Optimisation and characterisation of hydrochar production from spent coffee grounds by hydrothermal carbonisation

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1 **Highlights**

- 2 - Hydrothermal carbonisation (HTC) upgrades spent coffee grounds into high-density solid fuels
- 3 - Optimised HTC conditions yield ~64% hydrochar with a calorific value of 31.6MJ.kg⁻¹
- 4 - HTC improve the hydrochars atomic carbon content, fuel ratios and calorific values significantly
- 5 - Hydrochars have a remarkably low ash content (< 2%) and 16 priority PAH concentrations (< 3mg.kg⁻¹)
- 6 - Energy balance favours viability of HTC of spent coffee grounds for coal-substitute production

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Abstract

Current ways of managing Spent coffee grounds (SCGs) are uneconomical and have significant environmental impacts. Alternative approaches, such as hydrothermal carbonisation (HTC), which can utilise their rich organic matter for energy recovery purposes are essential. Here we present, a response surface methodology (RSM) for understanding the combined interactive effects due to the main HTC operating conditions, i.e. reaction temperature and residence time, as well as optimising them to produce hydrochar from SCGs of maximal yield and calorific value. The fuel properties and combustion behaviours of hydrochar were further evaluated to assess its suitability to replace coals for energy applications. Depending on the operating conditions, the atomic carbon content and calorific values of the hydrochar were significantly improved: by 11.2-30.7% and 15.8-44.7% respectively. The highest hydrochar calorific value recorded, 33.5MJ.kg⁻¹, resembled that of anthracite and dry steam coal, generally used in the UK. At optimal conditions of ~216°C and 1hr - guided by the RSM - a maximal hydrochar yield of ~64% and a calorific value of 31.6MJ.kg⁻¹ are feasible. Using this as a benchmark, the 500,000 tonnes of SCGs generated annually in the UK has the potential of replacing 4.4% of the coal used for electricity generation in the country.

Keywords

Spent coffee grounds, Hydrothermal carbonisation, Hydrochar, Renewable energy, Response surface method

1. Introduction

Access to clean and sustainable energy is an important challenge, which poses a threat to both developed and emerging economies. About 81.7% of world energy is derived from fossils [1]. With fossil fuels depleting, the need to meet ever-increasing energy demands, largely driven by rising global population and rapid urbanisation, suggests the availability of energy resources cannot lag behind strategic economic growth projections. More importantly, growing environmental concerns and evidence of climate change associated with the use of fossils means the role of sustainable renewable energy in the global energy mix cannot be over-emphasised. Renewable energy sources currently contribute a meagre 13.4% of world total primary energy supply [2], and to reduce over-reliance on fossils without compromising energy security plans, increasing the share and access to affordable, clean renewable energy will be imperative. Furthermore, increasing renewable energy in the global energy mix will be critical to addressing environmental and ecological concerns such as minimising fugitive emissions, waste reduction and environmental protection.

The annual production of coffee, a beverage consumed globally, has increased steadily since 2011, reaching 9.54 million tonnes globally in 2017 [3]. Accordingly, the generation of spent coffee grounds (SCGs), the solid residue remaining after brewing coffee, has also increased. An estimated 650kg of SCGs is produced from brewing one tonne of coffee, translating to more than 6 million tonnes of SCGs generated per year [4]. The enormous amount of SCGs generated is generally considered as a waste, largely underutilised (most ends up disposed in landfills [5]) and lacks economic value but incurs significant disposal costs. For example, applying the UK standard landfill tax rate [6], the estimated 500,000 tonnes of SCGs produced annually in the UK [7] translates to £44.4 million in landfill disposal costs. Aside from the cost implications associated with SCGs disposal, improper SCGs management bears significant pollution, environmental contamination and fugitive gas emission risks [4]. The potential release of toxic residual substances (e.g. caffeine, tannin and phenols) left in SCGs, leachate release and greenhouse gas (GHG) emissions from decomposition in landfills makes them phytotoxic and hazardous to the environment [5, 8].

SCGs, however, are rich in organic matter containing cellulose (8.6–13.3wt.%), oil (10–20wt.%), hemicellulose (30–40wt.%) and lignin (25–33wt.%) [9], which makes them attractive for energy recovery purposes. Direct use of pure SCGs as logs or pellets in commercial pellet boilers has proved to be impractical, as this has resulted in a lower boiler efficiency accompanied by significant emissions of particulate matter and nitrogen oxidants [10]. While anaerobic co-digestion of SCGs with other substrates such as sewage sludge is promising, studies have indicated mono-digestion of SCGs substrate is prone to failure and has long-term stability limitations [11–12]. Studies have also investigated the conversion of SCGs, mostly for liquid biofuels production, such as biodiesel, bioethanol and bio-oil using transesterification, enzymatic hydrolysis and pyrolysis/hydrothermal liquefaction processes respectively [5, 9, 13–15]. These processes usually require particular feedstock conditions (e.g. very low moisture/ash content, high carbon density); pre-treatment stages (e.g. homogenisation of feedstock; drying; extractions); use of a highly reactive environment (e.g. high temperature, pressure, inert atmospheres); and/or the use of chemicals, mostly derived from fossils. For example, the relatively high temperature regimes (400–600°C) associated with pyrolysis and the requirement of dried feedstock

will have significant energy and cost implications for managing SCGs, which are typically high in moisture (50–60wt.%) [13]. Also, studies have shown that oil extraction techniques employed during biodiesel production of SCGs are both time and energy intensive, require a significant amount of solvents and have low productivity [16–17]. These inevitable requirements raise questions about the sustainability of these processes and call for the investigation of suitable alternatives.

Hydrothermal carbonisation (HTC) is a thermochemical process that is particularly well suited for managing wet substrates such as SCGs. HTC is distinguished by the use of wet feedstock >50wt.% moisture – such as SCGs – obviating the need for energy-intensive drying before or during the process. HTC utilises relatively mild temperature regimes (180–250°C) under autogenous pressure conditions to convert biomass organics into a carbonaceous (coal-like) solid, i.e. hydrochar and organic-rich process liquor. The efficacy of HTC to convert a variety of feedstocks – including pure substances such as cellulose and glucose [18–19]; lignocellulosic biomass [20–21]; livestock waste [22–23]; sewage sludge and human waste [24–25] – has been reported. The preclusion of chemical use/microbial cultures; absence of fugitive gas emissions; relatively mild temperatures and processing times; and overall process efficiency make HTC an environmentally friendly option for addressing SCGs waste [26]. Hydrochars, the solid product derived from HTC, have desirable properties which have diverse applications, including bioenergy production [20, 24]. Despite the technological potential of HTC, however, there are still a paucity of information on statistically optimised conditions for realising best-quality hydrochar for energy applications. To the best of our knowledge, no work has been done to optimise the yield and energy properties of SCGs for hydrochar production. Bioenergy production from biowaste such as SCGs is both timely and relevant, particularly in the UK, considering its strategic plans to phase out the generation and use of coal power by 2025 as part of concerted efforts to meet emission targets [27]. Projections indicate that bioenergy will play a significant role in the energy security and clean growth strategy in the UK, as electricity generation from coal (which has declined significantly since 1998, from a record high of 144.95TWh in 2006 to a record low of 22.51TWh in 2017, with a corresponding increase in baseload supply from bioenergy sources – from 2.93TWh to 17.70TWh over the same period [28]) is now being replaced low-carbon technologies. Furthermore, polycyclic aromatic hydrocarbons (PAHs), mainly emitted from incomplete combustion of fuel, particularly indoors, are of environmental concern due to their carcinogenicity potentials [29]. No information exists on the environmental risks which can result from using hydrochar produced from SCGs (for energy application purposes) by the way of their potential PAHs emissions.

The main objective of this work was to present, for the first time, important experimental and statistical information on the potential of the HTC process to address SCGs waste (instead of sending it to landfill), while also realising quality hydrochar suitable for bioenergy application by means of a design of experiment – response surface methodology (DoE-RSM). The DoE-RSM is a proven and widely reported approach for investigating the combined interactive effects between independent (input) variables on a process. They are particularly useful in process optimisation to yield responses (outputs) for all possible combination of inputs within an experimental space to allow the identification of optimal conditions. Unlike the conventional approach of changing one single variable at a time, fewer experimental runs are required for process optimization, thereby making the approach time and resource-effective. The DoE-RSM approach was adopted in particular in this work to further understand HTC process operating

conditions (i.e. residence time and reaction temperature), interactions during HTC conversion of SCGs and to enable the development of appropriate models which will enable the prediction of the optimum operating conditions required for the synthesis and recovery of desired hydrochar properties. The specific objectives of this study were to:

- (a) investigate the potential of the HTC process to address underutilised SCGs waste by upgrading this into solid fuel of enhanced fuel properties and further illustrate improvements in the structural, fuel and combustion properties of SCGs hydrochar to support their suitability for replacing coals;
- (b) study the effects of HTC operating parameters (reaction temperature, T , and residence time, t) on the yield and characteristics of hydrochar obtained, and to present optimum HTC operating conditions for producing high-value hydrochar (based on yield and calorific value) by means of a DoE-RSM approach; and
- (c) evaluate the energy efficiency of using the HTC process for producing hydrochar from SCGs and further assess the possible environmental risks of using hydrochar as a renewable solid fuel (by means of 16 toxic PAHs evaluation) to additionally demonstrate their potential as a viable coal substitute.

2. Materials and methods

2.1 Materials

SCGs waste was collected from a café outlet within Loughborough university, Leicestershire, UK. The current study used SCGs consisting of Arabica and Robusta (80%: 20%) blend and with a moisture content of 52.4% (as received). The physical and chemical characteristics of the SCGs used in this study are shown in Table 1. All samples were stored as received between 3 and 5°C to minimise microbial growth and decomposition. However, samples were brought to room temperature for all HTC experiments and/or analyses.

2.2 HTC experiments

HTC experiments were carried out in a 2L PTFE vessel placed in a high-pressure stainless-steel tubular reactor (Berghof Ltd, Germany) rated at 300°C and 200 bar. The reaction temperature was measured via a thermocouple placed centrally within the PTFE reactor vessel and connected to a BTC-3000 regulator, which maintained a set reaction temperature during the HTC process. A PT-100 pressure sensor also measured autogenously generated pressure inside the vessel. Raw SCGs were mixed with de-ionised water at a solid: water (w/w) ratio of 1:10 for each experimental run. Following carbonisation, the reactor vessels were cooled to room temperature and the carbonised materials removed and filtered with a 63µm mesh sieve. The solids, i.e. hydrochars, were dried at 105°C for 24hrs. The hydrochar yield was estimated using Equation 1.

$$\text{Hydrochar yield, } H_y (\%) = \frac{\text{Wt. (dried) of hydrochar}}{\text{Wt. (dried) of raw SCG}} \times 100 \% \quad \text{Equation 1}$$

2.3 Experimental design

A DoE-RSM by means of faced-centred central composite factorial design (CCF) was used to fit two *responses*, i.e. hydrochar yield and calorific value (by means of their higher heating value, HHV) as a function of two *factors* i.e. HTC reaction temperature, $T(^{\circ}\text{C})$ and residence time, t (hr). The influence of the two *factors* on the structural, chemical and fuel properties of the hydrochar recovered from the HTC process liquor were also investigated. The CCF design, coded at $\alpha = \pm 1$, requires three levels for each factor and consisted of 13 runs in total: four factorial points, four axial points and five centre points to provide quality prediction and improve model reliability. The carbonisation reaction temperature (Factor A) was thus coded at 180°C, 200°C and 220°C, while residence temperature (Factor B) was coded at 1, 3 and 5 hours. The residence time required did not include the time expended to reach the desired reaction temperature. Regression analysis was used to derive a second-order polynomial equation of the general form presented in Equation 2.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 + \dots + \varepsilon \quad \text{Equation 2}$$

where y is the measured response, i.e. H_y , HHV;

x_1 and x_2 are the independent factors, i.e. T , t ;

β_0 ; β_1 & β_2 ; β_{11} & β_{22} ; β_{12} are the intercept, linear, quadratic & interaction coefficients respectively; and

ε is the experimental error.

A JMP statistical software (licenced to Loughborough University, UK) was used carry out the DoE-RSM design and all statistical tests/analyses.

2.4 Characterisations

2.4.1 Dried SCGs feedstock and hydrochar

Dried SCGs and hydrochar recovered from each HTC operating condition investigated were characterised using a suite of analytical techniques, as follows:

- Proximate analysis – moisture content (MC), volatile matter (VM) and ash content – was conducted using Navas TGA-2000A analyser (Navas Instruments, USA), adopting ASTM D7582-15 [30].
- Elemental analysis – carbon (C), hydrogen (H) and nitrogen (N) content – was conducted using a CHN analyser (CE-440 Elemental Analyzer, Exeter Analytical Inc., UK), adopting ASTM D5373-16 [31].
- The calorific values of the samples were measured using a bomb calorimeter (Automatic Isoperibol Calorimeter, Parr Instrument, USA), based on the ISO 1928:2009 Standard [32].
- Surface morphologies of samples were examined on a LEO 1530VP Field Emission Gun Scanning Electron Microscope (FEG-SEM).
- Imaging was conducted at an accelerating voltage of 5kV primary electron beam current of approximately 200pA.

Thermogravimetric analysis was carried out using a thermogravimetric analyser (Q5000IR TGA, TA Instruments, UK). Between 10mg and 30mg of the representative sample was placed in a platinum crucible and heated under atmospheric pressure, with an airflow rate of 50ml.min⁻¹. Weight loss and the corresponding weight loss rate, i.e. derivative TG (DTG), of samples were measured

continuously under non-isothermal conditions, with a temperature range of 20–700°C at a constant heating rate of 10°C.min⁻¹. The 16 toxic PAHs compounds were analysed to assess potential risk associated with the use of hydrochar as solid fuel. Briefly, extraction was conducted using 1g of sample with 10ml of dichloromethane (DCM) (with added p-terphenyl) as the extraction solvent. The mixture was left on a mechanical shaker for an hour. Extracts were cleaned up during extraction with Florisil. After extraction, they were filtered and were analysed by gas chromatography–mass spectrometry (GC–MS) (GC model Agilent 6890N fitted with a 5975C-MS detector). The GC used was equipped with a Rxi-5MS column (20m x 0.18mm internal diameter, 0.30µm film thickness). Helium was used as the carrier gas, supplied at 0.8mlmin⁻¹. The oven was programmed as follows: temperature ramp to 45°C then to 250°C (at 55°C.min⁻¹) for 2 mins and, finally, to 320°C (at 40°C.min⁻¹) and held isothermally for 4 mins. Extraction efficiency was measured by spiking a blank with a known amount of a PAHs spiking mixture (50uL x 200ug/mL) and subjected to the same analytical procedure.

2.5 Energy balance calculations

Net energy, Q_{net} , was determined from the energy used for hydrochar production and the energy produced from the combustion of hydrochar. The input energy, Q_{in} , did not consider energy expended to heat up the HTC system, since this would vary depending on reactor type, design and operational conditions/procedures [23]. Q_{in} was based on the sum of energy required to heat both the moisture and dry contents of SCGs feedstock during the HTC process and was estimated as:

$$Q_{in} = m_w (H_{w, HTC} - H_{w, 25}) + m_s C_s (T_{HTC} - 25) \quad \text{Equation 3}$$

where m_w , m_s are water and solid contents of the biomass: water mix respectively;
 $H_{w, HTC}$, $H_{w, 25}$ are enthalpies of water at HTC reaction temperature and at 25°C respectively;
 C_s is specific heat capacity, i.e. 2.5kJ.kgK⁻¹ (assuming mean value for dried coffee between 25°C and 210°C [24] ; and
 T_{HTC} is the HTC reaction temperature.

Energy output, Q_{out} , was estimated from the combustion of hydrochar Q_{HC} , as presented in Equation 4:

$$Q_{out} = m_{HC} * HHV_{HC} \quad \text{Equation 4}$$

where m_{HC} , HHV_{HC} are dried mass (kg) and HHV (MJ.kg⁻¹) of SCGs hydrochar.

Finally, an estimation of hydrochar-electricity generation potential in the UK was evaluated based on Equations 5:

$$\text{Fraction of coal replaceable by hydrochar in the UK is estimated as: } \frac{E_{HC}}{E_C} \times 100\% \quad \text{Equation 5}$$

where E_{HC} is electricity from hydrochar production; and
 E_C is UK electricity from coal.

3. Results and discussions

3.1 Optimisation of hydrochar yield and calorific value

3.1.1 Hydrochar yield

HTC operating conditions played a crucial role in determining hydrochar yield. The impact of HTC conditions, i.e. reaction temperature, T , and residence time, t , on hydrochar yield investigated through the DoE-RSM is shown in Figure 1.

Figure 1 Response surface plot of hydrochar yield, showing the effects of **T** and **t** at various operating conditions

Figure 1 shows hydrochar yield is influenced by reaction temperature, **T**, and residence time, **t**, as hydrochar yield decreased with increase in both **factors** – forming a curve-shaped response surface. However, reaction temperature, **T**, had a more significant influence on hydrochar yield than residence time, **t**. Elevating reaction temperature from 180°C to 220°C resulted in a net 13.5% decrease in hydrochar yield, while the decrease in yield associated with increasing residence time from 1 to 5hrs for all reaction temperatures investigated (with most significant at 220°C) was 8.3%. Evidently, increasing the severity of the HTC operating conditions leads to a higher degree of thermolytic decomposition, fragmentation and solubilisation of SCGs macromolecules, resulting in decreasing solid yield [34]. The highest decrease in hydrochar yield was observed when reaction temperature was increased from 200°C to 220°C, consistent with the temperature ranges effective for significantly decomposing SCGs hemicellulose and lignin content [26, 35], while also triggering substantial cellulose degradation (above 210°C) under hydrothermal conditions [36].

The response surface plot further illustrates the impacts of both operating conditions when the effects tests for each parameter – reaction temperature, **T** ($F_{ratio} = 61.58$; **p-value** = <0.0001) and residence time, **t** ($F_{ratio} = 12.84$; **p-value** = 0.0072) – were critically examined. Furthermore, and more importantly, hydrochar yield was also found to be significantly affected by an interaction effect of reaction temperature and residence time (**T x t**: $F_{ratio} = 6.44$; **p-value** = 0.035) and a quadratic effect due to reaction temperature, i.e. T^2 (T^2 : $F_{ratio} = 5.57$; **p-value** = 0.046), evident from the curvature seen in Figure 1. The response surface model implies that the linear, interaction and quadratic effects are significant for optimising hydrochar yield. The model fitted to optimise hydrochar yield was observed as a good fit, **RMSE** = 1.39, **R²** = 0.92 at **p-value** = 0.0002, and is represented by Equation 6.

$$H_y (\%) = 65.28857 - 1.9016t - 4.165T - 1.65Tt - 1.7069T^2 \quad \text{Equation 6}$$

In terms of their physical qualities, the hydrochar obtained retained its brownish black colour and was friable and easily ground into powder. The textural qualities of the hydrochar suggest it could be used either in powdery form or compacted into high-density solid fuel briquettes.

3.1.2 Optimisation of hydrochar calorific value

The calorific value of hydrochar is an important characteristic that enables its assessment as a solid fuel and determination of key energy parameters – such as, energy densification and energy yield – for comparative evaluation with conventional fuels. The effect of HTC on the SCGs feedstock was observed to generate significant calorific value improvement (% HHV improvement), i.e. up to a 44.7% increase over raw SCGs (see Table 1). In contrast to the hydrochar yield trend, the calorific value of hydrochar increased as reaction temperature and residence time were increased respectively. SCGs hydrochar yielded calorific values that were greater than low-rank fuels such as peat (17.1MJ.kg^{-1}), lignite ($17.6\text{--}21.9\text{MJ.kg}^{-1}$), bituminous coal ($30.2\text{--}31.0\text{MJ.kg}^{-1}$) and comparable to anthracite coal ($31.8\text{--}34.5\text{MJ.kg}^{-1}$) [37–39]. At 220°C , the hydrochar calorific value – i.e. 33.5MJ.kg^{-1} – was greater than house coal (30.1MJ/kg) and coals reported in power stations and other industrial applications ($24.2\text{--}32.8\text{MJ.kg}^{-1}$) in the UK [39]. This suggests the use of SCGs hydrochar either as a stand-alone solid fuel for domestic energy consumption (e.g. for cooking and heating) or as one that can substitute/be co-combusted with coals of similar heating value for energy generation. The increased calorific value of biomass after carbonisation is a peculiar phenomenon of the HTC process, which has also been reported extensively [20, 40–41]. The energy enrichment factor (EEF) was observed to increase with increasing process conditions from 1.16 to 1.45, with the highest densification recorded at 220°C (Table 1). These results are similar to those reported for hydrochar produced from municipal solid waste (MSW) (EEF increase from 1.01 to 1.41 [42]) and support evidence that HTC promotes energy densification in hydrochar. Energy yield (E_v), which provides a means for assessing the energy recoverable from chars, averaged 83.3% over the operating conditions investigated. In spite of the decreasing hydrochar yield, the high calorific value of hydrochar promoted a high-energy yield per unit weight of hydrochar produced.

Figure 2 shows the response surface plot obtained for hydrochar calorific value, illustrating the impact of reaction temperature and residence time. The surface plots indicate slopes for both reaction temperature and residence time, suggesting that both factors influenced the calorific values of hydrochar.

Figure 2 Response surface plot of hydrochar calorific value, showing the effects of **T** and **t** at various operating conditions

The effects statistical tests for each **factor** were observed to be significant: reaction temperature, **T** ($F_{ratio} = 986.19$; **p-value** = <0.0001) and residence time, **t** ($F_{ratio} = 82.98$; **p-value** = <0.0001). Unlike hydrochar yield, interaction and quadratic effects were not significant in the predictive model of hydrochar calorific values due to high **p-values** > 0.2. Hence a linear model is most appropriate for optimising hydrochar calorific values. The model fitted to optimise hydrochar yield was also observed as a good fit, **RSME** = 0.19, **R²** = 0.99 at **p-value** <0.0001, and is represented by Equation 7:

$$HHV (MJ.kg^{-1}) = 30.0724 + 0.7117t + 2.4533T \quad \text{Equation 7}$$

3.1.3 Optimum HTC operating conditions for recovering SCGs hydrochar

Optimising HTC operating conditions for the recovery of hydrochar fuel is crucial, particularly from a process development perspective. An ideal, cost-effective HTC process should be characterised by lowest possible reaction temperature and residence time for maximal hydrochar yield and highest calorific value possible. Based on the DoE-RSM employed in this study, we discovered that for the given HTC parameter space investigated, a maximal hydrochar yield of 63.9% and 31.6MJ.kg⁻¹ calorific value could be obtained at optimum operating condition **T = 216.4°C** and **t = 1hr**. When compared with HTC operating conditions that have been used for different feedstocks in the literature, and considering up to 350°C [43] and 96hrs [44] have been reported, the optimal condition from the current study is relatively mild for addressing SCGs waste, yet promises a high hydrochar mass yield (typical reported range: 36–80wt.% [26; 45–46]) and calorific value (typical reported range: 14–28MJ.kg⁻¹ [19; 41–42, 47]). Furthermore, the optimum condition reported in this study would represent huge cost and energy savings from the process development and economic viability perspectives when compared to other operational ranges: 380°C–700°C and up to 24hrs

employed in previous studies to recover solid fuel (<40% yield and 32MJ.kg⁻¹ heating value) from SCGs involving pyrolysis processing [48–50].

3.2 Hydrochar properties: proximate and elemental composition

The proximate and elemental analyses were of the well-established thermochemical properties of solid fuels. These were conducted to further illustrate the hydrochar fuel properties produced at the different operating conditions investigated, as presented in Table 1.

Table 1 Fuel properties of SCGs and hydrochar

	Raw SCGs	180°C			200°C			220°C		
		1hr	3hr	5hr	1hr	3hr	5hr	1hr	3hr	5hr
<i>Proximate composition (db.)</i>										
VM (%)	77.91	76.37	72.61	71.96	69.35	68.69	67.92	66.09	66.11	63.93
Ash (%)	1.60	0.80	0.97	0.97	0.98	0.96	1.05	1.08	1.11	1.29
FC (%)*	20.49	22.84	26.42	27.07	29.67	30.35	31.03	32.83	32.78	34.78
Fuel ratio	0.26	0.30	0.36	0.38	0.43	0.44	0.46	0.50	0.50	0.54
<i>Elemental composition</i>										
C (%)	53.94	60.00	63.11	63.42	65.45	65.56	66.15	68.69	69.42	70.51
H (%)	7.06	7.49	7.31	7.13	7.12	7.11	7.28	7.35	7.39	7.36
N (%)	2.29	2.29	2.46	2.54	2.61	2.66	2.66	2.85	2.78	2.98
O (%)*	36.72	30.22	27.12	26.91	24.81	24.67	23.91	21.11	20.40	19.15
<i>Carbon properties</i>										
C _{Char}		76.09	79.73	78.42	80.63	79.36	79.77	80.48	77.42	71.77
C _{DF}		1.11	1.17	1.18	1.21	1.22	1.23	1.27	1.29	1.31
%C increase		11.24	17.01	17.57	21.35	21.54	22.64	27.35	28.71	30.72
<i>Energy properties</i>										
EEF		1.16	1.20	1.24	1.28	1.30	1.32	1.39	1.40	1.45
% HHV improvement		15.75	20.11	23.65	27.59	29.79	32.05	38.62	39.74	44.68
E _v (%)		79.17	81.84	82.47	84.78	84.75	85.89	87.60	84.05	79.43

* Estimated by difference

Carbon retained in hydrochar (wt.%), $C_{char} = \frac{\% C \text{ in hydrochar} \times \text{mass of hydrochar recovered}}{\% C \text{ in raw SCG} \times \text{mass of raw SCG}}$

Percentage carbon increase (%), $\%C \text{ increase} = \frac{\%C \text{ in hydrochar} - \%C \text{ of raw SCG}}{\%C \text{ of raw SCG}} \times 100\%$

% HHV improvement = $\frac{HHV \text{ of hydrochar} - HHV \text{ of raw SCG}}{HHV \text{ of raw SCG}} \times 100\%$

Carbon densification factor, $C_{DF} = \frac{\% C \text{ in hydrochar}}{\% C \text{ in raw SCG}}$

Energy enrichment factor, $EEF = \frac{HHV \text{ of hydrochar}}{HHV \text{ of raw SCG}}$

Energy yield, $E_v (\%) = EEF \times H_v (\%)$

3.2.1 Proximate composition

The proximate analysis of raw SCGs revealed volatile matter (VM) of 77.9% and a considerably low fixed carbon (FC) of 20.5%, resulting in lower fuel properties. When compared with hydrochar recovered after the carbonisation conditions investigated, VM decreased by 13.9% coupled with a corresponding increase in FC by 14.3%, indicating improved and higher energy density and, by extension, enhanced fuel properties of the hydrochar. This is due to the carbonisation process, as observed in previous studies [20, 40]. For direct combustion purposes, lowering volatile matter in combustible hydrochar carbon is particularly beneficial for reducing pollutant emissions and preventing a decline in combustion efficiency. Clearly from Table 1, FC and VM of SCGs hydrochar are dependent on operating conditions: FC indicated a positive correlation while VM indicated a negative correlation as operating conditions become severe.

Of particular interest is the ash content observed in the hydrochar. The detrimental impacts of high ash content in fuels during combustion are well known and documented. Essentially, ash content influences the choice of combustion and gas-cleaning technologies. Fly ash formation, ash deposit formation, ash storage and ash management (utilisation/disposal logistics) also depend on the ash content of a fuel [51–52]. Therefore, from an energy application perspective, fuels with a low ash content are more beneficial. Hydrochar ash content is predominantly influenced by feedstock type and operating conditions. For example, studies have reported ash contents ranging between 4 and 11.5% in hydrochar derived from lignocellulosic biomass, including barley straw, maize straw, watermelon, coconut fibre and eucalyptus leaves [53–54]. Likewise, 21–29% ash content has been reported for hydrochar recovered from fish waste [55], while swine manure, poultry litters and sewage sludge hydrochars have had ash contents reported of up to 27.8% [22], 30.4% [23] and 46.7% [24] respectively. In contrast, all SCGs hydrochar ash contents are remarkably low, less than 2% for all operating conditions investigated. From an energy perspective, the low ash content of SCGs hydrochar would be highly advantageous if they were used as a solid fuel and would ultimately contribute to reduced fouling, deposition, agglomeration/slagging issues and the overall operating costs associated with gas-cleaning technologies and ash management.

The combustibility of the solid fuel, indicated by the fuel ratio (i.e. ratio of FC to VM), was determined. It was realised that increasing the severity of the HTC operating conditions resulted in a remarkable effect on hydrochar fuel ratios, suggesting improved combustibility of hydrochar. When compared with raw SCGs, the fuel ratio of the hydrochar increased significantly – from 0.26 to 0.54; the highest fuel ratio was observed at 220°C. The SCGs hydrochar fuel ratios were also observed to be higher than those reported in previous studies [24, 55].

3.2.2 Elemental composition

Remarkably, HTC initiated significant changes in the elemental composition of the hydrochar recovered from SCGs. Consistent with previous studies [19, 56], a majority of the atomic carbon content (up to 80.6wt.%) from the starting feedstock was retained in the solid hydrochar, thus demonstrating the sequestration potential of the HTC process. Changes in elemental composition were also observed to be dependent on carbonisation conditions. An increase in the carbon content of hydrochar, and a corresponding decrease in the oxygen content, was observed for all hydrochars recovered at the carbonisation conditions investigated. Up to 30.7% carbon increase was recorded due to carbonisation effects (See Table 1). The carbon densification factors of the chars, which were greater than 1 in all cases, were comparable to the values in another study ranging between 1 and 1.8 [56]. Accordingly, HTC increased the carbon content and carbon densities of the SCGs hydrochar.

With both parameters measured independently, a strong correlation ($R^2 = 0.98$) between calorific values and the carbon content of both raw SCGs and processed hydrochar was observed, as shown in Figure 3. This further implies the increased carbon content effect of the HTC process and produces higher hydrochar heating values. Furthermore, unlike most coal with less than 2% nitrogen content but up to 7.2% sulphur content [37], the absence of sulphur and relatively low nitrogen content of SCGs hydrochar (less than 3wt.%), will contribute to reduced emissions of unwanted nitrogen oxides during combustion.

1 The molar ratios of H/C and O/C were also estimated from elemental compositions and were analysed with a van Krevelen diagram,
 2 as shown in Figure 4, to further understand the reaction pathways associated with the HTC of SCGs. Figure 4 shows the atomic
 3 ratios moving from upper right to lower left, illustrating both the progression of the carbonisation process and how increasing the
 4 HTC operating conditions intensified the degree of carbonisation. Also, Figure 4 provides evidence that the HTC of SCGs is
 5 predominantly governed by dehydration and decarboxylation reactions, as the H/C and O/C ratios decreased significantly – by
 6 20.5% and 60.7% respectively. These results further suggest changes in the structural elemental compositions of hydrochar solid
 7 fuels, which favour energy application purposes.

8
 9 **Figure 3** Correlation of hydrochar calorific values (MJ.kg^{-1}) against carbon content (%)

10
 11 **Figure 4** Atomic ratios H/C against O/C for raw SCGs and hydrochar at varying operating conditions investigated, illustrating the delineation
 12 of reaction pathways from raw SCGs to 180°C, carbonisation progression trend ($R^2 = 0.98$) and a transitional region between low-rank and
 13 high-rank coals

3.3 Hydrochar properties: Surface morphology of SCGs hydrochar

SEM micrographs enabled the examination and analysis of microstructural changes of the hydrochar produced by the HTC process at the varying carbonisation conditions. Figures 5A & B show the SEM images of raw SCGs and SCGs hydrochar, revealing interesting and distinctive surface morphologies. Raw SCGs exhibit a rough and irregular surface morphology, consistent with those reported in a previous study [57]. In comparison, irrespective of the varying carbonisation conditions, SCGs hydrochars showed distinctive morphologies that suggest the HTC process resulted in a major transformation of SCGs hydrochar surface morphologies. SCGs hydrochars at all reaction temperatures and residence times showed similar morphological patterns, characterised by tunnelling features, pore formation/enlargement and microstructural fragmentations. While more discernible porous features are exhibited at 1hr and 3hr residence times, a proliferation of smaller fragments scattered irregularly in and around the porous/rough surfaces of the hydrochars can be observed at 5hr residence times. These observations further support the thermolytic decomposition, fragmentation and devolatilisation reactions characteristic of the HTC process [24, 34]. The SCGs hydrochars' enhanced porous features could promote air access and distribution, resulting in higher thermal reactivity during combustion. In addition, these porous features could be harnessed for other applications, such as removal of contaminants.

Figure 5 SEM micrographs: (A) raw SCGs; (B) hydrochar recovered from SCGs at conditions investigated (scale: 10µm; Mag: x500)

3.4 Hydrochar properties: Thermal combustion behaviour

Thermogravimetric analysis (TG) is an established technique for evaluating the combustion behaviour of fuel materials. Fuel burning characteristics, revealed by the TG-DTG curves, are paramount to assess thermal reactivity and decomposition stages as temperature increases. The TG-DTG profiles of raw SCGs and hydrochar are presented in Figures 6 and 7; these reveal marked differences in the combustion profiles of raw SCGs in comparison to the hydrochar.

Figure 6 TG profile of raw SCGs and hydrochar obtained at varying operating conditions

Figure 7 DTG profile of raw SCGs and hydrochar obtained at varying operating conditions

Basically, the decomposition of raw SCGs and their hydrochars involved several discrete stages. These began with a dehydration stage – depicted on the DTG profile (Figure 7) by the small discrete peaks summing about 60°C, which occurred between 20°C and 100°C for the hydrochar and between 35°C and 160°C for the raw SCGs, summing at 55°C. This stage corresponds to the residual (adsorbed) moisture loss present in all materials, evident by the <0.03%/°C weight loss rate for the hydrochar and about 0.08%/°C for the raw SCGs. No other distinctive peak was observed below 200°C. After the dehydration phase, the raw SCGs exhibited two additional main stages. The first stage occurred between 160°C and 460°C and had a maximum peak and weight loss rate of 288°C and 0.76%/°C respectively. This stage is attributed to the volatile matter release associated chiefly with the decomposition of the hemicellulose and cellulose components of raw SCGs [58]. The final stage, summing at 502°C, occurred between 460°C and 550°C; this corresponds to the degradation of the raw SCGs lignin component [59].

However, close examination of the DTG curves (Figure 7) obtained for the hydrochars reveals three distinct peaks after moisture removal. The first prominent weight loss noticeable on the combustion profile occurred between 100°C and 250°C, with distinctive peaks about 215 ± 5°C – which is attributed to light volatile release. This is followed by another set of prominent peaks occurring between 250°C and 370°C, summing about 315 ± 15°C. This is also consistent with volatile matter combustion. A significant weight loss rate between 0.2 and 1.15%/°C (depending on the operating conditions) occurred at the **secondary** volatile release stage for all hydrochar samples. Interestingly, it was observed that only hydrochar recovered at and after 200°C 3hr exhibited this **two-phased** volatile release stage. The preliminary volatile release phenomenon observed indicates the presence of short-chain hydrocarbons [60], resulting from the decomposition of SCGs long-chain polymers during the HTC process. Short-chain hydrocarbon monomer proliferation with increasing reaction temperature could explain why the preliminary volatile release peak becomes more prominent for hydrochars obtained at and after 200°C. This further implies that significant degradation of SCGs lignocellulosic content during the HTC process began about 200°C. Lastly, the final prominent peak summing about 482 ± 10°C was observed between 370°C and 550°C and is attributed to char combustion.

3.5 Hydrochar properties: PAHs

Assessing PAHs emissions associated with the combustion of hydrochar is highly important to provide information regarding their toxicity and potential environmental risk, especially when considering their use as a renewable fuel. Total PAHs and individual contributions from the 16 priority PAHs provide this important information. From Table 2, the total 16 priority PAHs of all hydrochars was found to be below 0.8mgkg⁻¹, except for those recovered at 220°C 3hr, which was 2.74mgkg⁻¹; this was largely due to three-ring PAHs – fluorene, phenanthrene and anthracene. When compared with conventional sources of fuel, total PAHs observed from SCGs hydrochar are lower than those reported for coal, dung cake and domestic firewood, as illustrated in Table 3. Importantly, benzo (a) pyrene, one of the potent carcinogen PAHs [29], was found to be < 0.01mgkg⁻¹ for all hydrochars; this is significantly lower than those reported for peat briquettes (0.8mgkg⁻¹); birch and pine firewood (1.6–8.2mgkg⁻¹) [61]; and various forms of wood fuel (5.3–13.2mgkg⁻¹) [62–63].

1 **Table 2** Concentration (mg.kg⁻¹) of 16 priority PAHs in SCGs and hydrochar

Ring number	Priority PAH	Raw SCGs	180°C 1hr	180°C 3hr	180°C 5hr	200°C 1hr	200°C 3hr	200°C 5hr	220°C 1hr	220°C 3hr	220°C 5hr
2	Naphthalene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.04	0.11	0.01
	Acenaphthylene	< 0.01	0.02	< 0.01	0.05	0.08	0.14	0.29	0.20	< 0.01	< 0.01
	Acenaphthene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.09	0.03	< 0.01	< 0.01
3	Fluorene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.03	0.01	0.28	< 0.01
	Phenanthrene	0.04	0.07	0.04	0.07	0.05	0.06	0.08	0.38	1.99	< 0.01
	Anthracene	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	0.02	0.05	0.36	< 0.01
	Fluoranthene	0.03	0.03	< 0.01	< 0.01	< 0.01	0.06	0.05	< 0.01	< 0.01	< 0.01
4	Pyrene	0.03	0.04	< 0.01	< 0.01	< 0.01	0.03	0.05	< 0.01	< 0.01	< 0.01
	Benzo (a) anthracene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Chrysene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Benzo (b) fluoranthene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01	< 0.01
5	Benzo (k) fluoranthene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01	< 0.01
	Benzo (a) pyrene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Dibenzo (a,h) anthracene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01	< 0.01
6	Indeno (1,2,3-cd) pyrene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.03	< 0.01	< 0.01	< 0.01	< 0.01
	Benzo (g,h,i) perylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01
Total PAH (16)		0.10	0.19	0.05	0.15	0.15	0.42	0.63	0.72	2.74	0.04

2 **Table 3** Total PAHs of solid fuels

Substrate	HTC conditions	Total 16 PAHs (mgkg ⁻¹)	References
Maize silage, leftover foods, biogas plant digestate, grass greenery and sewage sludge	A commercial two-stage HTC process: 230°C, 15mins (stage 1) and 180°C, 75mins (stage 2)	0.5–12	[64]
Wheat straw, poplar wood and olive residues	180°C–230°C	1.8–5.0	[65]
Orange pomace	170°C–260°C	Below detection	[66]
MSW	160°C–240°C	1.378–177.7	[67]
SCGs hydrochar	180°C–220°C	0.04–2.74	Current study
50 different biochars	250°C–900°C	0.07–3.27	[68]
Anthracite coal	n/a	0.95–2.0	[69]
Rice husk briquettes	n/a	140	[69]
Dung cake	n/a	3.1–5.5	[63]
Domestic firewood	n/a	2.0–114	[29]

3 Unlike biosolids, compost and soil, legalised thresholds and frameworks for PAHs limits in hydrochar are still evolving. Standard
 4 PAHs in biosolids in the European Union (EU) range from 3 to 6mgkg⁻¹ [70], while US-Environmental Protection Agency (EPA) limits
 5 PAHs to 6mgkg⁻¹ for all 16 priority PAHs [65]. Using these as benchmarks, total PAHs reported for all SCGs hydrochars in this study
 6 were below regulatory limits and thus pose no health/environmental risks for their adoption as renewable solid fuel.

7 3.7 Energy efficiency of hydrochar

8 Analyses of process energy consumption and energy recovery are important to assess their economic feasibility. As illustrated in
 9 Table 4, and based on the approach used in this work, the amount of input energy, Q_{in} , required for the carbonisation of SCGs
 10 biomass/water mixture is largely influenced by the moisture content of the mixture. This is similar to observations reported on
 11 the HTC of poultry litter [23]. Energy output, Q_{outs} , which depends on hydrochar yield and heating value, was up to 2.3MJ at 220°C.

At the operating conditions investigated in this work, HTC of SCGs results in a net energetically positive energy balance. Depending on the operating conditions, 30 to 40% of hydrochar combustion energy can provide the input energy necessary for the production of SCGs hydrochar. An estimation for hydrochar-electricity generation potential from SCGs in the UK was determined based on Table 5 and Equation 5. Accordingly, using SCGs for solid fuel recovery could substitute 4.4% of energy currently generated from coal in the UK.

Table 4 Energy balance averaged for all residence times, t

HTC Reaction temperature	Energy input, Q_{in}			Energy output, Q_{out}	Fraction of Q_{out} required for Q_{in} (%)
	Energy to heat water (kJ)	Energy to heat dry SCGs (kJ)	Total energy to heat mixture (kJ)	Total energy from hydrochar (kJ)	
180°C	673.9	4.4	678.3	2236.2	30.3
200°C	765.3	4.9	770.2	2352.3	32.7
220°C	858.8	5.5	864.3	2303.3	37.5

Table 5 Parameters and estimation for hydrochar-electricity generation potential

Parameters	Symbol	Value	Reference
UK quantity of SCGs generated per year (tonnes)	M_{SCGs}	500,000	[7]
Optimised hydrochar yield (%)	H_y	0.64	Current study
Optimised hydrochar calorific value (GJ/tonnes)	HHV_{HC}	31.6	Current study
Efficiency of coal-fired power plants	η	0.35	[39]
UK electricity production from coal in 2017 (TWh)	E	22.51	[28]
From Equation 5:			
Electricity from hydrochar production, E_{HC} (GJ) = $\eta * M_{SCGs} * H_y * HHV_{HC}$		3,539,200	
UK Electricity production from coal, E_c (GJ) in 2017 = $3.6 \times 10^6 E$		81,036,000	
Fraction of coal replaceable by hydrochar in the UK (%)		4.37	

Conclusion

A hydrothermal carbonisation (HTC) process was demonstrated in this paper as an alternative approach to addressing the enormous spent coffee grounds (SCGs) waste generated annually, such that the huge cost and environmental implications associated with the current landfilling approach could be avoided while also promoting the recovery of bioenergy products. For the first time, HTC process parameters were optimised to realise high-value energy-densified hydrochar from SCGs by means of a response surface methodology. Following the HTC process, characterisation of the hydrochar's structural, chemical and fuel/energy properties indicated they were significantly enhanced when compared to raw SCGs. From an energy applications perspective, the extremely low ash content (< 2%) and high calorific value of the hydrochar (higher than required for power stations and other industrial applications) supports its potential suitability to substitute/replace coal as a stand-alone solid fuel or to be co-combusted for domestic and industrial energy application purposes. The health/environmental risks that could be posed by hydrochar combustion were evaluated by means of 16 PAHs, revealing total concentrations below statutory limits, i.e. less than 3mg/kg, and significantly below conventionally used domestic/industrial fuels. The recovery of hydrochar from SCGs adopting the

HTC process was also found to have a net energy balance, which favours the economic viability of the process. Hence, addressing SCGs waste by the HTC process represents a sustainable utilisation of bio-resources and promotes diversification of fuel supplies and energy security, while at the same time reducing biomass residues/wastes and preventing disposal costs, environmental contamination and localised fugitive emissions due to landfilling. However, extensive experimental runs and hydrochar characterisations at the predicted optimized conditions should constitute future work. This is crucial to realise consistent hydrochar product from SCGs processing. In addition, a comprehensive techno-economic analysis of the HTC process for recovering bioenergy from SCGs need to be carefully assessed to justify scalability. This is also important to provide economic basis to support the HTC technology. While the absence of sulphur and low nitrogen content in SCGs hydrochar may ultimately lead to a decrease in hazardous NO_x, SO_x and particulate emissions, additional investigations are needed to establish performance and emission levels – especially when deployed as stand-alone solid fuel or used in co-combustion with similar coal ranks in residential stoves/boilers, for example. Such practical applications for hydrochar are needed to further understand its suitability as renewable fuel. The sustainability of SCGs waste as a renewable fuel substrate and life cycle assessment to understand the environmental footprint of HTC technology for converting SCGs into a solid fuel should also constitute future work in this area.

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