



Thermochemical characterisation of hydrochar from agricultural waste and its efficiency as a supplement with solid fuel

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ABSTRACT

Circular approaches to revalorise waste biomass from agriculture and food production sectors are crucial for developing a sustainable bioenergy strategy. For instance, while the demand for edible mushroom cultivation has increased globally, the production generates a substantial amount of waste biomass, known as Spent Mushroom Substrate (MS). Thermochemical biomass conversion technologies such as hydrothermal carbonisation offers a robust strategy to produce "hydrochar" from the wet biomass and can be used downstream for various environmental applications. In this study, we assess the feasibility of MS-derived hydrochar for energy application, specifically as a blend with coal. The key parameters for the hydrochar production such as temperature, time and moisture content were optimised (205 °C, 3.65 h, and 73.18 %, respectively) using a statistical tool "Response Surface Methodology (RSM)" to obtain a carbon material with higher yield and calorific value. The hydrochar from MS exhibited an acidic pH (4.42), increased fixed carbon content (23.7 %), reduced sulphur content (0.26 %), coarser porous surface, enhanced oxygenated functional groups (hydroxyl, carboxyl and ketonic) and the formation of minerals like Sodium Carbonate (NaCO₃), whewellite (CaC₂O₄·H₂O) and gypsum (CaSO₄). Combustion behaviour of hydrochar was also assessed using calorimetry and thermogravimetry, specifically to test different coal and hydrochar blends on the feasibility of using hydrochar as a supplement to conventional solid fuels. Our results suggest that a blend of 20 % hydrochar with 80 % coal as an ideal blending ratio (with a calorific value of 27.65 MJ kg⁻¹) highlighting the use of hydrochar as supplement with conventional fuel like coal.

1. Introduction

Circular economic approaches to valorise waste biomass from agriculture and food production section is critical to develop a sustainable bioenergy strategy. For instance, edible mushroom cultivation has gained momentum recently with global per capita mushroom consumption ranging between 1 and 4.7 kg yr⁻¹ having regional variations in China (14 kg yr⁻¹), Australia (3.2 kg yr⁻¹), North America (3 kg yr⁻¹)

and Europe (2 kg yr⁻¹) [1,2]. It has been estimated that the global mushroom market size will rise from 15.25 million tonnes in 2021 to 24.05 million tonnes in 2028 [3]. Mushroom production creates a substantial quantity of waste biomass after harvesting, referred to as Spent Mushroom Substrate (MS), and is produced in huge amount i.e., 5 kg of substrate is generated for each kg of mushrooms produced [1]. Currently, these biomasses are managed through disposal in landfills, composting and incineration [4]. However, MS are rich in carbon and

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thus effective valorisation strategies can find downstream application in various environmental domains such as second-generation biofuel.

Valorisation strategies of the MS can include different biomass conversion technologies such as chemical, biological, thermal, and thermochemical processes [5,6]. Specifically, thermochemical conversion has been suggested as the most preferred strategy owing to the production of carbon material with higher energy content in comparison with other biomass conversion technologies [7] and it includes hydrothermal carbonisation (180–250 °C), hydrothermal liquefaction (50–350 °C), pyrolysis (500–600 °C), gasification (600–1000 °C) and combustion (800–1000 °C) [8,9]. Hydrothermal Carbonisation (HTC) offers a robust strategy in wet-waste management without the prior need to remove the moisture content [10]. In this process, the wet waste is subjected to temperatures within a range of 180 and 250 °C under autogenerated pressure conditions for 5–240 min with a water-to-biomass ratio up to 1:9 [11]. The final product, referred to as “Hydrochar”, can be used for multiple environmental applications in terms of energy storage, wastewater treatment and carbon sequestration [5]. Hydrothermal carbonisation is synonymously called as wet torrefaction producing the resultant product hydrochar, while pyrolysis results in the production of biochar [12]. The factors governing hydrochar’s carbon content and yield include temperature, feed water pH, water to biomass ratio, residence time, and the feedstock composition among which the latter serves as a critical factor influencing the final hydrochar properties [13,14]. Challenges and opportunities in hydrochar production process has been recently discussed in the work by Sadish and colleagues [15].

The energy properties and thermal behaviour of hydrochar pose a significant similarity to conventional non-renewable energy sources such as coal and lignite [16]. It has been well established that among the carbon materials produced from biomass, hydrochar exhibited a higher relative increment in calorific value due to the removal of volatile matter and harbouring increased fixed carbon content, thus resulting in higher heat generation capacity during combustion [17]. This property of hydrochar can offer it as an excellent substitute to coal for industrial heat and power generation through co-combustion process. Moreover, the utilisation of these substitute carbon materials renders lower SO_x and NO_x emissions in the industrial power sector with additional energy recovery and scrubbing of flue gases thereby maintaining air quality. It has been suggested that these biomass derived carbon materials could be substituted between 2 % and 10 % along with coal to curb CO₂ emissions by 1–5% in the steel industry [18]. In the socio-economic perspective, the ethical issues related to illegal coal mining and its associated hazard due to the presence of Naturally Occurring Radioactive Materials (NORMs) could be overcome by the practical implication of biomass derived carbon materials [19,20]. An earlier work by Marija and colleagues on the production of hydrochar from spent mushroom performed a detailed analysis on the effect of HTC temperature, surface functionalities, energy properties and thermogravimetric kinetics on the final product [21]. However, there is a knowledge gap on producing a hydrochar with optimised temperature, time, and moisture content along with conclusive evidence on mineralogical composition, elemental dispersion within the skeletal matrix and the feasible applicability of using hydrochar as a supplementary entity to conventional solid fuel in the energy domain. The employment of geochemistry tools to characterize hydrochar would help in engineering this carbon material for specific energy and environmental applications which distinguishes the novelty of this work. Moreover, the individualistic and interactive effect of production parameters on the hydrochar characteristics need to be studied for specific environmental applications. In this study, we examined the feasibility of Spent Mushroom Substrate derived hydrochar for energy application with the specific objectives to i) perform a comprehensive characterisation of hydrochar derived from MS including elemental composition, surface functionalities, structural morphology, combustion behaviour, and energy characteristics and ii) Test the thermal behaviour of hydrochar and potential use as a

supplement with coal (i.e. different blends of coal:hydrochar).

2. Experimental methods

2.1. Sample collection, processing and storage

The spent mushroom substrate (MS) was collected from a local mushroom production unit in Belfast, Northern Ireland, United Kingdom. The reason to choose this region is due to the notable fact that the current annual mushroom production is around 23,000 tonnes and this accounts for 10 % of all mushrooms and 40 % of organic mushrooms sold across the United Kingdom which corresponds to an estimate of 40 % horticultural output from Northern Ireland [22,23]. The composition of MS is subjectable to variation according to the local mushroom production practices. For instance, a substrate in Northern Ireland is made of soya hull, oak and wheat bran, while a substrate in India/China contains rice/wheat harvest residues, chicken manure, corn cob, saw dust and horse manure [24,25]. For characterization, the substrate was dried in the hot air oven at 105 °C until the moisture content (64.7 %) was completely removed and stored under airtight conditions until downstream analysis [26]. To perform hydrothermal carbonisation, the undried MS was used and the moisture content was adjusted according to the requirements for the optimisation.

2.2. Hydrothermal carbonisation

Hydrothermal carbonisation was performed in a 100 mL hydrothermal autoclave reactor (Techinstro, India) at a pre-determined solid to liquid ratio (1:1.5 to 1:9), followed by purging with nitrogen (N₂) (>99 % purity) and subsequently sealed. The reactor was then placed in a pre-heated oven at the appropriate temperature (180–250 °C) for the required time (0.5–6 h) [11]. The carbonisation reaction was quenched by placing the reactor in cold water (~10–15 °C) at the end of the residence time. The resultant carbonised product is the Spent Mushroom Substrate derived Hydrochar (HMS). It was subsequently dried, grinded, sieved (100 µm), and stored in an airtight container until further characterisation and application.

2.3. Characterisation of the feedstock and hydrochar

The pH of the samples was measured in a 1:5 suspension of sample and 0.01 M CaCl₂ (w/v basis) to exclude the influence of electrolytic interaction [27]. The proximate analysis (Moisture content, Volatile matter, ash content and fixed carbon) was performed using the standard American Society for Testing and Materials (ASTM D3172-13, 2021) protocol [28]. The ultimate analysis (CHNSO content) of the samples was performed using the elemental analyser Elementor Vario EL III (ASTM D5291, 2021). The X-Ray Diffraction of the samples was analysed by Malvern Panalytical X’Pert Pro Multi-Purpose X-Ray Diffractometer (Model no: DY1610) at a working voltage/current of 45kV/40 mA with a scan speed of 1.7° min⁻¹ between a 2θ range of 5 and 65° under the X-ray wavelength of 1.54 Å [29]. The presence of functional groups and their related vibrations were determined using a JASCO (FT/IR-4100) Fourier Transform Infrared Spectrometer over a wave-number range of 4000 to 400 cm⁻¹. The structural morphology of the samples was analysed using a Focused Ion Beam Field Emission Scanning Electron Microscopy (FIB-FESEM), TESCAN S8215G at an acceleration voltage of 120 kV, prior to which the samples were subjected to sputter coating with gold particles for enhanced imaging [30].

2.4. Optimisation of hydrochar production

In this study, the design of experiments for Response Surface Methodology (RSM) was performed using the statistical software “Design-Expert” (version 11) from Stat-Ease Inc. The statistical significance of these factors was established with analysis of variance (ANOVA). The

resultant graphical outputs were used to identify the impact of each factor on the desired outcomes, the interaction between the process parameters and revealed potential abnormalities in the data. The factors responsible for hydrochar production (temperature, time, and moisture content) are referred to as “process parameters” with each having a range of levels and the expected quantitative outcomes of the resultant product (hydrochar) are termed as “responses”. The range of each process parameter for hydrochar production included 180–240 °C (temperature), 1–6 h (time), and 65–80 % (moisture content). Routinely, the combination of each level of factors would result in a very high number of experiments. However, this can be surpassed by the utilisation of the RSM methodology that minimises the number of experimental runs by suggesting specific experiments with random combination of factor levels. The appropriate responses for these recommended experiments were analysed by the software thereby providing the optimised parameters for hydrochar production. These responses include hydrochar yield (%) and the higher heating value (MJ kg⁻¹). The selected design for the optimisation process was the Central Composite design, which formulated cubical sample space with randomized experimental recommendations.

2.5. Energy properties of coal and hydrochar blends

Conventional coal used for domestic utilities (BBQ coal) was obtained from a local market and mixed with hydrochar at different blending ratios and their Higher Heating Values (HHV) were determined using a digital bomb calorimeter (Toshniwal, model: DT100). The hydrochar yield, energy densification and the energy yield/energetic recovery efficiency were calculated using the following equations (1)–(3) [11].

$$\text{Hydrochar yield (\%)} = (\text{Mass of Hydrochar} / \text{Mass of feedstock}) \times 100 \quad (1)$$

$$\text{Energy Densification} = \text{HHV of Hydrochar} / \text{HHV of feedstock} \quad (2)$$

$$\text{Energetic recovery efficiency (\%)} = \text{Hydrochar yield} \times \text{Energy Densification} \quad (3)$$

The CO₂, NO₂ and SO₂ emissions of the feedstock, hydrochar and the coal:hydrochar blends have been estimated for 100 % combustion using the following equations (4)–(6) [31]. The estimate equation was modified and calculated using the elemental carbon and ash content of the samples in the current study. Although, the obtained values denote approximate emissions, absolute quantification is required for validation with the scaled-up studies.

$$\text{CO}_2 \text{ emission (kg)} = (1 - \text{Ash Content}) \times \frac{\text{C content of sample}}{100} \times \frac{\text{MW of CO}_2}{\text{AW of C}} \quad (4)$$

$$\text{NO}_2 \text{ emission (kg)} = (1 - \text{Ash Content}) \times \frac{\text{N content of sample}}{100} \times \frac{\text{MW of NO}_2}{\text{AW of N}} \quad (5)$$

$$\text{SO}_2 \text{ emission (kg)} = (1 - \text{Ash Content}) \times \frac{\text{S content of sample}}{100} \times \frac{\text{MW of SO}_2}{\text{AW of S}} \quad (6)$$

Where, MW is the Molecular weight of the emitted gas and AW is the atomic weight of the element. These estimates were calculated with the assumption that all these elements in the samples will be converted to the corresponding gases during combustion.

The thermogravimetric analysis (TGA) and Differential Thermogravimetry (DTG) of the samples (25–30 mg) was performed in an

aluminium oxide crucible (85 µL) using NETZSCH TG 209F1 Libra TGA/DTG analyser up to a maximum temperature of 1000 °C at a varying heating rate of 10 and 20 °C min⁻¹ under a dynamic nitrogen atmosphere (gas flow: 50 mL min⁻¹, >99 % purity) to determine their thermal stability and the combustion behaviour [21]. The combustion parameters such as ignition temperature (T_i), maximum weight loss rate (dm/dt)_{max}, maximum peak temperature (T_m), and burnout temperature (T_b) were also determined by the TG-DTG tangent method.

3. Results and discussion

3.1. Optimisation of hydrochar production using Response Surface Methodology (RSM)

In order to obtain specific combination of process parameters to produce an optimised hydrochar, we designed the experiment based on the Response Surface Methodology using the Design Expert software. The criteria of optimisation included conditions to maximise hydrochar yield and Higher Heating Value (HHV) along with minimal standard errors. The selected design for the optimisation resulted in the recommendation of 30 experimental runs with a randomized distribution among the different combination factors levels (Fig. 1). The experiments of these 30 runs were performed and the appropriate responses were entered in the software to perform RSM (Table 1). The best model to be fitted for the values was obtained from the outputs from the software after the individual analysis of the responses. The best fitted model for the hydrochar yield was found to be cubical, while the Higher Heating Value (HHV) was fitted using quadratic model followed by the Analysis of Variance (ANOVA) test for each response.

The Model F-value of 25.69 and P-value of 0.0001 for hydrochar yield highlighted that the derived model was significant (Supplementary Table S1). P-values less than 0.05 indicated model terms are significant while, values greater than 0.1 indicated the model terms are not significant. In this case A (Temperature), B (Time), C (Moisture content), AB, B², A²B, C³ are significant model terms. A negative Predicted R² implied that the better response predictor to be the overall mean rather than the current model. Adeq Precision measured the signal to noise ratio wherein a ratio greater than 4 is desirable and the obtained ratio of 22.239 indicated an adequate signal. In the case of Higher Heating Value (HHV) the Model F-value of 3.80 and P-value of 0.0062 indicated that the model was significant (Supplementary Table S2). Here B, C, B² were determined as significant model terms. The Predicted R² of 0.1686 was

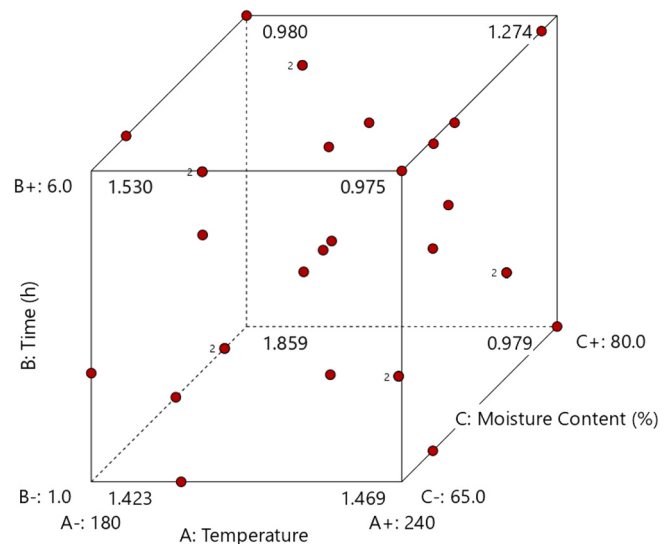


Fig. 1. Diagram indicating distribution pattern of the runs at the different factor levels.

Table 1

Responses of randomised runs suggested by the Design Expert Software for RSM optimisation.

Run	Space Type	Factor 1	Factor 2	Factor 3	Response 1	Response 2
		Temperature (°C)	Time (h)	Moisture Content (%)	Hydrochar Yield (%)	Higher heating value (MJ Kg ⁻¹)
1	Interior	201	4.9	65.3	86.27	13.52
2	Interior	191	1.9	79.9	88.50	12.17
3	Interior	216	4	69.3	85.59	12.79
4	Interior	198	5.8	76.3	79.71	12.17
5	Interior	227	4.8	74.5	74.19	15.82
6	Plane	224	6	69.7	75.45	14.46
7	Edge	240	6	78.5	60.46	14.11
8	Interior	197	2.4	69.7	93.13	11.76
9	Plane	219	1	75.2	84.40	11.68
10	Interior	238	2.5	76.2	79.04	14.16
11	Interior	226	2.7	65.2	85.41	13.10
12	Plane	240	4.7	69.5	73.66	14.03
13	Interior	207	3.3	74.7	83.89	15.16
14	Edge	180	1	73.2	99.78	11.79
15	Plane	196	3.9	80	78.16	14.19
16	Plane	216	2.3	80	84.5	12.18
17	Interior	197	2.4	69.7	92.36	12.48
18	Plane	220	4.3	80	73	14.76
19	Edge	197	1	65	99.23	11.79
20	Plane	219	1	75.2	83.65	12.36
21	Edge	180	6	68.4	90.01	13.04
22	Vertex	180	6	80	79.16	13.78
23	Vertex	240	1	80	90.5	12.97
24	Edge	240	1	68	98.95	11.38
25	Vertex	240	6	65	72	12.75
26	Interior	181	4.3	75.4	82.87	14.31
27	Interior	238	2.5	76.2	78.36	14.86
28	Edge	180	2.8	65	95.90	11.41
29	Interior	181	4.3	75.4	83.02	15.01
30	Interior	198	5.8	76.3	80.51	12.88

not as close to the Adjusted R^2 of 0.4646 as per the expectation, i.e. the difference is more than 0.2. The obtained Adeq Precision ratio of 7.634 indicates an adequate signal. The derived equations help to predict the response for each factor levels and identify their relative impacts on comparing the factor coefficients.

The equation of fitted cubical model for the hydrochar yield is:

$$Y_1 = 82.82 - 8.73A - 5.87B - 9.33C - 2.87AB + 0.1320AC + 0.1922BC + 0.7065A^2 + 2.62B^2 - 0.1707C^2 - 0.4319ABC - 5.61A^2B - 1.20A^2C - 1.56AB^2 + 2.11AC^2 - 0.2031B^2C - 1.92BC^2 + 2.70A^3 + 1.70B^3 + 5.72C^3.$$

The equation of fitted quadratic model for HHV is:

$$Y_2 = 13.96 + 0.4749A + 0.9018B + 0.5691C - 0.0359AB + 0.1048AC + 0.0450BC + 0.3441A^2 - 1.36B^2 - 0.5538C^2$$

In these equations, A is the coded value of temperature; B is the coded value of residence time and C is the coded value of moisture content. These coefficients denoted the individualistic and interactive effects of the factors with the positive sign denoting a synergistic relation and a negative denoting an antagonistic relation between them.

We observed a good correlation with the predicted and observed values for the recommended runs confirming the reliability of the developed models (Fig. 2a and b). The 3-Dimensional variation of the individual response values are shown in Fig. 2c and d with the colour gradient representing a range of values i.e. red colour being higher value and the blue colour being the lower value of the responses. The perturbation plots (Fig. 2e and f) were used to determine the individualistic and interactive effects of process parameters for the hydrochar production. Specifically, it helps to evaluate the interdependencies of process factors and monitor the corresponding changes in the target parameters (i.e., responses) [11]. It is evident that increasing the severity of the process parameters decreased the hydrochar yield as all three factors followed a similar trend on this response. In case of HHV, time exhibited a parabolic correlation with a midpoint around 4 h which showed a higher response value while temperature and moisture content

exhibited a second level control over this response. The weightage of these factors to produce hydrochar with the higher value of responses would result in the approximation around 200 °C temperature, 4 h time and 73 % moisture content. The analysis was performed based on the predetermined constraints thus resulting in the prediction of an optimised run. Based on the combination of process parameters (30), the recommended solutions for optimum conditions were determined (Table 2) and the solution with the highest desirability value was used as the optimum process condition for hydrochar production. The process temperature of 205 °C for 3.65 h residence time with the moisture content of 73.18 % showed the highest desirability of 74 % (0.747) thereby representing it as the optimised run for the design. The optimised run for the hydrochar production was performed and it resulted in properties with the expected values of yield and Higher Heating Value.

3.2. Characteristics of MS and HMS

3.2.1. pH

The pH (Table 3) of HMS was more acidic (4.42) in comparison to its feedstock (MS) (4.92), which is due to its organic origin and related organic acid production during mushroom production [32,33]. However, during the HTC process due to the formation of hydronium ions and its direct effect on the substrate i.e. cellulose degradation at the HTC temperature (200 °C), the pH of the hydrochar was further reduced [34]. This can be further supplemented by the production of acidic functional groups (such as phenolic, lactonic, and carboxylic) and an increase in the proportion of acidic elemental composition (such as silicon, iron, and aluminium) during the process [34]. It has also been suggested that there is an inverse relation between the pH of hydrochar and its ash content (specifically, acidic inorganic compounds) [35]. A similar trend was observed in the current work where the acidic nature of hydrochar was observed due to an increase in the inorganic composition i.e., ash content and elemental composition of the hydrochar. Higher abundance of oxygenated functional groups (C=O, COOH) and leaching of OH groups into the liquid counterparts were also shown to be a contributing

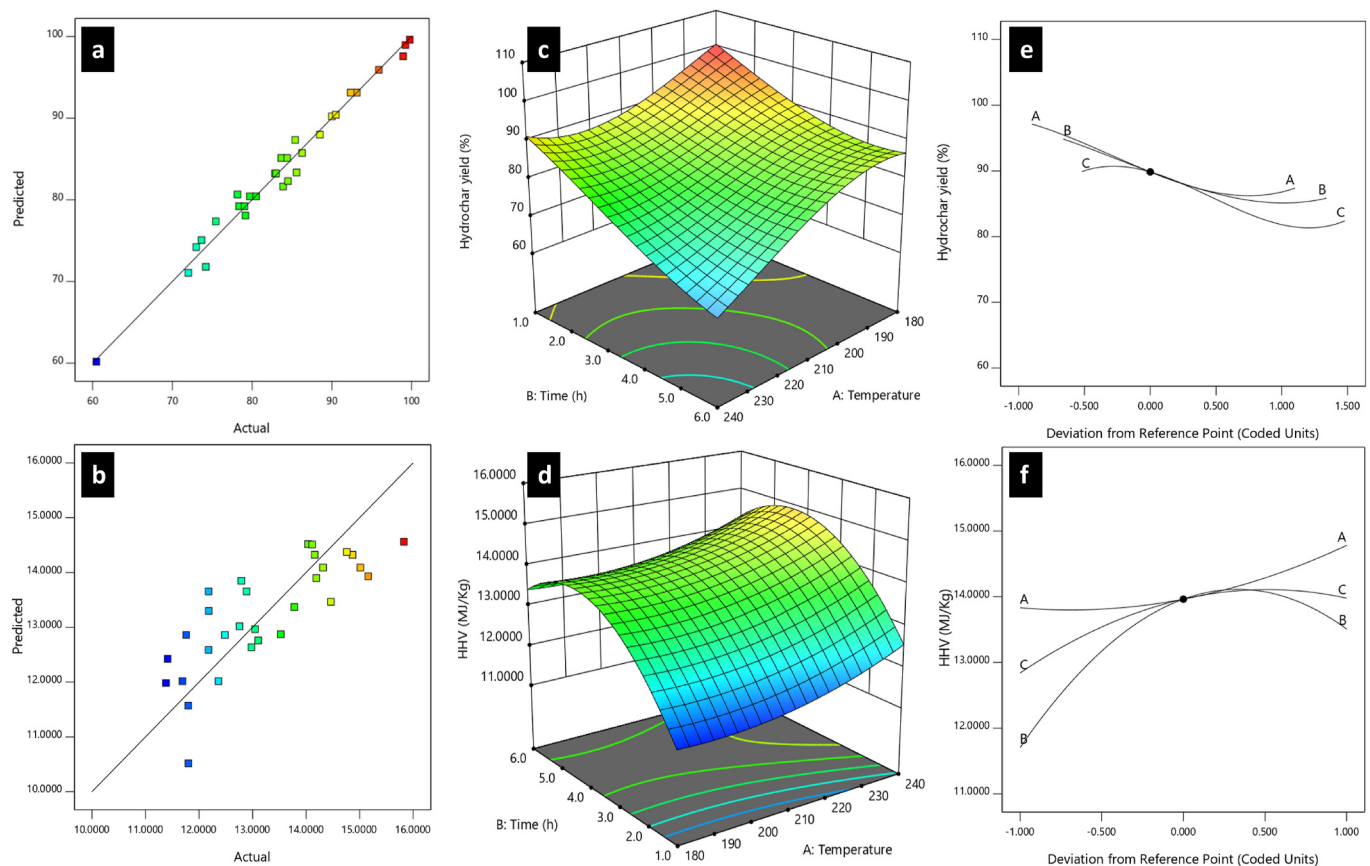


Fig. 2. Predicted vs actual response values (a & b), 3D plot of responses (c & d) [X1 axis – Time (h); X2 axis – Temperature (°C) and Y axis – Response at 72.5 % moisture content; Colour gradient representing Red – highest values; and Blue – Lowest Values], and Perturbation plot of process parameters (e & f) for Hydrochar yield and Higher Heating value [A – Temperature (°C); B - Residence time (h) and C - Moisture content (%)]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2

Solutions for the optimisation of Hydrochar.

No.	Temperature (°C)	Time (h)	Moisture Content (%)	Expected Outcomes		
				Hydrochar yield (%)	HHV (MJ Kg ⁻¹)	Desirability
1	204.83	3.65	73.18	83.26 ± 0.98	13.98 ± 0.37	0.747
2	204.84	3.67	73.09	83.20 ± 0.98	13.98 ± 0.37	0.731
3	204.74	3.68	73.22	83.05 ± 0.98	13.99 ± 0.37	0.657
4	204.84	3.70	73.16	83.05 ± 0.98	14.00 ± 0.37	0.632

factor for the acidic pH [7]. Similar trends have been observed in recent research on the hydrothermal carbonisation of garden waste (pH 6.8 to 5.5) [36], wood (pH 6.2 to 3.6) [34], paper board mill sludge (pH 6.36 to 5.79) [11].

3.2.2. Proximate composition of feedstock and hydrochar

The proximate analysis (Table 3) of the samples was used to compare the volatile matter, ash content and the fixed carbon content between the MS and HMS. We observed that the volatile matter content of HMS decreased from 77.1 % to 69.1 % (8 % relative reduction) during HTC but the fixed carbon content increased from 18 % to 23.7 % (5.7 % relative increase). This confirmed the aromaticity and the severity of the carbonisation process at a higher degree of carbon polymerisation. In addition, the ash content of HMS increased from 4.8 % to 7.1 % (2.3 % relative increase) as compared to its feedstock. Reduction in the volatile matter content could be due to the chemical dehydration and decarboxylation reactions during the HTC process. Increase in fixed carbon content could be due to the aromatisation of carbon with attributed repolymerisation reactions. Enhanced fixed carbon content ensured easy

ignitability of the material and thus promoting maximum weight loss during combustion with reduced pollutant emissions [37]. However, the relative loss of volatile matter (8 %) in the HMS was higher in comparison to the relative increase in fixed carbon content (5.7 %) potentially highlighting the conversion of residual volatile compounds to aqueous and gaseous fractions [38]. The decomposition of complex organic fractions (carbohydrates, proteins, cellulose, and hemicellulose) in the feedstock and subsequent dispersal to the aqueous and gaseous fractions during HTC could be contributed to the loss of volatile matter [39]. The retainment of acidic elements (such as silica, aluminium, and iron) in the hydrochar increased its ash content and influenced its acidic nature [40]. After HTC, there was a significant increase in the fuel ratio from 0.23 to 0.34. This confirmed the preferred fuel capability of hydrochar rather than the feedstock, since the desired value is within the range of conventional coal (0.1–0.4) [41]. Comparison of the volatile matter, ash content and fixed carbon of the HMS with other hydrochars produced from paper board mill sludge (PSH) [11], waste food (WFH) [42], Tobacco residue (TRH) [43], swine manure (SWH) [44], and Corn cob (CCH) [45] revealed a similar trend (Fig. 3a). We can clearly

Table 3

Physico-chemical Characterization of Spent Mushroom Substrate (MS) and its derived hydrochar (HMS).

S. No.	Parameter	MS	HMS
1.	pH	4.92 ± 0.01	4.42 ± 0.03
2.	Proximate Analysis (%)		
	Moisture content	64.7 ± 0.16	71.5 ± 0.46
	Volatile matter	77.1 ± 0.39	69.1 ± 0.36
	Ash content	4.81 ± 0.28	7.11 ± 0.54
	Fixed carbon	18 ± 0.67	23.7 ± 0.89
3.	Fuel Ratio	0.23 ± 0.09	0.34 ± 0.01
4.	Ultimate Analysis (%)		
	Carbon	41.26 ± 0.31	49.33 ± 0.26
	Hydrogen	6.7 ± 0.1	5.63 ± 0.07
	Nitrogen	1.8 ± 0.02	1.69 ± 0.01
	Sulphur	0.29 ± 0.01	0.26 ± 0.02
	Oxygen	45.14 ± 0.29	35.97 ± 0.32
5.	H/C ratio	1.94 ± 0.03	0.82 ± 0.01
6.	O/C ratio	1.36 ± 0.02	0.55 ± 0.02
7.	Total Aluminium (mg kg ⁻¹)	1033.33 ± 145.29	1600 ± 115.47
8.	Total Iron (mg kg ⁻¹)	733.33 ± 45.29	1633.33 ± 88.19
9.	Total Sodium (mg kg ⁻¹)	1000 ± 57.73	1366.67 ± 8.19
10.	Total Magnesium (mg kg ⁻¹)	6866.67 ± 1034.94	11966.67 ± 491.03
11.	Total Calcium (mg kg ⁻¹)	14666.67 ± 1186.49	29033.33 ± 2861.42
12.	Total Phosphorus (mg kg ⁻¹)	800 ± 115.47	1233.33 ± 66.67
13.	Total Potassium (mg kg ⁻¹)	8066.67 ± 409.60	11033.33 ± 808.97
14.	Total Manganese (mg kg ⁻¹)	666.67 ± 66.67	1066.67 ± 120.18
15.	Total Copper (mg kg ⁻¹)	1000 ± 152.75	2166.67 ± 240.37
16.	Total Zinc (mg kg ⁻¹)	633.33 ± 88.19	1166.67 ± 88.19
17.	Total Silicon (mg kg ⁻¹)	1300 ± 57.73	1733.33 ± 8.19

*Samples analyzed under moisture free basis.

*Values represent average of three replicates.

observe that after hydrothermal carbonisation there was an active reduction in the volatile matter content of all the hydrochars (Supplementary Table S3).

3.2.3. Elemental composition of feedstock and hydrochar

We performed the ultimate analysis (Table 3) of the MS and HMS to observe the differences in elemental composition. Whilst we observed an

increase in carbon content (41.26 %–49.33 %) there was a decrease in the cases of hydrogen (6.7 %–5.63 %), nitrogen (1.8 %–1.69 %), sulphur (0.29 %–0.26 %) and oxygen content (45.14 %–35.97 %). The change in the elemental composition during the HTC process, especially that of atomic H/C and O/C ratios can have a greater influence on the coalification factor of the hydrochar [46]. The increase in carbon content and decrease of hydrogen and oxygen due to dehydration, decarboxylation, and demethylation reactions resulted in the cumulative reduction of atomic H/C and O/C ratios caused [47]. This reduction in the H/C and O/C ratios enhances the energy storage capability for fuel application and can promote the hydrophobicity of the hydrochar which was visually confirmed through the settlement of solids in the bottom of the reactor with a supernatant aqueous part [11]. The resultant hydrochar had H/C and O/C ratios in the peat region and this is due to the optimisation constraint of the current study that aimed for an hydrochar having a better yield and a higher HHV. Increasing the HTC process severity will position the resultant hydrochar in the region of coal and lignite. Due to presence of oxygenated functional groups and the loss of moisture during the HTC process, it exhibited hydrophobic properties [47]. The H/C ratio of HMS reduced from 1.94 to 0.82, while the O/C ratio reduced from 1.36 to 0.55, as shown in the Van-Krevelen diagram (Fig. 3b). This analysis, including a comparison with other hydrochars from the literature, confirmed the coalification degree of the carbon material and the severity of intermediate reactions (Supplementary Table S3) [26]. In comparison to its feedstock, the HMS exhibited a fuel status with its presence in the region of the low-grade carbon material. However, the fuel status could be improved by increasing the HTC process with a specific focus on the energy output [41]. Sulphur content of the solid fuel is an important factor to be considered in relation to their SO_x emissions during combustion. During the HTC process, the sulphur content in the HMS has been reduced significantly (0.29 %–0.26 %), implying a potential reduction in the SO_x emission. Although this level of sulphur is well below the permissible limit (0.5 %), the acquired reduction (0.03 %) will curb the potential sulphur emissions at an industrial scale by 300g per ton of hydrochar burned. It has been suggested that the reduction in sulphur could be due to the hydrothermal transformation of sulphur from available to unavailable forms (such as thiophene-S, aromatic-S and thiazole-S) and its subsequent leaching into the HTC liquid fraction [48].

The cumulative effect of HTC process influenced the elemental composition of the biomass in the reactor (Table 3). We observed a

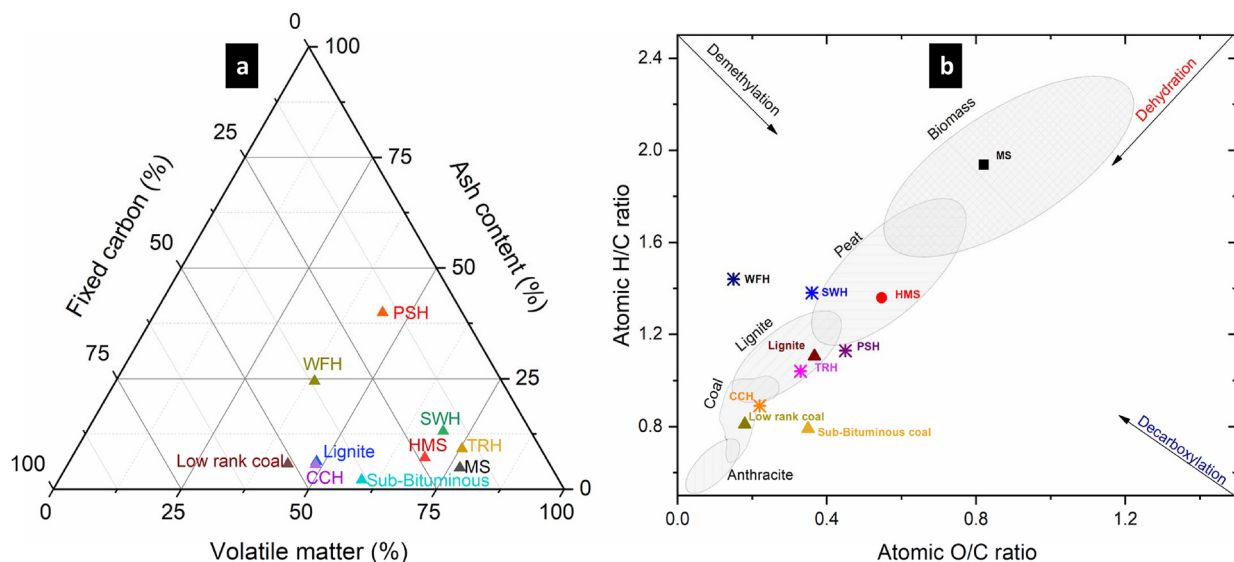


Fig. 3. a) Ternary diagram of proximate fluctuations in different hydrochar and b) Van-Krevelen diagram for assessment of coalification degree [Legend: Paper board mill sludge (PSH), Waste Food (WFH), Tobacco Residue (TRH), Swine Manure (SWH), Corn Cob (CCH), Spent Mushroom Substrate (MS) and its derived hydrochar (HMS)].

significant increase in the total nutrient and metal content due to the supplementary effect of the carbonisation process and a similar trend was noted in the study by Wilk and Colleagues [49]. It is possible that these elements are embedded into the skeletal matrix of the hydrochar thereby enhancing its application in the specific environmental domain. For instance, iron and aluminium can promote the adsorption of nutrients in anionic forms (sulphates and phosphates) while the other metals (such as zinc, copper and molybdenum) serve as a critical co-factor for enzymes involved in microbial metabolisms during Anaerobic Digestion such as hydrolysis and fermentation of polysaccharides [15,50,51]. However, the high values for copper and zinc in the HMS also highlight that the hydrochar would not be acceptable as a soil amendment by industry & Eco labels furthering the argument as a biomass fuel [52]. This could be overcome by increasing the moisture content of the feedstock during HTC and subsequent removal of these elements from the leachates [39].

3.2.4. Surface functionalities by FTIR

In order to observe the changes in the surface functionalities, we used the Fourier Transform Infrared Spectroscopic (FTIR) analysis of the hydrochar and its feedstock (Supplementary Fig. S1). The observed FTIR peaks in the MS indicated the presence of:

- Complex molecules like cellulose and hemicellulose (variably stretched broad band between 3200 and 3600 cm^{-1})
- Phenolic -OH groups (identified due to the rounded tip at 3260 cm^{-1}).
- Amino acids (vibration of aliphatic methyl groups between 2800 and 3000 cm^{-1} was identified with a centroid at 2900 cm^{-1} representing the C-H stretching of amino acids).
- Protein amide functional groups (1500 cm^{-1} represented the carboxylic stretching band).
- C-O-C functional group (ether) due to alcohol dehydration reactions (sharp peak around 1000 cm^{-1} corresponded to the asymmetric stretching).

After the HTC process, we observed a significant change in the functional groups, specifically the oxygenated ones (such as hydroxylic, carboxylic, and aliphatic methyl groups). The FTIR spectra suggested a gradual weakening of the OH stretching (around 3200-3400 cm^{-1}) due to the dehydration reactions during the HTC process, which could be confirmed by the reduction in the H/C and O/C ratios of hydrochar [53]. The conversion of peaks corresponding to -CH_x aliphatic methyl groups (1400-1500 cm^{-1}) to a sharpened and narrowed version was observed, indicating the influence of polymeric decomposition reactions resulting in the predominance of aliphatic structures (-CH_x) (Areeprasat et al., 2014). The reduction in the amide stretching (-NH₂) around 1500 cm^{-1} was due to protein hydrolysis during the HTC process [10]. In addition, the reduction at C=O stretching groups confirmed the occurrence of decarboxylation reactions during the HTC process [54]. This reduction could be attributed to the production CO₂ and its dissipation into the negligible gaseous fraction produced from the process.

The washing of hydrochar either with ethanol or milli Q water resulted in changes in terms of functional group. The ethanol and Milli Q water washed hydrochar exhibited enhanced stretching of phenolic (OH), aliphatic (CH), carboxylic (CO) and C-O-C groups. Specifically, the oxygen containing functional groups have shown to express higher intensity after water washing, freezing or microbial aging [55]. This change in surface functionality can enhance the adsorptive ability of hydrochar and promotes potential application as an adsorbent in wastewater treatment. Moreover, the reduction in the aliphatic hydrocarbon groups could also contribute to the reduced phytotoxic effect of hydrochar when used for soil amelioration [56].

3.2.5. X-Ray Diffraction of feedstock and hydrochar

The X-Ray Diffractometry (XRD) analysis of the MS and HMS

revealed the structure of both materials to be amorphous with the presence of several mineral elements (Fig. 4). The amorphous nature of carbon in the MS can be attributed to presence of biomass derived organic cellulose and hemicellulose [57]. An enhanced diffraction in the peaks of HMS, between 10 and 30° (2 θ), was observed possibly due to the intense decomposition of amorphous carbon during the HTC process. This resulted in the appearance of several crystalline peaks despite the amorphous nature of the carbon material [58]. The HTC process resulted in significant change of peaks that can be attributed to Quartz and Calcite, potentially due to simultaneous decomposition with the aromatic lignocellulosic structures. This could result in the production of mild acids during HTC process followed by the enhancement of the surface porosity and a potential elemental leaching into the aqueous fraction which requires further quantification and validation [14]. Further repolymerisation during the HTC process resulted in the fixation of these minerals with the stable carbon structures thereby promoting intensified crystallized mineral formations like Sodium Carbonate (NaCO₃), Whewellite (CaC₂O₄·H₂O) and Gypsum (CaSO₄) [59].

3.2.6. Structural morphologies by Scanning Electron Microscopy

Comparison of the structural morphologies between the MS and HMS, using the Scanning Electron Microscopy (SEM), revealed noticeable differences on the surface of hydrochar in (Fig. 5a and b). After HTC, the smooth surface of the feedstock has turned into a rougher surface due to the fragmentation of hydrothermal susceptible compounds like hemicellulose resulting in a residual porous surface and it was confirmed on comparison with a previous study [11]. The subsequent carbonisation of these fragments leads to the formation of

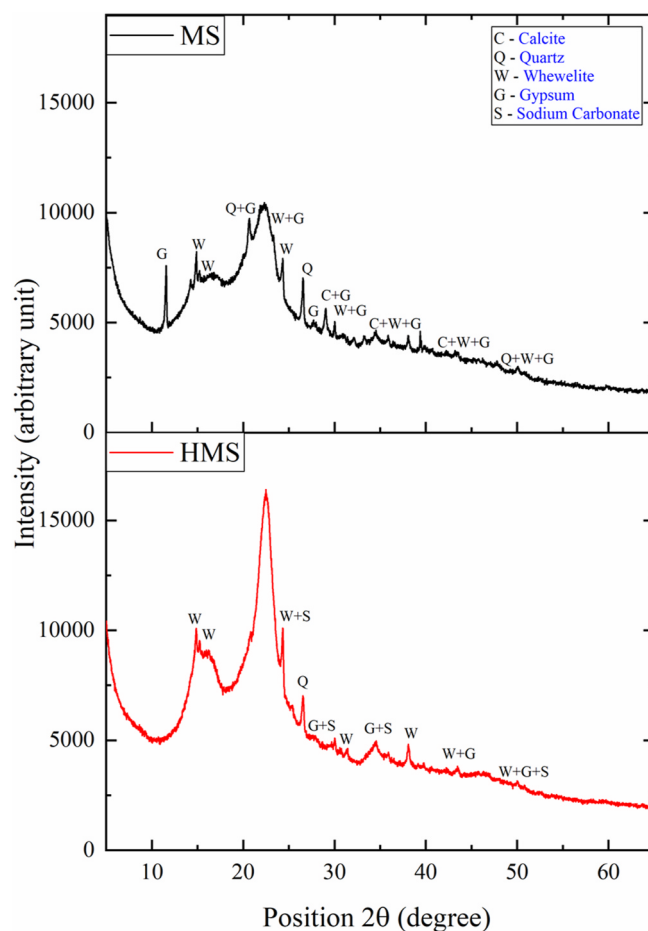


Fig. 4. X-Ray Diffractometry graph of Spent Mushroom Substrate (MS) and its derived hydrochar (HMS).

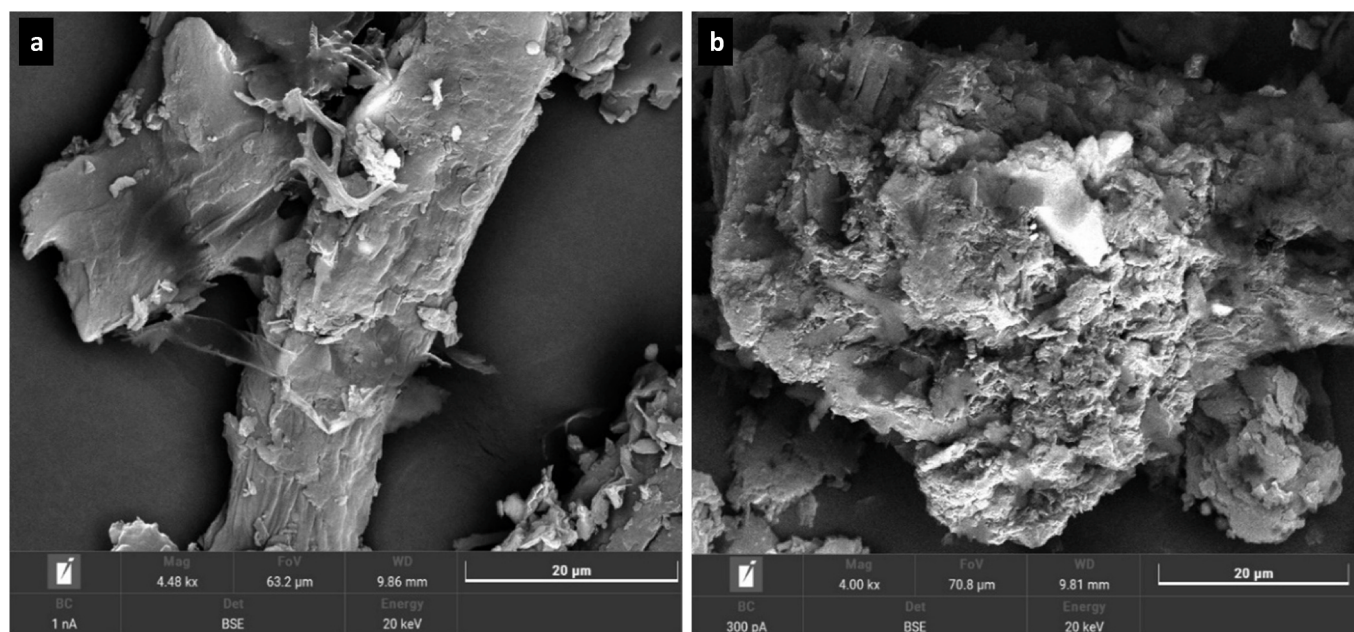


Fig. 5. Scanning Electron Microscopy of a) Spent Mushroom Substrate (MS) and b) MS derived hydrochar (HMS).

spherical shaped agglomerated structures due to the deterioration of cellulose. These shapeshifted dispersions in the form of honeycombs or fluffed sponges on the surface are generally available at the micro-metre or nano-metre scale [60]. In terms of the texture, the long-sheathed particles of the feedstock are converted to short, interlinked carbon microspheres. The intensity of fragmentation and pore formation

depends on several factors of the HTC process such as temperature, residence time, moisture content, feedstock type and pH [61]. The cumulative effect of intermediate reactions during HTC (depolymerisation, devolatilization, demethylation, dehydration and repolymerisation) is responsible for the acquired surface characteristics of hydrochar [62].

The compositional data map of MS and HMS from the EDAX analysis

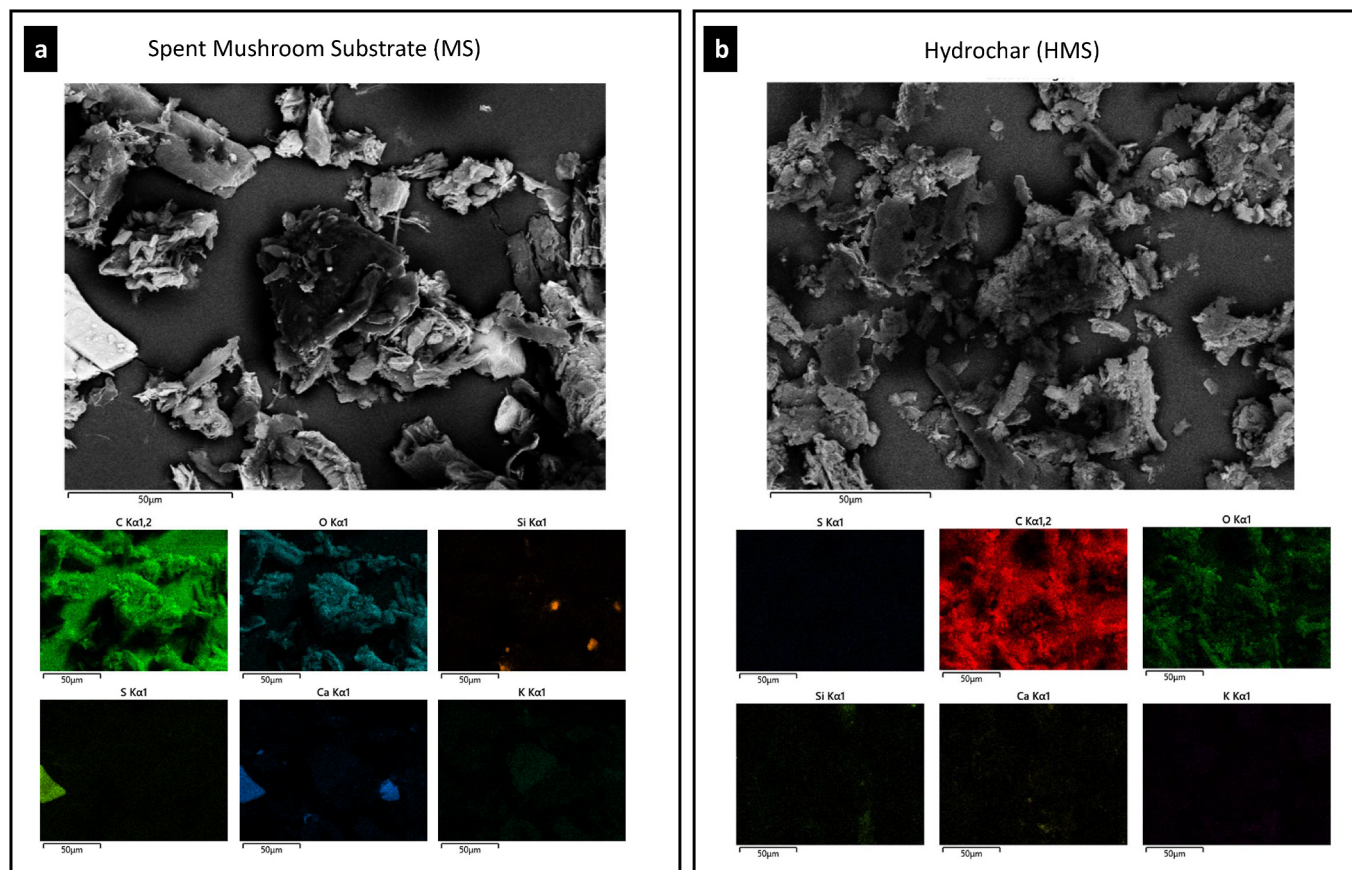


Fig. 6. EDAX compositional data map of Spent Mushroom Substrate (MS) (a) and MS-derived hydrochar (HMS) (b).

(Fig. 6a and b) provided conclusive visual evidence for the quantitative elemental change during the HTC process. The intensified colour of carbon matrix in hydrochar in comparison to its feedstock confirmed the carbonisation [63]. The presence of calcium and sulphur at a particular position in the MS sample visually confirmed the presence of Gypsum. Moreover, we also observed a gradual dispersion of elements (such as Si, Ca and S) into the skeletal matrix of hydrochar, possibly due to the sub-reactions during the HTC process and subsequent fixation to form micro-crystalline structures which was evident from the X-Ray Diffractometry (Section 3.2.5) [59].

3.3. Energy characteristics of hydrochar

The energy characteristics of the hydrochar and its feedstock was used to study the impact of the HTC process (Table 4). The higher heating value (HHV) increased from 11.32 to 13.97 MJ kg⁻¹ after hydrothermal carbonisation and the relative increment in the HHV was found to be 23.4 %. The lower heating value (LHV) is a derivative value of HHV excluding the heat of vaporisation of water [64]. This net calorific value is the absolute quantity of heat released from burning samples and was increased by 35.2 % after hydrothermal carbonisation. HMS had a lower HHV compared to hydrochar from other feedstocks (Supplementary Table S3), however given the process severity with an additional aim to get a higher hydrochar yield, the energy densification has happened substantially. This helps to create a valorisation potential for the spent mushroom substrate rather than conventional management options. It could be seen from Table 1 that adjusting the process severity could produce HMS with an HHV of 15.8 MJ kg⁻¹ thereby achieving comparably closer value to sub-bituminous coal (16.8 MJ kg⁻¹) [64]. The carbonisation increased the value of energy densification ratio to be more than 1 due to the loss of hydrogen and oxygen content. An intensified energy densification ratio is ideal for any thermochemical conversion of a biomass and its subsequent application in the energy sector [38]. The energy yield of the hydrochar was determined to be 88.4 %, and it was calculated based on the obtained hydrochar yield (71.6 %) and energy densification ratio (1.23). The energy yield indicates the recoverable energy from the hydrochar with respect to its precursor's calorific value [64]. The energy parameters of the hydrochar produced in this study was compared with the other hydrochars (Supplementary Fig. S2) from different feedstocks such as paper board mill sludge (PSH) [11], macadamia nut (MNH) [38], olive tree (OTH) [65], Camellia shells (COH) [66], organic waste (OWH) [67], and microalgae (MAH) [68]. It was evident from these studies that all the hydrochars showed an energy densification ratio above 1, however the variation in their yield due to the levels of corresponding production parameters influenced the final recoverable energy from hydrochar (Supplementary Table S4).

3.3.1. Thermo-gravimetric analysis of hydrochar

The combustion behaviour of a sample and its effectiveness as a solid fuel is generally assessed by the thermogravimetric analysis i.e., evaluation of the sample weight loss corresponding increase in the temperature. Moreover, the Differential Thermogravimetric curve (DTG)

Table 4
Energy characterization of optimised hydrochar.

No.	Parameter	MS	HMS
1.	Higher Heating Value (MJ kg ⁻¹)	11.32 ± 0.25	13.97 ± 0.46
2.	Lower Heating Value (MJ kg ⁻¹)	7.95 ± 0.27	10.75 ± 0.47
3.	Energy Densification	–	1.23 ± 0.04
4.	Hydrochar Yield (%)	–	71.6 ± 0.61
5.	Energetic recovery efficiency/Energy yield (%)	–	88.4 ± 2.74

*Values represent average of three replicates.

analysed the weight loss rates at specific temperatures. There was a significant change in the pattern of weight loss at increased temperatures due to hydrothermal carbonisation (Table 5). The TGA/DTG profiling of hydrochar showed a significant change in the proportion of weight loss at different stages of combustion in comparison to the MS (Fig. 7a and b). These differences can be due to changes in the reactive components of the hydrochar than its feedstock [69]. In the previous studies, it has been highlighted that the weight loss occurs in three main decomposition phases i.e., Phase I: 0–200 °C (loss of moisture and small organic molecules), Phase II: 200–400 °C (volatilization of organic entities) and, Phase III: 400–700 °C (burning of fixed carbon) [11]. Although, a similar trend was observed in the current study, specific shift in the phase temperature was recorded.

In this study, two different ramping temperatures (10 °C and 20 °C min⁻¹) were used to run the process. The variation in the heating rates help to efficiently predict the combustion behaviour and optimise the thermal decomposition process. The multi-stage weight loss of the mushroom substrate (Table 5) for 10 °C min⁻¹ heating rate at Phase I (up to 225 °C), Phase II (226–360 °C), and Phase III (361–686 °C) were 11.18 %, 45.84 % and 15.02 %, respectively. For the heating rate 20 °C min⁻¹, the weight loss at Phase I (up to 229 °C), Phase II (230–375 °C), and Phase III (376–701 °C) were 11.27 %, 47.84 %, and 14.58 %, respectively. Notably, the Phase II weight loss for the MS had 2 sub-divisions with the first interval corresponding to the degradation of hemicellulose, proteins, lipids and carbohydrates while the second interval denotes the decomposition of lignin and cellulose particle and it was found to vary among the two heating rates, i.e., 10 °C min⁻¹ (225 °C–278 °C–360 °C) and 20 °C min⁻¹ (223 °C–281 °C–375 °C).

Whilst the difference in ramping temperatures had negligible influence in the weight loss pattern, it influenced the rate of thermal decomposition of the sample. However, there was a change in the distribution of mass loss with respect to different phases after the HTC process. The weight loss in the Phase I (~11 %–10 %) highlighted the reduction in the moisture content of hydrochar and could also be attributed to the decomposition of long chained polymers to short, structured hydrocarbons [70]. The temperature boundaries of the HMS in Phase I was found to be up to 233 °C and 242 °C for the heating rates 10 °C min⁻¹ and 20 °C min⁻¹, respectively. The Phase II reduction for 10 °C min⁻¹ (234 °C–372 °C) and 20 °C min⁻¹ (243 °C–383 °C) were 41.14 % and 41.64 %, respectively. This phase exhibited an exponential decline in rate of weight loss compared to other phases [58]. We observed a gradual combustion in the Phase III of the weight loss due to the rapid continuation from the previous phase. Typically, the weight loss increased from 15 to 16 % at this specific phase thereby indicating the increase in stable aromatic carbon content of the sample. A similar trend was observed in a previous work where a higher abundance of fixed carbon improved the mass loss at the third phase of TGA [71]. The thermal decomposition between 700 and 1000 °C were found to be in negligible proportions (around 2 %) for all the samples and is attributed to the loss of stable aromatic structures, Si bonded lignin molecules, and other inorganic constituents [21]. The rate of weight loss at the second phase was more than that of third phase possibly due to the higher thermal stability of the organic entities in the form of fixed carbon and its higher abundance in the hydrochar [72].

The combustion behaviour and the thermal stability of the solid fuel were assessed by the parameters such as ignition temperature (T_i), maximum peak temperature (T_m), and burnout temperature (T_b). Ignition temperature is the point where the fuel starts to burn. Burnout temperature is the point indicating the complete combustion of the fuel. The maximum peak temperature is the point with the maximum weight loss rate of the fuel (dm/dt_{max}). It could be noticed that HMS has higher T_i and T_m values than MS indicating its lower reactivity towards combustion thereby reducing the fire risk and improving the storage safety of the fuel. Moreover, higher T_b values of HMS than MS ensured the thermal stability and longer period of complete combustion. These observed changes after the HTC process is due to the reduction volatile

Table 5

Different stages of weight loss during thermo-gravimetric analysis.

Sample	Heating rate (°C/min)	T _i (°C)	T _m (°C)	T _b (°C)	(dm/dt) _{max} (% min ⁻¹)	Weight loss (%)			
						Phase I	Phase II	Phase III	
MS	10	225	317	686	-5.86	11.18	11.9	33.94	15.02
	20	229	327	701	-11.61	11.27	10.83	37.01	14.58
HMS	10	233	339	719	-6.6	10.11	41.14		16.56
	20	242	349	735	-12.84	9.89	41.64		16.27

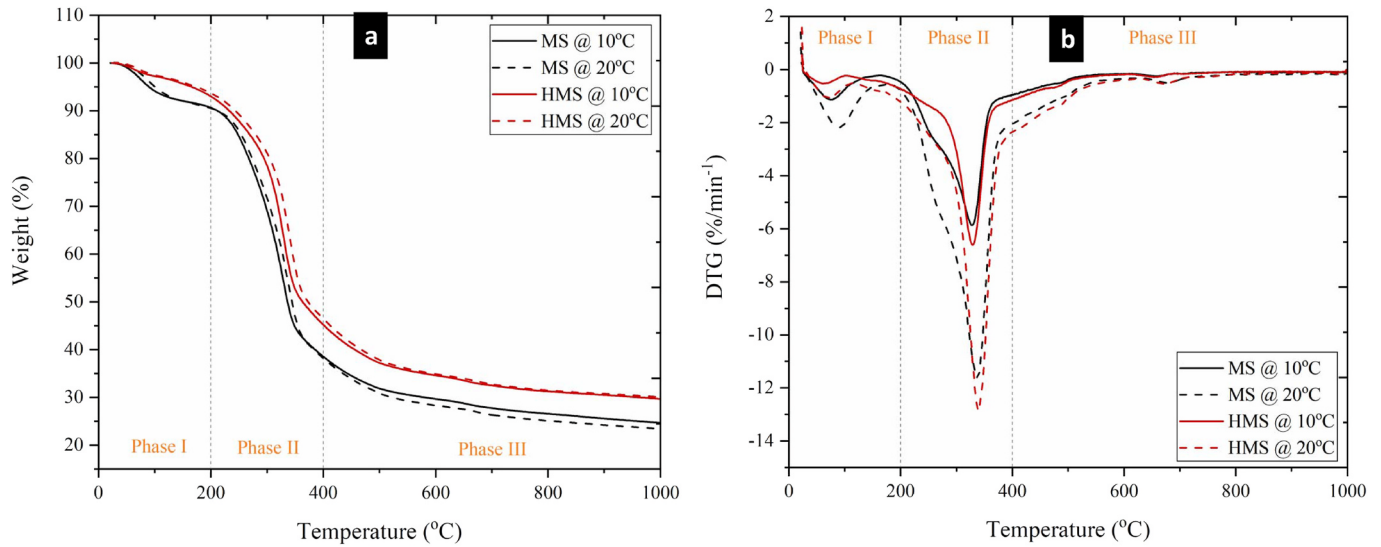


Fig. 7. a) Thermogravimetric (TGA) and b) Differential Thermogravimetric (DTG) curves of Spent Mushroom Substrate (MS) and its derived hydrochar (HMS).

matter and increase in the fixed carbon content [21]. The phase after T_b indicated the presence of inorganic constituents or ash content in the sample. After HTC, it could be seen that there was an increase in ash content due to the retainment of mineral constituents after the HTC process [73].

3.4. Higher heating value of the coal:hydrochar blends

We tested the higher heating values of coal and hydrochar blends at different proportions (Fig. 8). It was observed that there was a significant decrease in the calorific value with the corresponding increase in the hydrochar proportion [11]. Although, the coal: hydrochar blend of 90:10 showed the highest calorific value (28.45 MJ kg⁻¹), we did not observe a statistically significant difference when compared to 80:20 blend (27.65 MJ kg⁻¹) or the calorific value of coal (28.85 MJ kg⁻¹). Based on this observation, 80:20 of Coal:Hydrochar blend can be an ideal blend using spent mushroom substrate derived hydrochar as an alternative solid fuel supplement, since it suggests an option for an in-situ waste management and with comparable energy values to coal. In the context of 100 % biomass dedicated facilities, a pilot scale study could help in valorising the biomass through HTC process. With our lab-scale work on hydrochar, we estimated that around 30–50 % of the output energy from hydrochar could be used to process the next batch of waste. However, this needs to be investigated in an elaborated scaled-up study. Previous research on hydrochar has showed that it possesses a lower ignition point when compared to conventional solid fuels [40]. This would result in the enhanced energy densification ratios and subsequently increase energy recovery efficiencies [41]. Moreover, in terms of sulphate emissions, blending with low sulphur containing hydrochars could be an interesting strategy to curb the emissions within the permissible limits [74]. The estimation of gaseous emissions during combustion revealed that using 20 % hydrochar as a supplement with coal could reduce CO₂, NO₂ and SO₂ emissions by 5.3 %, 6.8 % and 10.6

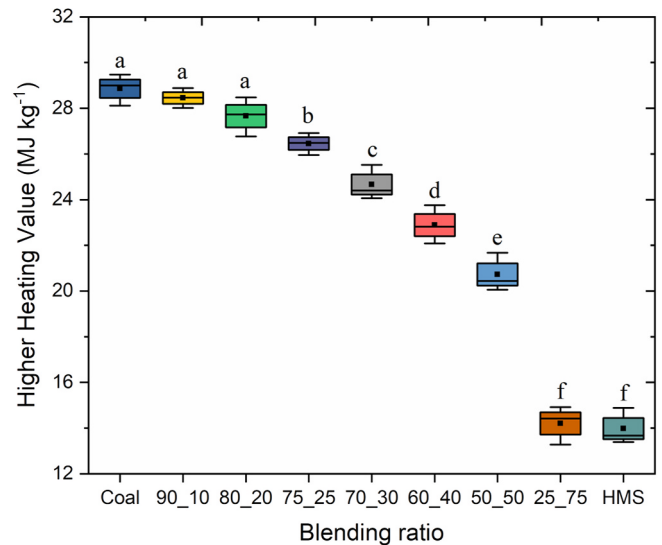


Fig. 8. Higher Heating Values of Coal and hydrochar blends.

%, respectively (Supplementary Table S5).

4. Conclusion

In this work, we highlight the potential use of hydrothermal carbonisation to valorise biomass waste from mushroom production. The optimisation of the hydrochar production factors showed that a process temperature of 204 °C for 3.65 h at 73.18 % moisture content produce a carbon material from spent mushroom substrate with higher yield and calorific value. The hydrochar produced exhibited a yield of 71.6 % and

a higher heating value of 13.97 MJ kg⁻¹ depicting its potential suitability as an alternative to solid fuel. However, Co-HTC with other biomass will help to reduce the ash generation and related corrosion in the industrial boilers. The usage of coal hydrochar blend at 80:20 blending ratio confirmed the feasibility of its application in industrial boilers with lower gaseous emissions. Furthermore, scaled up studies need to be performed with a specific focus on the improved energy values at an industrial level. The energy characterisation and thermogravimetry have ensured the application of hydrochar in the renewable energy domain thereby promoting circular economy through agro-waste management.

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CRediT authorship contribution statement

Sadish Oumabady: Writing – original draft, Visualization, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Satish K. Bhardwaj:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization. **Sangeetha Piriya Ramasamy:** Writing – review & editing, Investigation. **Shamsudeen U. Dandare:** Resources, Investigation. **Ruben Sakrabani:** Resources. **Rory Doherty:** Writing – review & editing, Supervision, Resources. **Sree Nanukuttan:** Supervision, Resources. **Deepak Kumaresan:** Writing – original draft, Supervision, Resources, Project administration, Conceptualization.

Data availability

Data is available in the manuscript

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biombioe.2024.107299>.

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