Turning Brewery Waste into Paper: Brewer's Spent Grain as an Alternative Fiber in Sustainable Paper Innovation

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Brewer's spent grain is a significant byproduct of the brewing industry, composed mainly of cellulose, hemicelluloses, lignin, and polysaccharides (arabinoxylans). It is primarily used for agricultural purposes, such as animal feed. However, it also presents an alternative option as a substitute for wood cellulose in certain paper grades. This study investigates the strength contribution of mechanically macerated BSG at different amendment levels and evaluates its potential application in producing paper products. The tensile index decreased by 46% when 40% BSG was substituted. However, 20% of the tensile index was recovered through the addition of strength and retention aids. This indicates that BSG may be used in certain paper grades in combination with a suitable wet end chemistry package without significant degradation of mechanical properties.

Keywords: Brewer's spent grain, paper properties, physical properties, chemical composition

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INTRODUCTION

Brewer's spent grain (BSG) is the largest by product of the brewing process amounting to 85% of the total side streams[1,2]. Reinold reported that for every 100 liters of beer produced, 20 kg of spent grain can be separated from the wort[3]. In 2015, the market for beer in the United States was 141,379,804 barrels. Craft brewers accounted for 24,076,864 barrels[4]. That is 717,735 MT of BSG produced by Craft brewers or 17% of the total BSG. It is estimated that the total secondary market for spent grain is approximately 2.4 million tons[5]. According to the Brewers Association, the more than 2700 small, independent craft brewers in the United States provide this spent grain for use as animal feed to local farmers. However, due to the large volume of spent grain produced, a significant portion of it is often discarded as compost or sent to landfills[6].

Most of the innovations that brewers have undertaken involve burning the spent grain for energy or using it to make other edible products. These efforts are typically limited to individual craft brewers. BSG has the potential to be a high-value by-product that provides an environmental solution to landfill and brewery carbon footprints. There are opportunities to produce biofuels, as a filler in polymers, or use spent grains as a substitute for wood pulp in certain types of paper.[7,8,9,10,11].

Research has been conducted to evaluate the pulping of BSG, resulting in the successful production of a fiber slurry with potential for paper production[12]. Investigations have been conducted into the soda pulping of BSG. However, for this investigation, mechanical treatment was considered the simple and most economic treatment of the BSG for use as a substitute for wood cellulose. The resulting pulp is a mixture of cellulose, hemicellulose, lignin, and polysaccharides, as well as husks present in the BSG. Spent grain contains on a dry weight basis, approximately 15-18% cellulose,

24-31% hemicellulose, and 2-3% starch[13]. Lignin is another significant component representing approximately 10-28% of the weight[14].

The non-fibrous components of BSG can hinder the development of strength in the final paper sheet. To address this issue, BSG was mechanically treated to break down the larger components and increase the relative bonded area. An experimental design was used to evaluate the effect of different levels of BSG replacement on paper strength properties. This was followed by an evaluation of the wet end chemistry on the resulting optimal substitution level. The proposed approach can produce a suitable BSG based fiber substitute using low mechanical energy.

EXPERIMENTAL

Raw Materials

Brewer's spent grain (BSG) was obtained from Big Time Brewery, a local microbrewery located in the University District of Seattle, Washington and from North Idaho Mountain Brew, Wallace, Idaho. The BSG was washed multiple times with distilled water using a Williams Standard Pulp Testing Apparatus. Its moisture content was determined, and subsequently, the BSG was disintegrated in a laboratory disintegrator for one minute to break down larger components. The energy applied to the fiber to achieve sufficient breakdown of the BSG was 1.08 kJ/g OD. The Port Townsend paper mill in Port Townsend, Washington provided unbleached Northern softwood Kraft pulp. The softwood species used was a mixture of Douglas fir (*Pseudotsuga menziesii*) and Western Hemlock (*Tsuga heterophylla*). Cationic polyacrylamide (cPAM) was supplied by BASF, Florham Park, New Jersey. Poly-DADMAC was supplied by Aldrich Chemical. Sodium sulfate was obtained from Sigma Aldrich, St. Louis, MO, USA, CAS 7757-82-6.

Methods

Carbohydrate Composition

Brewer's spent grain contains cellulose, hemicellulose, lignin and monosaccharides. Samples were oven dried then treated in a laboratory mill fitted with a 40-mesh screen prior to digestion. The milled biomass residual was extracted with 150 ml of a 1:1 dichloromethane; acetone mixture according to TAPPI T204 cm-97[15]. 3.0 grams of biomass was weighed out and placed into a tared glass thimble. The BSG was extracted using a Soxhlet extraction apparatus equipped with an Allihn condenser for 24 hours.

The extracted solids were placed in an oven to dry. The oven dried sample was weighed in preparation for acid hydrolysis. A modified Klason method was used to determine the arabinose, galactose, glucose, xylose, and mannose content of the brewer's spent grain.[16,17]. To hydrolyze the biomass, 0.2g of it was mixed with 3.0 milliliters of 72% H_2SO_4 for 120 minutes. The samples were transferred to Wheaton serum bottles with a working volume of 200 mL, which were stoppered and crimp-sealed. After diluting them to 115 mL with deionized water, they were autoclaved at 121°C for 60 minutes[18].

The concentration of monomeric sugars (arabinose, galactose, glucose, xylose and mannose) was measured on a Dionex (Sunnyvale, CA, USA) high-performance liquid chromatography (HPLC, ICS-3000) system equipped with AS (auto sampler), ED40

(electrochemical detector), dual pumps and anion exchange column (Dionex, CarboPac PA1) according to ASTM method E1758-01[19]. Deionized water at 1.0 mL/min was used as eluent and post column addition of 0.2 M NaOH at a flow rate of 0.5 mL/min ensured optimal baseline stability and detector sensitivity. Ten microliters of each sample was injected after filtration through a 0.2 μm syringe filter (Restek Corp., Bellefonte, PA, USA). Standards were prepared containing arabinose, galactose, glucose, xylose and mannose to mirror the concentration range of the samples. Fucose was added to all samples as an internal standard for Dionex HPLC instrument to calibrate peaks[20,21]. Fucose was selected as the internal standard as it is similar to the sugars of interest and produces a peak that does not overlap with target sugars (EPA Test Method). A stock solution was produced at 5.0 mg/mL. Samples were diluted as appropriate, fucose was spiked at 0.870 mg/mL as an internal standard and filtered through 0.22 μm syringe filters (Restek Corp., Bellefonte, PA, U.S.). Sugar calibration standards were treated in the same manner as the samples.

The response of the target sugar was normalized to the response of the internal standard. The ratio of the target sugar peak area (A_S) to the internal standard peak area (A_{IS}) in each sample was compared to the ratio of the calibration standard peak area (C_S) to the internal standard peak area (C_{IS}) to determine the response factor, see Equation 1.

$$RF = (A_S * C_{IS})/(A_{IS} \& C_S). \quad (1)$$

Ash Determination

The percentage of ash was determined using ASTM D1102[22]. Empty crucibles were placed in a muffle furnace for two hours at 550 °C prior to use. They were then placed in a desiccator and allowed to cool to room temperature. The tare weight of each crucible was then determined. 1 gram of oven brewer's spent grain was placed in a crucible and covered. The contents were ignited in a muffle furnace at 600 °C for 3 hours. The crucibles were then removed and placed in a desiccator until cool to room temperature.

Moisture Content

Moisture content was determined by weight difference before and after heating at 105 °C for 4 hours for each raw material according to NREL 510[23]. Samples were placed in a desiccator prior to weighing and allowed to cool to room temperature.

Refining of Unbleached Softwood Kraft Pulp

Port Townsend pulp was analyzed in a fiber quality analyzer and the ratio of Douglas Fir to Western Hemlock was determined by microscopy. A Testing Machines Incorporated PFI (Papirindustriens Forskningsinstitutt) mill was used to produce a beater curve on the unbleached softwood pulp to establish the ideal refining level versus strength development in advance of scaling up for a pilot paper machine run according to TAPPI T248[24]. Five levels of refining were selected; 0, 2500, 5000, 7500, and 10,000 revolutions. 30g of unbleached softwood baled pulp was weighed out and disintegrated in a British disintegrator for each refining treatment. The resulting pulp slurry was drained and adjusted to a consistency of 10%. The force on the fibers by the beater roll is 3.33 N/mm of bar length. Freeness was determined according to TAPPI T227[25]. Temperature was measured and freeness adjusted accordingly.

Fiber Surface Charge

Fiber charge was determined using a Mutek particle charge detector, PCD04. The unit is a reciprocating piston inside a cylindrical plastic (PTFE) vessel, Figure 1. 10 mL of filtrate is place into the vessel where charged particles in the colloidal solution are adsorbed onto the cylinder and piston surface. The induced streaming potential is measured by electrodes in the plastic vessel that develop from the action of the piston. The filtrate sample is titrated with a cationic polyelectrolyte with known concentration and charge density such as DADMAC. The ionic charge of the filtrate has been neutralized when the streaming potential reaches zero. The amount of added cationic or anionic polyelectrolyte is used to calculate the charge density of the pulp slurry using equation 2.

$$q = V*c/m \quad (2)$$

Were q is the surface charge of the fiber [eq/g], V is the volume of the titrant [L], c is the concentration of the titrant [eq/L] and m is the solids content in the sample [g]. The net positive charge of the dissolved and colloidal substances (DCS) may originate from the dissociation of uronic type carboxylic groups in anionic hemicelluloses[26].

Brewer's spent grain may be either cationically or anionically charged colloidal material, composed primarily of cellulose, hemicellulose, lignin and polysaccharides suitable as a substitute for wood cellulose. "Charge Demand" has been defined as the amount of a high-charge polyelectrolyte required to neutralize the net ionic charge of dissolved and colloidal substances (DCS). The surface charge, as defined by Wagberg, of the brewer's spent grain, if not addressed, will adversely affect the performance of retention aid, sizing, and dry strength and fiber-fiber interactions[27,28].

Hand sheet Preparation

The difficulties inherent to the production of paper using brewer's spent grain (BSG) stem from the heterogeneous composition of this material, which comprises barley grain husk, pericarp, and pieces of endosperm. Hand sheets were produced initially with no wet end chemistry to isolate the contribution of the BSG and the interaction with the wood fibers. The electrical conductivity of the refined bleached softwood pulp was adjusted to 1000 µs·cm-1 using sodium sulfate prepared to a 1.0% solution in water according to a method described by Lenze**Error! Bookmark not defined.**. cPAM, prepared as a 0.25% solution in water, was added to the slurry at 0.05% (W/W), followed by an additional five minutes of agitation[29,30]. Hand sheets were produced to 60 $g \cdot m^{-2}$ according to the standard TAPPI procedure T205[31]. The hand sheets were wet pressed using an automatic sheet press.

Conditioning

Hand sheets were conditioned in a TAPPI humidity laboratory for 24 hours prior to testing at a relative humidity of 50 +/-2% and a temperature of 23 +/- 1 °C [32].

Physical Testing

Uniaxial tensile tests were performed using a Thwing Albert EJA 1760 following the standard TAPPI procedure T494[33]. Evaluation of tear resistance was completed using a CY708B (Jinan CYEEYO) tear tester according to TAPPI method T414[34]. Scanning

electron microcopy (SEM) images were obtained with a Sirion XL30 (ThermoFisher) scanning electron microscope operated at 5 kV. Before SEM observation, all samples were platinum-sputtered using an EM ACE600 (Leica) to a depth of 4 nm.

Experimental Design

Four levels of brewer's spent grain substitution by weight were evaluated; 0%, 40%, 50%, and 60%. The intent was to maximize the displacement of wood cellulose while maintaining sufficient sheet properties to allow processing on a pilot paper machine. Ten hand sheets were produced at each substitution level. Determinations were carried out in triplicate.

RESULTS AND DISCUSSION

Composition

The total polysaccharide content of the BSG, shown in Table 1, proved to reflect the raw biomass used in producing beer (43–46%)[35,36]. The lignin content ranged from only 20–21%.

Table 1. Brewer's spent grain acid hydrolysis composition data. (95% confidence interval shown)

Sugar	Percentage Composition
Arabinose	5.41% +/-0.18
Galactose	0.65% +/-0.01
Glucose	26.69% +/-0.46
Xylose	11.45% +/-0.57
Mannose	0.46% +/-0.14
Total Sugars	44.65% +/-1.29
Acid Insoluble Lignin	12.67% +/-0.35
Acid Soluble Lignin	7.96% +/-0.17

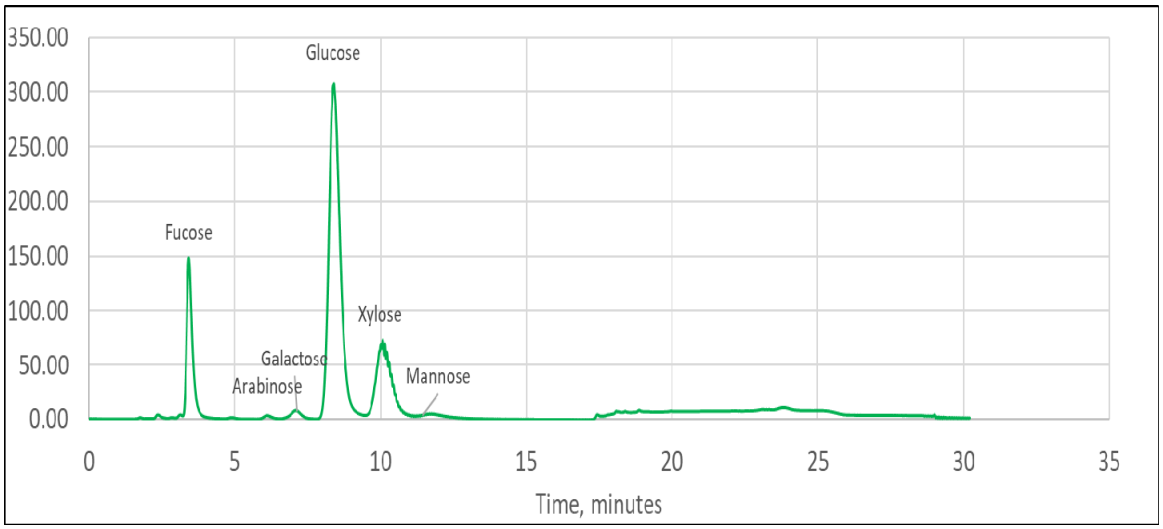

Figure 1. HPLC graph of sugars in hydrolysis sample

The pulp was determined to be 30% Douglas Fir and 70% Western Hemlock with a length weighted fiber length of 2.34 mm, see Figure 2a. The percentage of fines was 5.45%. Based on the refiner curve, the Port Townsend pulp was refined to a Canadian standard freeness target of 450 giving a tensile index of 44 N-m/g for this preliminary investigation.

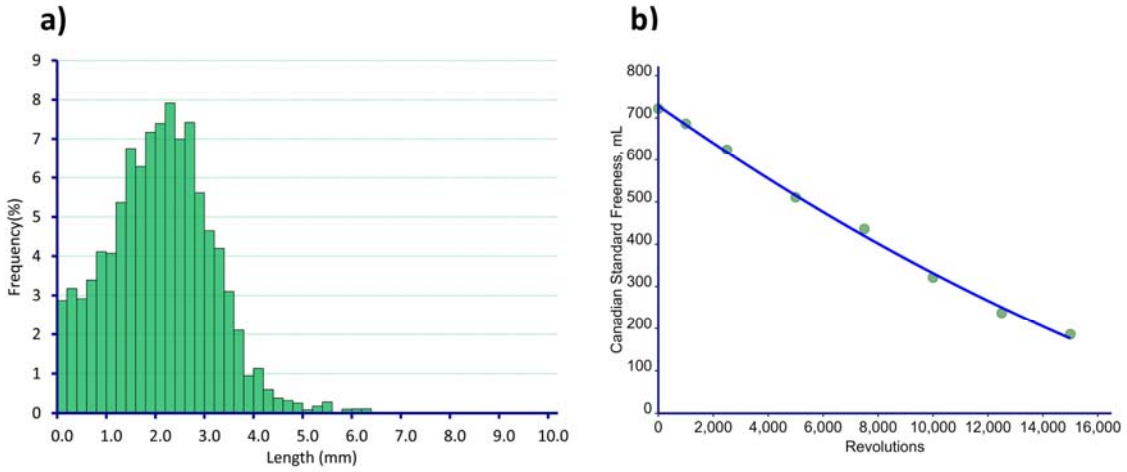

Figure 2 a) Fiber quality analysis showing length weighted average fiber length of softwood pulp, b) PFI revolutions versus Canadian standard freeness.

The cationic charge density of BSG was found to be significantly higher than that of unbleached wood pulp. Lignocellulosic biomass usually has anionic surface charge attributed to the dissociation of carboxylic acid functional groups[37]. This negatively impacted the formation of bonds between wood fibers and BSG components and adversely impacted the adsorbtion of polyelectrolytes between the fibers in initial hand sheet forming. The BSG was washed with deionized water to reduce the dissolved charge. Subsequently, the electrical conductivity of the refined unbleached softwood pulp and BSG slurry was adjusted to 1000 µs/cm through the addition of sodium sulfate.

At the 40% weight percentage of BSG, the tensile index relative to the unsubstituted sheet dropped by 46.2%. Increasing the content of BSG to 50% by weight resulted in an additional 10% decrease in tensile index and the variation in sheet stability increased. The loss in tensile index was linear up to 60% substitution, see Figure 3a. At the 60% substitution level, sheet integrity was compromised as physical handling resulted in rapid failure of the paper.

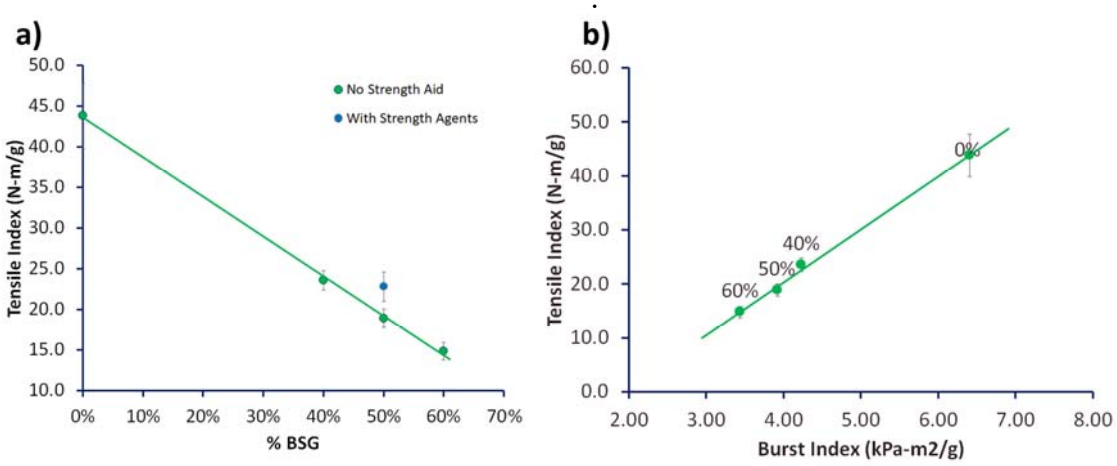

Figure 3 a) Tensile index at varying BSG substitution levels and with retention aid. b) Tensile index versus burst index at each substitution level.

Burst index followed a similar but less dramatic trend. At 40% substitution, burst index declined by 34%, but only an additional 5% reduction as the mass of brewer's spent grain was increased to 50%. Figure 3b displays a plot of tensile index versus burst index

Table 2. Average Tensile and Burst index at varying substitution levels. (95% confidence interval shown)

% Composition	Tensile Index N-m/g	Burst Index (kPa-m2/g)
0%	43.8 +/-3.9	6.41 +/-0.60
40%	23.6 +/-1.2	4.23 +/-0.20
50%	18.9 +/-1.1	3.92 +/-0.20
60%	14.8 +/-1.1	3.44 +/-0.29
50% w/chem	22.8 +/-1.8	5.09 +/-0.22

The tensile energy absorption (TEA) for the BSG-amended hand-sheet is lower for a given amount of stretch. This indicates that the extensibility and inter-fiber bonding fibers developed during refining has been reduced by the addition of BSG[38]. A plot of the normalized stretch as a function of normalized TEA (N-m/g) (Figure 4) was found to have proportionality factors of 1.16 and 1.28. Typical proportionality factors for unbleached pine range from 1.31 to 1.39[39]. The linear relationship between TEA and the product of tensile strength and stretch depicted in Figure 4 is consistent with other reports in the literature[40]. The addition of retention aid did not offset the reduction in TEA.

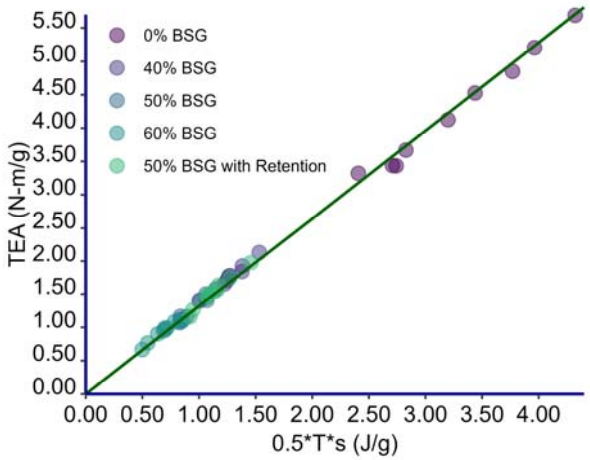

Figure 4. TEA Index versus the product of tensile index and stretch for BSG amended hand-sheets.

Scanning electron micrographs of the dried sheet at 40% substitution demonstrate the relative size difference between wood fibers and the brewer's spent grain components.

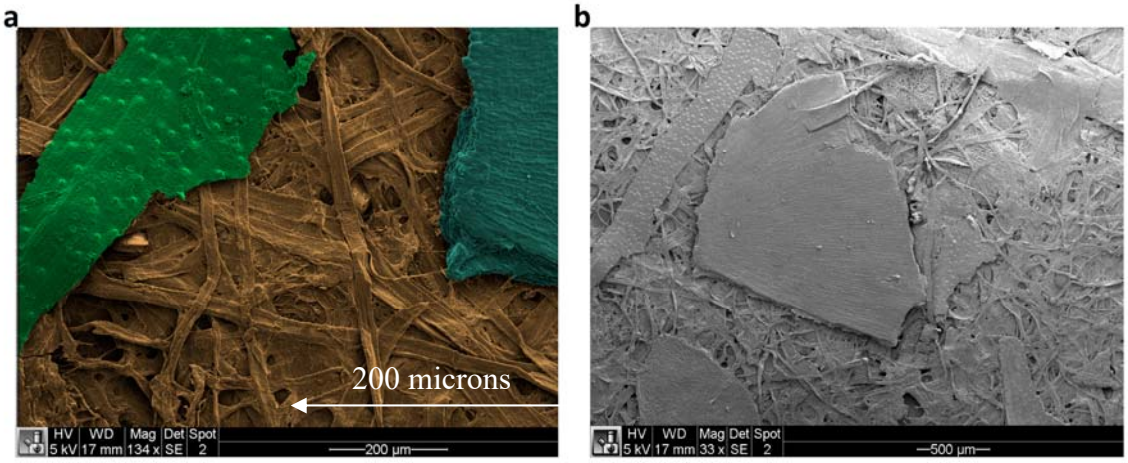

Figure 5 a) SEM of hand sheet with 40% BSG –magnification 134x, b) magnification 33x.

CONCLUSIONS

1. Above 40% substitution, homogeneity of the hand sheet produced was too variable to provide reproducible results. At a 40% substitution level, paper performance was adequate to exceed the minimum bursting strength specifications for a 60g/m^2 sheet of 60kPa.
2. The minimum tensile requirement for bond paper was not met by the base paper. It was 1.4kN/m versus the required 1.7kN/m. Addition of strength aid was shown to offset this[41].
3. Brewer's spent grain does provide a suitable material to displace wood fiber at or below 40% addition provided sufficient pre-treatment is performed to deal with the

colloidal charge present and wet end chemistry is applied to improve strength characteristics. The hand feel and appearance of the sheet may limit the extent of its' application to artisan type papers.

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