Valorization of Brewery Spent Grain for Biochar Production through Fixed-Bed Pyrolysis

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Introduction

Brewery spent grain (BSG) is the major solid by-product of the brewing industry, accounting for approximately 85% of the solid residues generated during beer production. Its composition is dominated by lignocellulosic fractions, proteins, and residual lipids, which makes BSG a potentially valuable renewable feedstock rather than a material intended only for low-value disposal or animal feed [1,2]. Nevertheless, freshly generated BSG contains a high moisture fraction and is highly susceptible to microbial deterioration, which restricts its storage stability and increases handling and disposal costs. These limitations have stimulated the development of strategies capable of integrating brewery residues into circular-bioeconomy routes and converting their organic fraction into higher-value products [1,2].

Thermochemical conversion is particularly attractive for lignocellulosic residues because it can simultaneously reduce waste volume and generate energy carriers and carbonaceous materials. Among the available routes, pyrolysis converts biomass under oxygen-limited conditions into three major product fractions: a solid carbon-rich material (biochar), condensable vapors recovered as bio-oil, and non-condensable gases [3]. The relative distribution of these fractions is governed by operating parameters such as final temperature, residence time, particle size, heating conditions, and biomass loading, which influence heat transfer, devolatilization, vapor residence, secondary cracking, and char-forming reactions [3,4].

For BSG, the biochar fraction is of particular interest because carbonization can transform an unstable brewery residue into a more thermally stable carbonaceous material. BSG-derived biochars have been investigated as precursors for activated carbon and as functional carbon materials for adsorption, environmental remediation, and energy-related applications [4-6]. Previous studies have also shown that the preparation conditions and particle characteristics can substantially affect the physicochemical performance of BSG-derived carbon materials [5,6]. Consequently, understanding how pyrolysis conditions affect both product yield and the properties of the resulting solid is essential for defining efficient routes for brewery-residue valorization.

In this context, the objective of this work was to evaluate the conversion of BSG by fixed-bed pyrolysis, emphasizing the production of biochar and the experimental distribution of biochar, bio-oil, and pyrolysis gas. The effects of residence time, final pyrolysis temperature, particle size, and biomass loading were investigated. In addition to product yields, the biochar obtained under the condition that maximized carbon enrichment was evaluated by elemental analysis and spectroscopic and thermal characterization to verify the structural transformations associated with carbonization.

Materials and Methods

BSG was obtained from pilot-scale brewing operations conducted at the Polytechnic School of the University of São Paulo (USP), Brazil. The residue originated from a representative malt blend composed of approximately 70 wt.% Pilsner malt, 20 wt.% Munich malt, and 10 wt.% Carapils malt. After collection, the material was homogenized, refrigerated, dried, and subsequently classified by particle size before pyrolysis.

Pyrolysis experiments were performed in batch mode using a laboratory-scale fixed-bed system composed of a thick-walled borosilicate glass tube positioned horizontally inside an electrically heated tubular furnace. The biomass was placed in the central heating zone, and the samples were heated from room temperature to the selected final temperature at 10 °C min^{-1}. No external carrier or reactive gas was supplied. The reactor outlet was connected to a helical condenser maintained at 5 °C by a thermostatic bath. Condensable products were recovered in a collection flask, whereas non-condensable gases were directed to a gas sampling bag.

A one-variable-at-a-time experimental strategy was used. Residence time was varied from 30 to 300 min, final temperature from 400 to 1200 °C, particle size from 200 to 800 µm, and biomass loading from 2 to 8 g. Biochar yield was calculated from the mass of solid recovered after cooling relative to the initial dry biomass mass. Bio-oil yield was determined gravimetrically from the collected condensable fraction, and gas yield was calculated by mass difference. The biochar selected for further characterization corresponded to the condition that produced the highest carbon content: 700 °C, 120 min, 800 µm, and 8 g. Elemental composition was determined by CHN analysis, and the selected biochar was additionally evaluated by FTIR, TGA, and Raman spectroscopy.

Results and Discussion

Figure 1 presents the experimental distribution of biochar, bio-oil, and pyrolysis gas as a function of the four investigated operating variables. Residence time exerted a comparatively modest effect on product distribution. Biochar remained within approximately 27-33 wt.% over 30-300 min and reached its highest value near 120 min, while the gaseous fraction remained dominant at approximately 65-71 wt.%. Bio-oil was consistently low, generally between 1 and 4 wt.%. The limited variation after 120 min indicates that the main devolatilization and solid-forming reactions had already occurred, whereas longer exposure mainly favored secondary reactions involving volatile compounds. This behavior is consistent with the general response of lignocellulosic materials under prolonged slow-pyrolysis conditions, in which vapor cracking becomes increasingly relevant after primary devolatilization [3,7].

Temperature produced a more pronounced shift in the balance among products. Biochar yield increased from approximately 32 wt.% at 400 °C to about 39-40 wt.% at temperatures of 700 °C and above. In parallel, the gas fraction decreased from approximately 65 wt.% at 400-500 °C to about 59-60 wt.% above 700 °C, while bio-oil remained between approximately 2 and 4 wt.%. The stabilization of product distribution above 700 °C suggests that the principal thermochemical transformations controlling solid recovery had largely been completed by this temperature. The observed plateau is relevant from a processing perspective because further heating above 700 °C produced only limited changes in product yield, while necessarily increasing the thermal demand of the process. Similar effects of temperature on carbonization, volatile release, and the evolution of biochar properties have been widely reported for biomass-derived chars [7,8].

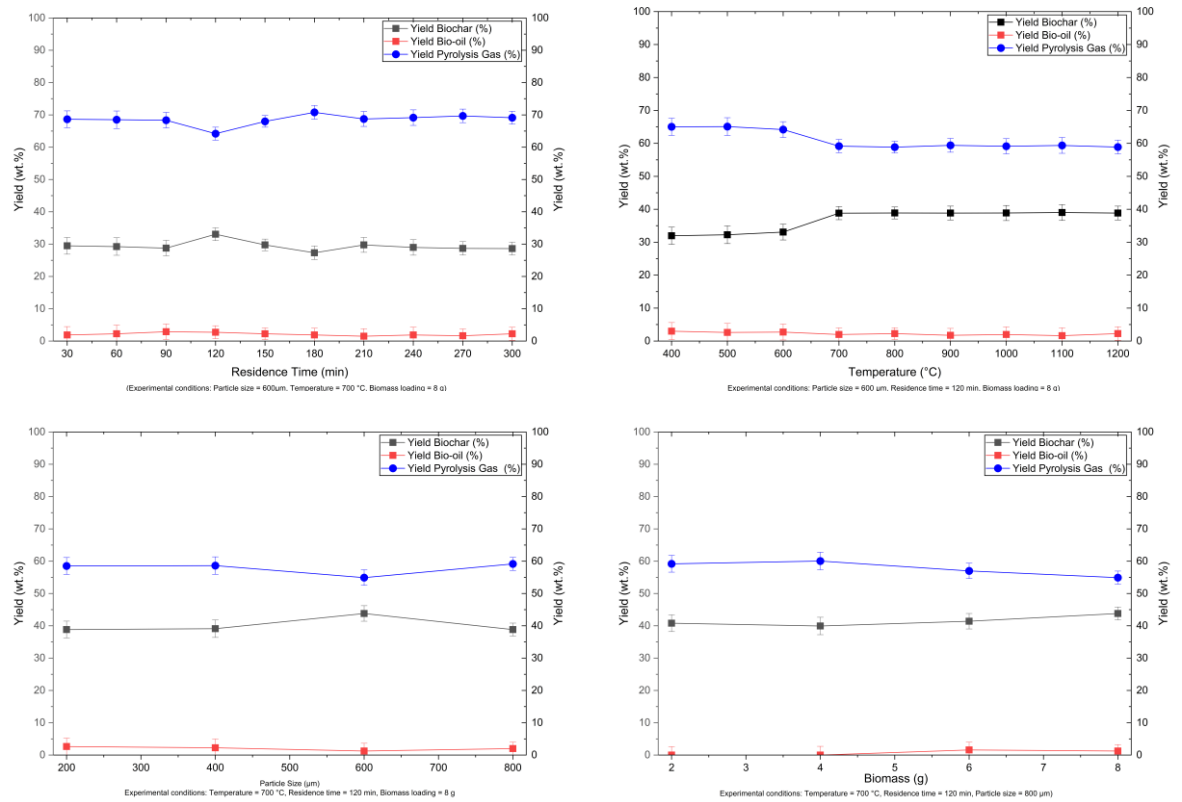

Figure 1. Effect of (a) residence time, (b) pyrolysis temperature, (c) particle size, and (d) biomass loading on the distribution of biochar, bio-oil, and pyrolysis gas obtained from BSG.

Particle size also changed the relative formation of solid and gaseous products. Biochar yield increased from approximately 39 wt.% at 200 µm to a maximum of about 44 wt.% at 600 µm, followed by a slight decrease at 800 µm. The maximum biochar yield coincided with the minimum gas yield, approximately 55 wt.%, at 600 µm. This result suggests that the intermediate particle size provided a favorable balance between heat penetration and volatile transport. Smaller particles can favor rapid devolatilization, whereas larger particles develop longer diffusion paths and internal gradients that may alter secondary reactions. Therefore, the condition that maximized solid recovery was not necessarily the same condition that maximized the degree of carbonization.

Biomass loading had a moderate but systematic influence. Increasing the amount of BSG from 2 to 8 g slightly increased biochar formation and reduced the gas fraction, whereas the bio-oil fraction remained low and showed no clear trend. A thicker biomass bed can increase resistance to heat and mass transfer and prolong the contact of volatile intermediates with the solid phase, thereby favoring repolymerization and secondary char-forming reactions. Considering all yield experiments, the process showed a clear tendency toward biochar and gas production rather than liquid recovery. The highest biochar yield was associated with approximately 120 min, temperatures at or above 700 °C, particle size near 600 µm, and higher biomass loading. This behavior agrees with studies showing that process variables strongly determine the distribution and physicochemical characteristics of pyrolysis products from BSG and other lignocellulosic residues [3,7,8].

Product yield alone, however, does not describe the quality of the solid fraction. Elemental analysis demonstrated a progressive enrichment of carbon as the pyrolysis severity

increased. The raw BSG contained 41.69 ± 0.09 wt.% carbon, whereas the highest carbon content measured in the produced biochars was 75.31 ± 0.58 wt.%. This maximum was obtained at 700 °C, 120 min, 800 µm particle size, and 8 g biomass loading. Notably, the particle size associated with the highest carbon content (800 µm) differed from that associated with the highest biochar yield (600 µm), indicating a trade-off between maximum solid recovery and maximum carbon enrichment. The carbon increase was accompanied by a strong decrease in hydrogen and in the fraction calculated by difference, consistent with dehydration, decarboxylation, decarbonylation, and devolatilization reactions that remove hydrogen- and oxygen-containing compounds and promote the formation of a more condensed carbonaceous matrix [8].

FTIR analysis of the biochar produced under the highest-carbon condition is shown in Figure 2. Compared with the functional-group profile expected for the lignocellulosic precursor, the biochar exhibited a weak broad O-H band in the 3200-3600 cm^{-1} region and only weak aliphatic C-H contributions near 2900 cm^{-1}. In contrast, the 1600-1700 cm^{-1} region became more prominent and was associated with aromatic C=C structures and/or conjugated carbonyl groups. Bands in the 1000-1300 cm^{-1} region, attributed to C-O-containing groups and possible mineral contributions, were comparatively weak. These changes indicate extensive loss of oxygenated functionalities and increasing predominance of condensed aromatic structures, which are characteristic of advanced carbonization [8].

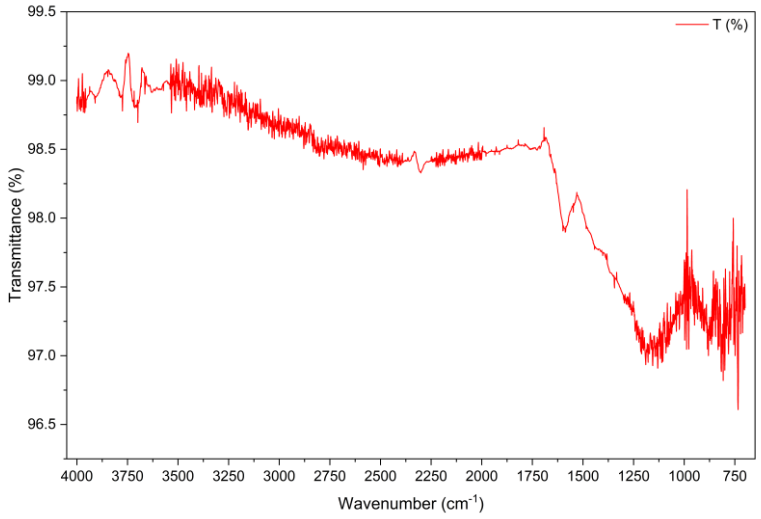

Figure 2. FTIR spectrum of the biochar produced at 700 °C, 120 min, 800 µm particle size, and 8 g biomass loading.

Thermogravimetric analysis (Figure 3) further confirmed the structural stabilization of the selected biochar. Only a small initial mass loss was observed below approximately 120 °C, associated with adsorbed moisture and residual light volatile compounds. The main mass-loss event occurred approximately between 200 and 400 °C and was attributed to residual oxygenated functionalities and thermally unstable organic structures that remained after pyrolysis. Above 400 °C, mass loss became progressively slower, indicating the predominance of more thermally resistant aromatic carbon structures. The absence of abrupt decomposition at higher temperatures is consistent with the formation of a stabilized carbonaceous matrix [9].

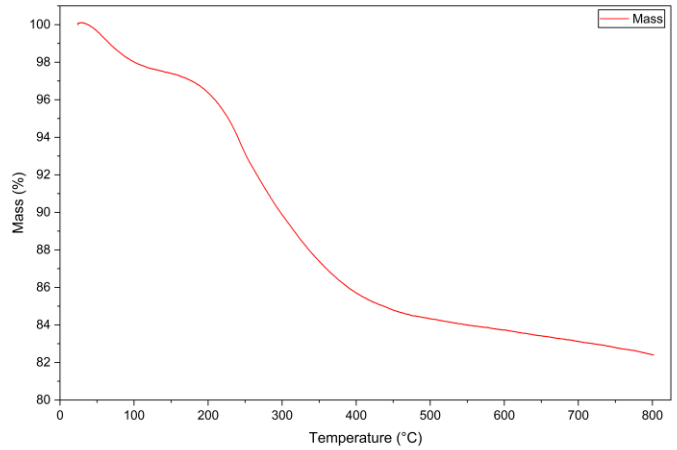

Figure 3. TGA curve of the biochar produced at 700 °C, 120 min, 800 µm particle size, and 8 g biomass loading.

Raman spectroscopy provided complementary information on carbon organization (Figure 4). The spectrum displayed the characteristic D band at approximately 1350 cm^{-1} and G band near 1580 cm^{-1}. The D band is associated with structural disorder and defects in aromatic carbon, whereas the G band is related to vibrations of sp^2-hybridized carbon atoms. The relatively high intensity of the D band compared with the G band indicates that the biochar remained predominantly disordered and only partially ordered, rather than developing a highly graphitic structure. Such a response is typical of biochars produced from lignocellulosic materials at intermediate pyrolysis temperatures, in which aromatization occurs without complete graphitic ordering [10]. Taken together, the yield data, carbon enrichment, FTIR, TGA, and Raman results demonstrate that BSG can be converted into a carbon-rich and thermally stable biochar. The relatively high carbon content combined with the structural features observed after pyrolysis supports the use of this material as a precursor for subsequent activation and other value-added carbon-material applications.

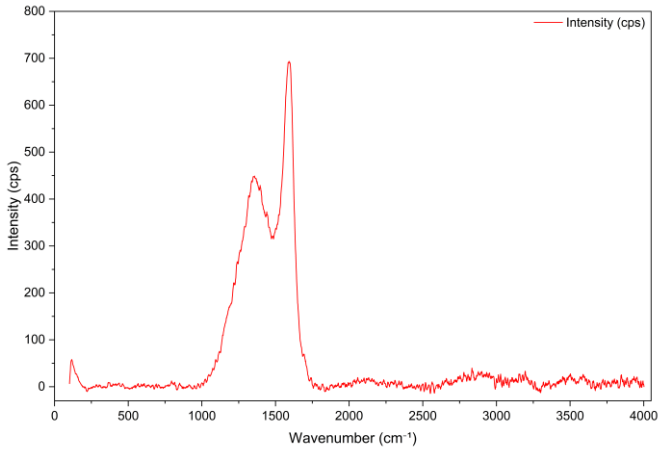

Figure 4. Raman spectrum of the biochar produced at 700 °C, 120 min, 800 µm particle size, and 8 g biomass loading.

Conclusions

The results demonstrate that brewery spent grain can be effectively valorized through fixed-bed pyrolysis, converting a highly perishable agro-industrial residue into a carbon-rich solid while simultaneously generating gaseous and minor liquid fractions. Operating conditions

controlled product distribution, with temperature and particle size producing the clearest changes in solid recovery. Bio-oil remained below approximately 4 wt.% throughout the investigated conditions, confirming that the adopted process favored carbonization and gas formation rather than liquid-product production. A residence time close to 120 min, temperatures of at least 700 °C, an intermediate particle size near 600 µm, and higher biomass loading favored biochar yield.

Importantly, the operating condition that maximized solid yield did not match the one that produced the highest carbon enrichment. The highest carbon content, 75.31 ± 0.58 wt.%, was obtained at 700 °C, 120 min, 800 µm, and 8 g. The corresponding FTIR profile showed a marked reduction in oxygenated and aliphatic functionalities and a predominance of aromatic structures, while TGA demonstrated enhanced thermal stability and Raman spectroscopy confirmed the development of a defect-rich, predominantly disordered aromatic carbon matrix. These complementary results show that optimization of BSG pyrolysis should consider not only the amount of biochar recovered but also the chemical and structural quality of the resulting material.

Overall, the study supports pyrolysis as a technically promising route for integrating brewery spent grain into circular-bioeconomy strategies. The produced material combines high carbon content and thermal stability with an initial carbonaceous structure suitable for further modification. Future activation or surface-development steps may expand its applicability as an adsorbent, catalyst support, or advanced carbon material, increasing the value recovered from brewery residues.

Acknowledgments

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