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Hydrothermal Carbonization of Brewer’s Spent Grains: a Pathway for Brewery Waste Valorisation

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Brewer’s spent grains (BSG), the primary byproduct of beer production, are typically used as animal feed but hold significant potential for sustainable valorisation. The present study explores the application of the hydrothermal carbonization (HTC) process to transform high-moisture BSG into hydrochar, a versatile carbonaceous material with applications in energy, agriculture, and environmental sectors. Using a Design of Experiments – Response Surface Methodology (DoE-RSM), the combined effects of process operating conditions on hydrochar yields and properties were analyzed. HTC experiments were conducted at various temperatures (200–260 °C), times (30–210 min), and solid contents (5–25 wt %). Results showed that rising temperature and extended reaction time enhanced carbonization, reducing the H/C and O/C ratios, while enriching the energy content. Hydrochars with carbon contents up to 72 wt % and higher heating values up to 30.8 MJ/kg, were obtained. Optimization studies identified specific HTC conditions to maximize selected properties and process yields. Processing at 215°C with 23.5 wt % solids for 30 minutes ensured maximum carbon yield, leading to a hydrochar with properties comparable to lignite. Bioassay tests confirmed the potential agricultural utility of BSG-derived hydrochar as soil amendment. HTC can therefore assume an important role in the valorisation of BSG, aiding in waste reduction and contributing to circular economy models by transforming brewery byproducts into a valuable resource for agriculture, energy, and environmental applications.

* 1. Introduction

Brewer’s spent grains (BSG) are the main byproduct of beer brewing, consisting mostly of barley husks. BSG is traditionally used as animal feed, but its potential for more sustainable applications has gathered interest (Mainardis et al., 2024), particularly due to the significant quantities produced globally (around 30 million tons annually). This significant volume of BSG presents both challenges and opportunities for waste management and resource utilization. The greatest challenge in implementing any valorisation pathway lies in the material's high moisture content (typically 70–80%).

Hydrothermal carbonization (HTC) has proven to be a sustainable thermochemical technology to harness waste biomasses with elevated humidity level (Wang et al., 2018). Conducted in aqueous environment at mild temperatures under self-generated pressure, it converts biomass into a carbonaceous solid called hydrochar. The versatility of hydrochar has led to a wide range of applications, i.e., solid biofuel (Basso et al., 2016), electrode material in energy storage devices (Nicolae et al., 2020), adsorbent for wastewater treatment (Mahmood Al-Nuaimy et al., 2024), and soil amendment (Khosravi et al., 2022). Unlike other thermochemical processes, HTC bypasses the need for energy-intensive feedstock pre-drying, enabling its application to various high-moisture waste biomasses.

The present study examined the effect of operative parameters on the yields and characteristics of the hydrochar obtained from BSG. The influence of process variables was investigated through the Design of Experiments – Response Surface Methodology (DoE-RSM), a useful approach for process analysis, prediction, and optimization. The optimal HTC process variables capable to ensure set goals were assessed.

Among the various potential uses of hydrochar, there is increasing interest in its use as an organic growing medium in gardening and horticulture (as a peat substitute in potting mixes) or as a soil amendment in open-field agriculture (Islam et al., 2021). In the present study the suitability of the hydrochar produced from BSG for agronomic applications was investigated. The suitability of BSG hydrochar was assessed in terms of potential phytotoxicity through bioassay tests according to the Italian law (Decreto Legislativo 29 Aprile 2010, n. 75, 2010).

* 1. Materials and Methods
		1. Feedstock

Brewer’s spent grains (BSG) were provided by a local craft brewery (Birrificio Artigianale La Staffetta, Calci, Pisa, Italy). The as-received sample had a moisture content of 70.8 wt %. To improve sample preservation for the experimental campaign, BSG were dried at 105 °C. The main physicochemical characteristics of the feedstock, including Volatile Matter (VM), Fixed Carbon (FC), Ash, C, H, N and O contents, and Higher Heating Value (HHV), are listed in Table 1.

Table 1: BSG characterization (dry basis)

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| VM (wt %) | FC (wt %) | Ash (wt %) | C (wt %) | H (wt %) | N (wt %) | O (wt %) | HHV (MJ/kg) |
| 79.07 | 17.49 | 3.44 | 47.56 | 6.57 | 3.16 | 39.27 | 19.55 |

* + 1. Experimental design

The DoE-RSM approach was used to plan the HTC experimental campaign. The following process variables were recognized as independent variables (factors), with the chosen levels indicated in parentheses:

* A: Temperature (low level: 200 °C; high level: 260 °C)
* B: Time (low level: 30 min; high level: 210 min)
* C: Solid content (low level: 5 wt %; high level: 25 wt %).

The independent variable levels were selected based on insights from literature (Wang et al., 2018), preliminary trials, and inherent process limitations. This ensured an experimental design space representative of practical operating conditions while being sufficiently broad to capture trends in hydrochar yield and properties, thereby allowing for process optimization. An RSM approach with a face-centred Central Composite Design (CCD) was selected to unveil potential non-linear interactions between factors. The randomised design matrix, comprising 20 runs, is reported in Table 2.

To assess process performance, the following responses were evaluated: hydrochar yield (Y), hydrochar carbon content, carbon yield, hydrochar H/C and O/C atomic ratios, hydrochar ash content, hydrochar higher heating value (HHV), energy densification (ED), and energy yield (EY). Hydrochar yield, carbon yield, ED, and EY were defined as stated in Eqs (1) to (4).

|  |  |
| --- | --- |
|  | (1) |
|  | (2) |
|  | (3) |
|  | (4) |

The Design Expert® 13 software (Stat-Ease, USA) was used to identify significant models for each response.

* + 1. Hydrothermal carbonization experimental tests

HTC experimental tests were performed using a 0.3 L reactor (Parr, USA), equipped with mechanical stirring, heating system, temperature and pressure sensors, and a process controller (Parr, USA). Tests were conducted at different reaction temperatures, reaction times, and solid contents, following the design matrix displayed in Table 2. At the beginning of each test, the reactor was loaded with BSG and deionised water to achieve the desired solid load. At the end of the test, the obtained slurry was recovered, and the solid product (i.e., hydrochar) was separated by filtration, rinsed with deionised water, dried at 105 °C, and weighed. Hydrochar samples were characterized by proximate analysis, ultimate analysis and HHV determination.

Table 2: Experimental design matrix for HTC tests

|  |  |  |  |
| --- | --- | --- | --- |
| Run | A: Temperature (°C) | B: Time (min) | C: Solid content (wt %) |
| 1 | 260 | 30 | 25 |
| 2 | 230 | 120 | 5 |
| 3 | 200 | 30 | 5 |
| 4 | 260 | 120 | 15 |
| 5 | 230 | 120 | 15 |
| 6 | 230 | 120 | 15 |
| 7 | 260 | 210 | 25 |
| 8 | 200 | 30 | 25 |
| 9 | 230 | 120 | 15 |
| 10 | 260 | 30 | 15 |
| 11 | 200 | 210 | 5 |
| 12 | 260 | 210 | 25 |
| 13 | 230 | 30 | 5 |
| 14 | 230 | 120 | 15 |
| 15 | 230 | 120 | 25 |
| 16 | 200 | 210 | 5 |
| 17 | 230 | 120 | 15 |
| 18 | 230 | 120 | 15 |
| 19 | 230 | 210 | 15 |
| 20 | 200 | 120 | 15 |

A thermogravimetric Q-500 analyser (TA Instruments, USA) and a TruSpec CHN Elemental Analyser (LECO, USA) were employed for proximate and ultimate analysis, respectively. An AC-500 Calorimeter (LECO, USA) was used for HHV measurement.

* + 1. Phytotoxicity tests

Hydrochar phytotoxicity was evaluated through bioassays employing *Lepidium sativum* L. (cress) as a model species, in accordance with the Italian regulation (Decreto Legislativo 29 Aprile 2010, n. 75, 2010) and the methodology outlined by APAT (APAT, 2003). Germination and growth tests were performed as reported by Barontini et al. (2024). The germination index (Ig) was computed according to the expression in Eq(5):

|  |  |
| --- | --- |
|  | (5) |

where *Gt* and *Gc* are the average number of germinated seeds in the treated and the control Petri dishes, respectively, while *Lt* and *Lc* are the average root lengths of the treated and control samples.

The growth index (Gm) was determined using the expression in Eq(6):

|  |  |
| --- | --- |
|  | (6) |

where *Gt* and *Gc* represent the mean plant dry weight in the treated and in the control pots, respectively.

The Shapiro-Wilk test (95% confidence interval) was used to check normal distribution of data. Then, the difference between the control and the treatment in the germination and growth tests were analyzed by unpaired *t*-test (p ≤ 0.05). Statistical analysis of the bioassays was accomplished using GraphPad software (GraphPad, USA).

* 1. Results and Discussion
		1. Hydrochar production and process optimization

The DoE-RSM approach was employed to investigate hydrochar production from BSG, focusing on its suitability for various applications. HTC process yields and hydrochar properties were examined in relation to operating conditions.

The HTC process was shown to effectively transform BSG into hydrochar, reducing volatile matter and enriching both the fixed carbon and carbon contents. These transformations are attributed to the key reactions involving biomass macrocomponents, like hydrolysis, dehydration, decarboxylation, condensation, aromatisation, and polymerisation (Funke and Ziegler, 2010). Carbon content in the hydrochars varied between 60.7 wt % (Run 8) and 72.0 wt % (Run 7), indicating enrichment relative to the raw BSG (Table 1). The C content increased with rising temperatures and prolonged residence times, with temperature having a more pronounced effect than reaction time. Conversely, hydrogen and oxygen contents exhibited a decline with increasing process severity, because of dehydration and decarboxylation mechanisms. Therefore, increases in the temperature and residence time led to decreases in the H/C and O/C ratios, reflecting the development of aromatic structures in the carbonization process. HTC led to a change in the biomass elemental composition shown in Figure 1 according to the Van Krevelen method. The Van Krevelen diagram in Figure 1 plots the atomic H/C and O/C ratios for the hydrochar produced in different conditions, compared with the same ratios in the original BSG. Lower ratios signify enhanced carbonization and the formation of coal-like structures. The results in Figure 1 clearly highlight that HTC converted the lignocellulosic biomass into products resembling lignite or sub-bituminous coal.

The variations in the elemental composition also enhanced the HHV of the hydrochar with respect to the original BSG. The HHV of hydrochar improved with increased reaction temperature and time, reaching up to 30.8 MJ/kg (run 7). Energy densification ratios ranged from 1.32 to 1.57, indicative of enhanced fuel quality. It is also worthwhile noting that hydrochar exhibited a reduction in the ash content compared to that of the raw BSG, with some hydrochars achieving values as low as 1.1 wt %. These properties highlight the potential of BSG hydrochar as a low-ash solid biofuel. The observed values and trends are consistent with the findings of previous studies (Poerschmann et al., 2014).



*Figure 1: Van Krevelen diagram obtained for BSG and BSG-derived hydrochars (run details in Table 2).*

The operating conditions not only influence the physicochemical properties of the produced hydrochar but also exert a significant impact on process yields.

The hydrochar yield showed a significant sensitivity to temperature and solid content. The mass yield increased with higher solid contents, but decreased at elevated temperatures, consistently with the degradation of biomass components. Carbon yield relies on both hydrochar mass yield and hydrochar carbon content, as defined in Eq(2). The Analysis of Variance indicated temperature and solid content as significant factors for carbon yield, with the Design Expert® software suggesting a reduced quadratic model. The mathematical model, expressed in coded values, is shown in Eq(7):

|  |  |
| --- | --- |
|  | (7) |

The equation expressed in coded factors is helpful for assessing the relative influence of the factors by comparing their coefficients. The correlation between the factors and the response can be visually represented using response surface graphs. Figure 2a shows the response surface for carbon yield as a function of temperature and solid content (time is not significant). The adequacy of the model was verified by diagnostic plots. The agreement between the experimental values and the predicted model values was demonstrated by the close clustering of points along the straight line in the predicted versus actual values plot in Figure 2b.

Optimization studies identified specific HTC conditions for the maximization of selected responses. Regarding carbon yield, its maximization could be useful in the perspective of a potential use of hydrochar to produce high value-added carbonaceous materials, or for soil applications. The optimization of the carbon yield generated the following set of operating conditions: 215 °C reaction temperature and 23.5 wt % solid content.

To verify the model prediction capability, validation runs were carried out in the optimal conditions identified (since time is a not significant factor, the minimum reaction time, i.e., 30 min, was chosen). For all the validation runs carried out, the observed responses fell within the ranges predicted by the model.

Processing BSG at 215°C with 23.5 wt % solid content for 30 minutes yielded a hydrochar with properties comparable to lignite, potentially suitable for soil applications. The suitability of the BSG hydrochar for agronomic applications was investigated through phytotoxicity assessment.



*Figure 2: Response surface plot for carbon yield as a function of temperature and solid content (a) and diagnostic plot of predicted model values vs. experimental data for carbon yield (b).*

* + 1. Phytotoxicity assessment of BSG-derived hydrochar

As shown in Figure 3a, the Ig was lower in *L. sativum* plants treated with water extract of BSG hydrochar (85.2 vs 100 %) and a similar reduction was also observed in terms of Gm (78.5 vs 100 %, Figure 3b). This suggests the presence of some phytotoxic compounds generated by the HTC process which influence both the germination (acute effect) and the growth of *L. sativum* plants (chronic exposure for 21 days). However, for both the indexes values are higher than those allowed by the Italian regulation (>60 % *sensu* Decreto Legislativo 75/2010 and s.m.a.) for a soil amendment.



Figure 3: a) Germination index (Ig) of Lepidium sativum under control conditions (CTRL) or treated with the water extract of Brewer’s spent grains-derived hydrochar (BSG-HC). b) Growth index (Gm) of L. sativum in control conditions (CTRL) and after treatment with BSG-HC. Different letters indicate significant differences between controls and treated samples.

This indicates that the hydrochar derived from BSG could still be considered suitable for agronomic applications. Recent studies, such as those by Karatas et al. (2022), have made significant advances in understanding hydrochar phytotoxicity and methods to reduce its toxic effects, aiming to minimize the formation of phytotoxic compounds and improve the effectiveness and safety of hydrochar.

* 1. Conclusions

HTC enables the production of a high-quality hydrochar with different potential applications, ranging from energy generation to soil improvement, while leveraging BSG as a sustainable waste feedstock. This highlights that HTC can make a significant contribution to the valorisation of BSG, aiding in waste reduction and contributing to circular economy models by transforming brewery byproducts into valuable resources for agriculture, energy, and environmental purposes.

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