they were used to calculate parameters at the various reaction temperatures and times used in this study and then compared with the corresponding experimental results. The predicted results obtained from the model equations were close to the experimental results having

standard errors ranging between 0.02–7.41% (for hydrochar yield, with $R^2 = 0.66$), 0.02–7.41 (for HHV, with $R^2 = 0.50$), 0.25–6.19% (for energy yield, with $R^2 = 0.70$), 0.24–4.85% (for energy densification, with $R^2 = 0.50$), 0.28–7.97% (for hydrochar carbon recovery, with $R^2 = 0.90$), 0.03–37.97% (for liquid phase carbon recovery, with $R^2 = 0.97$), 0.03–5.49% (for hydrochar carbon storage factor, with $R^2 = 0.84$), 0.52–3.44% (for methane yield from Buswell equation, with $R^2 = 0.64$), and 0.12–20.11% ($R^2 = 0.83$) for methane yield using the correlation of Franco et al. (2007). The relatively low standard errors and **acceptable** regression coefficients indicate that the models can be considered **reasonable** for determining the listed responses within the range of the investigated parameters.

Rather than relying on maximising the characteristics of individual parameters, model criteria were set to optimise the following: hydrochar and energy yields, hydrochar energy content and densification, hydrochar and liquid product carbon characteristics, and methane yields. Hydrothermal carbonisation at 180°C for 60 min and 200°C for 30 min proved to be **the best** operating parameters for achieving hydrochar having optimal characteristics; **these were yield (66.30–70.20%), HHV (17.70–7.90 MJ/kg), energy yield (73.00–76.90%), energy densification (1.09–1.10) and carbon recovery (57.80–60.70%), and methane yields (50.30–61.30%)**. These predictions were confirmed by experiments conducted in triplicate and showed means deviations less than 5% for HTC at 180°C for 60 min, and less than 3% for HTC at 200°C for 30 min (**Table S4**).

The models showed that there were no significant differences ($p < 0.05$) between the predicted values of the key parameters referred to above for carbonisations at 180°C for 60 min and 200°C for 30 min, which gave standard errors between 0.00–4.29%, or

0.00–5.06 for carbonisation at 200°C for 15 min. As a result of this it was revealed that carbonisations carried out at either 180°C for 60 min or 200°C for 15 min or 30 min resulted in hydrochars having the same characteristics as those obtained from the predicted results. This suggests that continuous-scale carbonisation can be performed at either of these operating conditions for effective carbonisation and to enhance methane yields from the liquid phase. The ultimate selection of operating parameters would require a more detailed investigation into process energetics. It was observed that the higher hydrochar energy and methane yields, and hydrochar carbon recovery were obtained at lower reaction temperatures (140°C and 160°C) and moderate temperature and shorter reaction time (180°C for 30 min). However, filtration to separate the liquid-phase from the hydrochar at these conditions or in shorter reaction times proved to be difficult; taking a long time to filter and yet the hydrochar contained high moisture. Also, it took long time to heat the reactor and its contents to the required temperature at these conditions, which suggests that heat transfer may not be effective on a large-scale or continuous HTC operation at these conditions, and this is an important consideration.

4. Conclusions

Reaction conditions exert a significant effect on the characteristics of all the products obtained by hydrothermally carbonising primary sewage sludge. Models were developed here which could aid in the identification of reaction conditions to tailor such products for specific end uses. Hydrothermal carbonisation at 180°C for 60 min and 200°C for 30 min resulted in hydrochars having optimal characteristics and also for obtaining optimum carbon recovery in the liquid by-product. These reaction conditions also gave optimal methane yields. Further experimental studies would need to be conducted to confirm predicted methane yields from the liquid by-products.

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Table 1 – Physical and chemical characteristics of PSS feedstock and hydrochar

Sample	Proximate Analyses				Ultimate Analysis				Yield [%]
	Moisture	Ash	Volatile Matter ^a	Fixed Carbon ^a	C	H	N	O ^b	
	[%]	[% db]	[% db]	[% db]	[%]	[%]	[%]	[%]	
Feedstock (dried)	8.17	27.54	68.56	3.90	36.63	5.79	5.29	52.30	
Hydrochar									
140°C–240 min	5.25	22.89	75.97	1.14	37.15	5.34	4.56	52.95	74.64
160°C–60 min	5.47	33.03	63.67	3.30	37.69	5.76	4.50	52.05	81.13
160°C–120 min	5.37	31.81	66.17	2.02	38.02	5.63	4.31	52.04	71.08
160°C–240 min	4.56	34.40	64.33	1.27	38.07	5.43	3.62	52.88	67.11
180°C–30 min	4.81	33.46	63.01	3.53	37.83	5.48	4.11	52.58	70.74
180°C–60 min	4.35	34.05	63.14	2.81	37.93	5.38	3.80	52.89	67.18
180°C–120 min	4.25	37.65	60.44	1.92	38.16	5.32	2.81	53.71	64.31
180°C–240 min	3.70	39.17	57.37	3.46	38.29	5.19	2.75	53.77	61.87
200°C–15 min	4.26	35.87	63.14	1.00	37.69	5.40	3.14	53.77	69.32
200°C–30 min	4.58	36.29	62.30	1.42	37.85	5.39	3.04	53.72	66.83
200°C–60 min	4.01	35.93	62.98	1.18	37.95	5.22	2.75	54.08	64.06
200°C–120 min	3.29	38.07	60.44	1.50	38.86	5.16	2.65	53.34	61.26
200°C–240 min	3.63	38.94	55.33	5.73	39.24	5.12	2.55	53.09	60.54

^a 100 – (moisture + ash + volatile matter). ^b Calculated as difference between 100 and total of C/H/N. db = dry basis.

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Table 2 – Compounds identified in the liquid fraction produced during hydrothermal carbonisation of primary sewage sludge

Sample	Compounds	Total Peak Area (%) ^a	Sample	Compounds	Total Peak Area (%) ^a
140°C 240 min	2-methylbutanoic acid	1.188	200°C 15 min	2-methylbutanoic acid	0.291
	2-methylpentanoic acid	0.847		2-methylpropanoic acid	0.675
	2-methylpropanoic acid	1.180		3-methylbutanoic acid	2.300
	3-methylbutanoic acid	3.198		4-methylpentanoic acid	1.005
	4-methyl phenol	0.344		4-methyl phenol	0.557
	Acetic acid	3.800		5-methyl-2-furancarboxyaldehyde	0.350
	Benzene acetic acid	0.087		Acetic acid	29.205
	Butanoic acid	4.494		Benzene acetic acid	0.179
	Hexanodecanoic acid	0.030		Butanoic acid	3.567
	Pentanoic acid	1.135		Pentanoic acid	1.027
	Propanoic acid	7.886		Propanoic acid	7.991
160°C 240 min	2-methylbutanoic acid	1.897	200°C 240 min	1-pyrrolideneethanamine	2.333
	2-methylpentanoic acid	0.460		1,3-Cyclopentanedione, 4	4.596
	2-methylpropanoic acid	0.843		2-ethyl-3-methyl pyrazine	1.539
	3-methylbenzofurane	0.105		2-methyl-2-butenic acid	0.351
	4-methyl phenol	0.770		2-methyl-2-phenyl 1H-indole	1.375
	Acetic acid	13.274		2-methylpentanoic acid	0.271
	Benzene acetic acid	0.255		2-methoxy-4, 4, 5-trimethyloxazoline	0.773
	Butanoic acid	5.489		2-pyrrolidone	0.152
	Pentanoic acid	1.007		3-methylbutanoic acid	0.440
	Propanoic acid	17.513		3-pyridinol	0.850
180°C 30 min	2-methylpropanoic acid	0.534		4-fluorothiophenol	1.205
	3-methylbutanoic acid	0.531		4-methyl phenol	0.834
	4-methyl phenol	0.611		6-methyl-3-pyridinol	0.418
	Acetic acid	8.083		Acetamide	1.010
	Benzene acetic acid	0.259		Acetic acid	9.008
	Butanoic acid	4.292		Benzene, 1,2-dichloro-4	0.795
	Indole, or 2,3-Benzopyrrole	0.515		Benzene acetic acid	0.906
	Pentanoic acid	0.939		Benzene propanoic acid	0.125
	Propanoic acid	7.601		Butanoic acid	3.053
180°C 240 min	2-Cyclopenten-1-one	0.254		Formic acid	1.421
	2-Methyl hexanoic acid	0.499		Glycerin	1.089
	3-ethoxy-4-methoxyphenol	0.362		Pentanoic acid	1.735
	3-pyridinol	0.362		Propanoic acid	7.872
	4-methyl phenol	0.800			
	5-isobutylpyrimidine	0.276			
	Acetamide	1.085			
	Acetic acid	10.790			
	Benzaldehyde	0.140			
	Benzeneacetic acid	1.511			
	Benzenepropanoic acid	0.199			
	Butanoic acid	4.593			
	Butanoic acid derivative	1.545			
	Formic acid	0.535			
	Pentanoic acid	1.785			
	Propanoic acid	8.965			
	Phenol	0.229			
	Trichloromethyl Benzene	0.536			
	Triphenyl phosphine	8.789			

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