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Designing a Circular Economy for the Brewing Industry: Pyrolysis-Based Biochar Production  
from Brewing Waste Streams and Relative Greenhouse Gas Assessment

By

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THESIS

Submitted in partial satisfaction of the requirements for the degree of

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of the

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# Abstract

In 2020, global beer production reached a staggering volume of 1.82 trillion hectoliters, resulting in the generation of 36.4 million metric tons of brewers spent grain (BSG) (Zeko-Pivač et al. 2022). BSG primarily consists of the husk, pericarp, and seed coats of barley, making it a highly fibrous material. Trace amounts of silica, polyphenols, insoluble protein, and oils may also be present (Mussatto et al. 2006). The water content of BSG ranges from 60-90%; which allows naturally present microbes spoil the material within a few months of cold, sealed storage and within days of room temperature sealed or open air storage (Briggs et al. 2004; Mallen & Najdanovic-Visak 2018). The water content also contributes to the weight of BSG, increasing transportation costs and resource demand for disposing grain offsite. Traditionally, brewers donate their BSG to farmers as animal feed, however there is growing interest in alternative opportunities to valorize the grain. This research first provides an overview of the current BSG-derived products on the market, including dog treats, compound extraction, industrial materials, and beyond. Subsequently, it evaluates a biorefinery model which converts BSG into biochar using waste caustic material from the brewing process, specifically considering optimization of each step in the protocol to produce a biochar product. The ideal production parameters were found to be 1 day of soaking BSG in caustic at a dosage rate of  $\leq 5$  moles per 100 g unprocessed BSG at ambient temperature, followed by draining of the liquid fraction, drying of the BSG until constant weight, grinding until uniform particle size, and pyrolysis at 700 °C with a heating rate of 5 °C/min, holding the sample for at least 1 hour of residence time with constant inert gas flow throughout the heating and cooling process. The resulting biochar was

appropriate for water filtration or soil amendment systems within the brewing industry (assuming further processing), which would allow brewers to build circular economy model. The proposed method was then evaluated via a greenhouse gas (GHG) assessment, to determine the efficacy of implementing this system in industry. The findings of this study concluded that landfilling BSG released nearly 3 kg  $CO_2e$  per kg unprocessed BSG, while processing BSG into biochar at the lab scale resulted in lower emissions of 1.175 kg  $CO_2e$  per kg unprocessed BSG. Based on these results, it is strongly recommended that BSG is diverted from landfills and utilized in more environmentally sustainable ways, such as through biochar production, composting, or a relative biorefinery process. By adopting a circular economy model for BSG, breweries can contribute to resource efficiency, waste reduction and the creation of sustainable value chains.

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# Chapter 1: Brewers' Spent Grain (BSG)

## Application's Towards Biorefinery Models

### 1. Introduction

Fermented alcoholic beverages have played a fundamental role in evolving societies for over 10,000 years ([Liu et al. 2018](#)), there is even scholarly discourse suggesting that beer was foundational in the advancement of economic trade ([Bamforth 2009](#)). Although the original fermentation process was rudimentary and yielded a beverage distant from modern day beer, our comprehension of this intricate process has improved remarkably over time. Contemporary beer production utilizes meticulously refined techniques which have been heavily adapted from the original principles. Beer is manufactured with four standard ingredients: water, malted barley, hops, and yeast; each are vital, contributing a variety of characteristics that formulate modern-day beer.

#### 1.1 Barley and Malt

Barley is recognized as one of the world's most important cereals, after wheat, maize, and rice. It is most frequently used for beer production or animal feed. Barley grains are composed of three main parts: a small embryo or germ, a large endosperm filled with starch particles which are held in place by a protein matrix, and the bran (the seed coat, the aleurone layers, and the pericarp layers) ([Mussatto et al. 2006](#)). This is displayed in Figure 1. The pericarp is waxy and

semi-waterproof, there is a clear boundary between the inner and outer regions of the kernels where the pericarp interfaces with the semi-permeable seed coat (Mussatto et al. 2006). The surrounding husk acts primarily as protection for the kernels, and is composed primarily of lignocellulose (Mussatto et al. 2006). On average, barley granules contain 11.97% protein, 1.93% ash, 1.81% lipids, and 63.42% starch (Czuchajowska et al. 1998; Quinde et al. 2004; Izydorczyk et al. 2000); Table 1. These values may vary depending on genotype (waxy, non-waxy, high-amylose, high-starch, etc.).

Figure 1. Barley Grain Structure

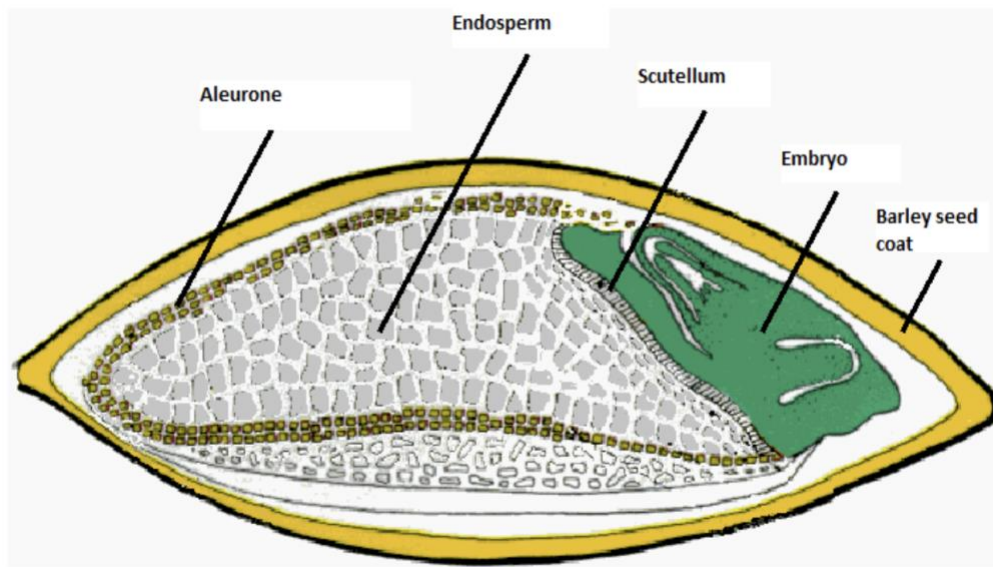


Image from (Chetrariu and Dabija 2020)

Table 1. Barley Compositions from Literature

Source	Protein	Ash	Lipids	Starch
<u>(Czuchajowska et al. 1998)</u>	12.5 - 15.5	2.11 - 3.01	2.16 - 2.65	65.2 - 67.6
<u>(Quinde et al. 2004)</u>	9.8	0.85	1.14	-
<u>(Quinde et al. 2004)</u>	12	2.38	-	-
<u>(Izydorczyk et al. 2000)</u>	12.2 ± 0.4	-	-	60.7 ± 1.0
<b>Average</b>	<b>11.97</b>	<b>1.93</b>	<b>1.81</b>	<b>63.42</b>

After harvesting, barley is cleaned and graded according to size (2.5, 2.4, 2.2, 2.0 mm) (Mussatto et al. 2006). After controlled dormancy (4-6 weeks), barley is malted. During the malting process, kernels are steeped in water, which is changed every 6-8 hours, for two days held between 15-18°C. The grains' moisture content increases to 42-48% which initiates germination and aleurone metabolism (Mussatto et al. 2006). The barley then enters the germination vessel where it is treated with a humid air flow that activates inherent enzymes which modify the starchy endosperm; full modification takes 6-7 days. The grains are then slowly dried and subsequently kilned to develop desirable organoleptic properties and enhance its overall sensory characteristics.

## 1.2 The Brewing Process

At the start of brewing, malted barley is milled, and combined with temperature-controlled water, initiating the mash stage. The alteration of temperature triggers enzymatic activity, leading to conversion of starch into fermentable sugars. The mash yields two distinct fractions:

1) insoluble fragments that settle at the bottom of the vessel, creating a natural filtration system, and 2) a sweet liquid known as wort that permeates through the grain bed. To achieve wort clarification, a continuous recirculation process called vorlaufing is employed, wherein the wort is circulated over the top of the grain bed. Once suitably clarified, the liquid is transferred to a kettle to begin boiling, in a process called lautering. Concurrently, water continuously flows over the top of the grain bed and then to the kettle, this is referred to as sparging. The lautering process concludes when the kettle reaches its maximum capacity. At this stage, any residual liquid left in the lauter tun is drained, while the solid fraction of the grains, known as brewer's spent grain (BSG), remains in the lauter tun, or a mash filter if the brewery is equipped with one. Depending on the scale and capabilities of the brewing system, BSG is manually or mechanically removed.

## 2. Brewer's Spent Grain

In 2020, global beer production reached a staggering volume of 1.82 trillion hectoliters, resulting in the generation of 36.4 million metric tons of BSG ([Zeko-Pivač et al. 2022](#)). This significant quantity has gained considerable attention in recent years. However, applications for BSG are limited primarily because of its high-water content, typically ranging from 60-90%. Consequently, naturally present microbes spoil the material within a few months of cold, sealed storage and within days of room temperature sealed or open air storage ([Briggs et al. 2004](#); [Mallen & Najdanovic-Visak 2018](#)). Water content also contributes to the weight of BSG, thereby increasing transportation costs and resource demand for disposing grain offsite. Traditionally,

brewers offer their BSG to farmers as animal feed. In this arrangement, farmers retrieve the grain from the brewery site, therefore the only cost is incurred by the farmer's travel. However, this solution is not viable for breweries located in urban areas or far from animal farms.

Majority of inner-city breweries compost their grain and others send it to the landfill. As BSG decomposes in a compost, or aerobic fermentation, setting it releases carbon dioxide, which is a potent greenhouse gas (GHG). As BSG decomposes in a landfill, or anaerobic degradation, setting it releases methane which is a more potent GHG than carbon dioxide. When BSG is sent to a landfill, all potential to reuse or benefit the environment is lost, however, when it is sent to compost, nutrients can still be recovered and used such as in a soil system. Therefore, composting is more desirable than landfilling.

To prevent loss of nutrients and damage to the environment, there is a growing trend in exploring the various applications for BSG. Briefly, it can be dried and used in baked goods, undergo chemical processing to extract compounds such as polysaccharides or antioxidants, or undergo biotechnological processing for microorganism cultivation and enzyme production, among many other opportunities. This review considers both literature- and market-based valorization techniques.

## 2.1 BSG Composition

BSG is the major solid waste stream generated during beer production, constituting approximately 85% of the total by-products (Mussatto et al. 2006). Because the brewing process is highly selective, BSG is constituted primarily of the husk, pericarp, and seed coats of

the cereal grains. However, there may be trace amounts of silica, polyphenols, insoluble protein, and oils (Mussatto et al. 2006). The composition of BSG varies depending on several including quality and grain species, malting, and mashing conditions (time, temperature, volume ratios), the use of adjuncts, and salt incorporated during the mashing stage.

There are many studies available to elucidate the macronutrient and fiber content of BSG. Table 2 presents data compiled from 11 different studies, providing an estimate of the macronutrient composition of BSG. On average, BSG contains 38.22% total carbohydrates, 7.33% fat, 21.82% protein, 2.73% ash, and 44.71% fiber. It is worth noting that these values sum up to nearly 115% instead of 100%, indicating inconsistencies across the BSG. The largest standard deviation, reflecting the highest fluctuation, was observed in total carbohydrates at 17.17%, followed by total fiber at 9.90%. Similarly, Table 3 consolidates data from 12 different studies to estimate the fiber composition of BSG. According to these studies, the total fiber composition of BSG comprises approximately 23.59% cellulose, 31.27% hemicellulose, and 15.26% lignin. However, the standard deviations for these components were 10.34%, 8.22%, and 6.67%, respectively, again highlighting variability in the reported studies.

Table 2. Macronutrient Composition of Brewer's Spent Grain

<b>Source</b>	<b>Total Carbs</b>	<b>Fat</b>	<b>Protein</b>	<b>Ash</b>	<b>Total Fiber</b>
<u>(Waters et al. 2012)</u>	64.88	7.12	22.13	1.13	48.22
<u>(Serena and Knudsen 2007)</u>	52.5	-	21.5	0.5	-
<u>(Dhillon et al. 2012)</u>	34.5-43.3	7.9 ± 1.4	23.9 ± 1.24	2.6 ± 0.3	-
<u>(Makowska et al. 2013)</u>	-	8.53 ± 0.03	25.49 ± 0.66	3.76 ± 0.17	-
<u>(Canedo et al. 2016)</u>	39.10 ± 0.57	-	17.96 ± 0.21	4.42 ± 0.07	-
<u>(Kanauchi et al. 2001)</u>	-	10.6	24	2.4	59
<u>(Castro and Colpini 2021)</u>	-	1.61 ± 0.10	18.14 ± 0.25	2.34 ± 0.07	-
<u>(Bravi et al. 2021)</u>	24.58 ± 0.71	6.75 ± 0.16	18.58 ± 0.02	2.96 ± 0.10	38.52 ± 0.12
<u>(Bravi et al. 2021)</u>	34.97 ± 1.94	6.40 ± 0.09	15.91 ± 0.05	2.63 ± 0.05	33.01 ± 2.76
<u>(Lynch et al. 2021)</u>	12.6	9.7	31	3.6	44.8
<u>(Sibhatu et al. 2021)</u>	-	-	21.4 ± 0.06	3.7 ± 0.06	-
<b>Average</b>	<b>38.22</b>	<b>7.33</b>	<b>21.82</b>	<b>2.73</b>	<b>44.71</b>
<b>Standard Deviation</b>	<b>17.17</b>	<b>2.73</b>	<b>4.26</b>	<b>1.16</b>	<b>9.90</b>
<b>Minimum</b>	<b>12.60</b>	<b>1.61</b>	<b>15.91</b>	<b>0.50</b>	<b>33.01</b>
<b>Maximum</b>	<b>64.88</b>	<b>10.60</b>	<b>31.00</b>	<b>4.42</b>	<b>59.00</b>

Table 3. Fiber Composition of Brewer's Spent Grain

Source	Cellulose	Hemicellulose	Lignin	Unit
(Kanauchi et al. 2001)	43	36.9	20.1	% fiber
(Pedro Silva et al. 2004)	25.3	41.9	16.9	dry mass (%)
(Mussatto and Roberto 2006)	16.78	28.42	27.78	g/100g
(Xiros et al. 2008)	12	40.2	11.5	w/w%
(Meneses et al. 2013)	21.73 ± 1.36	19.27 ± 1.18	19.4 ± 0.34	g/100g
(Serena and Knudsen 2007)	14.7	-	12.6	g/100g
(Terrasan and Carmona 2015)	22.32	32.81	16.94	%
(Dhillon et al. 2012)	13.8 ± 2.4	30.0 ± 4.2	12.4 ± 1.3	% DW
(Makowska et al. 2013)	17.81 ± 0.94	28.8	5.14 ± 0.25	% dm
(Kanauchi et al. 2001)	43	36.9	20.1	% weight
(Castro and Colpini 2021)	23.99 ± 1.63	-	3.35 ± 0.45	%
(Sibhatu et al. 2021)	28.7 ± 0.02	17.5 ± 0.05	16.9 ± 0.04	g/100g
<b>Average</b>	<b>23.59</b>	<b>31.27</b>	<b>15.26</b>	<b>w/w</b>
<b>Standard Deviation</b>	<b>10.34</b>	<b>8.22</b>	<b>6.76</b>	<b>w/w</b>
<b>Minimum</b>	<b>12.00</b>	<b>17.50</b>	<b>3.35</b>	<b>w/w</b>
<b>Maximum</b>	<b>43.00</b>	<b>41.90</b>	<b>27.78</b>	<b>w/w</b>

Microscopic analysis has confirmed the presence of fibrous tissues within BSG, originating from the surface layers of barley grain (Mussatto et al. 2006). These are primarily the arabinoxylan, lignin, and cellulose fibers demonstrated in Table 3. Because the brewing process is optimized for starch (and therefore soluble sugar) removal, BSG contains higher levels of protein and fiber compared to starch. The vitamin and mineral composition of BSG can vary depending on the



grains, water, and salt additions used during brewing. Commonly found minerals include calcium, cobalt, copper, iron, magnesium, manganese, phosphorus, potassium, selenium, sodium, and sulfur (Huige 2006). The most prevalent vitamins include biotin, choline, folic acid, niacin, pantothenic acid, riboflavin, thiamine, and pyridoxine (Huige 2006). There are also protein bound amino acids, including relatively large amounts of leucine, valine, alanine, serine, glycine, glutamic acid, and aspartic acid, while tyrosine, proline, threonine, arginine, and lysine are present in smaller quantities (Huige 2006).

A study by Naibaho and Korzeniowska found that the water holding capacity of eight different varieties of BSG ranged from 3.06 to 4.34 g/g, and the oil holding capacity ranged from 1.92 to 2.22 g/g. The same study also evaluated the color characteristics of these samples using the L\*, a\*, and b\* test which describes a color based on lightness-darkness (L\*), redness to greenness (a\*), and yellowness to blueness (b\*). The results demonstrated that the L\* values ranged from 58.44 to 63.73% indicating lightness, the a\* values ranged from 3.73 and 5.57 indicating mild redness, and the b\* values ranged from 14.61 to 17.12 indicating yellowness (Naibaho and Korzeniowska 2021). Overall, the composition and properties of BSG can vary significantly depending on factors such as the beer style, use of adjuncts, initial characteristics of the barley, and specific processing techniques employed.

## 2.2 Shelf Life of BSG

The major limiting factors for valorizing BSG are its high water activity and high fermentable sugar concentration. These make BSG highly unstable and susceptible to rapid deterioration

from microbial activity. After 30 days of storage in gunnysacks, a study by [Sodhi et al. \(1985\)](#) identified eight isolates of microorganisms on BSG: *Aspergillus*, *Fusarium*, *Mucor*, *Penicillium*, and *Rhizopus* ([Mussatto et al. 2006](#)). Drying can be used to extend the shelf life of BSG, which simultaneously decreases the weight and therefore transportation costs and storage needs; however, the drying process increases energy use. Drying temperature, energy usage, and ventilation of the oven is important to consider prior to adapting this method. A study by [Tang et al. 2004](#) found that superheated steam methods can be utilized for drying BSG while reducing environmental impact, improving drying efficiency and enhanced recovery of the inherent compounds ([Mussatto et al. 2006](#)).

## 2.3 Brewer's and BSG

After hosting conversations with over ten craft breweries located within a 55-mile radius of Davis, CA, ranging from production sizes of 7-40 barrels (217-1240 L) a day, it was found that all have established arrangements with local farmers for the pickup of their BSG directly from their sites. The brewer's provided several reasons for utilizing this recovery method: (1) historical effectiveness: donating BSG to farmers has been a long-standing, effective, and convenient method of disposal; (2) cost considerations: the cost associated with implementing new systems or equipment is the largest barrier; (3) mutual benefits: donating to farmers is beneficial for both parties; (4) environmental friendliness: compared to landfilling, donating BSG is seen as an eco-friendly option; (5) time efficiency: farmers' immediate response and timely pickup align with the brewery's needs; (6) space optimization: breweries can manage

with a small dumpster, rather than having to store large quantities of BSG onsite until landfill pickup.

However, some breweries expressed frustration with the reliance on farmers, noting that they have experienced some unreliability when they stopped picking up without much notice. One brewery previously explored the option of composting BSG in silos, but the cost was prohibitive for near-future implementation. Another brewery emphasized the importance of return on investment and convenience when considering alternative valorization methods, further confirming the largest barrier to BSG upcycling is the cost of new equipment and the processing required.

When asked about their satisfaction with their current BSG disposal, most breweries indicated their contentment. Some shared some further comments that they have had difficulty building reliable relationships. One brewery noted that if their farmer stopped showing up on time, they would end the relationship because timeliness is of utmost importance to them.

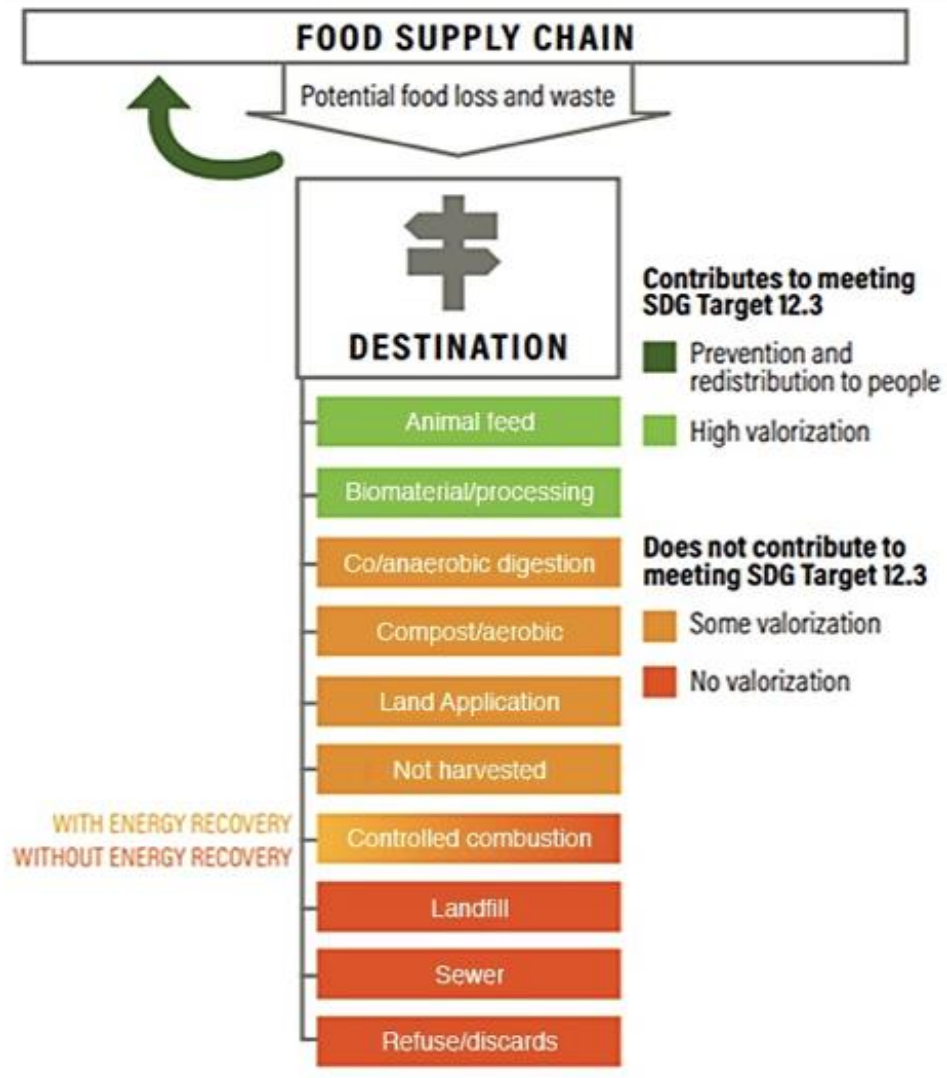
When asked if they would be interested in new technologies to upcycle their grain there was a general trend that they were currently rather unconcerned about finding a new use for the grain. However, some expressed interest in exploring profit-generating processes, provided they are timely and reliable. One brewery mentioned a previous attempt at making dog treats, but the cost-benefit analysis proved unsustainable. These conversations elucidated the reasons

why many small-scale breweries continue to rely on local farmers for BSG pickup, and the existing barriers to changing this protocol.

## 2.4 BSG for Circular Economy Models

In September 2015, the United Nations General Assembly released 17 Sustainable Development Goals (SDGs), with targets for each goal. SDG 12 aims to ensure sustainable consumption and production patterns. More specifically, SDG Target 12.3 aims to reduce global per capita food waste by 50% at the retail and consumer levels, while minimizing food losses in the production, postharvest, and supply chains by 2030. Champions 12.3, a collaborative group of executives from various industries working on SDG 12.3, released a study denoting the optimal uses for potential food loss and waste, as demonstrated in Figure 2.

Figure 2. Hierarchy of solutions for diverting food waste to meet UN SDG 12.3.



(Champions 12.3 and Hanson 2017)

The reuse of BSG in a new application is often considered environmentally friendly and can help achieve this goal; however, it is vital to consider the emissions associated with the reuse of BSG to confirm or deny that hypothesis (*see Chapter 3 for an analysis*). One approach to fostering sustainable practices is through the adoption of a circular economy model. According to The US Environmental Protection Agency (EPA), a circular economy “reduces material use, redesigns

materials to be less resource intensive, and recaptures ‘waste’ as a resource to manufacture new materials and products” ([United States Environmental Protection Agency 2021](#)). This was designed to counteract the linear economy model in which resources are extracted from Earth, manufactured into products, and then discarded as waste ([United States Environmental Protection Agency 2021](#)). The food and beverage industries, in particular, are responsible for considerable usage of finite natural resources, and release of GHG emissions to our ecosystem. It is crucial for these industries to adopt circular economy principles. By-products of food and beverage processing, such as BSG, are still valuable resources that, if used intentionally, can be recovered into value-added products ([Cortés et al. 2020](#)). In the case of BSG, a circular economy model can be achieved, with respect to Figure 2, by converting it into biomaterials that can be utilized (1) in barley, hop or yeast growing/processing, (2) directly in the brewing process, or (3) in a manufacturing process that directly feeds into the brewing industry (i.e. 6-pack rings). By adopting a circular economy model for BSG, breweries can contribute to resource efficiency, waste reduction and the creation of sustainable value chains. This approach can transform perceptions of BSG into a valuable resource with multiple applications, encouraging sustainable practices within the brewing industry.

It is crucial to minimize the disposal of BSG in landfills and sewers, as denoted by Figure 2. If organic matter is left to decompose, it is typically broken down by naturally present microorganisms which require oxygen to function. When this occurs in a landfill, the waste becomes buried under other waste materials and therefore the system is depleted of oxygen. As a result, the organic waste gets broken down by anaerobic microorganisms, or those which

do not require oxygen. Anaerobic decomposition releases biogas as a by-product, which is roughly 50% methane and 50% carbon dioxide, both of which are potent GHGs (National Resource Defense Council and Hu 2020). In a landfill, every ton of BSG releases around 514 kg CO<sub>2</sub> GHG equivalent (Mitri et al. 2022). GHGs are detrimental to our environment because, among many other reasons, they trap heat in the atmosphere and contribute to global warming. According to the National Resource Defense Council and Hu (2020), around 94% of food waste gets sent to the landfill in the US because this is how our solid waste infrastructure was designed.

### 3. Literature-Based Applications for BSG

The opportunities for utilizing BSG are vast and continually increasing since it is available in massive quantities all year round. BSG's main application has been limited to animal feed, though there have been many research studies aiming to determine ideal applications for BSG. Due to the extensiveness of published papers elucidating the ample opportunities to valorize BSG, the following summarizes applications outlined in literature-review style publications on the applications for BSG. The applications are presented in Figure 3.

#### 3.1 Biochar/Activated Carbon

BSG can be processed into biochar after thermal-physical or chemical activation, and carbonization to produce a highly porous material which has applications in numerous industries ranging from water treatment, a filler in cement, GHG adsorption, soil amendment,

supercapacitors and beyond. When processed effectively, BSG biochar is comparable to that made from wood, sugarcane, grape or olive bagasse, and hazelnut shells ([Mussatto et al. 2006](#)). It is an effective adsorbent material, removing volatile organic compounds, dyes, water contaminants and other undesired compounds from different systems ([Mussatto et al. 2006](#); [Jackowski et al. 2020](#); [Chetrariu and Dabija 2020](#)). *See more on biochar from BSG in Chapter 2.*

## 3.2 BSG for a Biorefinery & Biogas Production

SDG 7 addresses the need to ensure universal access to affordable, dependable, and sustainable energy sources. To contribute to this goal, biorefineries have emerged as a pivotal solution. Biorefineries are defined as a unique facility that efficiently converts biomass into energy and other value-added byproducts. The resulting products often include biochar or bio-oil, bioethanol, biobutanol, xylitol, fermentable carbohydrates, enzymes, phenolic compounds, and more ([Pabbathi et al. 2022](#)). These versatile systems often employ a combination of production techniques to yield multiple product, thus enhancing efficiency ([Pabbathi et al. 2022](#)).

Biogas production utilizing various waste streams has been an established practice for decades ([Emmanuel et al. 2022](#)). Importantly, BSG has higher calorific values than commonly used waste streams, making it a desirable source for biogas production. BSG exhibits a gross calorific value of 20.14 MJ kg<sup>-1</sup>dry mass, making it a promising substrate for heat generation through combustion ([Mussatto et al. 2006](#); [Emmanuel et al. 2022](#)). The composition of biogas primarily comprises methane (40-75%) with carbon dioxide (25-55%), with trace amounts of hydrogen



sulfide, ammonia, nitrogen, oxygen, and hydrogen ([Chetrariu and Dabija 2020](#); [Emmanuel et al. 2022](#)). Although biogas is recognized as a clean, recyclable, and efficient fuel, its current production is made primarily (96%) with fossil fuels, contributing to environmental pollution ([Chetrariu and Dabija 2020](#)).

The production of biogas from BSG involves hydrolysis to completely degrade the material, and methanogenesis to convert it into volatile fatty acids, acetates, butyrate, propionate, and methane ([Chetrariu and Dabija 2020](#)). Utilizing BSG onsite at breweries for biogas production would offer economic and environmental advantages by eliminating the need for costly and energy-intensive transportation. Anaerobic digestion of BSG to produce biogas can achieve a conversion rate exceeding 80%, and can be even more efficient with pretreatments (chemical, physical, biological, hybrid, etc.) BSG contains substantial amounts of lignin and cellulose, which pose limitations on biogas production. Use of pretreatments which disrupt the lignocellulosic fibers and expose polysaccharides can enhance enzymatic hydrolysis and the fermentation process ([Emmanuel et al. 2022](#)). Common pretreatments include microwave-assisted alkali pretreatment, 5% addition of biochar, or anaerobic co-digestion ([Jackowski et al. 2020](#); [Emmanuel et al. 2022](#)). While the heat generated from BSG combustion has the potential to meet the energy demands of breweries, it should be noted that the process simultaneously generates air pollutants including nitrogen and sulfur oxides. Therefore, it is critical to consider the emissions associated with the combustion process when assessing the effectiveness of utilizing BSG for brewery energy demands ([Mussatto et al. 2006](#)).

BSG can also be used as a solid fuel, with carbon content ranging from 45-49% (dry basis) which is comparable to other commonly used lignocellulosic biomasses ([Jackowski et al. 2020](#)).

However, the high moisture content of BSG poses a significant challenge to its efficient use as a solid biofuel because it requires an additional step, increased energy, and specialized equipment ([Jackowski et al. 2020](#)).

### 3.3 Agriculture

BSG has a high concentration of phosphorus and potassium, making it suitable for direct application to soils as a nutrient source to enhance crop health ([Jackowski et al. 2020](#)). The incorporation of BSG into soils can promote microbial diversity, fostering the soil's ability to sequester carbon and act as a carbon sink ([Jackowski et al. 2020](#)). Additionally, the inclusion of BSG in soil improves the water holding capacity of the soil, leading to better moisture retention and potentially enhancing crop productivity ([Jackowski et al. 2020](#)). There are multiple opportunities to utilize BSG in agriculture, particularly in barley and hop production to create a circular economy model for beer.

### 3.4 Building and Industrial Materials

Cellulose has long been employed in a variety of industrial products because of its structure, biodegradability, and water resistance. The high concentration of fiber in BSG enables its utilization to enhance the porosity of ceramic bricks and other building materials, making it a potential substitute for sawdust in such applications ([Jackowski et al. 2020](#); [Mussatto et al.](#)

2006; Chetrariu and Dabija 2020; Pabbathi et al. 2022). The fibrous nature of BSG also makes it suitable for paper production specifically including the manufacturing of paper towels, business cards, coasters, and more (Mussatto et al. 2006). Researchers have also explored the potential applications of BSG in rubber and organic polyurethane foam particularly for reinforcing tires, biodegradable packaging, and polystyrene trays (Jackowski et al. 2020; Chetrariu and Dabija 2020). BSG can improve thermal stability and various physico-mechanical properties, such as apparent density and compression resistance (Chetrariu and Dabija 2020; Pabbathi et al. 2022). When utilized in food packaging or biofilm applications, BSG can contribute antioxidant and antimicrobial properties (Pabbathi et al. 2022). In summation, the versatile nature of BSG makes it applicable in diverse industrial applications.

### 3.5 Animal Nutrition

BSG has traditionally been widely used as animal feed, particularly for cattle. The utilization of BSG as an economical alternative to forage in cattle feed supply can avoid the cost of drying, but the high moisture content and microbial instability of the grain mean that it will only last for 3-5 days before spoiling. The two major drawbacks to this are (1) transportation is expensive due to the weight of the grain, (2) high protein and polysaccharide concentration encourages microbial growth and BSG deterioration (Terefe 2022). However, several preservation methods can be employed to prevent these issues, including drying (solar, freeze, or oven), freezing, ensiling (alone or in combination with other animal feeds), using additives (Silo-King GPX preservatives, xylanase, carbohydrase (econase) and protease (alcalase), urea and lime, sodium formate, calcium propionate, formic and propionic acids, acetic acid, NaCl, NaOH, HCl, and

H<sub>2</sub>SO<sub>4</sub>) (Terefe 2022).

BSG is a great source of fiber and protein for cattle and can be consumed without any further processing. When combined with cost-effective nitrogen sources, BSG becomes a complete protein, offering high nutritional value (Huige 2006). In a study by (Belibasakis and Tsirgogianni 1996), BSG incorporation into cow diets resulted in increased milk, milk total solid content, and milk fat yields. However, the concentrations of glucose, total protein, albumin, urea, triglycerides, cholesterol, phospholipids, sodium, potassium, calcium, phosphorus, and magnesium in blood plasma were unaffected (Belibasakis and Tsirgogianni 1996).

BSG demonstrates potential as a nutritious diet amendment for rats, hamsters, chicken, cows, fish, and pigs, if administered and dosed properly (Mussatto et al. 2006). A nutritional study investigating the effects of incorporating wet BSG as a substitute for maize silage, soya bean meal, and wheat bran in cattle diets revealed promising results. The treatment group that received wet BSG had higher milk yield along with increased milkfat content and total milk solids yield, when compared to the control group fed ground maize, maize silage, soya bean meal, and wheat bran (McCarthy et al. 2013; Belibasakis and Tsirgogianni 1996). BSG contains arabinoxylans and  $\beta$ -glucans which, when consumed by animals, “promote the activity of beneficial bacteria particularly species from three genera of *Bifidobacterium*, *Enterococcus*, and *Lactobacillus*” (Lao et al. 2020). The degradation of BSG leads to increased production of short-chain fatty acids (SCFA), which serve as an energy source for anaerobic microbes. The elevation of SCFA concentrations has been associated with various improvements including enhanced

nutrient absorption, modified rumen bacteria, improved intestinal architecture, increased antioxidant potential, regulation of glucose and lipid metabolisms, strengthened immunity, and suppression of pathogens (*Salmonella* and *Escherichia coli*) (Lao et al. 2020). However, not all animals incur the same responses to these prebiotics, therefore appropriate managerial considerations are imperative for BSG to be an effective prebiotic such as the age, health and species of the animals, feeding routine, living conditions, and food safety measures (e.g., monitoring for mycotoxin which can counteract its prebiotic effects) (Lao et al. 2020). With proper balance and management, BSG has the potential to improve animal health.

Another study particularly evaluated the use of BSG as fish feed. The most important yet expensive ingredient in aquafeeds is protein, often made with fishmeal and soybean meal yet these sources are not economically sustainable because of stagnant production and competitive markets (Karlsen and Skov 2022). BSG offers an attractive alternative to soybean and fishmeal because of its relatively high protein content, considerable amino acid profile, low market price, and consistent production. However, prior to implementation into aquafeeds, BSG must be refined which is both energy- and time-demanding. Another approach to enhance the sustainability of aquafeeds is to use BSG as a composting agent, improving the cultivation and sustainability of plant-based ingredients for aquafeeds. Although this may mitigate some environmental impact associated with soybean meal or other plant-based aquafeeds, it will not solve the nutritional deficiencies of these sources. The study concluded it was more climate-smart and economical to valorize BSG through other means, considering the extensive refinement required to produce BSG-derived protein for aquafeeds (Karlsen and Skov 2022).

### 3.6 Compound Extraction

Numerous fractions of BSG can be extracted and purified, including arabino-oligoxylosides, cellulose, glucose, non cellulosic polysaccharides, acetic and hydroxycinnamic acids, hydroxybenzoic acids, xylitol, antioxidants, oligosaccharides, arabitol, lactic acid, functional proteins, lipids, and more (Mussatto et al. 2006; Jackowski et al. 2020; Xiros and Christakopoulos 2012). A comprehensive review conducted by (Bonifácio-Lopes et al. 2020) details the advantages and disadvantages of various extraction techniques, highlighting that no technique comes without disadvantages. The techniques discussed include: supercritical carbon dioxide, autohydrolysis, alkaline hydrolysis, solvent extraction, ultrasound assisted extraction, dilute acid hydrolysis, enzymatic hydrolysis, microwave assisted extraction, and ultrafiltration (Bonifácio-Lopes et al. 2020).

BSG contains significant amounts of phenolic compounds, and there are various methods of extraction available, although the efficient extraction of these compounds remains a challenge. Common methods include extraction with organic solvents, enzymatic, and alkaline reactions, and solid-liquid extraction (SLE) (Guido and Moreira 2017). In a study by (Guido and Moreira 2017), SLE using 60 % (v/v) acetone for 30 minutes at 60°C was found to be the most efficient method for extracting antioxidant phenolic compounds (9.90 mg gallic acid equivalents/g dry BSG) (Guido and Moreira 2017). Newer, advanced, and environmentally friendly methods have been developed to address the limitations of traditional extraction techniques such as extraction time, solvent consumption, extraction yields, and reproducibility. Updated methods

include pressurized fluid extraction, supercritical extractions, microwave-assisted extraction (MAE), and ultrasound-assisted extractions ([Guido and Moreira 2017](#)). Among extraction methods, MAE (15 minutes, 100°C, 20 mL of solvent, maximum stirring speed) was efficient for extracting polyphenols, particularly ferulic acid, from BSG; the yield (1.31 ± 0.04 % (w/w)) was five-fold more efficient than SLE ([Guido and Moreira 2017](#)). Another study by ([Xiros and Christakopoulos 2012](#)) confirmed that enzymatic approaches for BSG solubilization and recovery of components are favorable compared to chemical treatments, which can lead to destruction of valuable components during the process ([Xiros and Christakopoulos 2012](#)). Biotechnological approaches, specifically for fractionating carbohydrates, proteins, and phenolic acids, were found to be ideal. However, chemical pretreatments are often necessary to enhance the accessibility of carbohydrates and hydrolytic enzymes ([Xiros and Christakopoulos 2012](#)). Proteins can also be extracted using alkaline treatment, alkaline pretreatment with diluted acid, hydrothermal pretreatment, carboxylate salt-urate deep eutectic solvents, or ultrasounds for enzymatic hydrolysis ([Jackowski et al. 2020](#)). This process is considered more efficient and economical when optimized for the simultaneous fractionation of fibers and proteins.

Further research is essential to comprehensively understand extraction mechanisms, scale-up potential, and overall efficiency of the processes. Thus, a fractionation process which enables the extraction of multiple bio-products from BSG to yield a biorefinery may be the most climate-forward and economical solution.

### 3.7 BSG as a Substrate

Researchers have utilized BSG in a variety of biotechnological processes, such as mushroom cultivation, actinobacteria cultivation, extraction of value-added products (ferulic and - coumaric acids, xylose, arabinose), cultivation of xylitol or arabitol ([Mussatto et al. 2006](#)). To achieve successful utilization, BSG must undergo pretreatments that hydrolyze cellulose and hemicellulose into sugars which are consumable by microorganisms. The most commonly used pretreatments include the application of acids, high temperatures (120-210°C), and pressure (< 10 atm) ([Jackowski et al. 2020](#)). BSG is predominantly employed as a substrate for fungi growth to produce enzymes ( $\alpha$ -amylases, cellulases, hemicellulases) ([Jackowski et al. 2020](#)).

## 4. Product-Based Applications for BSG

### 4.1 Human Food Products

As demonstrated in Figure 2 presented by Champions 12.3, recovering wasted food and transforming it into new food products is considered the most effective method of recovery. To promote and support these efforts, a team of experts established the Upcycled Food Association (UFA). In 2020, a team of experts (Harvard Law School, Drexel University, World Wildlife Fund, Natural Resources Defense Council, ReFED, and others) collaborated to define upcycled food as those which “use ingredients that otherwise would not have gone to human consumption, are procured and produced using verifiable supply chains, and have a positive impact on the environment” ([Upcycled Food Association 2023](#)).



Through research, networking and policy advocacy, the UFA aims to build a food system where all food is “elevated to its highest and best use” ([Upcycled Food Association 2023](#)). The association has outlined four main objectives: (1) attracting more investment to the upcycled industry, (2) improving the upcycled business network, (3) improving the upcycled supply chain, (4) increasing consumer demand for upcycled products. The UFA envisions a circular economy of food in which consumers prevent food waste with the products they buy. An important driving force behind this movement is the fact that, according to Project Drawdown, reducing food waste is the top solution to global warming ([Upcycled Food Association 2023](#)).

The low cost and high nutritional value of BSG make it an ideal product for recovery and incorporation into the food chain. As a result, numerous researchers and companies have developed a wide range of new food products. However, the texture and water content of BSG after recovery pose significant challenges to its effective utilization in food production. To overcome this, BSG can be processed into a flour product, enabling its use in a variety of applications: breads, muffins, cookies, mixed grain cereals, cakes, waffles, pancakes, tortillas, snacks, doughnuts, brownies, pizza dough, granola bars, chips, protein bars, pasta, pie crust, and so on ([Mussatto et al. 2006](#)). The color of BSG flour is another barrier to use, because it is a darker brown than most bleached flour products. There are a variety of patented processes to recover BSG into food products while maintaining desired visual and organoleptic properties. BSG flours present a variety of beneficial properties in food, as described by ([Huige 2006](#)): (1) ease of blending, (2) calorie content is roughly half that of most cereal flours, (3) high water

absorption capacity, (4) contains valuable minerals including Ca, P, Fe, Cu, Zn, and MG, (5) low-fat absorption, (6) uniform color, milk flavor and aroma, (7) high fiber content, (8) high protein content.

A study by [\(Hassona 1993\)](#) examined the nutritional impact of incorporating BSG into breads. The findings demonstrated that BSG improved the protein and essential amino acid content of breads by 50 and 10%, respectively. The fiber content of BSG-supplemented breads was also doubled while containing approximately 7% fewer calories [\(Hassona 1993\)](#). BSG primarily consists of the aleurone, scutellum and germ fractions of germinated barley, which makes it rich in non-cellulosic polysaccharides and glutamine-rich protein [\(Fastnaught 2001; Mussatto et al. 2006\)](#). These fractions have been associated with various health benefits, as determined in a study by [\(Fastnaught 2001\)](#) which evaluated the impact of BSG incorporation into the diets of rats. The study revealed that BSG ingestion resulted in increased fecal weight, accelerated transit time, increased cholesterol and fat excretion and decreased gallstones [\(Fastnaught 2001\)](#). BSG has also been recognized as a prebiotic treatment option for patients with ulcerative colitis, as it increases stool butyrate concentration [\(Bamba et al. 2002; Kanauchi et al. 2001\)](#). Furthermore, BSG exhibits anti-inflammatory effects due to its ability to increase butyrate concentration and its high concentration of *Bifidobacterium* sp. and butyrate producing *Eubacterium limosum* [\(Kanauchi et al. 1999\)](#). In summation, BSG has a positive impact on nutritional composition of food products while simultaneously delivering desirable food properties and meeting SDG 12.3. For these reasons, a variety of companies have developed food products utilizing BSG, as outlined in Table 3.

Table 3. Food Products on the Market Made from BSG

Brand	UFA Certified as of June 2023?	Product Name(s)
Evergrain	Yes	Everpro (Original, Neutral, Clear)
Upcycled Foods Inc / Regrained	Yes	Regrained Supergrain+ Supergrain+ Sourdough Systems Supergrain+ Protein Crisps Supergrain+ Multigrain Flakes
Grain 4 Grain	Yes	Pancake & Waffle Mix (Original, Chocolate) Barley Barley Flour 1-to-1 Replacement Flour Seasoned Coating (Chili Paprika, Lemon Pepper)
Brewer's Foods	No	Flatbreads (Sesame Pretzel, Sea Salt, Everything) Pita Chips (Sea Salt, Rosemary) Brewer's Cookies (Chocolate Chip Sea Salt)
Rise	No	Spent Grain Super Flour
Green Bowl Foods	Yes	Hifibe
US Foods	Yes	Hilltop Hearth Pub Grain Hamburger Bun
Act	Yes	Act Bar (Cashew Coconut, Peanut Butter) <i>Note: Made with Regrained Supergrain+, no other BSG</i>

## 4.2 Dog Food & Treats

While BSG is primarily reserved for cattle, it is also an excellent source of protein and fiber for other animals. Many breweries and standalone companies have been utilizing BSG in dog food treats as a cost-effective source of fiber. There are multiple products on the market, however, most are not yet certified by the UFA. Table 4 outlines the dog treats currently available for purchase.

Table 4. Animal Food Products on the Market made from BSG

<b>Brand</b>	<b>UFA Certified as of June 2023?</b>	<b>Product Name(s)</b>
Portland Pet Food Company	No	Bacon Brew Biscuits Beef Broth Brew Biscuits Pumpkin Brew Biscuits
Leashless Lab	Yes	Upcycled Beer Grain Dog Treats (Cheese, Pumpkin Berry, Peanut Butter)
Bare Bites	No	Brew-Yahs! Dog Treats
Frequency 528 Brewing	No	Spent Grain Dog Treats
Doggie Beer Bones	No	Crunchy Treats (Peanut Butter, Turmeric, Pumpkin) Soft & Chewy Treats (Bacon, CBD Bacon)
The Crafted Bone	No	Peanut Butter Bones (Large, Small)
Brew'ed Biscuits	No	Brew'ed Biscuits (Apple Cinnamon, Peanut Butter, Pumpkin Sweet Potato)
Hungry Hound	No	Beer Grain Treats

## 4.3 Product Innovations

Numerous product innovations have been developed using BSG, offering potential applications within brewery and taproom settings. These innovations aim to replace traditionally wasteful items and contribute to the establishment of a circular economy. It is important to note that a life cycle analysis (LCA) or greenhouse gas assessment (GHGA) on the production of these products is crucial to evaluate their environmental burden as compared to traditional production processes. As these innovations become more widely adopted, they will become more scalable and cost-effective. For visual references of all the mentioned products, refer to Addendum (Figure 4).

### 4.3.1. Furniture

Franck Gossel, a France-based designer, founded Mobilier in 2018, driven by his passion for beer and sustainable design. The first product was a brewed stool which gained recognition for its impermeability and durability. The brewed stool is composed of 98% BSG and a recyclable, and formaldehyde-free volatile organic compound, resulting in a near net-zero carbon footprint. Mobilier collaborates with a French factory to replace their typical raw materials with Mobilier's formula, actively avoiding the need for a new industry or processing line. Gossel shared that Mobilier's furniture line aims to "reinvent the relationship between the beer and its consumers [by] sitting on a stool made out of spent grains, a material we actually end up drinking" ([Design Wanted 2020](#)).

In a commissioned partnership with Heineken, Spain-based designer Omayra Maymó created a pedestal that utilizes BSG as the primary ingredient. Maymó's design embodies Heineken's efforts to reduce  $CO_2$  emissions throughout their production and distribution chains. The BSG is combined with cement, resulting in a lighter yet durable mixture. The final product is a set of modular blocks and a bronze glass which can be configured numerous ways to meet the design and functionality needs of a particular space ([DesignWanted 2021](#)).

Weihsiang (Sean) Chiu, a US-based designer, collaborated with Strong Rope Brewery in Brooklyn, NY, to design a stool made with BSG. Similar to Maymó and Grosse, Chiu's design draws inspiration from compressed materials like medium-density fiberboard and recycled cork. Chiu used water based wood glue, water, and BSG in his formulation, creating a singular compressed product material that can be used as a stool-top, coaster, or service tray ([Chiu 2018](#)).

Designer Noemi Niederhauser presented her line, Wastematter, at Milan Design Week 2022. The Wastematter line of products utilizes BSG and an organic binding to yield a material similar to plywood with a unique texture ([Niederhauser 2022](#)). Niederhauser intends to use this material for new fields of design and furniture in the future.

These four furniture designs, along with others that utilize BSG as the primary construction material, provide a unique way to connect consumers with upcycled products and demonstrate the impact of repurposing previously overlooked by-product materials.

### 4.3.2. Packtechs and Packaging

Eco Six Pack Ring (E6PR) offers “the first eco-friendly six-pack ring made from by-product waste” which performs as effectively as the traditional plastic counterpart, both in wet and dry conditions (E6PR n.d.). The rings are compostable and biodegradable, E6PR advertises that they contribute to circularity because they can ultimately be used in soil to produce more barley and more beer, generating additional BSG. E6PR currently has over 50 customers in the beverage industry utilizing their uniquely sustainable 6-pack ring. The rings are compatible with manual (40 cans per minute), mid-speed (80 cans per minute), and high speed (1,200 cans per minute) applicators. The rings have also been certified for toxicity (containing no pesticides or volatile substance), palletizing, and transportation (pallet structure, stacking and stability verified), and the jolt test (E6PR is strong enough to hold the cans while shaking them in a Jolt Test Machine) (E6PR n.d.).

Similarly, Trebodur has designed what they deemed the “mabeerial” which is made entirely from BSG without any additional binders, making it 100% BSG (Stoll and Schrempf 2022).

Trebodur can be used as a substitute for paper and plastic materials such as packtechs, serving trays and coasters. At the end of its lifecycle, it can be composted contributing to soil health.

A group of graduate students from University of California, Santa Barbara conducted a case study on the effectiveness of producing 6-pack carriers and coasters in a business model they

deemed Ingrain. Their prototype involved 25:75 proportion of BSG to recycled fiber (office paper and cardboard) which demonstrated optimal flexibility ([Dunning et al. 2016](#)).

In summation, the utilization of BSG in the production of sustainable materials and packaging solutions not only promotes circularity and reduces environmental impact but also showcases the innovative potential of repurposing overlooked resources in various industries.

#### 4.3.3. Tableware and Cutlery

Although cutlery products made from BSG are not readily available on the market, a few researchers and designers have developed prototypes of these products. The FriendlyKnife project in Poland is iterating a process for making eco-friendly cutlery from BSG which is fully biodegradable and compostable ([FriendlyKnife n.d.](#)). The FriendlyKnife team is also developing coasters, plates, and drinkware, and testing their product line against fragility, flexibility, and strength tests. A team out of Belgium, Ecoware, also worked on cutlery made with BSG as the main ingredient. The team won the KICK Challenge at KU Leuven in 2021, and shared that they were particularly focused on product development, manufacturing, and building partnerships ([KU Leuven KICK 2021](#)). Although the sector still has ample room for growth, these designs demonstrate the potential for further advancements in tableware and cutlery.

#### 4.3.4. Coasters

Among the companies and designers previously mentioned (Chiu, Trebodur, FriendlyKnife, Ingrain), Maine Coasters & Bio Boards is also developing a coaster product utilizing BSG. While



Chiu, Trebodur, and FriendlyKnife's designs utilize BSG as the primary ingredient and add a binder, Maine Coaster's design blends pine and spruce pulp from Maine's paper industry with other additives, BSG, and vegetable dyes for aesthetic purposes ([Sampson 2018](#)). The team designed their prototype at the University of Maine Process Development Center and began commercial production at paper mills in Maine. The coasters are biodegradable and meet Forest Stewardship Council and Sustainable Forestry Initiative certifications. They also meet all commercial standards for absorbency, wet-strength, and printability for beer and beverage applications ([Sampson 2018](#)). The Ingrain team also developed a coaster prototype utilizing a 50:50 proportion of BSG to recycled fibers (office paper and corrugated cardboard) ([Dunning et al. 2016](#)).

#### 4.3.5. Trays

Among the works of Chiu, Trebodur, and Heineken, there are other researchers focusing on the development of service trays using BSG. A study by ([Ferreira et al. 2019](#)) explored the use of BSG in disposable trays. The study identified that the optimal material composition was 60% BSG with potato starch, chitosan, and glyoxal ([Ferreira et al. 2019](#)). Trays formulated with this concentration of BSG demonstrated the highest flexural strength both before and after contact with water. Furthermore, the BSG trays displayed greater flexural strength compared to expanded polystyrene (EPS) reference trays, although this was not true after absorbing water ([Ferreira et al. 2019](#)). Coating the trays with beeswax improved flexural strength, creating a cost-effective and easily processed tray that could be an appropriate alternative to EPS with further optimization ([Ferreira et al. 2019](#)). Notably, the cellulose, lignin, xylitol, and

arabinoxylan fractions of BSG have the greatest impact on the success of BSG as a substitute for conventional packaging materials ([Qazanfarzadeh et al. 2023](#)).

#### 4.3.6. Biorefinery Considerations

A comprehensive review by ([Qazanfarzadeh et al. 2023](#)) highlighted the key factors to consider in an optimal biorefinery system for the production of trays from BSG, emphasizing the need to balance “extraction efficiency, energy consumption, environmental impacts, tangible upscaling, and operating cost.” The study identified several critical variables for this application, including the BSG drying technique, pretreatment chemicals, solvent recovery, energy requirements, GHG emissions, and the product yield ([Qazanfarzadeh et al. 2023](#)). These considerations should be applied to all processes for upcycling BSG into new products, particularly when comparing them to traditional production techniques. It is essential to account for scalability, as small-scale production systems may face challenges in outperforming larger-scale counterparts.

## 5. Future Uses

In theory, the utilization of BSG has the potential to be integrated into nearly every single industry sector, as depicted by Figure 3. However, it is the responsibility of researchers to ascertain the efficacy of integrating BSG as a replacement for conventional materials in the production of these items. On a small-scale, it may inadvertently impose a greater environmental burden than large-scale production of the traditional counterparts. But, in an ideal world, all BSG (and even more ideally, all wasted food) would be saved along the value

chains and repurposed. However, achieving vision will take decades of work, consumer education, governmental incentives, infrastructure changes, readjustment of the job market, and other multifaceted undertakings to come to fruition. Consequently, it is imperative that researchers and developers undertake projects that can be seamlessly implemented into existing processing chains, ensuring scalability, and facilitating their adoption until a monumental shift in infrastructure becomes feasible. Figure 3 demonstrates what this can look like in a taproom setting, with a small list of the potential for BSG in various items underneath.

Figure 3. Potential for BSG Utilization in Taproom Settings



<b>Infrastructure &amp; Agriculture</b>	pavement, rubber, roadside drainage systems, bio-solarization, composting, soil amendment
<b>Table &amp; Serve-ware</b>	plates, napkins, cups, trays, utensils, coffee stirrers, serving utensils, beer-tap handles
<b>Furniture</b>	seating, lampshades, countertops, tables
<b>Décor</b>	soap dishes/dispensers, vases, bowls, planters, tiles, clocks, napkin holders, candle holders, flight racks
<b>Flooring &amp; Walls</b>	wood replacement, tiles, cork replacement

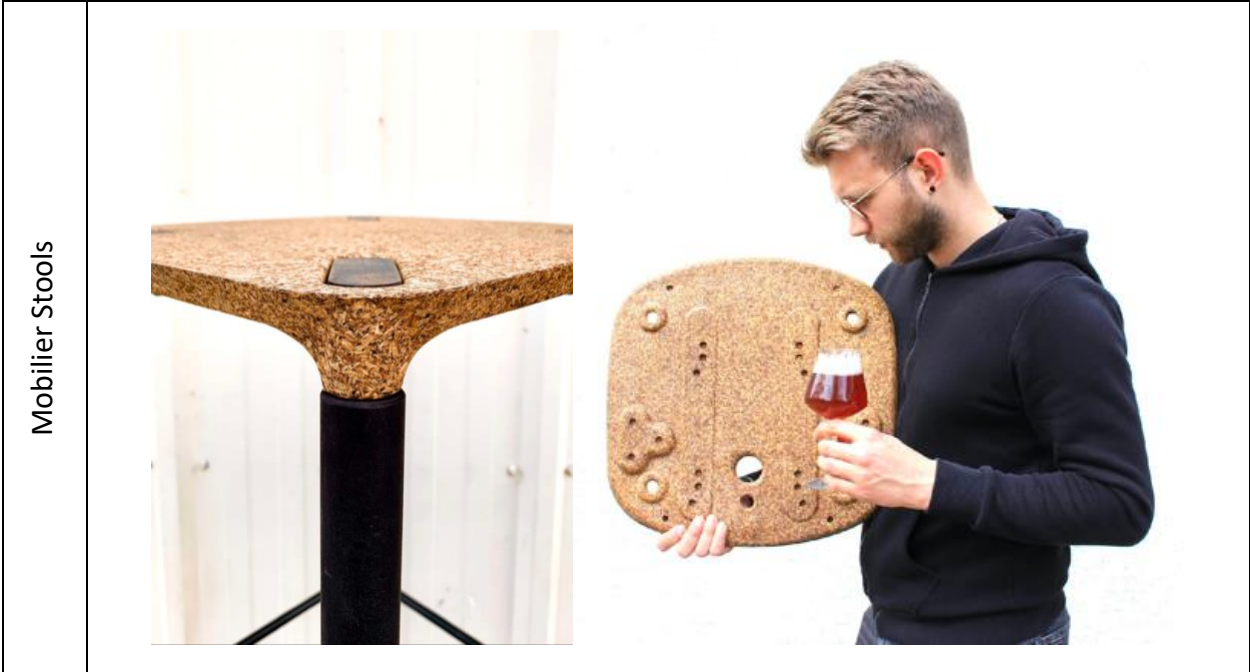
*Image Adapted from (Brewbound 2021)*

The following chapters will consider the use of BSG for biochar production (Chapter 2), specifically evaluating the parameters of production that are ideal for optimized biochar. The

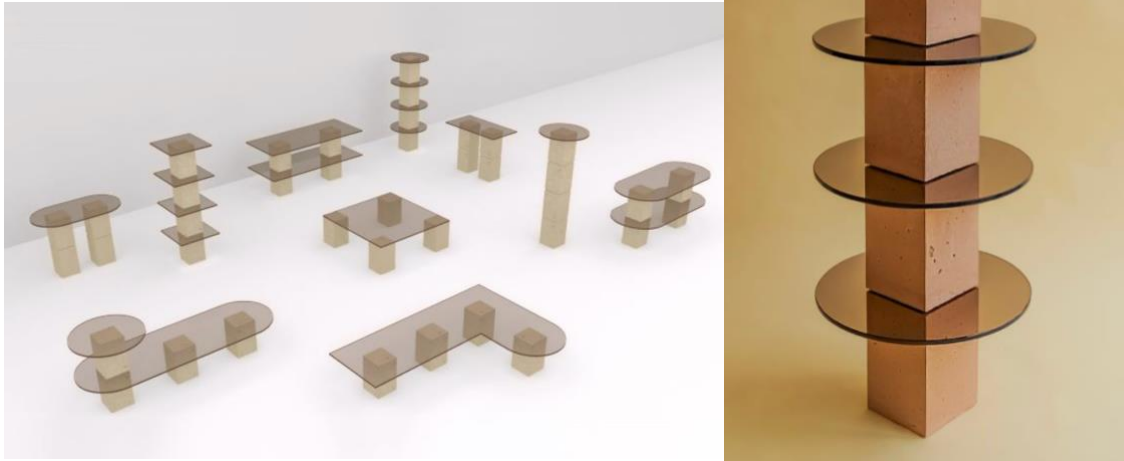
designed protocol will then be evaluated in a greenhouse gas assessment (Chapter 3) to determine if this upcycling opportunity is more or less desirable than landfilling the grain.

## 6. Addendum

Figure 4. Product Innovations Utilizing BSG



Maymó Modular Blocks



Weihsiang Chiu Stools



Wastematter Configurable table



Ecoware Tableware



E6PR Six Pack Ring



Trebodur Mabeerial Packtechs





Ingrain's Beer Packaging

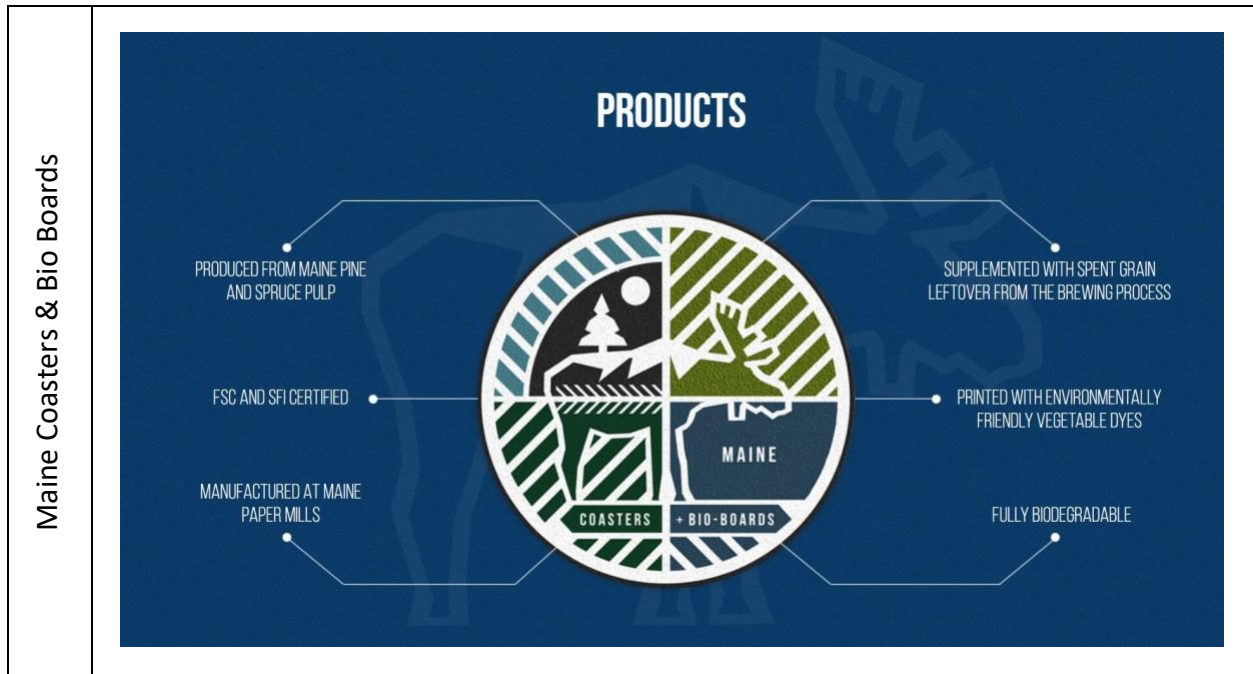


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Heineken Greener Bar Skimmers



**Skimmers**



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# Chapter 2: Producing Biochar from Brewer's

## Spent Grains

### 1. Introduction

#### 1.1 Biochar

The process of biochar production is over 2,000 years old but has been gaining more attention since 2010 for its various environmental applications ([International Biochar Initiative 2015](#)). The International Biochar Initiative (IBI) defined biochar as “a solid material obtained from thermochemical conversion of biomass in an oxygen-limited environment” ([International Biochar Initiative 2015](#)). Where biomass is “the biodegradable fraction of products, waste and residues of biological origin from agriculture (including vegetal and animal substances), forestry, and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste (including municipal solid waste)” ([International Biochar Initiative 2015](#)). Some biomass residues can be high in cellulosic components, sugar content and/or oil content so it is vital that the specific components of interest in biomass materials are identified prior to processing ([Capareda 2022](#)). The initial biomass directly affects biochar characteristics (porosity, organic carbon content, pH, etc.) and therefore impacts what applications the resulting char is suitable for. To qualify as biochar under IBI standards, the feedstock/biomass must not contain more than 2% by dry weight of contaminants/diluents. Where diluents are defined as “inorganic material that is deliberately

mixed or inadvertently commingled with biomass feedstock prior to processing” ([International Biochar Initiative 2015](#)). Diluents, such as soils, clays and gravel must be considered because they will not react the same way as biomass but are often intermixed with feedstock biomass depending on prior collection or processing methods ([International Biochar Initiative 2015](#)). The IBI differentiates between processed and unprocessed feedstocks and has different sampling requirements relevant to each category. If the diluent added to BSG as a pretreatment does not constitute 10% or more (dry basis) of the feedstock material, BSG is categorized as a biochar feedstock IBI Test Category A. This means that it needs only be evaluated for the most basic properties of biochar.

Biochar is differentiated from charcoal, and other carbon products by its predetermined use: biochar is intended for environmental management. This can include soil remediation, improved resource efficiency, preventative care against pollution, greenhouse gas (GHG) mitigation and so on ([International Biochar Initiative 2015](#)). Biochars are highly porous, amorphous materials. Generally, they contain virtually zero heavy metals, and exceptionally low nitrogen and ash concentrations while maintaining a high surface area, and adsorption capacity ([Rodriguez Correa et al. 2019](#); [Surampalli et al. 2014](#)). Biochar’s also offer a low degree of aromatization, resulting in higher porosity and reactivity; this is correlated with their high surface areas, and effectiveness for electrical conductivity ([Rodriguez Correa et al. 2019](#); [Surampalli et al. 2014](#)).

## 1.2 Biomass Precursors

According to the European Biochar Certificate (EBC), only biomass can be used to produce biochar, no fossil carbon; the EBC offers a list of appropriate biomass types which can be used for biochar production (EBC 2010). Biochar should contain carbon content and ash only, however the elemental composition can vary depending on the biomass, pretreatment and processing conditions (Yaashikaa et al. 2020). Because of this, it is vital that the biomass selected is appropriate for the desired qualities of the biochar that will be produced.

This research utilizes brewer's spent grain (BSG), which is the major waste stream from beer production, as the biomass precursor. At the start of the brewing process, barley (and sometimes other grains) is combined in a water bath which is heated at specific temperatures to activate enzymes and complete optimized soluble sugar extraction from the grains into the water. The pericarp layer of barley is waxy, and therefore has waterproof characteristics which create an interface between the interior and exterior portions of the barley kernel. Once sufficient sugar extraction has transpired, the insoluble fraction of the steeped grains are filtered out of the system; this waste stream, denoted BSG, represents about 85% of the total by-products generated during brewing (Mussatto et al. 2006). As expected, the major constituent of BSG is the insoluble husk-pericarp-seed coat of barley grains; though, BSG also contains silica, polyphenols, and trace amounts of water insoluble protein and oils (Mussatto et al. 2006). Depending on the brewing recipe, BSG can have residues from wheat, rice, maize or other adjuncts used during mashing. BSG composition can also vary based on the quality and harvest time of barley, as well as malting and mashing conditions. On average, BSG is 70% fiber

(dry basis); specifically containing 18.03 w/w% cellulose, 36.83 w/w% hemicellulose, and 18.73 w/w% lignin as elucidated in Table 5.

### 1.3 Biochar Production

There are a variety of methods to produce biochar, all of which significantly impact the volume of yield. Common variations to biochar production include the biomass precursor, treatment, temperature, heating rate, pressure, and residence time. Temperature has the most significant overall impact on biochar characteristics (Yaashikaa et al. 2020; Ahmad et al. 2014). There are six main methods for biochar production: slow pyrolysis, fast pyrolysis, hydrothermal carbonization or torrefaction, gasification, flash carbonization and torrefaction, though pyrolysis (slow or fast) is the most commonly used (Yaashikaa et al. 2020). The temperature ranges for each of these methods is outlined in Figure 5. Depending on the temperature and time controls, the end-product can be a solid (biochar), liquid (bio-oil), or gas (syngas) (Surampalli et al. 2014). The yield ranges for each of the biochar production methods are outlined in Figure 6.

Figure 5. Temperature Ranges for Different Biochar Production Methods

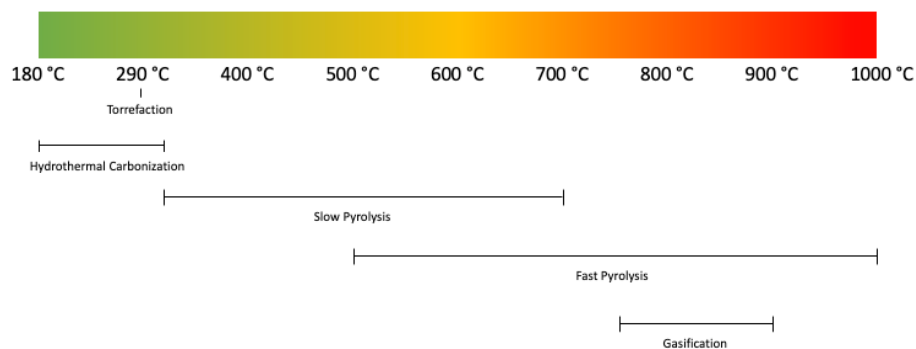
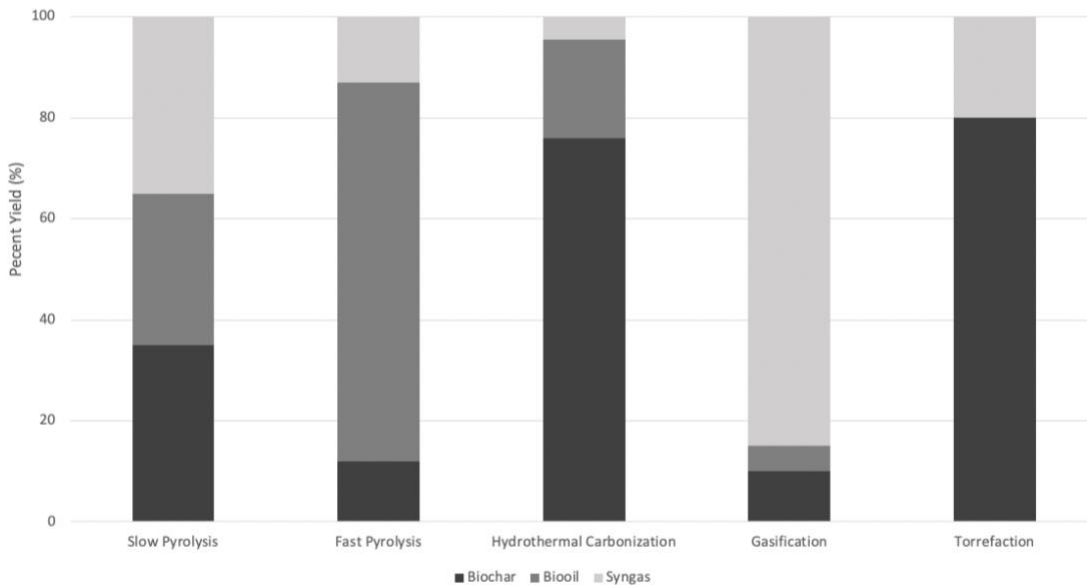


Figure 6. Percent Yield of Biochar, Bio-oil, and Syngas for Different Biochar Production Methods



### 1.3.1 Pyrolysis

Pyrolysis is direct thermochemical decomposition of lignocellulosic biomass materials in the absence of oxygen, and under highly specific time, and temperature controlled conditions

([Surampalli et al. 2014](#)). The temperature range is between 250-900°C, altering the

temperature and time controls can alter the end-product and yield solid (biochar), liquid (bio-oil), or gas (carbon dioxide, carbon monoxide, hydrogen, syngas - C1-C2 hydrocarbons) fractions

([Surampalli et al. 2014](#)). There are two common types of pyrolysis: slow and fast. The

characterization is dependent on temperature, heating rate, residence time and pressure. Slow

pyrolysis is characterized by low heating rates (5-7°C/min), and longer residence time (1h) ([Roy](#)

and [Dias 2017](#); [Pelaez-Samaniego et al. 2022](#); [Yaashikaa et al. 2020](#)). According to a review by

([Roy and Dias 2017](#)), the yield of slow pyrolysis is 20-50% bio-oil, 25-35% biochar, and 20-50%

gas. This process lends to repolymerization of organic carbons, which in turn yields higher

volumes of biochar compared to fast pyrolysis ([Kan et al. 2016](#)). Fast pyrolysis is characterized by high heating rates ( $>100^{\circ}\text{C}/\text{min}$ ), short residence time ( $<2\text{s}$ ), and moderate peak temperatures ( $400\text{--}600^{\circ}\text{C}$ ). The yield of fast pyrolysis is 60-75% bio-oil, 10-25% biochar, and 10-30% gas ([Roy and Dias 2017](#)). There is also a less commonly defined intermediate style of pyrolysis. The parameters of intermediate pyrolysis are peak temperatures of  $300\text{--}450^{\circ}\text{C}$ , heating rate of  $200\text{--}300^{\circ}\text{C}/\text{min}$ , and residence time of  $\sim 10$  min. According to the review by ([Roy and Dias 2017](#)), the yield of intermediate pyrolysis is 35-50% bio-oil, 25-40% biochar, and 20-30% gas.

Lignocellulosic biomass materials are composed of three fibrous components: cellulose, hemicellulose, and lignin. They often contain trace amounts of ash and extractives. Cellulose is a macromolecule which forms strong microfibrils that act as the skeleton of the cell wall ([Wang et al. 2017](#)). Cellulose polysaccharides are composed of unbranched glucose chains which are linked by  $\beta$ -(1-4)-glycosidic bonds ([Pelaez-Samaniego et al. 2022](#)). Every other glucose molecule in the cellulose chain is inverted, allowing the formation of the long-chain polymeric carbohydrate. Cellulose primarily links to hemicellulose and lignin molecules through hydrogen bonds. Hemicellulose and lignin link primarily through covalent and hydrogen bonds forming the inner space of the cell wall ([Wang et al. 2017](#)). Hemicellulose is a branched heterogeneous biopolymer composed of pentoses, hexoses, sugar acids, and organic acids ([Pelaez-Samaniego et al. 2022](#)). Lignin is also a heterogeneous biopolymer but it is majorly composed of aromatic structures ([Pelaez-Samaniego et al. 2022](#)).

A review by [\(Wang et al. 2017\)](#) compiled data on the lignocellulose composition of 28 different biomass materials including 17 tree barks, a variety of rice, wheat and corn straw and some miscellaneous agriculture and herbaceous biomasses. The cellulose content ranged from 40-60%, while the hemicellulose content ranged from 15-30% and the lignin content ranged from 10-25% [\(Wang et al. 2017\)](#). It was also found that wood biomass contained less extractives and ash than agricultural and herbaceous biomass. However, a review of the lignocellulosic composition of BSG found an average of 22.4 % cellulose, 28.79% hemicellulose and 15.46% lignin, as demonstrated in Table 5. This lower level of cellulose can be attributed to the functional differences between the crops; barley contains more non-structural carbohydrates (such as starch, which makes it effective in brewing) than trees which need stronger structure.



Table 5. Lignocellulosic Composition of BSG from Literature

Source	Cellulose (w/w%)	Hemicellulose (w/w%)	Lignin (w/w%)
<u>(Pedro Silva et al. 2004)</u>	25.3	41.9	16.90
<u>(Mussatto and Roberto 2006)</u>	16.8	28.4	27.80
<u>(Xiros et al. 2008)</u>	12.0	40.2	11.50
<u>(Meneses et al. 2013)</u>	21.7	19.3	19.40
<u>(Serena and Knudsen 2007)</u>	14.7	-	12.60
<u>(Terrasan and Carmona 2015)</u>	22.3	32.8	16.94
<u>(Dhillon et al. 2012)</u>	13.8	30.00	12.40
<u>(Makowska et al. 2013)</u>	17.8	28.80	5.14
<u>(Kanauchi et al. 2001)</u>	43.0	36.90	20.10
<u>(Giacobbe et al. 2019)</u>	-	19.00	21.00
<u>(Assefa and Jabasingh 2020)</u>	28.7	41.30	16.90
<u>(Castro and Colpini 2021)</u>	24.0	9.44	3.35
<u>(Sibhatu et al. 2021)</u>	28.7	17.50	16.9
<b>Average</b>	<b>22.40</b>	<b>28.79</b>	<b>15.46</b>
<b>Standard Deviation</b>	<b>8.58</b>	<b>10.58</b>	<b>6.55</b>

## 1.4 Effect of Pyrolysis Operational Variables on Biochar

### 1.4.1 Temperature

As a result of temperature change, lignocellulosic components can undergo various reactions including depolymerization, fragmentation, and cross-linking. Hemicellulose and cellulose decompose within narrow temperature ranges of 220-315°C and 314-400°C respectively. Lignin decomposes in a much broader temperature range of 160-900°C (Yang et al. 2007). There are

three main phases of cellulose conversion: formation of anhydro-cellulose, depolymerization, and char production ([Akhtar et al. 2018](#); [Pelaez-Samaniego et al. 2022](#)). The first degradation reaction in pyrolysis of cellulose is a cleavage of the glycosidic groups and dehydration, then anhydro-cellulose is formed ([Zhang et al. 2011](#); [Pelaez-Samaniego et al. 2022](#)). Above 300°C, cellulose depolymerization occurs, forming anhydro-oligosaccharides and anhydro-saccharides ([Wang et al. 2012](#)). Within the temperature range of 380-800°C, char is formed ([Pelaez-Samaniego et al. 2022](#)). In fast pyrolysis there is rapid volatilization which encourages levoglucosan development alongside solid biochar ([Yaashikaa et al. 2020](#)). Levoglucosan then dehydrates to hydroxymethyl fufural which ultimately decomposes into bio-oil and/or syngas ([Yaashikaa et al. 2020](#)). However, the hydroxymethyl furfural can also undergo a series of reactions including aromatization, condensation and polymerization to ultimately yield biochar rather than bio-oil or syngas ([Yaashikaa et al. 2020](#)).

Pyrolysis of hemicellulose first involves depolymerization of the backbone, followed by oligosaccharide formation and cleavage of glycosidic bonds ([Shen et al. 2010](#)). Intermediated products undergo a variety of reactions: depolymerization, decarboxylation, intramolecular rearrangement, and aromatization which either forms biochar or decomposes into bio-oil or syngas ([Yaashikaa et al. 2020](#); [Shen et al. 2010](#); [Pelaez-Samaniego et al. 2022](#)). Decomposition of lignin is more complex because of the intricate structure, however it also yields more char than cellulose or hemicellulose ([Azadi et al. 2013](#)). In lignin pyrolysis, hydrogen and other weaker bonds are cleaved first, then  $\beta$ -O-4 linkages ([Pelaez-Samaniego et al. 2022](#)).

Temperatures above 350°C will encourage cleavage of the  $\beta$ -O-4 linkages which releases free

radicals ([Liu et al. 2015](#)). Free radicals take protons from other molecules yielding decomposed compounds, the reactions of free radicals yield polyaromatic char ([Yaashikaa et al. 2020](#); [Liu et al. 2015](#)). As a result of these processes, biochar yield will vary across different peak temperature and heating rate ranges.

#### 1.4.2 Heating Rate

Heating rate also impacts biochar characteristics. As heating rate increases, the surface area and pore volumes of biochar increase but biochar yield decreases. A study by ([Uzun et al. 2010](#)) found that increasing the heating rate from 5 K/min to 700 K/min caused the yield of biochar from tea waste to decrease from 34.3% to 27.1%. Similarly, a study by ([Zhao et al. 2018](#)) evaluating how altering pyrolysis variables for rapeseed stem biochar production found that as the heating rate increased from 1 °C/min to 5 °C/min yield of biochar increased. However, when the heating rate increased from 5° C/min to 20 °C/min, yield of biochar decreased ([Zhao et al. 2018](#)). They also found that as heating rate increased from 10° C/min to 30 °C/min surface area increased, however when the heating rate was increased to 50 °C/min surface area decreased ([Zhao et al. 2018](#)).

#### 1.4.3 Residence Time

Residence time is described as the time biomass is held at the peak pyrolysis temperature. A study by ([Liang et al. 2016](#)) found that at a peak pyrolysis temperature of 300 °C, an increase in residence time resulted in lesser biochar yield. However, at a peak pyrolysis temperature of 600 °C, residence time had negatable impacts on yield and pH of biochar ([Liang et al. 2016](#)).

#### 1.4.4 Pretreatments

Naturally, cellulose is tightly bound with hemicellulose through lignin and hydrogen bonds, therefore biomass high in cellulose often do not have micro- or nano-fiber structures (Jin et al. 2021). This structure makes it extremely important to impart some form of pretreatment, separation or functionalization of biomass cellulose prior to biochar production (Jin et al. 2021). These methods should be relatively simple, economically feasible and use/cause minimal environmentally detrimental chemicals (Ravindran et al. 2018). This process must safeguard the desired fraction (polysaccharide or lignin) (Ravindran et al. 2018). The effect pretreatments have is based on their mode of action which can be chemical, physical, or biological (or a combination) alterations of a material that ultimately disorder the structure. This includes microwave radiation, hydrothermal, enzymatic, acid hydrolysis, acid-alkali treatment, and more.

#### 1.4.5 Chemical Pretreatments

A common pretreatment method for BSG is soaking in a chemical solution, acidic or alkaline; this process is often referred to as alkaline or kraft pulping. In this study caustic, a NaOH- or KOH-based solution, was used to pretreat BSG. Caustic materials induce delignification, or the removal of lignin, to break down the lignocellulosic structures in BSG (Brányik et al. 2004; De et al. 2020). Specifically, the alkaline elements of caustic break fracture the relatively weak carbon-oxygen ether bonds naturally found in lignocellulose structures, yielding lignin (Wool and Susan Sun 2011). Treatment with NaOH induces disruption of lignin, yielding more pure cellulose

and hemicellulose fractions. Removing lignin improves the efficiency and effectiveness of pyrolysis, yielding more and higher-quality biochar (Wool and Susan Sun 2011).

#### 1.4.6 Biological Pretreatments

In the scope of biological pretreatments, ligninolytic enzymes like lignin peroxidase (LiP), manganese peroxidase (MnP), and laccase are commonly used because of their selectivity to degrade lignin. These ligninolytic enzymes degrade lignin to expose cellulose and hemicellulose. A study by (He et al. 2019) utilized an alcalase enzyme which successfully separated protein with an efficiency of 84%, yielding 43% (w/w) high protein product and more than 80% (w/w) high fiber product, primarily hemicellulose.

#### 1.4.7 Physical Pretreatments

Steam explosion and microwave-assisted extractions are common physical pretreatment methods. The process of steam explosion is more specifically a thermo-mechanical process. The system undergoes rapid heating and pressurization which causes steam to penetrate cellulose fiber via diffusion, there is then a sudden pressure release which through sheer force hydrolyzes glycosidic and hydrogen bonds ultimately yielding nanofibers (Islam and Rahman 2019). Microwave-assisted pretreatments selectively heat the polar parts of the biomass system, by directly producing heat inside the material; this reduces energy loss and therefore is more efficient and requires shorter residence time than other pretreatments (Jablonowski et al. 2021). Microwave-assisted pretreatments are often enhanced with chemical pretreatments to remove lignin first (Jablonowski et al. 2021).

## 1.5 Properties of Biochar

There are two categories of biochar properties that are significant when considering using biochar for water or wastewater treatment: chemical and physical.

### 1.5.1 Chemical Properties

The most important properties are pH, ion exchange capacity, total carbon, H/C<sub>org</sub> atomic ratio (as a proxy of degree of fused aromaticity), inorganic carbon and ash concentration ([Singh et al. 2022](#)). pH can influence the adsorption-desorption capacity of biochars, and this ultimately impacts adsorption-desorption reactions between biochar and contaminants ([Singh et al. 2022](#)). Specifically, ([Fidel et al. 2018](#)) found that biochar made at high pyrolysis temperatures (500, 600 °C) that had lower pH and saw less NH<sub>4</sub><sup>+</sup> sorption and more NO<sub>3</sub><sup>-</sup> sorption.

Total carbon is indirectly related to the ability for biochar to remove pollutants from solution, however higher concentrations of organic carbon and a low hydrogen to organic carbon atomic ratio makes biochar less degradable ([Singh et al. 2022](#)). Inorganic carbon is part of the ash concentration in biochar, and impacts the buffering capacity; calcite and dolomite are the most common forms of inorganic carbons on biochar's ([Singh et al. 2022](#)). Contaminants can adsorb or desorb onto calcite and dolomite sites, impacting the liming potential and pH of biochar ([Singh et al. 2022](#)). Condensation of aromatic structures displaces hydrogen atoms so the hydrogen to organic carbon atomic ratio informs about the concentration of condensed aromatic carbon in biochar; high concentrations of condensed aromatic structures improves the longevity of biochar, ([Singh et al. 2022](#)).

The ash concentration of biochar is considered inorganic residue that survives composition, it is typically composed of metal carbonates, silicates, phosphates, sulfates, chlorides, and oxyhydroxides ([Singh et al. 2022](#); [Singh et al. 2010](#)). Since these elements are generally soluble, the ash fraction can decrease over time due to dissolution into the surrounding environment. The ash fraction can also influence biochar liming potential, and precipitation reactions associated with salt presence ([Guo et al. 2020](#); [Singh et al. 2022](#)).

Ion exchange capacity involves both cation exchange capacity (CEC) which arises from biochar's negative charges, and anion exchange capacity (AEC) which arises from biochar's positively charged surface ([Singh et al. 2022](#)). Generally, CEC is more influential because it impacts heavy metal and cationic nutrient retention ([Graber et al. 2022](#)).

### 1.5.2 Physical Properties

The high porosity and specific surface area (SSA) of biochar allows it to readily bond with a variety of compounds. Porosity, by definition is the percent of particle volume not filled by solid ([Brewer et al. 2014](#)). The porosity of biochar is generally classified by the IUPAC conventions where micropores are < 2 nm, mesopores are 2-50 nm, and macropores are > 50 nm ([Everett 1972](#); [Singh et al. 2022](#)). According to a study by ([Brewer et al. 2014](#)) evaluating the porosity of grass and wood biochar's (n=21), macropores account for the majority of the total porosity. Total porosity of biochar remains relatively constant over a variety of pyrolysis temperatures, however the concentration of mesopores and nanopores increases with increasing temperature

(Singh et al. 2022). And, as pyrolysis temperature increases, functional groups containing oxygen dissipate, which decreases the CEC (Singh et al. 2022). And, as temperature increases SSA increases because ash content decreases and limits blockage of pores (Singh et al. 2022). The porosity and SSA influence the ability for biochar to retain organic compounds; biochar's pyrolyzed at high temperatures undergo more adsorption reactions, while biochar's pyrolyzed at lower temperatures undergo more partition reactions (Chen et al. 2008).

## 1.6 Biochar Uses

According to The Biochar Journal, there are at least 55 uses of biochar; major categories include animal farming, soil conditioning, building design, decontamination, biogas production, wastewater treatment and drinking water treatment, industrial uses, medicines, textiles, wellness, shield against electromagnetic radiation, and food conservation (Schmidt and Wilson 2014). However, as noted previously, biochar has great potential to be utilized in environmental management, particularly agricultural applications. The Biochar Journal notes that when a carbonaceous material is prepared for any of these 55 uses, it must later in its life cycle be applied to soil as a form of soil remediation (Schmidt and Wilson 2014). If that is not the case, it should be referred to as charcoal instead. The European Biochar Certificate (EBC) was developed as a resource to limit the risks of improper biochar usage, and reduce hazards to health and the environment during biochar production (EBC 2010). The EBC also provides a certification which ensures that biochar is being produced sustainably and safely and is appropriate for use in a variety of applications. The EBC defines biochar as a "porous, carbonaceous material that is produced by pyrolysis of biomass and is applied in such a way



that the contained carbon remains stored as a long-term C sink or replaces fossil carbon in industrial manufacturing. It is not made to be burnt for energy generation” (European Biochar Certificate 2023).

The International Biochar Initiative (IBI) explains that biochar production is a means of converting agricultural waste into a soil enhancer to increase soil biodiversity and discourage deforestation because of its high porosity which helps the soil retain nutrients and water (International Biochar Initiative 2022). The IBI also states that biochar can also be used to improve food security and crop diversity after soil has been depleted and/or there is inadequate water or chemical fertilizers. Similarly, biochar can improve the amount and quality of water by helping improve retention in soils. Biochar resists degradation and can trap carbon in soils for hundreds of years (International Biochar Initiative 2022). Once buried in the ground, it can sequester carbon and prevent nitrous oxide emissions positively decreasing greenhouse gasses around the globe, while adsorbing heavy metals and organic pollutants (International Biochar Initiative 2022; Singh et al. 2010).

Beyond soil amendment, biochar is effective at removing contaminants from water such as heavy metals, organic contaminants and pathogens (Singh et al. 2010). However, it is important to note that the effectiveness of biochar in any application is dependent on its chemical and physical properties, particularly stemming from the biomass used. It is vital that characteristics of biochar are analyzed prior to use in any of the potential applications.

## 2. Methods

This research aimed to understand two main questions: (1) can waste caustic be used as a pretreatment for biochar production from BSG without employment of stirring during soaking, (2) does utilizing waste caustic significantly improve the quality of the biochar for water filtration applications?

### 2.1 Producing Biochar from BSG

Specifically, BSG was produced in the UC Davis Anheuser Busch InBev Pilot Brewery on the 30 Liter Nano-brewhouse systems. The recipe was based on an ale style beer. Epsom salt and calcium chloride were added (ratio 2:1, respectively) to the mash water. The malt used was Two Row from Rahr Maltings and Munich II from Weyermann in a ratio of 1:0.04 g, respectively. They were milled in a Sieger two roller malt mill with a mill gap of 1.2 mm. A ramp-up style mash was conducted with an initial liquor:grist ratio of 3:1. The mash was held at a rest at 66°C for 30 minutes, followed by a ramp to 76°C with a water addition to yield liquor:grist ratio of 5:1. The mash was then immediately transferred into the lauter tun equipped with a false bottom and foundation/underlet water. The wort was vorlaufed for 10 minutes. Wort was then lautered into the kettle, when the wort level was about an inch over the grain bed, there was continuous sparging (6-10 L of 76°C water) in the lauter tun until kettle full was reached (33 L). The grain bed was then drained and allowed to rest in the lauter tun for thirty minutes. BSG was manually removed, then treated with caustic. Waste caustic (KOH or NaOH) was collected from the UC Davis Anheuser Busch InBev Pilot Brewery after being used to

clean in place (CIP) the 1.5-barrel brewhouse. The most common chemical used to clean are caustics (trade name: LERAPUR 283). Caustic materials are strong bases which chemically degrade organic material. The most common chemicals for caustic solutions used to CIP are sodium hydroxide (NaOH) or potassium hydroxide (KOH). The caustic used in this experiment is primarily KOH. When a brewery is CIP, caustic is combined with water; therefore, the waste stream from CIP is a semi-dilute caustic solution. The pH of caustic pre-dilution was found to be around 13.0, while the pH of caustic solution after being used to CIP the UC Davis pilot brewery was around 12.8. The caustic waste was continually evaluated for pH, calculations were conducted, and the volume needed to treat BSG with a given was determined according to the following series:

(a) Convert pH to  $[H^+]$ :  $pH = -\log [H^+]$  therefore  $[H^+] = 10^{-pH}$

(b) Convert  $[H^+]$  to  $[OH^-]$ :  $[OH^-] = \frac{1e-14}{[H^+]}$

(c) Consider what concentration of moles is desired (ex. 2.5 moles caustic per 100 g BSG)

(d) Use (c) to calculate the needed volume of caustic solution:

$$n = cv \quad \text{where } n = \text{moles desired, } c = [OH^-]$$

The resulting  $v$  value represents the volume (mL) of caustic solution needed per 100 g

BSG

(e) Scale the mL/100g value to an appropriate weight for BSG

Dosing of caustic was based on previous literature, see Table 6.

Table 6. BSG Treatment with Caustic

Variable	Total Variants	Batch 1	Batch 2	
			Set 1	Set 2
Moles of Caustic per 100g BSG	6	2.5	-	-
		5	5	5
		7.5	-	-
		10	10	10
		12.5	-	-
		15	15	15
Time Soaking (h)	3	24	24	24
		48	-	-
		72	72	72
Peak Temperature (°C)	4	400	400	400
		500	-	-
		600	-	-
		700	700	700

Table 7. Pyrolysis Time, Pyrolysis Temperature from Literature

Pyrolysis Temperature and Time			Pretreatment Concentrations		
Source	Pyrolysis Temp (°C)	Pyrolysis Time (h)	Source	Compound	Concentration
<u>(Cancelliere et al. 2019)</u>	400	-	<u>(Mussatto et al. 2006)</u>	NaOH	0.2M
<u>(Dudek et al. 2019)</u>	300	1	<u>(Low et al. 2001)</u>	NaOH	0.1M
<u>(Amoriello et al. 2020)</u>	400-500	-	<u>(Brányik et al. 2004)</u>	NaOH	2% w/v
<u>(Zhang and Wang 2016)</u>	400-700	2 at peak	<u>(Jung et al., 2017)</u>	NaOH	0.5M
<u>(Sousa et al. 2020)</u>	600-800	1-1.5	<u>(Hu et al., 2018)</u>	NaOH	0.1M
<u>(Yoo et al. 2021)</u>	300, 500, 700	2	<u>(Lee et al., 2019)</u>	NaOH	0.5M
<u>(Xi et al. 2014)</u>	300-700	2-4	<u>(Peng et al., 2019)</u>	NaOH	0.5M
<u>(Kukic et al. 2019)</u>	600	3	<u>(Zhang et al., 2019)</u>	NaOH	0.2, 0.5M
<u>(Machado et al. 2020)</u>	500, 600, 700	Held for 10, 30, 50 min	<u>(Alagha et al., 2020a)</u>	NaOH	0.1, 0.5M
			<u>(Sousa et al. 2020)</u>	KOH & NaOH	3:10
			<u>(Xi et al. 2014)</u>	NaOH/HCl	0.1N
			<u>(Kukic et al. 2019)</u>	KOH	4N at 1:3 ratio

BSG was soaked in the caustic solution for 24-96 h. It was then evenly spread on a baking sheet and dried in a convection oven with continuous air flow at 100 °C until the weight was constant (6 h, 25-30% weight recovered, Table 8). The samples were then ground in a Hamilton Beach Fresh Grind™ Coffee Grinder for one minute before pyrolysis.

Table 8. Effect of Drying Time on Weight Loss of Spent Grain Samples at 100 °C

Hours Drying (h)	Change in Mass of BSG (g)	
	Sample 1	Sample 2
0	114.60	114.32
2	84.22	81.74
4	0.04	0.42
6	0.00	0.00

The furnace was an Across International STF Series Horizontal Split Tube Furnace with a 60 mm diameter quartz tube, 3.5 KW rated output, maximum temperature of 1200 °C, K type thermocouple and a furnace cavity made of 1600 Polycrystalline 95% alumina fiber. The furnace came equipped with an outlet valve that connected to a vacuum port, however this was removed due to the amount of oil production during BSG pyrolysis. Instead, the outlet end of the quartz tube was equipped with a dryer duct vent and hose clamp. The other end of the dryer duct was secured directly to a fume vent. This set-up decreased the oil build-up on the outlet end of the quartz tube but also allowed the furnace to run without reaching a pressure that the quartz tube could not tolerate (>3 psi) since it was no longer a closed system. The furnace was cleaned after each run with 70% ethanol solution. The dryer duct was replaced after about 30 runs. The ground BSG samples (10 g) were transferred to the furnace crucibles. For preliminary data, three samples were loaded into the furnace for each run, in order of nitrogen flow from left to right: least concentrated caustic treatment to most. For formal data, the samples were randomized (for order in furnace and dosage). The furnace was purged with Nitrogen gas for 10 minutes, then set with the parameters outlined in Table 9.

Table 9. Furnace Settings

Step	Temperature Change	Heating Rate	Time (h)	PID
1	0 → 300 °C	5 °C / min	1	1
2	300 → Peak Temperature °C	5 °C / min	varies	2
3	Peak Temperature → Peak Temperature °C	-	1 or 2	2
4	Peak Temperature → 100 °C	5 min / 75 °C	varies	3

These parameters were determined based on previous literature (Table 7) and guidance from the furnace manufacturer. Nitrogen flow was stopped when the furnace cooled to 300 °C, samples were removed from the furnace once the temperature was at or below 100 °C. Samples were stored in plastic Falcon tubes for further analysis. The overall method to this point is outlined in Figure 7. Figure 8 provides an overview of the variables present in this protocol, indicating which were standardized and which were evaluated.

Figure 7. BSG to Biochar Processing Protocol

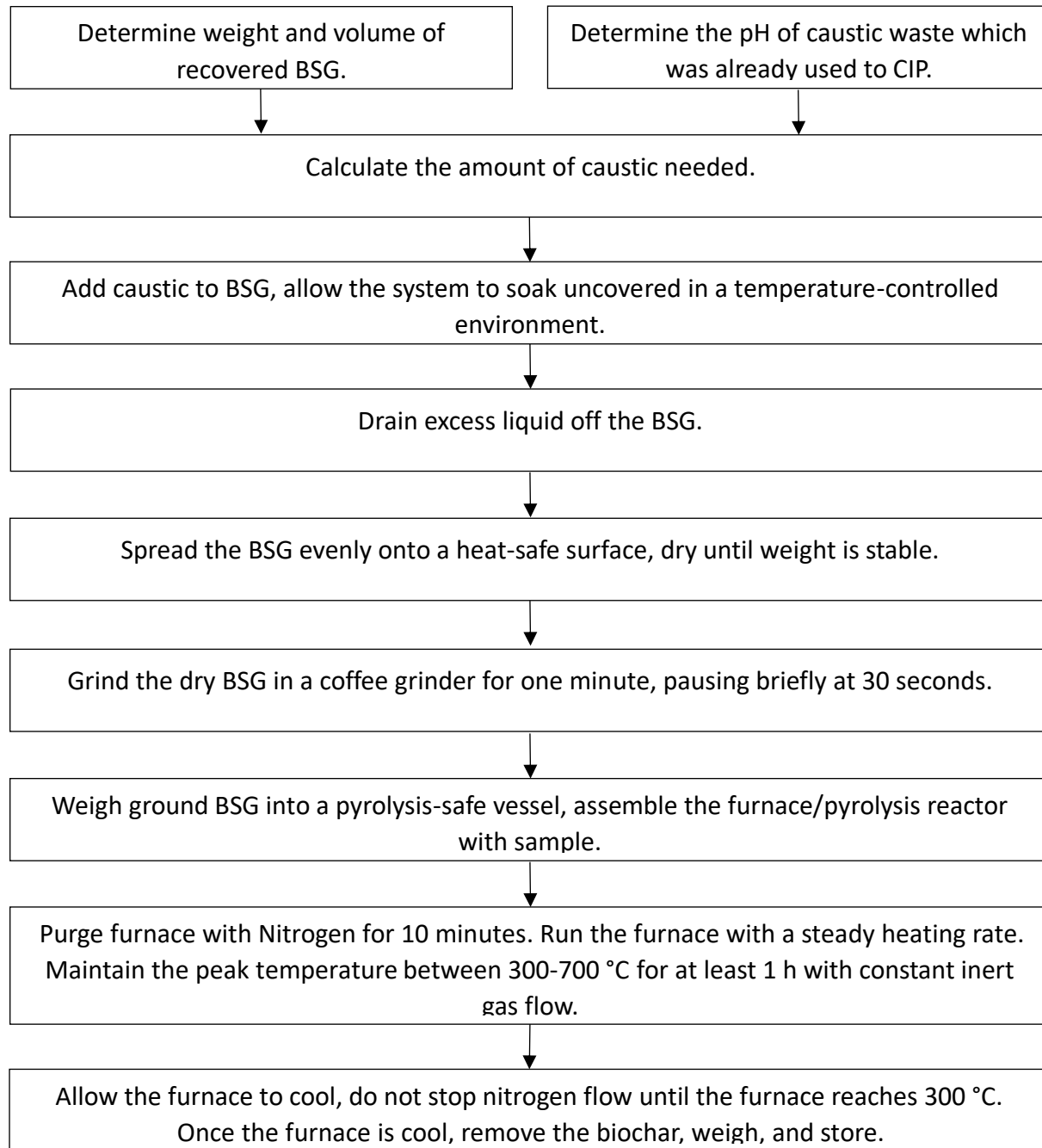
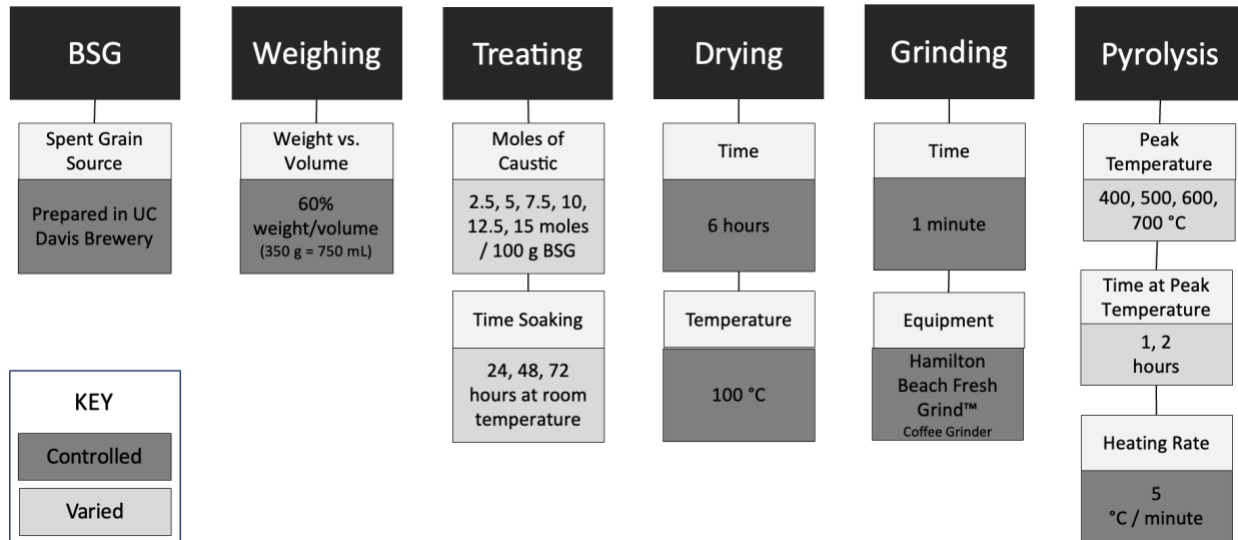




Figure 8. Variables, Producing Biochar from BSG



## 2.2 Evaluating BSG

The methods used to evaluate biochar quality were pH, liming potential, organic and inorganic carbon content, total porosity, and specific surface area according to the methods presented by [\(Singh et al. 2022\)](#).

### 2.2.1 pH

Biochar samples (250 mg) were weighed onto weighing paper, then transferred to 15 mL centrifuge tubes. DI water (5 mL) was added to each tube. Samples were mechanically shaken on a wrist action shaker for 1 h at room temperature. They then stood at room temperature for 1 h. The pH meter was calibrated using pH 7 and 10 buffers. pH of the suspension was

evaluated three times for each sample with rinsing the probe with DI water and blotting dry with a kimwipe between each measurement, values were averaged.

### 2.2.2 Liming Potential

Biochar (250 mg) was weighed onto weighing paper, then transferred to 15 mL plastic centrifuge tubes. Hydrochloric Acid (5 mL, 1 M) was added, the suspension was hand shaken to combine then mechanically shaken on an orbital shaker for 2 h at room temperature. The samples were left to settle overnight. The suspensions were titrated with 0.5 M NaOH with constant stirring until a neutral pH (~7.0) was reached. The volume of NaOH was recorded. A blank titration was performed to determine the volume of NaOH consumed by 1 M HCl without biochar. Equation 1 was used to determine the %  $CaCO_3$  equivalent.

$$\% CaCO_3 \text{ equivalent} = \frac{M*(b-a)*10^{-3}*100.09}{2*W} \quad \text{Eqn 1}$$

Where:

M = Standardized molarity of NaOH (mol L<sup>-1</sup>)

b = Volume of NaOH consumed (mL) by the blank

a = Volume of NaOH consumed (mL) by the biochar

10<sup>-3</sup> = Conversion from mL to L

100.09 = Molar mass of CaCO<sub>3</sub>

W = Mass of biochar (g)

2 = 1 mole of CaCO<sub>3</sub> consumes 2 moles of H<sup>+</sup>

### 2.2.3 Inorganic Carbon

Mason jars (8 oz or 0.24 L) were prepared by drilling a 1 cm hole in the lid of each, setting Styrofoam microfuge tube holders with two compartments into each, and equipping the lid with a layer of rubber that adhered to the lid so the jar could be pierced with a needle but resealed. Two replicates of biochar samples (250 mg) were weighed onto weighing paper, then transferred to 5 mL plastic microfuge tubes. One tube was labeled control, to that tube DI water (3.75 mL) was added, the tube was sealed and shaken to combine. The lid of the microfuge tube was unsealed, and the tube was set into a mason jar, labeled with the sample name and "control." DI water (1.25 mL) was added to the second replicate, the tube was sealed and shaken to combine. The lid of the microfuge tube was unsealed, and the tube was set into a mason jar, labeled with sample name. A second microfuge tube with no lid was added to each mason jar, then filled with 0.5 M NaOH (1.25 mL). The mason jars were sealed. Then, using a syringe, 30 mL of air was removed from each mason jar. Using a syringe, 2 M HCl (2.5 mL) was added to the biochar-containing microfuge tube for all non-control samples. The small hole in the rubber top was sealed with tape. The jars were allowed to rest at room temperature for 5 days, with some shaking to enhance the reaction. On day 6, The NaOH samples were removed from the jars, treated with two drops of 1 M BaCl<sub>2</sub> to precipitate the carbonate ion as BaCO<sub>3</sub>. The samples treated with BaCl<sub>2</sub> rested for 5 mins, then treated with two drops of phenolphthalein. The NaOH samples were then titrated with 0.2 M HCl to pH 8.3. The volume of 0.2 M HCl was recorded and used to determine the concentration of inorganic carbon (mg/g).

$$\text{Inorganic C} \left( \frac{\text{mg}}{\text{g}} \right) = \frac{12(V_{\text{control}} - V_{\text{sample}})}{2 * W} \quad \text{Eqn 2}$$

Where:

- $V_{\text{control}}$  = Total acid volume (mL) consumed by the non-acidified sample (control)
- $V_{\text{sample}}$  = Total acid volume (mL) consumed by the acidified sample
- $M_{\text{HCl}}$  = Concentration of HCl (mmol/mL) used for the titration
- 12 = Molar weight (mg/mmol) of C
- 2 = Number of mmol of OH<sup>-</sup> neutralized by each mmol of dissolved CO<sub>2</sub>
- W = Mass of biochar (g)

## 2.2.4 Total Organic Carbon

Total organic carbon (TOC) analysis was conducted by the University of California, Davis Analytical Lab in 2023. The analytical lab completed the AOAC Official Method 972.43, Microchemical Determination of Carbon, Hydrogen, and Nitrogen, Automated Method from the 16<sup>th</sup> Edition of the Official Methods of Analysis of AOAC International. Briefly, the protocol involves acid fumigation with hydrochloric vapor to remove inorganic carbon. The process of flash combustion converts organic and inorganic substances into combustion gases  $N_2$ ,  $NO_x$ ,  $CO_2$ , and  $H_2O$ . The detection limit is approximately 0.02% carbon (UC Davis Analytical Lab 2023).

### 2.2.5 Data Analysis

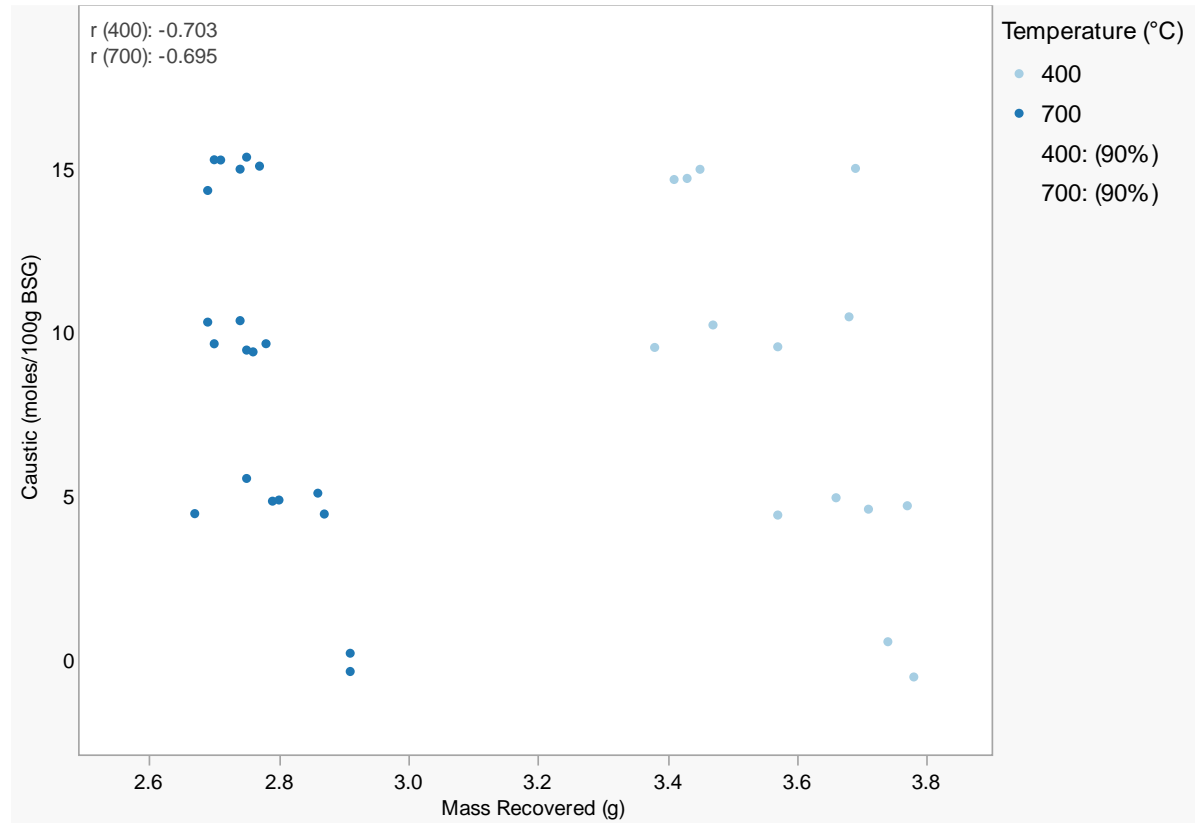
All data was analyzed using JMP Pro 17.0 Software. Tukey-Kramer tests were run with the JMP Pro software to evaluate the statistical differences between data points. All graphs were plotted using JMP Pro and Microsoft Excel Software. For each test, samples were evaluated in duplicates, and in randomized grouping with randomized order. Order was not random in TOC tests.

## 3. Results

### 3.1 Mass Recovered

The mass of biochar recovered was correlated with the peak pyrolysis temperature (Figure 9). Specifically, higher volumes of biochar were recovered for all samples pyrolyzed at 400 °C (3.59 g average) than at 700 °C (2.76 g average). Further, Figure 9 demonstrates that increasing caustic pretreatment concentration is correlated with increasing mass recovery. This data suggests that if mass recovery is the greatest concern, it is ideal to pyrolyze BSG at a lower temperature with low volumes of caustic pretreatment.

Figure 9. Mass of Biochar Recovered as it relates to Caustic Pretreatment Concentration and Pyrolysis Temperature



### 3.2 pH

The duration of immersion in caustic solution impacted pH values of the post-treatment (pre-drying) BSG. The sample set had varying caustic treatment dosages of 5.85, 7.8, and 13 moles per 100 g BSG. As time soaking increased, the resulting pH decreased, indicating that the solution underwent fermentation (Figure 10). A Tukey-Kramer HSD analysis found significant differences between the pH values; the 24-hour set was different than 48- and 72-hour sets (Table 10). The results suggest that the drop in pH is independent of the caustic dosage, and the

duration of immersion in caustic may impact the quality of the resulting biochar due to changing metabolite composition over time.

Figure 10. Impact of Time Soaking in Caustic on pH of BSG

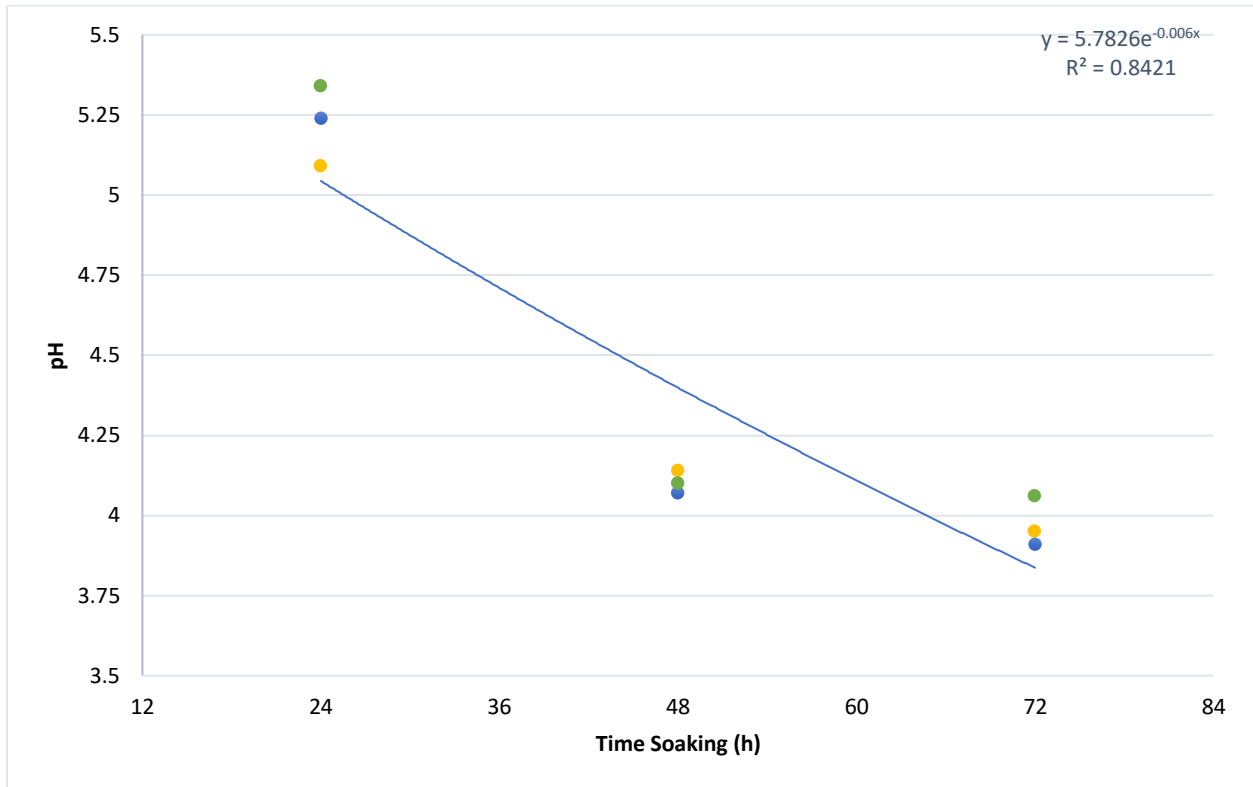


Table 10. Oneway Analysis of pH of BSG Filtrate by Hours Soaking

Hours Soaking (h)	N	Mean pH	Standard Deviation	Statistical Difference Letter
24	3	<b>5.22</b>	0.126	A
48	3	<b>4.10</b>	0.035	B
72	3	<b>3.97</b>	0.077	B

The pH of BSG changed after pyrolysis into biochar. Samples pyrolyzed at peak temperatures of both 400 °C and 700 °C, demonstrated increasing pH with increasing caustic pretreatment dosage, as hypothesized. Tukey-Kramer analysis determined that, for samples pyrolyzed at a peak temperature of 400 °C, caustic dosage has a significantly different impact on pH at dosage rates of 5 vs 15 moles of caustic per 100 g BSG (Table 11, Figure 11). Dosage of 5 moles yielded an average pH of 6.94, while dosage of 15 moles yielded an average pH of 8.69. However, there is an outlier data point (5 moles, 400 °C, pH = 6.23) which, when removed, changes the average pH for 5 moles to 7.18. With this average, no dosage rate has a significant difference on the pH of biochar produced at peak temperature 400 °C. For samples pyrolyzed at 700 °C, Tukey-Kramer analysis revealed statistically significant differences in the mean pH values of biochar (Table 11, Figure 11). Specifically, the pH of biochar samples treated with caustic dosages of 0 and 5 moles per 100 g BSG were significantly different from samples treated with caustic dosages of 15 moles per 100 g BSG. When a Tukey-Kramer analysis was run on biochar pyrolyzed at both 400 °C and 700 °C, dosage rate of 0 moles was significantly different from dosage rates of 10 and 15 moles per 100 g BSG (Table 11, Figure 11). Further, a dosage rate of 5 moles was significantly different than 15 moles per 100 g BSG. Therefore, regardless of peak temperature, the dosage rate of 5 moles does not alter biochar pH significantly from the control. However, dosage above 10 moles is significantly different from the control pH, and increasing dosage rate increases the difference in pH from the control. Based on this data, for a neutral pH, a low caustic dosage ( $\leq 5$  moles per 100 g BSG) is recommended.



Figure 11. Average pH of Biochar grouped by Caustic Pretreatment Dosage

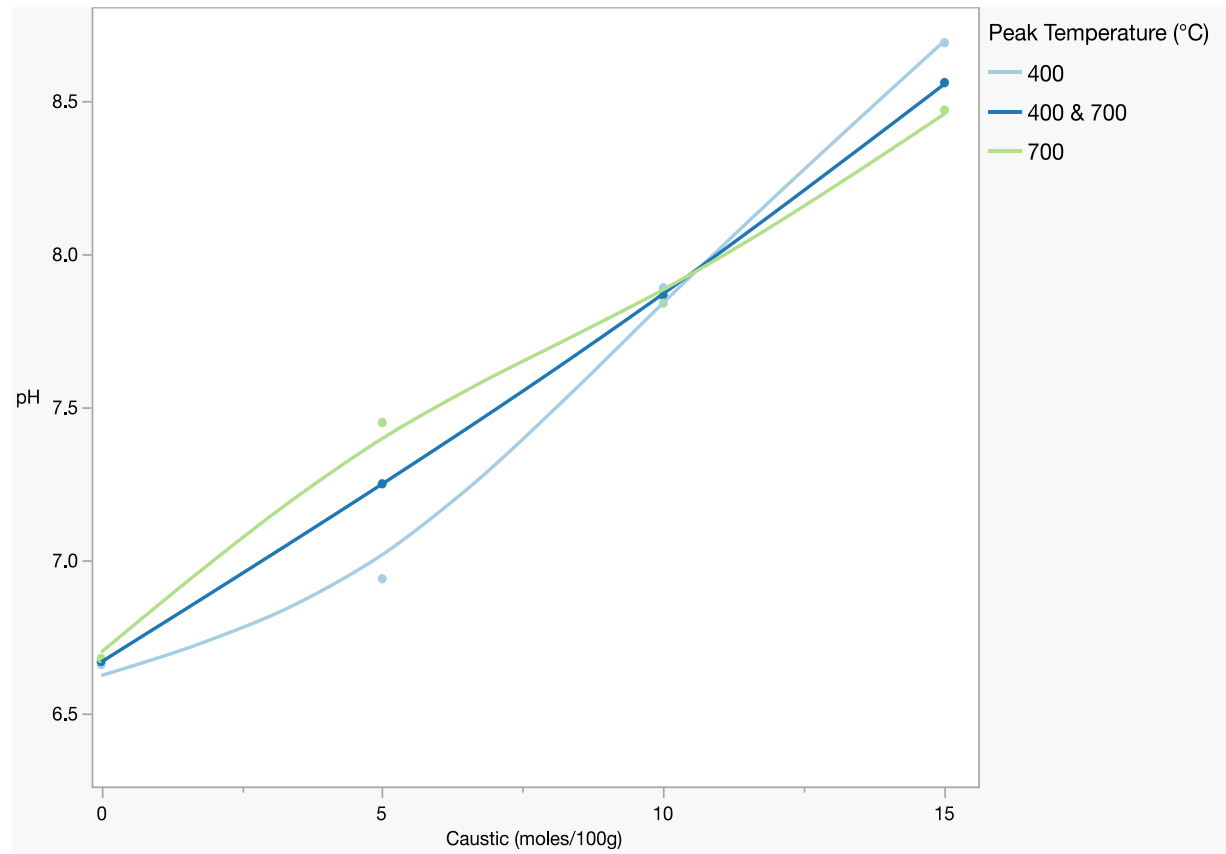


Table 11. Effect of Moles of Caustic Pretreatment Dosage on the pH of Biochar at Peak Temperatures 400 and 700 °C

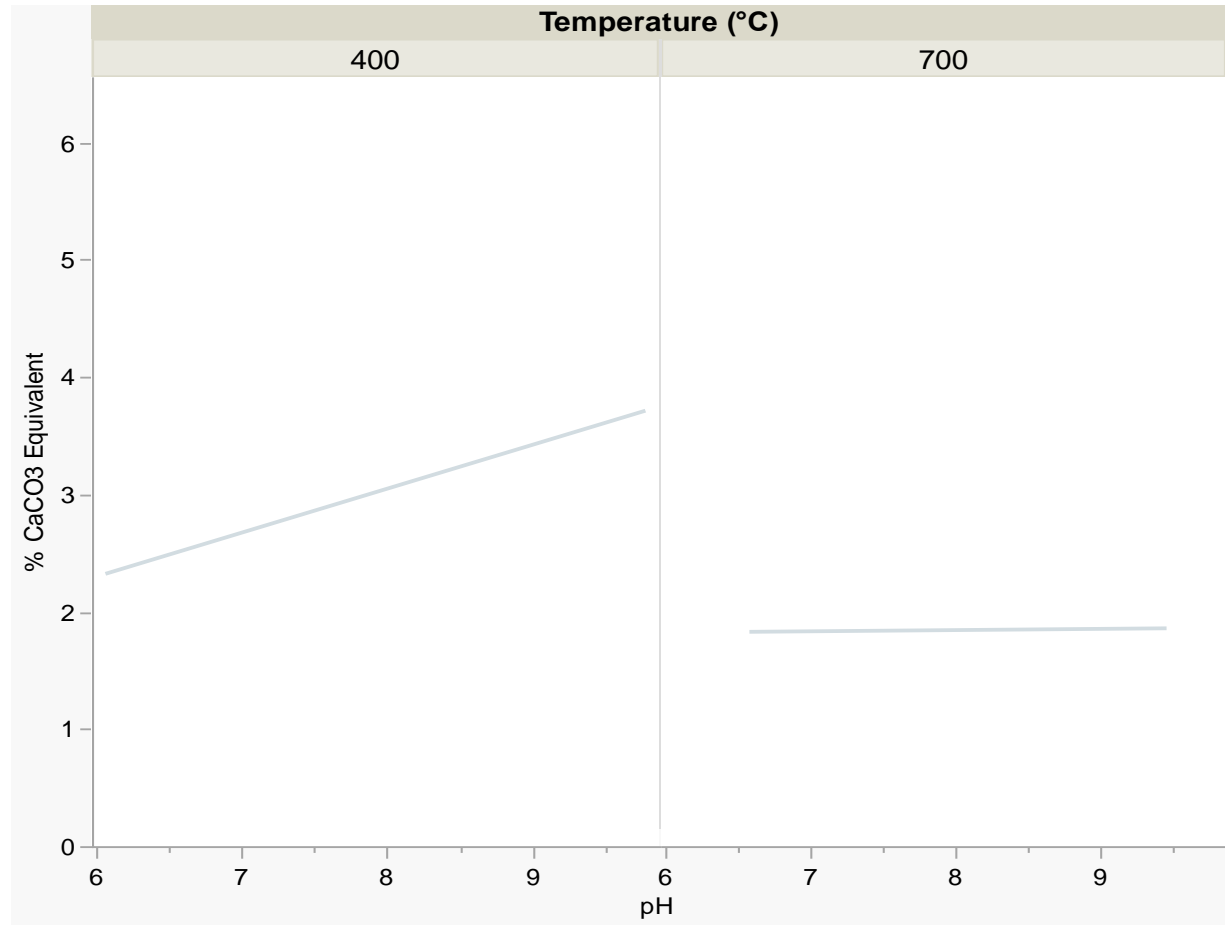
Peak Temperature 400 °C	Moles Caustic per 100g BSG	N	Mean pH	Standard Deviation	Statistical Difference Letter	
	0	2	6.66	0.014	A	B
5	4	6.94	0.483		B	
10	4	7.89	0.924	A	B	
15	4	8.69	0.986	A		
Peak Temperature 700 °C	Moles Caustic per 100g BSG	N	Mean pH	Standard Deviation	Statistical Difference Letter	
	0	2	6.68	0.042		B
5	6	7.45	0.338		B	
10	6	7.84	0.847	A	B	
15	6	8.47	0.502	A		
Peak Temperature 400 and 700 °C	Moles Caustic per 100g BSG	N	Mean pH	Standard Deviation	Statistical Difference Letter	
	0	4	6.67	0.028		
5	10	7.25	0.458		B	C
10	10	7.864	0.827	A	B	
15	10	8.56	0.069	A		

### 3.3 Liming potential

Liming potential is reported as an equivalent proportion to the liming effect of standard  $\text{CaCO}_3$  (%  $\text{CaCO}_3$  equivalent). When evaluated compared to pH, the results demonstrated a consistent %  $\text{CaCO}_3$  eq across varying pH, for all samples pyrolyzed at peak temperature 700 °C (n = 38, Figure 12). However, when pyrolyzed at peak temperature 400 °C, there was a slight increase in the liming potential of biochar samples with increasing pH (Figure 12). All samples, no matter the pyrolysis temperature, fell within the range of Class 1 biochar's (1-10%  $\text{CaCO}_3$  eq) (Singh et al. 2022). This data supports the previous finding that pyrolysis at peak temperature 700 °C produces the most desirable and consistent biochar. It is important to note, however, that results on the liming potential experienced similar difficulties to results from IOC analysis, due to the influence of human error in titrations; it would be ideal to confirm these results using techniques that avoid human error.

Figure 12. Effect of pH on Liming Potential ( $\% \text{CaCO}_3 \text{ eq}$ ) of Biochar at Pyrolysis Peak

Temperatures 400 and 700 °C



### 3.4 Inorganic Carbon

The inorganic carbon (IOC) concentration was evaluated for samples of biochar ( $n = 35$ ) produced at three different peak temperatures (400, 600, 700 °C); samples were tested in duplicates. Because of the variability in hand-titrating, the average calculated IOC value for all samples was below zero. The data is not presented because of high standard deviations.

However, based on this collection, the ash content was presumed to be relatively low for

biochar standards. Further ash content or IOC analysis without opportunity for human error would better confirm this.

### 3.5 Total Organic Carbon

TOC values were determined for 46 samples, with duplicates. Statistical analysis indicated no significant difference between TOC values across various caustic pretreatment concentrations (Table 12, Figure 9). Similarly, no trend was found amongst TOC values when considering the time spent soaking in caustic (Table 12, Figure 9). This data is partially skewed, for zero- and one-day soaking, the sample set included pyrolysis peak temperatures of 400 and 700 °C, while soaking for two- and three-days only included a pyrolysis peak temperature of 700 °C. When normalizing this to only include pyrolysis peak temperature of 700 °C, the statistical difference remained the same as presented in Table 12, yet the mean TOC values and relevant standard deviations were altered. The means and standard deviations were as follows, respectively; 0 days: 73.8% and 0.00, 1 day: 71.53% and 1.02, 2 days: 73% and 0.70, 3 days: 72.64% and 1.41.

There was a statistically significant difference in TOC values when considering peak temperature (Table 12, Figure 13). The average TOC value for samples pyrolyzed at 400 °C was 65.11%, while the average TOC value for samples pyrolyzed at 700 °C was 72.21%. This trend is further visible in Figure 14, where TOC values are separated by both peak temperature and moles of caustic. In summation, regardless of the concentration of caustic pretreatment, samples pyrolyzed at a peak temperature of 400 °C have less organic carbon than those pyrolyzed at 700 °C. There is a trend of decreasing TOC values with increasing caustic

treatment, however it is only slight. Similarly, there is a trend of decreasing TOC values with increasing days soaking in caustic, but it is only slight. Based on these trends, the ideal set of parameters for maximum TOC values is low caustic dosage ( $\leq 5$  moles per 100 g BSG), peak pyrolysis temperature of 700 °C, and 1 day soaking in caustic.

Table 12. Statistical Analysis of the TOC Concentration of Biochar

TOC by Moles of Caustic	<b>Moles of Caustic per 100g BSG</b>	<b>N</b>	<b>Mean TOC (%)</b>	<b>Standard Deviation</b>	<b>Statistical Difference Letter</b>
	0	4	<b>70.55</b>	3.57	A
	5	14	<b>70.25</b>	3.78	A
	10	14	<b>69.73</b>	3.63	A
	15	14	<b>68.91</b>	3.79	A
TOC by Pyrolysis Temperature	<b>Peak Pyrolysis Temperature (°C)</b>	<b>N</b>	<b>Mean TOC (%)</b>	<b>Standard Deviation</b>	<b>Statistical Difference Letter</b>
	400	16	<b>65.11</b>	1.65	B
	700	30	<b>72.21</b>	1.25	A
TOC by Days Soaking in Caustic	<b>Days Soaking in Caustic</b>	<b>N</b>	<b>Mean TOC (%)</b>	<b>Standard Deviation</b>	<b>Statistical Difference Letter</b>
	0	4	<b>73.00</b>	3.57	A
	1	30	<b>72.64</b>	3.57	A
	2	3	<b>70.55</b>	1.15	A
	3	9	<b>68.20</b>	1.18	A

Figure 13. One-way Analysis Plots of the TOC Concentration of Biochar by Moles of Caustic, Days Soaking in Caustic and Peak Pyrolysis Temperature

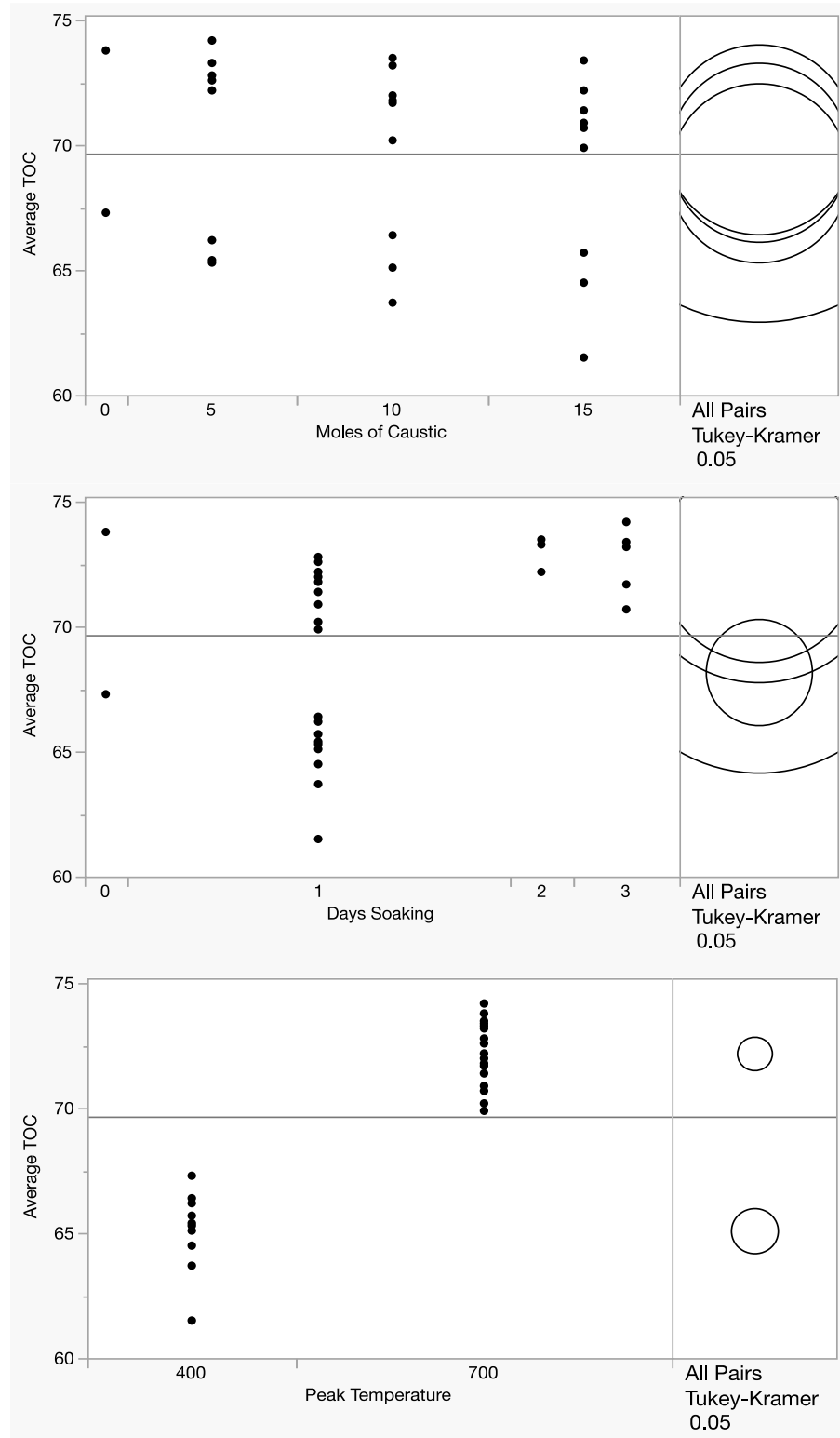
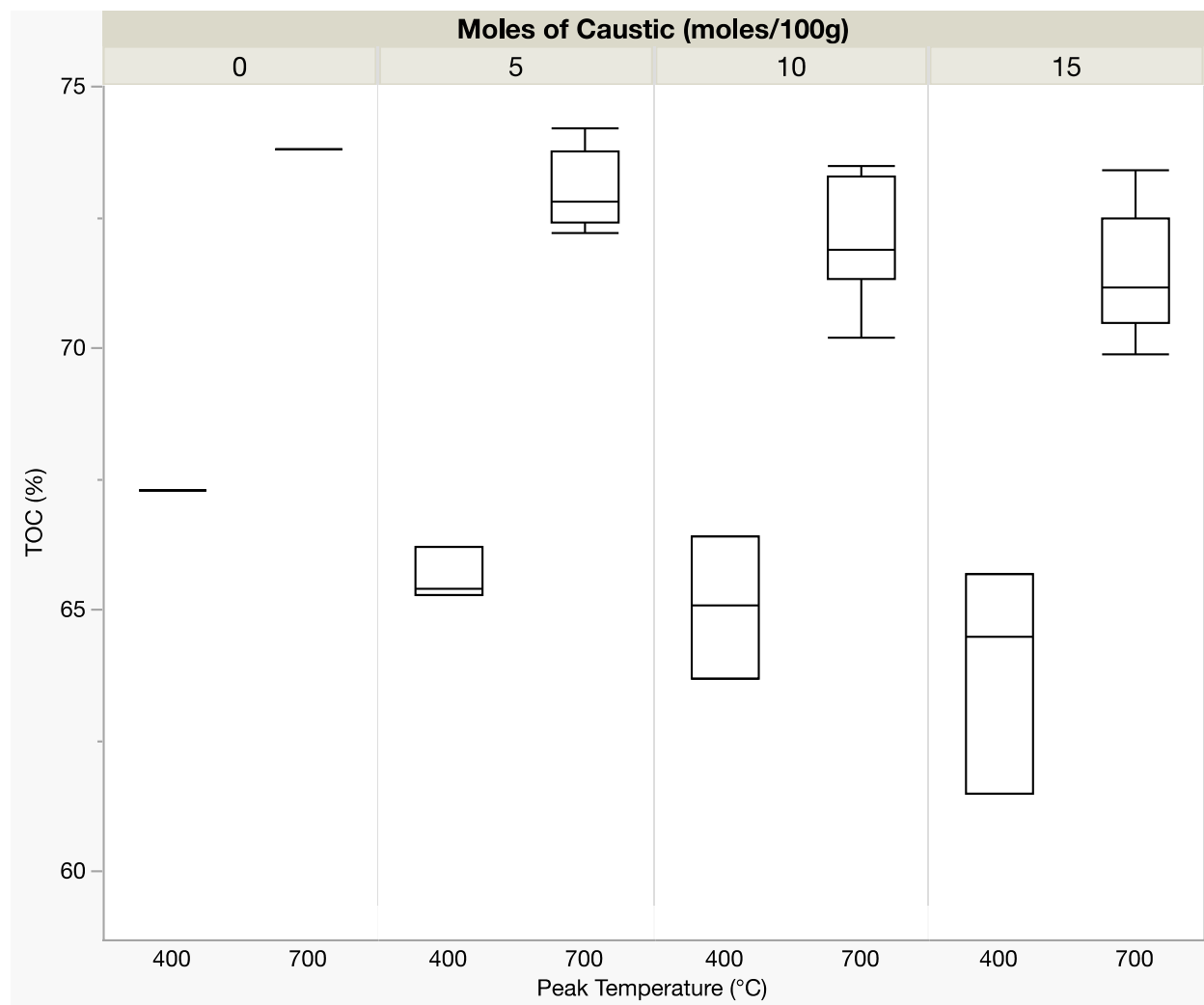


Figure 14. Average TOC Concentration of Biochar grouped by Peak Temperature and Moles of Caustic Pretreatment



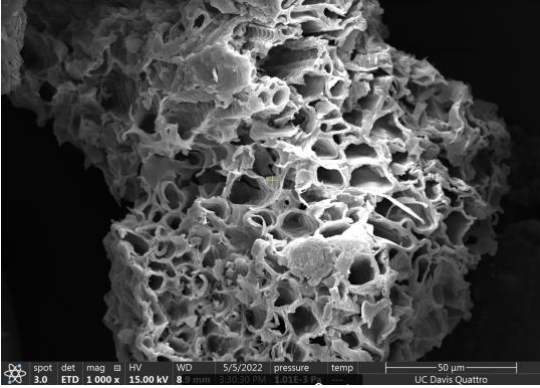
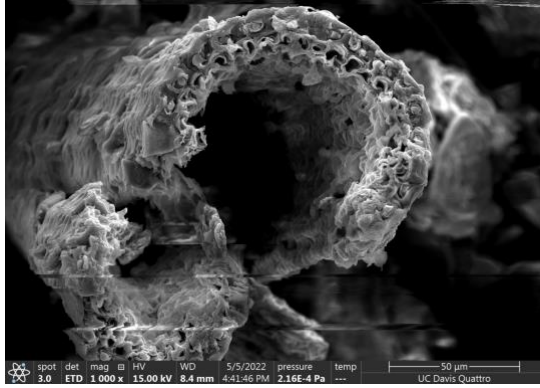
### 3.6 Physical Properties

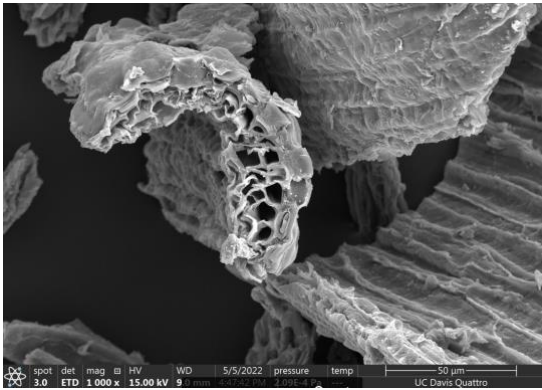
Scanning electron microscopy (SEM) images completed at the UC Davis Biological Electron Microscopy Facility are demonstrated in Table 13. The resulting images showed that all samples had highly porous structures. However, when comparing the images there are no visible differences observed relative to the peak temperature (400 or 700 °C) or caustic pretreatment



(5.85, 7.5, 10, 12.5, 13 moles per 100 g BSG). Instead, the micrographs displayed consistent pore distribution across all samples indicating that the temperature and pretreatment do not influence the visible microstructural properties of the biochar. It is, however, confirmed that the caustic pretreated BSG biochar structure is amorphous and heterogenous at pyrolysis peak temperatures of 400 and 700 °C.

Table 13. Scanning Electron Microscopy Images of Spent Grain Biochar at 50 µm

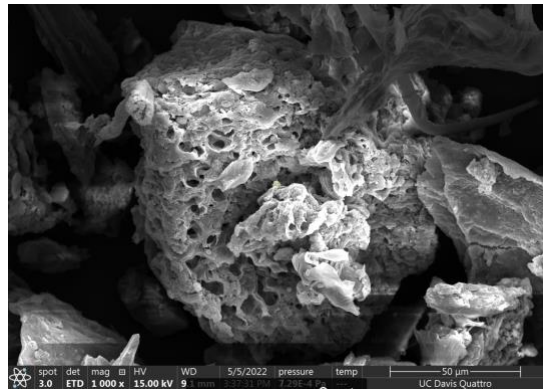
 Scanning Electron Microscopy (SEM) image showing the porous, interconnected structure of spent grain biochar. The image displays a complex network of fibers and voids, characteristic of a porous material. A scale bar at the bottom indicates 50 µm. Technical parameters at the bottom include: spot 3.0, det ETD, mag 1.000 x, HV 15.00 kV, WD 8.0 mm, 5/5/2022, pressure 1.01E-4 Pa, temp ---, UC Davis Quattro.	 Scanning Electron Microscopy (SEM) image showing the porous, interconnected structure of spent grain biochar. The image displays a complex network of fibers and voids, characteristic of a porous material. A scale bar at the bottom indicates 50 µm. Technical parameters at the bottom include: spot 3.0, det ETD, mag 1.000 x, HV 15.00 kV, WD 8.4 mm, 5/5/2022, pressure 2.16E-4 Pa, temp ---, UC Davis Quattro.
13 moles of Caustic / 100 g BSG 24 h Soaking Peak temp: 400 °C, 1 h	13 moles of Caustic / 100 g BSG 48 h Soaking Peak temp: 400 °C, 1 h



13 moles of Caustic / 100 g BSG

48 h Soaking

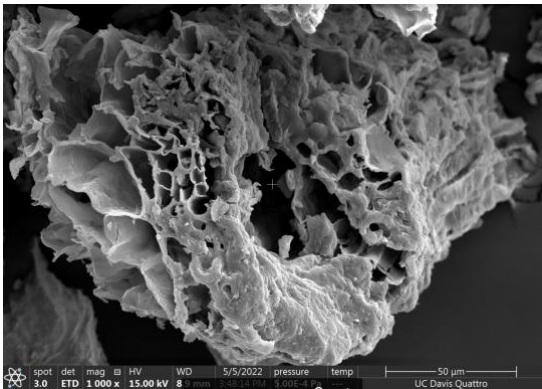
Peak temp: 700 °C, 1 h



5.85 moles of Caustic / 100 g BSG

24 h Soaking

Peak temp: 400 °C, 1 h



5.85 moles of Caustic / 100 g BSG

48 h Soaking

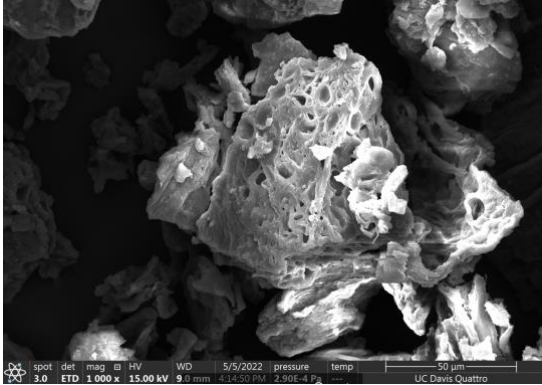
Peak temp: 400 °C, 1 h



5.85 moles of Caustic / 100 g BSG

48 h Soaking

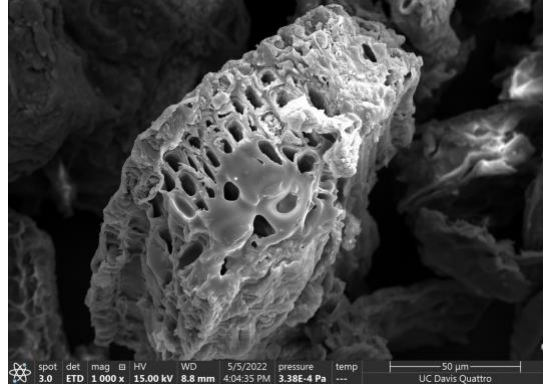
Peak temp: 700 °C, 1 h



7.5 moles of Caustic / 100 g BSG

24 h Soaking

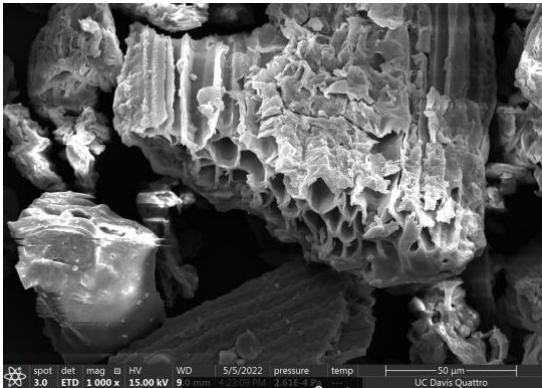
Peak temp: 400 °C, 1 h



10 moles of Caustic / 100 g BSG

24 h Soaking

Peak temp: 400 °C, 1 h



12.5 moles of Caustic / 100 g BSG

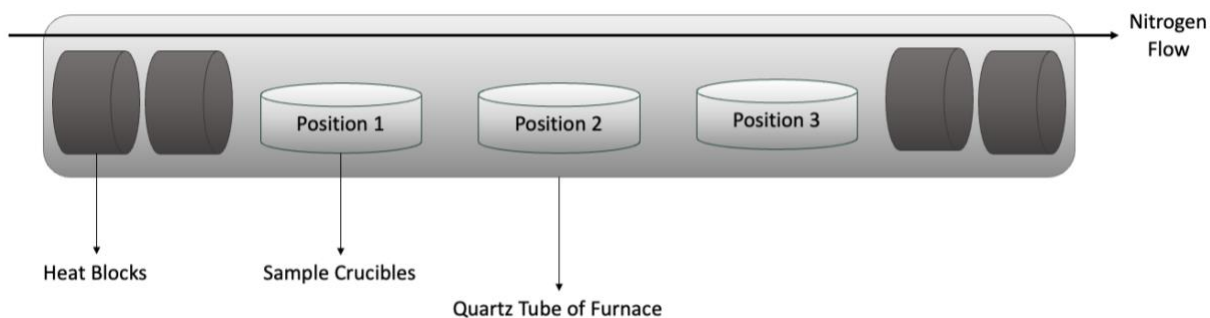
24 h Soaking

Peak temp: 400 °C, 1 h

### 3.7 Position in Furnace

There were some organoleptic differences noticeable to the researcher because of the sample's position in the pyrolysis furnace. Because of the direction of nitrogen flow, samples in position 3 (Figure 15) experienced a higher concentration of syngas pooling than position 1. As a result, samples from position 3 had stronger odor than samples from position 1. However, analysis of pH, liming potential, IOC and TOC showed no trends resulting from the positioning of the sample in the furnace.

Figure 15. Pyrolysis Furnace Position Influence



## 4. Discussion

In summation, the results of this research conclude that low-dosage ( $\leq 5$  moles per 100 g *unprocessed BSG*) of waste-caustic as a pretreatment method for biochar production from BSG is effective at improving desirable characteristics of the resulting biochar (mass recovered, liming potential, TOC, porosity). Specifically, to utilize this biochar for soil amendment, which is selective for alkaline samples, the recommended parameters are: 1 day of soaking BSG in

caustic at a dosage rate of  $\leq 5$  moles per 100 g unprocessed BSG at ambient temperature, followed by draining of the liquid fraction, drying of the BSG until constant weight, grinding until uniform particle size, and pyrolysis at 700 °C with a heating rate of 5 °C/min, holding the sample for at least 1 hour of residence time with constant inert gas flow throughout the heating and cooling process. After cooling, the biochar is ready for application. The resulting biochar would be expected to have a mass recovery of 25-30% initial weight, a neutral pH of  $\sim 7.5$ , a Class 1 categorized liming potential (1-10%  $CaCO_3$  eq), a high TOC (70-73%) and consistent porosity.

There are several avenues for recommended future research to advance understanding of the ideal parameters for producing BSG biochar with caustic as the pretreatment chemical. First, re-evaluation of the IOC and liming potential values utilizing methods that limit human error. Additionally, analysis of the CEC and porosity of the biochar would provide insight to confirm the optimal conditions for BSG biochar production. To validate the practicality and effectiveness of utilizing this biochar, soil application trials and water filtration trials would be recommended. Resulting data would allow future researchers to confirm the efficacy of adapting BSG as a biomass for biochar production in a circular economy model. Ultimately, these considerations would enhance the potential to close the loop on two major brewing industry waste streams.

## 5. Addendum

Figure 16. Importance of Volume when Weighing Spent Grain



Image Description: three samples of brewers spent grains soaked in caustic, all weigh 400 g.

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# Chapter 3: Net Greenhouse Gas Assessment on the Viability of Utilizing BSG to Produce Biochar

## 1. Introduction

### 1.1 Background

Beer, being one of the most widely consumed beverages globally, experienced significant production in 2020, with the world producing 1.82 trillion hectoliters ([Zeko-Pivač et al. 2022](#)). However, the sustainability of brewing raises concerns due to its substantial water requirements for production and cleaning, resulting in significant waste generation compared to product yield. The primary waste stream in brewing, aside from water, is brewer's spent grain (BSG), which refers to the husk, pericarp, and seed layers of barley that remain after extraction of soluble sugars from the grain. This fibrous by-product accounts for 85% of the total waste from beer production, with the remaining portions consisting of trub (hop solids, clarifying agents, yeast nutrient, and other ingredients added to the boiling stage) and yeast solids. In 2020, 36.4 million metric tonnes of BSG were disposed of as a result of beer production ([Zeko-Pivač et al. 2022](#)).

The Food and Agriculture Organization of the United Nations (FAO) introduced Sustainable Development Goal (SDG) 12.3, which calls for action to reduce food loss throughout the food supply chain. In line with this goal, Champions 12.3, a collaborative group of executives working

on SDG 12.3, conducted a study that presented the optimal hierarchy of solutions for valorizing food waste (Figure 2) (Hanson 2017). The top three solutions include: 1) prevention and redistribution to people, 2) diversion to animal feed, and 3) biomaterial/processing of waste. Notably, landfilling is considered “no valorization” and is an undesirable method of waste disposal (Figure 2).

Traditionally, the primary use for BSG has been animal feed (70%), while the rest is landfilled (30%) or used for biogas production (10%) (Mitri et al. 2022). While using BSG as animal feed is recommended by the FAO, it is not feasible for breweries located far distances from agriculture due to its high-water content, making it heavy to transport and highly unstable. Therefore, finding alternatives to landfilling is of great interest to the brewing industry aiming to align with sustainability goals. The decomposition of organic matter from food waste releases methane, a significant contributor to greenhouse gas (GHG) emissions. Considering the various approaches which fall under “biomaterial/processing” of food waste in the third position on Figure 2, there is some uncertainty regarding this ranking. Therefore, it becomes crucial to determine whether specific upcycling techniques for valorizing BSG imposes a higher or lower environmental burden than other destination options for BSG. Ideally, this would be via an evaluation of the GHG emissions associated with a system.

To address the quantification and reporting of GHG emissions and removals, the International Organization for Standardization (ISO) has developed a document titled ISO 14064-1:2018. This document outlines the principles and requirements for measuring and reporting GHG emissions



and removals. GHGs are defined as both natural and anthropogenic gaseous constituents of the atmosphere which absorb and emit radiation “at specific wavelengths within the spectrum of infrared radiation emitted by the Earth’s surface, the atmosphere and clouds” [\(ISO 2018\)](#). GHG emissions are typically categorized into three scopes: direct (generation of heat/power), indirect (purchasing electricity), emissions from the value chain (upstream purchasing, downstream usage, etc.). To conduct a comprehensive GHG assessment, a GHG inventory must be established, which includes a list of GHG sources, GHG sinks, and their quantified GHG emissions and removals. In this context, GHG sources refer to processes that release GHGs into the atmosphere, while GHG sinks refer to processes that remove GHGs from the atmosphere.

IEMA, a professional body for the environment and sustainability sectors, has made distinct statements about the global impact of GHGs including: (1) GHG emissions will contribute to have an environmental effect and contribute to climate change, and (2) climate change will lead to significant environmental effects on population, fauna, soil, and more. IEMA released a guide to assessing greenhouse gas emissions and evaluating their significance, emphasizing that the effects of GHGs are among the most challenging environmental issues.

## 1.2 Greenhouse Gas Assessment

Between 2010 and 2019, GHG emissions rose, although the rate of growth during this period was lower compared to 2000-2009 [\(Intergovernmental Panel on Climate Change \(IPCC\) and Working Group III 2022\)](#). Since 2010, net anthropogenic GHG emissions have increased across all major sectors globally, with urban areas witnessing a higher share of emissions

(Intergovernmental Panel on Climate Change (IPCC) and Working Group III 2022). However, emissions from fossil fuels and industrial processes have been reduced due to advancements in energy efficiency. Notably, improvements in industry, energy supply, transportation, agriculture and buildings have contributed to a lower carbon intensity of energy (Intergovernmental Panel on Climate Change (IPCC) and Working Group III 2022).

The purpose of a greenhouse gas assessment (GHGA) is to systematically evaluate the GHG emissions associated with a specific system. By quantifying the amount of GHGs released, researchers can assess the environmental footprint of a process and determine its climate-friendliness compared to alternative options. A GHGA shares similarities with an attributional life cycle assessment (LCA) in terms of techniques used, such as identifying a goal, scope, system boundaries, and conducting a life cycle inventory to understand the environmental impact of an existing system. However, the impact categories considered differ between GHGA and LCA. In an LCA, global warming potential (GWP) is typically one of the several impact categories considered, along with acidification, ecotoxicity, eutrophication, human toxicity potential, stratospheric ozone depletion, smog formation, cumulative energy demand, blue water consumption, land use, and others. Focusing primarily on quantifying and assessing GHG emissions allows for a quick determination of the carbon footprint of a system. Additionally, the system boundary in an LCA is often broader. A cradle-to-grave LCA covers phases from raw material extraction to end-of-life disposal. There are some LCAs, referred to as cradle-to-gate, which exclude end-of-life disposal if a specific scenario lends to this. Similarly, a GHGA can analyze data on energy consumption, fuel use, industrial and agricultural processes, waste

management, and land use depending on the defined scope of the system. Categories are selected based on the need to understand the largest contributors and overall magnitude of emissions, enabling decision-makers to identify areas for emission reduction or mitigation. In summary, GHGAs allow for targeted analysis of GHG emissions in a more focused and streamlined manner than an LCA.

For each impact category, characterization factors are used to translate an inventory flow into an impact indicator. In most cases, indicators utilize reference chemicals, summarizing a category as an equivalence to a reference chemical. The most used indicator is carbon dioxide ( $CO_2$ ). The evaluation of GWP involves determining a system's potential to emit a unit mass of gas, which, over a specified period, will exert cumulative radiative forcing, either directly or indirectly. The gasses typically identified and quantified include carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ), and nitrous oxide ( $N_2O$ ). These are expressed as  $CO_2$  equivalents ( $CO_2e$ ). The Intergovernmental Panel on Climate Change (IPCC) has estimated 100-year global warming potentials to convert non- $CO_2$  GHGs to  $CO_2e$ 's.  $CH_4$  has a conversion factor of 25, and  $N_2O$  which has a conversion factor of 298 (Griggs and Noguer 2002).

### 1.3 Brewing Industry Waste

BSG, the major waste stream generated during beer production, primarily consists of the husk, pericarp, and seed coats of crushed malted grains. It may also contain trace amounts of silica, polyphenols, insoluble protein, and oils (Mussatto et al. 2006). The composition of BSG can vary

depending on factors including grain quality, malting, and mashing conditions, the use of adjuncts, and salt incorporated during the mashing stage.

Several studies have examined the macronutrient and fiber content of BSG. Data from a variety of studies suggested that, on average, BSG contains 38.22% total carbohydrates, 7.33% fat, 21.82% protein, 2.73% ash, and 44.71% fiber (Waters et al. 2012; Serena and Knudsen 2007; Dhillon et al. 2012; Canedo et al. 2016; Kanauchi et al. 2001; Castro and Colpini 2021; Bravi et al. 2021; Lynch et al. 2021; Sibhatu et al. 2021). However, it is important to note that there are inconsistencies among samples, as the sum of these values is over 100%. The highest variance amongst values is observed in total carbohydrates and total fiber, respectively. The high-water activity and fermentable sugar concentration of BSG are major limiting factors for valorization, as they make it highly unstable and prone to rapid deterioration from microbial activity. Drying BSG can extend its shelf life, reduce weight and therefore transportation costs and storage needs, making it a valuable biomaterial for biorefinery applications. However, the drying process is often energy intensive, and therefore costly.

During the cleaning-in-place (CIP) process of brewing equipment, caustic chemicals, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) are commonly used. These chemicals often maintain a relatively high pH at the end of their use, indicating the need for neutralization before disposal. Instead of neutralizing and discarding these aqueous solutions, they can be recovered and reused as a pretreatment to enhance the quality of BSG for various valorization opportunities.

## 1.4 Biochar Production and Biorefinery model for BSG

Biochar, as defined by the International Biochar Initiative (IBI), is a solid material derived from thermochemical conversion of biomass in an oxygen-limited environment (International Biochar Initiative 2015). Biomass refers to the biodegradable portion of agricultural, forestry, and related industries' products, waste, and residues, as well as the biodegradable portion of industrial and municipal waste (International Biochar Initiative 2015). The characteristics of biochar, such as porosity, organic carbon content, pH, etc., are influenced by the type of biomass used in its production, including its cellulosic, sugar, fat components and contaminants.

Biochar is distinct from charcoal and other carbon products due to its predetermined use which is primarily environmental management. This can include soil remediation, resource efficiency improvement, pollution prevention, greenhouse gas (GHG) mitigation and so on (International Biochar Initiative 2015). Biochar's are highly porous, amorphous materials, typically containing negligible levels of heavy metals, low nitrogen and ash concentrations, while maintaining a high surface area and adsorption capacity (Rodriguez Correa et al. 2019; Surampalli et al. 2014). They also exhibit a low degree of aromatization, resulting in high porosity and reactivity which is correlated with high surface area, and electrical conductivity (Rodriguez Correa et al. 2019; Surampalli et al. 2014).

Utilizing BSG for biochar production can be a key technique employed in a biorefinery process for valorizing BSG. Biorefineries aim to maximize the utilization of waste streams by simultaneously producing various products from one initial waste source. The production of biochar from BSG generates bio-oil and syngas as byproducts, which can be utilized for energy applications or further purified to obtain their primary components for use as raw materials. The resulting biochar, being rich in carbon, can be applied in soil amendment, carbon sequestration, energy production and other applications. Implementing BSG in a biorefinery model has the potential to transform the brewing industry and contribute to a circular economy, revolutionizing the environmental impact associated with beer production. Additionally, this approach offers economic benefits, serving as a potential secondary income or cost reduction for breweries.

## 1.5 Post-Production Utilization of Biochar, Syngas and Bio-Oil

A study compiled data from 27 peer-reviewed papers that utilized LCA methodology to evaluate the environmental impact of pyrolysis-based biochar systems which specifically used biochar for soil amendment ([Matušík et al. 2020](#)). The selected studies were published between 2011 and 2019 from a variety of global regions. The functional units employed in these studies varied considerably depending on factors such as the use of wet or dry biomass, time, or land. The system boundaries also varied due to the inclusion of different feedstocks, particularly when the biomass was derived from waste streams. Majority of the studies adopted a system expansion approach to consider downstream utilization of syngas and bio-oil. The application rate of biochar to the soil exhibited significant variation across the studies (from 1 t/ha to 30

t/ha). Biochar stability also differed, most authors used conservative values (80% or lower) for the concentration of stable biochar.

Most of the studies considered the impact of biochar on soil, acknowledging its potential to increase crop yield, availability of nutrients, sorption of pollutants, have a positive impact on the microbial population in soils, and reduce methane and nitrous oxide emissions (Matušík et al. 2020). However, the overall impact of biochar on soil varied amongst studies depending on the specific benefits considered. Despite differences, the results of all 27 studies consistently demonstrated the trend that biochar-soil amendment systems benefit climate change mitigation (Matušík et al. 2020). The primary benefits are carbon sequestration driven by carbon storage from the biochar in soil, crop yield increase which reduces the use of fertilizer, and reduction of methane or nitrous oxide emissions from biochar (Matušík et al. 2020). For the studies that reported positive GWP values, biochar was found to be a method of mitigating the impact of crop production. When crop production was excluded, (Matušík et al. 2020) reported that the main source of GHG emissions was the pyrolysis system. However, these emissions were consistently offset by the carbon capture benefit of biochar and the energy production offsets achieved through the utilization of pyrolysis co-products, namely syngas and bio-oil.

Bio-oil and syngas are considered co-products due to their valuable uses in industrial applications. Therefore, it is important to consider the GHG savings achieved through utilization of these products. Bio-oil can be utilized in replacement of heating oil, or refined into gasoline,

ethanol and/or other chemical compounds ([Yoder et al. 2011](#)). Syngas, produced through pyrolysis, primarily consists of carbon dioxide, carbon monoxide, methane and hydrogen; it also has water vapor, hydrocarbons and condensable compounds ([Nunes et al. 2018](#); [Biogreen n.d.](#)). Syngas is combustible, making its primary use generating power and heat through stand-alone combined heat and power (CHP) plants or through co-firing the gas in large-scale power plants ([Biogreen n.d.](#)). By adopting a system expansion approach that considers the utilization of syngas and bio-oil from pyrolysis, this system can achieve fuel savings and emissions reductions by utilizing these co-products for heat and electricity generation to power the processing equipment.

## 1.6 Landfilling Biomass

To determine gas emissions from landfills, models are employed to predict methane generation based on the biological changes that occur during landfill decomposition. These models typically utilize a first-order kinetic equation which correlates methane production with the degradation of organic matter, while considering annual waste amounts and decomposition rates ([Mohsen et al. 2019](#)). In first-order models, such as LandGEM, methane production is assumed to be directly proportional to degradation of organic matter within the landfill.

LandGEM is a widely used first-order model in the United States, providing a framework to describe the behavior of landfills in terms of landfill gas generation ([Mohsen et al. 2019](#)). These models make estimating the amount of methane generated by landfills possible, therefore allowing for assessment of the environmental burden of these waste disposal sites. Quantifying



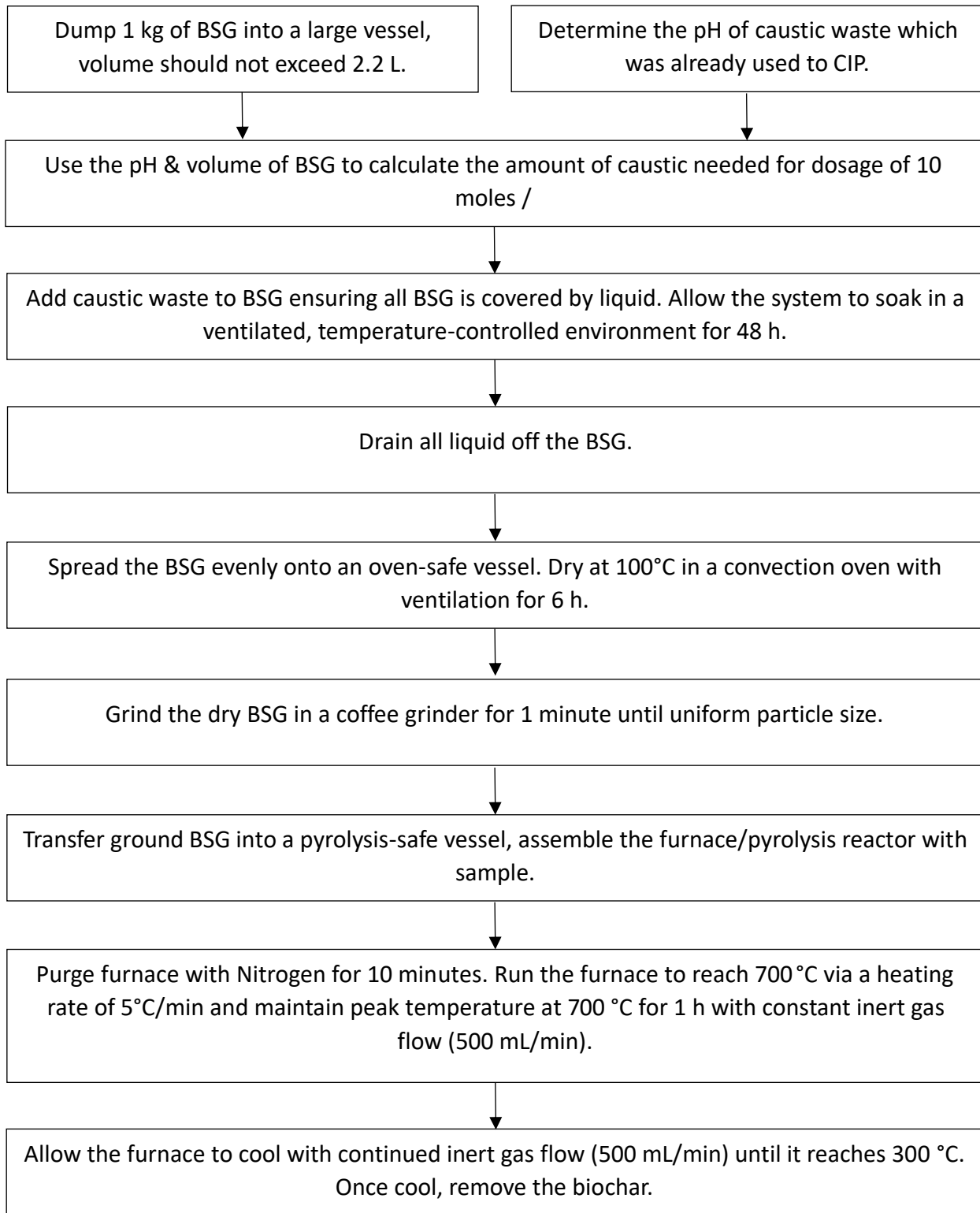
methane emissions from landfills allows for consideration of mitigation strategies to reduce the overall environmental impact.

## 2. Methods

### 2.1 Biochar Production Method

The overarching method used for biochar production in this study is described in detail in Chapter 2, Section 2.1, and illustrated in Figure 17 below. In this GHGA, a specific set of variables, which yielded an ideal biochar (*See Chapter 2*), was chosen to determine the GWP associated with the evaluated protocol. Briefly, BSG (produced on UC Davis Anheuser Busch InBev Pilot Brewery on the 30 Liter Nano-brewhouse systems) was soaked in waste caustic (collected after CIPing the UC Davis Anheuser Busch InBev Pilot Brewery 1.5-barrel brewhouse), at a dosage rate of 10 moles per 100 g BSG for a period of 48 h. After soaking, the caustic was drained off the BSG, then the BSG was dried for 6 h in a convection oven at 100 °C. The BSG was ground in a coffee grinder, then pyrolyzed in a 200 mm quartz tube furnace with a peak temperature of 700 °C for a residence time of 1 h.

Figure 17. BSG to Biochar Processing Protocol



## 2.2 GHG Assessment

### 2.2.1 Goal and Scope

The aim of this study was to assess the global warming potential of the method provided for converting BSG into biochar. By quantifying the greenhouse gas emissions associated with this process and comparing it to landfilling BSG, the overall environmental burden or benefit can be determined. This assessment explores the potential for creating a circular economy in the brewing industry by utilizing BSG for biochar production. Such an approach can effectively reduce waste generation, mitigate greenhouse gas emissions, and contribute to a more environmentally conscious brewing industry. Understanding the greenhouse gas implications of this practice supports informed decision-making and facilitates the adoption of sustainable practices.

The intended audience of this study includes brewing industry professionals, policymakers, and researchers. Brewing industry professionals can utilize this GHGA to assess the benefits of implementing biochar production in their facilities. Policymakers and environmental professionals can leverage the results to advocate for or shape policies and regulations that promote sustainable practices within the brewing industry, and potentially the beverage industry at large. The results can be used for comparative analysis, enabling stakeholders to evaluate the environmental performance of BSG-based biochar production in comparison to other waste management or biomass utilization practices. By openly sharing the results, the aim is to facilitate informed decision-making, encourage collaborations, and promote the adoption of sustainable practices in the brewing industry and beyond. The functional unit

chosen for this study is one unprocessed kg of BSG (collected directly from the lauter tun). This allows for data comparison with one unprocessed kg of BSG sent to landfill.

### 2.2.2 System Boundary

This study conducted an evaluation of biochar production at the bench scale, which imposed limitations on production volumes due to equipment size. It is important to note that scale-up of this system could enhance the accuracy of the environmental impact and potential benefits of this system. Scaling up would also represent more applicable conditions to help determine the feasibility and suitability on a larger scale.

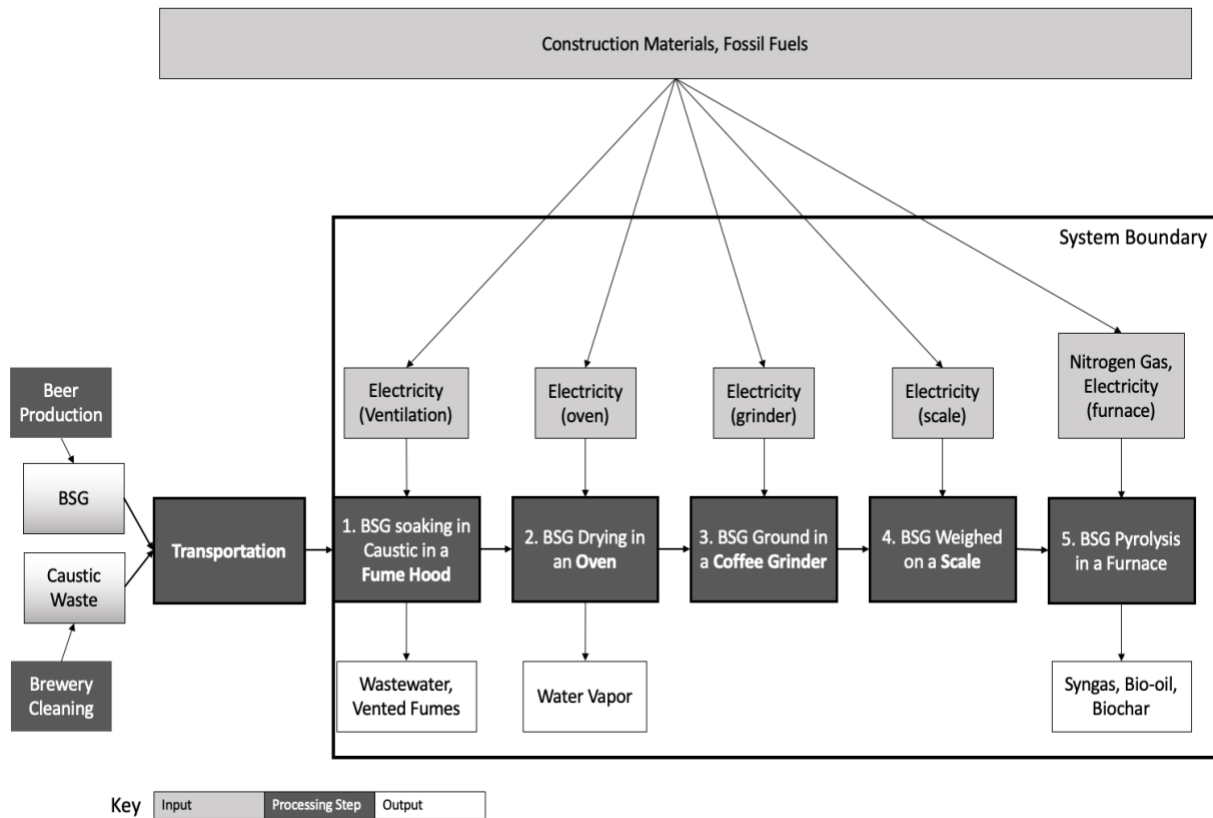
The boundaries of this system are depicted in Figure 18. Any item shown outside of the system boundary is considered background data, while items listed inside are considered foreground data. The system boundary excludes beer production and the production of brewery cleaning materials, as these processes will occur regardless of this valorization process. Transportation of BSG and caustic waste is excluded from the boundary. Although these steps will differ from the traditional brewing process, the distance is will vary depending on the location of the processing facility in relation to the breweries. The boundary also excludes the industrial production of equipment and materials used in this process, as they will vary depending on the size of the installed pyrolysis system.

The production process of BSG biochar involves six major steps: (1) soaking of BSG in caustic waste in a ventilated area, (2) drying of BSG in an oven, (3) grinding of BSG, (4) weighing of BSG,

and (5) pyrolysis of BSG. The primary inputs in steps 2, 3, and 4 are electricity use. Step 2 involves electricity and nitrogen gas.

The primary output of step 1 is wastewater, with consideration given to vented fumes. Step 2 mainly produces evaporated water. Step 5 results in the production of biochar as well as syngas and bio-oil, which are valuable commodities and therefore can be considered co-products. The system boundary concludes at biochar production because the various uses of biochar are specific to brewery systems, and the associated GHG emissions will vary considerably. It is assumed in this system that the source of electricity utilizes natural gas.

Figure 18. System Boundaries for a Greenhouse Gas Assessment on Making Biochar from BSG

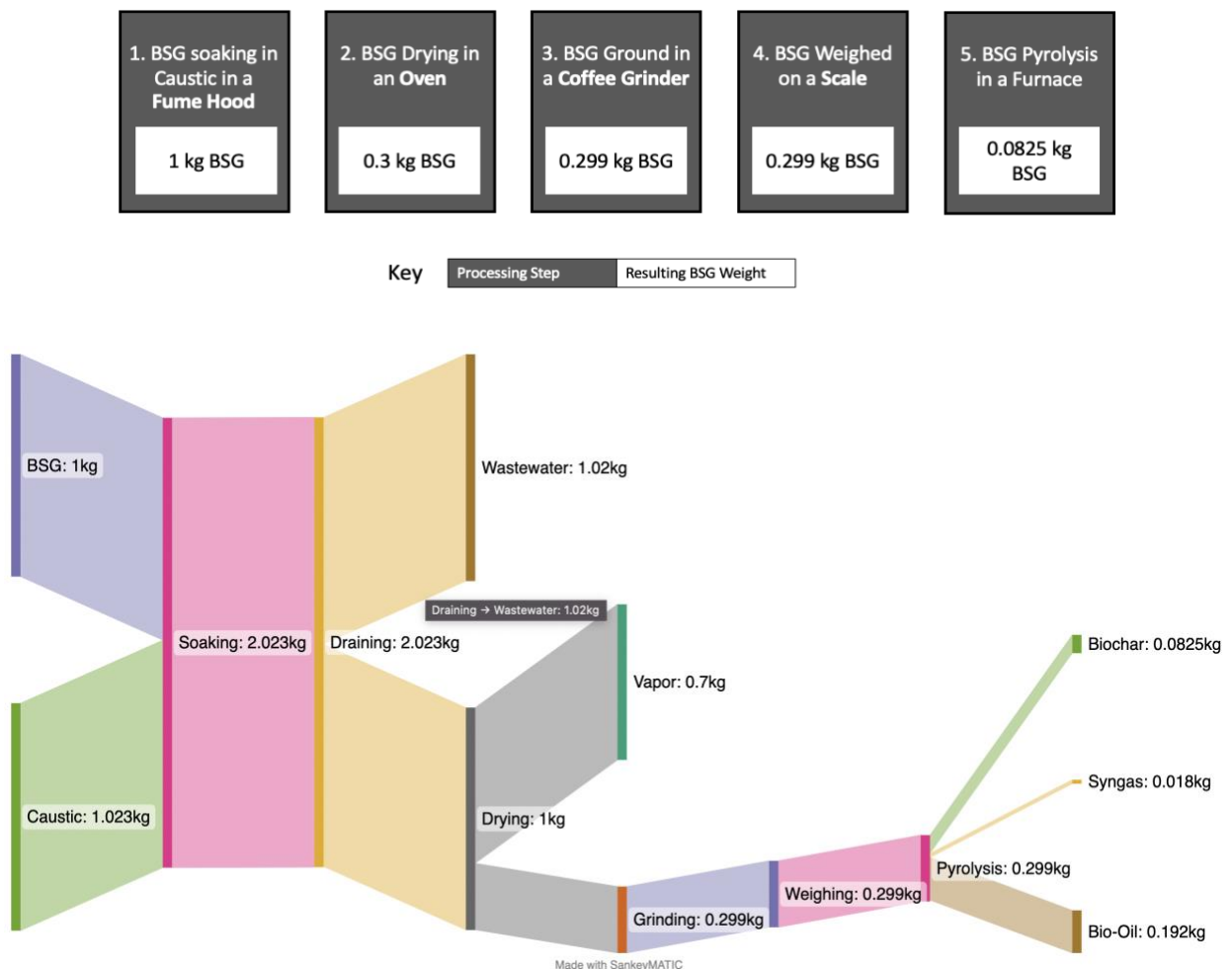


# 3. Results

## 3.1 Life Cycle Inventory

Data collection was categorized by the industrial phases (1-5) outlined in Figure 19. The resulting quantities of BSG after each phase, starting from 1 kg of unprocessed BSG are shown in Figure 19. Data was collected from the lab-scale protocol utilized by the researcher, and from publications on similar processes.

Figure 19. BSG Recovery Volumes throughout the Biochar Production Process



The major inputs for phase 1, soaking, were the electricity required for operation of a fume hood and the electricity required for operation of a scale. Fume hood data was collected using the Lawrence Berkeley National laboratory calculator for determining the energy usage of a fume hood, considering sash height and a variety of other parameters. The tool was set to Sacramento, CA with an opening of 62 by 29 in (horizontal by vertical), a face velocity of 100 ft/min, temperature maintenance at 55°F, a delivery air temp of 65°F, and energy type being fuel. It found that the closed fume hood would use 71.4 kWh/day which is equivalent to 257.04 MJ ([Lawrence Berkeley National Laboratory and Earth Advantage 2019](#)). Volume was adapted to consider the functional unit of 1 kg of unprocessed BSG. Specifically, 1 kg of BSG is equivalent to 220  $cm^2$ , while the fume hood volume is 11600  $cm^2$ . Therefore 1 kg of BSG needs 9.74 MJ for 48 h of soaking. Utilizing a scale with 10-watt power for 30 minutes, required 0.018 MJ.

The major outputs of phase 1 were wastewater drained off the grain after soaking, and vented fumes. The volume of wastewater was collected at the lab scale after caustic adsorption for 48 h. Per 1 kg of unprocessed BSG, 1.02 L of wastewater was drained via filtering the BSG solution over a cheesecloth. The filtrate had a pH value of 5.17, and therefore would require negligible neutralization treatment prior to discarding. In phase 1, BSG is maintained in a room temperature, moist environment where naturally present microbes can readily metabolize and release greenhouse gasses. Because of this output, the BSG vessels were held in a well-ventilated area, the fume hood. The volume of vented gas was determined at the lab scale by closing the system for 48 h and determining the volume of collected gas. The resulting volume

for 1 kg of unprocessed BSG was 109 mL, this was assumed to be primarily  $CO_2$ , and therefore had a weight of 0.074 kg. A study found that after fermentation of BSG, the total dissolved gas had a concentration of 0.72% dissolved  $CH_4$ , and the remaining gas was  $CO_2$  (Ran et al. 2021). Because of the significant drop in pH and increased presence of gaseous bubbles over the 48 h period, it was concluded that the main gas present is  $CO_2$  as a result of fermentation.

The major input for drying, phase 2, was electricity used to power the oven. The modeled equipment was a Shel Lab Forced Air Oven SMO3 110-120 Voltage. The wattage of this oven was 1610 W with a capacity of 85 L. At lab scale, 1 kg of unprocessed BSG was equivalent to 2.2 L, therefore per 1 kg of BSG, the oven utilized 0.915 MJ. The major output for drying was water vapor removed from the BSG. At lab scale, BSG lost 70-75% of its weight after drying, it was assumed that the water vapor produced from BSG drying was 0.7 kg per 1 kg of unprocessed BSG.

The major input for grinding, phase 3, was electricity required to power the coffee grinder. After drying, 1 kg of unprocessed BSG was equivalent to 0.3 kg of processed BSG. A 300 watt coffee grinder used for 1 minute was suitable for 0.3 kg dry BSG, requiring 0.018 MJ for use. There was some minor dust associated with this protocol, however, the total volume was considered negligible for environmental burden. After this stage, 1 kg of unprocessed BSG was equivalent to 0.299 kg of pretreated, dried, ground BSG.



The major input for weighing, phase 4, was electricity used to power the scale. Utilizing a scale with 10-watt power for 15 minutes, required 0.009 MJ. There was no considerable output for this phase.

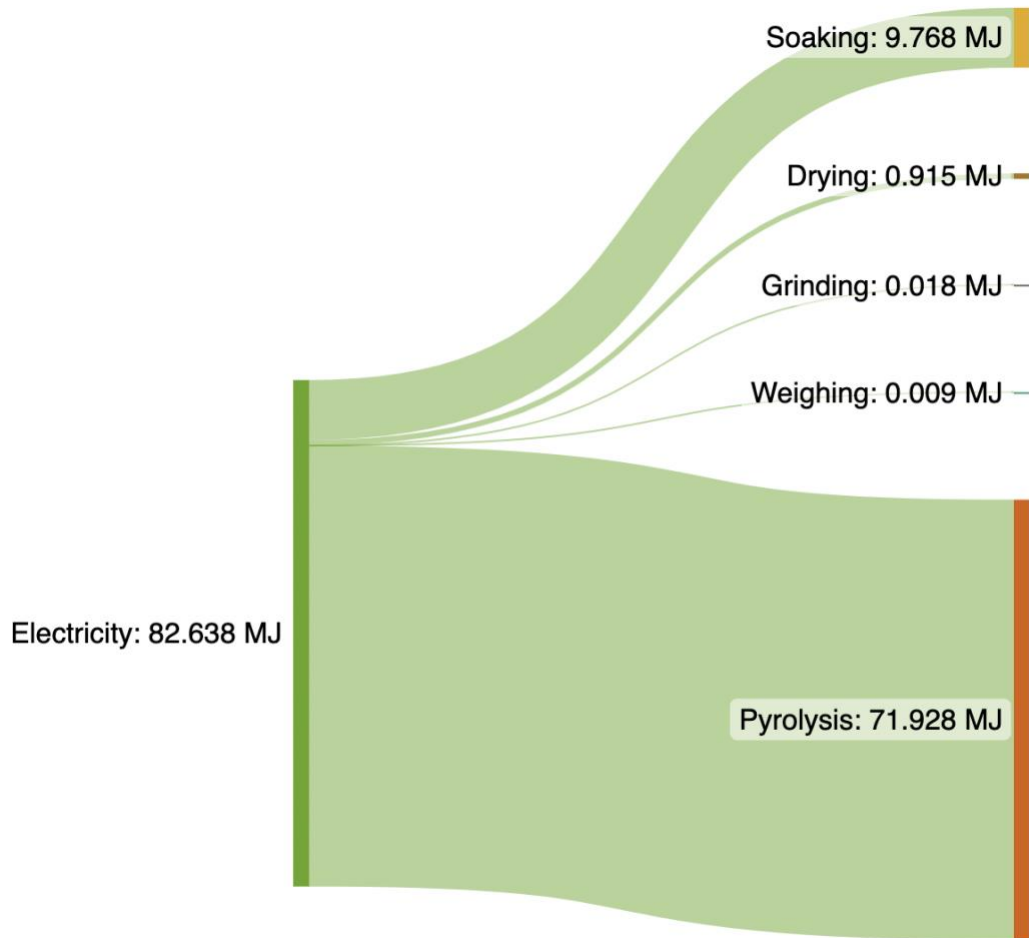
Phase 5, pyrolysis, required nitrogen gas and electricity as the major inputs. This GHGA considered a larger pyrolysis furnace than what the researchers had access to. At lab scale, researchers used the same style furnace; however, the quartz tube had a 60 mm diameter. The load limit for a 60 mm tube was small, only allowing 0.030 kg of dried, ground BSG in each run. Instead, this calculation assumes that a 200 mm diameter quartz tube could host 0.299 kg of dried, ground, BSG which is equivalent to the functional unit of 1 kg unprocessed BSG. The nitrogen gas flow rate was set to 500 mL/min and was active for 3 h and 40 min, therefore requiring 170 L per run. It is known that 1 L nitrogen is equivalent to 0.8083 kg (Fremantle and Finnemore 1908). Therefore, 137.41 kg of nitrogen were utilized per 1 kg of unprocessed BSG. For electricity, the furnace has a rated output of 6 kW, and therefore required 71.928 MJ. There were three major outputs of pyrolysis: syngas, bio-oil, and biochar; yield data for bio-oil and syngas was not collected at the lab-scale. A study considered the greenhouse gas impact of pyrolysis of switchgrass for biochar production (Brassard et al. 2018). The functional unit of the study was 1 Mg of BSG, yields of syngas and bio-oil were reported as percentage dry basis, therefore did not need to be converted. Biochar yield was 29% on a dry basis, bio-oil yield was 64.1% on a dry basis, and syngas yield was 6.1% on a dry basis (Brassard et al. 2018). This aligned with the present study yields, as biochar recovery averaged 27.6% or 0.0825 kg.

Therefore, bio-oil production was determined to be 0.192 kg, and syngas was 0.018 kg per kg of unprocessed BSG.

Table 14. Life Cycle Inventory

<b>Phase</b>	<b>Item</b>	<b>Amount per FU</b>	<b>Unit</b>
<b>Input</b>			
Soaking	Electricity (scale)	0.018	MJ
	Electricity (ventilation)	9.75	MJ
Drying	Electricity (oven)	0.915	MJ
Grinding	Electricity (coffee grinder)	0.018	MJ
Weighing	Electricity (scale)	0.009	MJ
Pyrolysis	Nitrogen Gas	137.5	kg
	Electricity	71.928	MJ
<b>Output</b>			
Soaking	Wastewater (pH 5.17)	1.02	kg
	Vented Fumes	0.024	kg
Drying	Water Vapor	0.7	kg
Pyrolysis	Biochar	0.083	kg
	Syngas	0.018	kg
	Bio-oil	0.192	kg

Figure 20. Sankey Diagram of Electricity Usage throughout Biochar Processing



Made with SankeyMATIC

### 3.2 Landfilling BSG Comparison

A study evaluated the cost-benefit analysis of greenhouse gas emissions associated with diverting food waste from landfills (Sanciolo et al. 2022). The food waste in question was generated by a restaurant during a 6-day work week, stored in bins without refrigeration, and picked up on a weekly basis. The study used a functional unit of 1 kg unprocessed food waste. It accounted for  $CO_2$  emissions resulting from the usage of grid electricity at the waste producer

site,  $CO_2$  emissions from fossil fuel consumption during transportation over a distance of 15 km, and  $CH_4$  emissions originating from the food waste at the landfill (Sanciolo et al. 2022). In the modeled scenario, the gasses were released into the environment rather than being collected for use.

The study revealed that the primary contributor to  $CO_2e$  emissions from landfilling food waste is the release of fugitive methane (3 kg of  $CO_2e$  per kg of food waste) (Sanciolo et al. 2022). Comparatively, transportation of the food waste to the landfill was a minor contributor, at 0.006 kg of  $CO_2e$  per kg of food waste (Sanciolo et al. 2022). The net emissions associated with landfilling increased proportionally with the volume of uncaptured methane released. Furthermore, the study demonstrated that capturing methane onsite at a landfill can reduce the environmental burden of landfilling BSG. Adapting the functional unit of the present study, the total emissions from landfilling 1 kg of unprocessed BSG would be 3.006 kg  $CO_2e$ .

The Sanciolo et al. study also examined various other scenarios including centralized composting, centralized composting of dehydrated food waste, food waste or diversion to wastewater treatment plants as a result of using aerobic digesters with liquid outputs or in-sink disposal (Sanciolo et al. 2022). In all of these scenarios, the  $CO_2e$  values were significant lower than landfilling; they ranged from 0.04 to 0.7 kg  $CO_2e$  per kg of food waste (Sanciolo et al. 2022). Composting and aerobic digestion proved to be more favorable compared to landfilling, with  $CO_2e$  values of 0.3 and 0.11 kg  $CO_2e$  per kg of food waste, respectively (Sanciolo et al. 2022).

However, the Sanciole et al. study did not provide data on the composition of the food waste utilized (Sanciole et al. 2022). Methane is primarily produced in a landfill setting when an oxygen-limited environment is formed, leading to anaerobic bacteria fermenting carbohydrates and amino acids. Since the carbohydrate and amino acid concentration of BSG is considerably smaller than that of generic food waste evaluated in the Sanciole et al. study, it can be presumed that the actual  $CO_2e$  generation is slightly less than 3 kg per kg unprocessed BSG (See Chapter 1, Table 2 for BSG composition data), but still greater than 1 kg  $CO_2e$  per kg unprocessed BSG.

### 3.3 Global Warming Potential (Impact Assessment)

#### 3.3.1 Input Phases

The United States Environmental Protection Agency (EPA) offers a GHG equivalencies calculator which was designed to convert emission or energy data into the equivalent amount of emissions. Utilizing this tool, values were determined from the impact categories (Table 14) and are presented in Table 15. Among the consumption categories, electricity usage for ventilation in phase 2 and electricity consumption for pyrolysis in phase 6 were the most significant contributors. Meanwhile, electricity usage for weighing in phases 2 and 5, electricity consumption in phases 3 and 4, and nitrogen gas usage in phase 6 were relatively insignificant.

### 3.3.2 Output Phases

GWP values were determined from the aforementioned impact categories (Table 1) and are presented in Table 15. Wastewater treatment emissions were calculated using a predictive model from the EPA (RTI International and US Environmental Protection Agency 2010). In this model, it was assumed that wastewater was sent to an activated sludge system for treatment with a methane correction factor for wastewater treatment value of 0, a conversion factor for maximum  $CO_2$  generation per unit of oxygen demand of 1.375, and a conversion factor for maximum  $CH_4$  generation per unit of oxygen demand of 0.5. The annual  $CO_2$  emissions from processing wastewater in this system were 316 Mg  $CO_2/year$ , or 3.16e5 kg  $CO_2e/year$ . The system processed 157.7  $m^3/hr$ , therefore, considering the functional unit where 1.02 kg of wastewater were produced per kg of unprocessed BSG, the wastewater processed from the evaluated system was 0.00076% of what the system processed per hour; this would equate to 6e-7 kg  $CO_2e/year$  for 1 kg unprocessed BSG. Fumes from fermentation were vented at a rate of 0.074 kg  $CO_2$  per kg of unprocessed BSG, and therefore emitted 0.074 kg  $CO_2e$  per kg of unprocessed BSG. The direct carbon sequestration value of biochar was estimated in terms of a carbon stability factor by utilizing equation 1.

$$CO_{2,sequest} = 3.66(1 - e^{(t_{1/2} \cdot \ln(0.5))/TH}) \quad \text{Eqn 1}$$

where 3.66 is the ratio of molecular weight of  $CO_2$  to that of C,  $t_{1/2}$  (the half-life of biochar in soil), and TH is the analytical time horizon (Hammond et al. 2011). The half-life of biochar in soil

was calculated using equation 3 from [\(Hammond et al. 2011\)](#). Equation 3 first required equation 2 to determine  $O:C$ .

$$O:C = \max \begin{cases} 0.6 - 0.00079T \\ 0 \end{cases} \quad \text{Eqn 2}$$

$$t_{1/2} = 1000e^{-7(O:C)} \quad \text{Eqn 3}$$

where  $T$  is the pyrolysis peak temperature. Using Equation 2,  $O:C$  was found to be 0.047. Using Equation 3,  $t_{1/2}$  was found to be 719 years. Using Equation 2,  $CO_{2,sequest}$  was found to be 3.63 Mg  $CO_2e$ /Mg feedstock processed when  $TH$  was 100 years [\(Hammond et al. 2011\)](#).

Sequestration values range from 0 to 3.66 Mg  $CO_2e$ /Mg feedstock processed, indicating that the studied pyrolysis conditions yielded an extremely effective carbon sequestration mechanism [\(Field et al. 2013\)](#). To consider the functional unit, 3.63 Mg  $CO_2e$  per Mg feedstock processed was converted to 8.928 kg  $CO_2e$  per kg of unprocessed BSG. Specifically, there are 30,082 seeds of barley per kg of barley plant [\(Jacobs 2016\)](#), one barley seed weighs 0.0436 g [\(Bertholdsson 1999\)](#), and BSG accounts of 31% of the original malt weight [\(Mussatto et al. 2006\)](#).

For the biorefining process, it was found that converting bio-oil into gasoline and diesel using the syngas from pyrolysis (Case 1) yielded a GWP value of -0.0275 kg  $CO_2e$  per kg unprocessed BSG [\(Dang et al. 2014\)](#). However, if the syngas (hydrogen) underwent steam reforming, and the

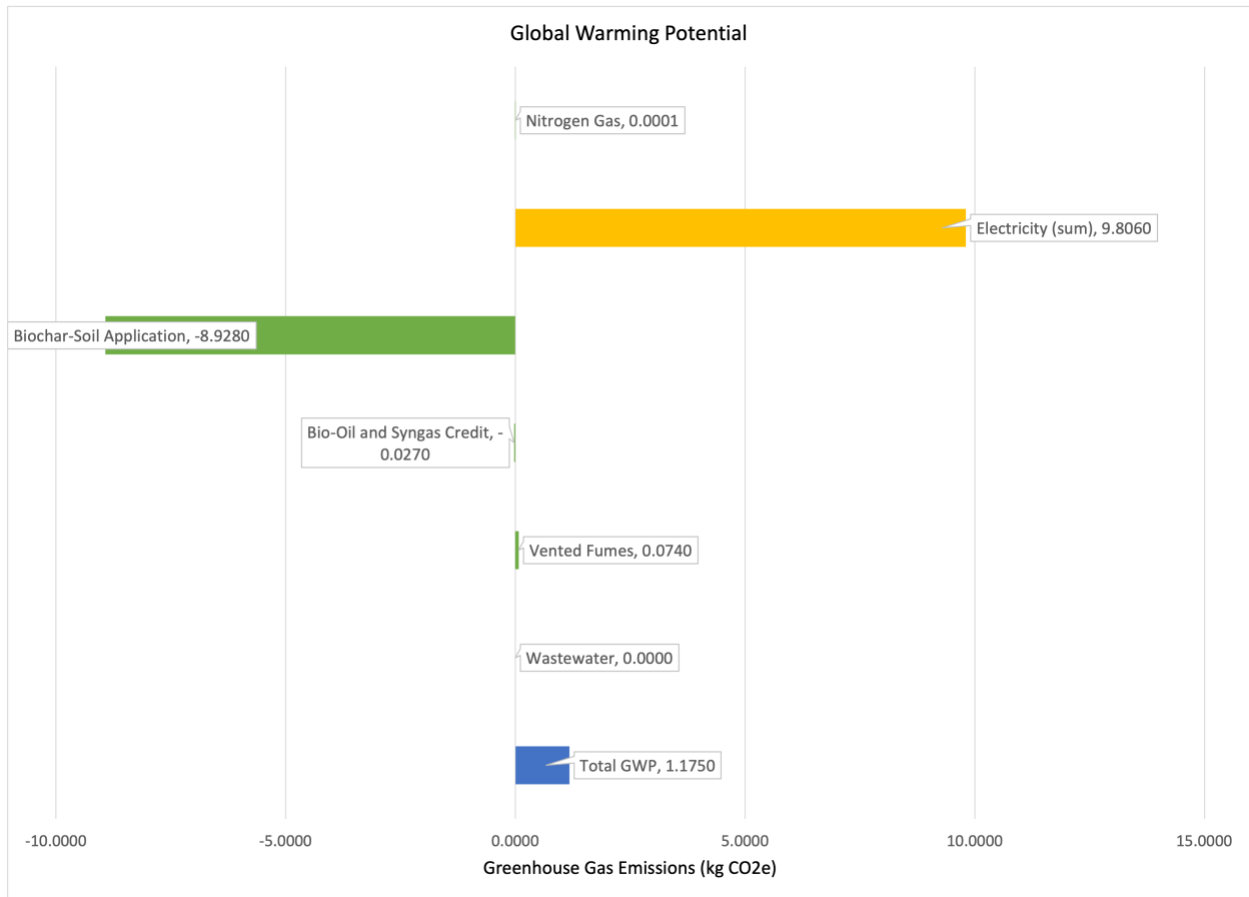
bio-oil was hydrogenated into gasoline and diesel (Case 2), a GWP value of -0.063 kg  $CO_2e$  per kg unprocessed BSG was found (Dang et al. 2014). In the referenced study, the biomass was corn-stover which was pyrolyzed at 500 °C with ambient pressure (Dang et al. 2014). Because of this difference, and a functional unit of 1 MJ of biofuel produced, data from the study has been extrapolated to match the current study. Based on these results, Case 2 has the more favorable GWP value, however, it also released a higher GWP value for biomass consumption and the pretreatment stage, respectively (8.80, 15.93 g  $CO_2e$  per MJ biofuel produced) than Case 1 (6.70, 12.13 g  $CO_2e$  per MJ biofuel produced). This must be considered when designing a biochar processing facility with bio-oil and syngas recovery. For this study, Case 1 was used as it requires less equipment and processing.

Table 15. GWP Impact Assessment

	Phase	Item	kg $CO_2e$
<b>Biorefinery Process</b>	<b>Input</b>	Electricity (sum)	9.806
		Nitrogen Gas	1e-4
	<b>Output</b>	Wastewater	6e-7
		Vented Fumes	0.074
		Biochar-Soil Application	-8.928
		Bio-Oil and Syngas Credit	-0.027
<b>Total</b>	Biorefinery GWP	1.175	
<b>Landfill</b>	<b>Total</b>	Landfill GWP	3.006



Figure 21. GWP Impact Assessment



As presented in Table 15, the primary category contributing to  $CO_2e$  production was the electricity consumed throughout the process, amounting to 9.8061 kg  $CO_2e$ . The most significant steps in terms of electricity use steps were pyrolysis, fume hood ventilation, and drying, in that order. The top  $CO_2e$  removal category was biochar-soil application (-8.928 kg  $CO_2e$ ). The overall GWP for this system was determined to be 1.175 kg  $CO_2e$  per kg of unprocessed biochar.

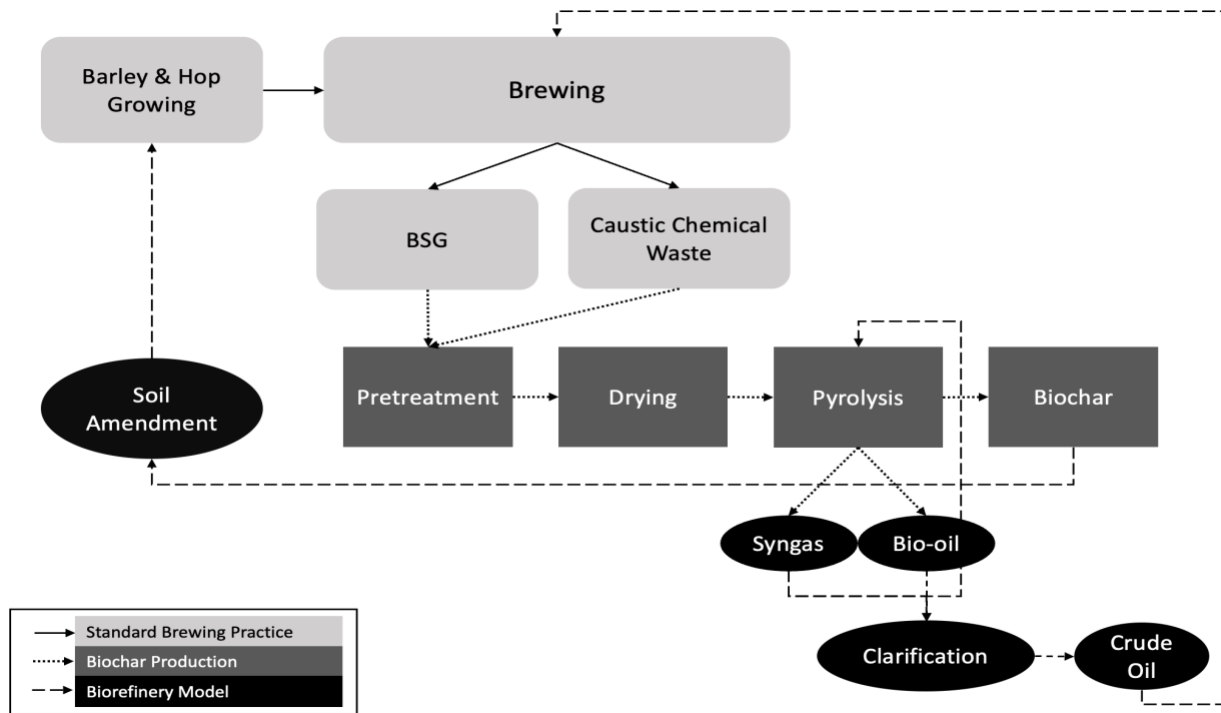
## 4. Discussion

The findings of this study concluded that landfilling BSG releases nearly 3 kg  $CO_2e$  per kg unprocessed BSG, while processing BSG into biochar at the lab scale results in a lower emission of 1.175 kg  $CO_2e$  per kg unprocessed BSG. Based on these results, it is strongly recommended that BSG should be diverted from landfills and utilized in more environmentally sustainable ways, such as through the biochar production, composting, or a relative biorefinery process. These alternative uses have the potential to significantly mitigate the environmental impacts associated with BSG disposal, particularly when built to a large scale in an urban area. The insights gained from this study can inform the development of policies and regulations aimed at minimizing the environmental impact of food waste disposal.

### 4.1 BSG Biochar Biorefinery Model for Breweries

The recommended biorefinery model, depicted in Figure 22, is primarily applicable to breweries who have the potential to expand their energy sources in their warehouse, and do not have access to local farmers who can utilize the BSG as cattle feed.

Figure 22. Biorefinery Model Converting BSG into Biochar



Ideally, this model would be adapted by a cooperative set of craft breweries located in one condensed urban area. In this setting, farmers would be less inclined to drive into the area and pick up the BSG, making diversion to animal feed unattainable for these breweries. A centralized biochar production facility would allow the craft breweries to send their BSG for processing, ultimately reducing the cost and material expenditure associated with transporting unprocessed BSG offsite, far out of the urban area, to a landfill or composting facility. Ideally, caustic waste from the craft brewery closest to the processing facility would be utilized to enhance the biochar. Utilizing caustic waste in processing removes the need to neutralize chemical waste prior to draining, and decreases the total wastewater produced in brewing facilities. Once processed, the biochar should be sent for soil amendment at a barley agriculture

site, because soil amendment is the most effective use of biochar for GHG reduction. The weight of BSG biochar is significantly less than that of BSG, therefore transportation of finalized biochar offsite from the centralized processing facility to a barley farm would be less resource intensive than transporting unprocessed BSG. Efforts should be made to minimize the distance for transporting biochar to barley growers.

At a BSG biochar processing facility, the syngas released during biochar production should be captured and utilized as an energy source. This would decrease the required energy input, thereby improving the overall energy requirements and consequently reducing GHG emissions associated with the biochar production process. Moreover, the syngas can also serve as an energy source to clarify the bio-oil produced during BSG processing if the bio-oil is being refined within the same facility. The clarified crude oil then has applications for gasoline, diesel fuel, and heating oil production which can be utilized in-house.

## 4.2 Biochar End-of-Life Use

The end-of-life use for biochar was not specifically considered in this model because it is not feasible to remove biochar from the soil once it has been applied for soil amendment. However, if the biochar was utilized in other potential applications (i.e water filtration, beer filtration, or supercapacitors) the biochar could be applied to soil as an end-of-life use. In these scenarios, the biochar would be impregnated with nutrients that could further benefit the soil.

## 4.3 Limitations

The most significant limitation for this study is the scale at which calculations were performed. Generally, as the scale increases, the cost (monetarily, energetically, and resource-wise) tends to decrease while maintaining the desired output, thereby improving the system. This analysis does not consider construction of the buildings or equipment used in the process, which could contribute to a higher GWP depending on the timeframe of the analysis.

There were many minor data collection limitations:

1. Collecting data on the pH of caustic waste proved challenging, and therefore confirmation was only obtained from a few breweries.
2. In the calculated model, the oven would need to be filled to full capacity, thereby potentially requiring drying time exceeding 6 h
3. The calculations for grinding were based on a small coffee grinder, which would not be efficient for large-scale production.
4. Although the recorded average nitrogen loss was 50 L per run, the calculations indicated a requirement of 170 L for the duration of the run, suggesting an error with the flow meter. The actual flow rate for nitrogen depleted was closer to 15mL/min while the flow meter read 5 L/min.
5. Regarding the syngas and bio-oil recovery calculations, the reference study employed an auger reactor (1 kg biomass per hour), while the present study used a smaller-scale pyrolysis furnace (30 g per run).

One final major limitation to consider is the extrapolation of data to calculate the GWP of utilizing biochar for soil amendment and recovering bio-oil and syngas for energy. The data collected utilizes different biomass precursors, and slightly different pyrolysis conditions. The biorefinery model excludes transportation of biochar to a farm for soil amendment, and transportation of BSG to a central processing facility.

#### 4.4 Future Considerations

The major factor that contributed to the GWP of this process was the electricity used in the pyrolysis step. It is presumed that employing larger-scale and more energy-efficient pyrolysis equipment would lead to a significant decrease in emissions. This straightforward modification would render the process more sustainable. Therefore, future studies should prioritize the implementation of this biochar production method on a larger scale to gather more robust and reliable data.

To mitigate the negative environmental impacts of the energy required for pyrolysis, the utilization of sustainable forms of electricity (i.e. solar panels, syngas from anaerobic digestion, recovered steam from the brewery, etc.) would be beneficial. Additionally, during the soaking phase, BSG could be left to soak in a ventilated area that is more energy efficient as the fume hood used in this scenario consumed a substantial amount of energy, contributing significantly to GHG emissions. While the electricity demand for oven usage was relatively smaller compared to pyrolysis and ventilation, it still contributed to overall emissions. Therefore, the adoption of a

more energy efficient oven or the use of sustainable forms of electricity would also be advantageous in this regard.

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# Thesis Conclusion

In summary, this research has unequivocally confirmed that BSG is a valuable by-product of the brewing industry. Beyond its traditional use as animal feed, it offers several possibilities that both both industry and academic researchers should continue to explore. When choosing the most appropriate valorization technique for a brewery to adapt, proximity to upcycling avenues (i.e. cattle feed, composting facilities, anaerobic digestion facilities, biorefinery models, material or food production facilities) should be a key consideration. Furthermore, adherence to the hierarchy of solutions outlined in Figure 2 (to meet the UN Sustainable Development Goal 12.3) should guide BSG utilization practices, with a primary goal of diverting it from landfills whenever possible.

The research findings have demonstrated the stark contrast between landfilling BSG, which releases nearly 3 kg  $CO_2e$  per kg unprocessed BSG, and processing BSG into biochar at the lab scale, which results in lower emissions of 1.175 kg  $CO_2e$  per kg unprocessed BSG.

While BSG exhibits vast potential for integration into various industry sectors, it is imperative for researchers to assess its efficacy as a suitable replacement for conventional materials in production processes. Small-scale utilization may inadvertently impose a greater environmental burden than large-scale production of the traditional counterparts. Achieving a future where all BSG and food waste is repurposed along value chains will require substantial efforts in areas such as consumer education, governmental incentives, infrastructure changes, readjustment of

the job market, and other multifaceted undertakings. In the interim, it is crucial that researchers and developers focus on projects which can be seamlessly implemented into existing processing chains, ensuring scalability, and facilitating their adoption until a broader shift in infrastructure becomes feasible.

This research also determined that low-dosage ( $\leq 5$  moles per 100 g unprocessed BSG) of waste-caustic as a pretreatment method for biochar production from BSG is effective at improving desirable characteristics of the resulting biochar (mass recovered, liming potential, TOC, porosity). Specifically, to utilize this biochar for soil amendment, which is selective for alkaline samples, the recommended parameters are: 1 day of soaking BSG in caustic at a dosage rate of  $\leq 5$  moles per 100 g unprocessed BSG at ambient temperature, followed by draining of the liquid fraction, drying of the BSG until constant weight, grinding until uniform particle size, and pyrolysis at 700 °C with a heating rate of 5 °C/min, holding the sample for at least 1 hour of residence time with constant inert gas flow throughout the heating and cooling process. After cooling, the biochar is ready for application. The resulting biochar would be expected to have a mass recovery of 25-30% initial weight, a neutral pH of  $\sim 7.5$ , a Class 1 categorized liming potential (1-10%  $CaCO_3$  eq), a high TOC (70-73%) and consistent porosity.

Finally, for any valorization technique considered by a brewery, it is imperative that a GHGA or LCA is conducted prior to implementation. This will allow the researchers to ensure that the chosen recovery method imposes a lower environmental burden than alternative options. This practice is critical for realizing the full potential of BSG in circular economy practices.