Utilization of brewery residues to produces granular activated carbon and bio-oil

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A B S T R A C T

Brewer's spend grain (BSG) and brewer's surplus yeast (BSY) are the main by-products from the brewery industry. The substantial production of these by-products contributes to economic losses in the production process, and may contribute to environmental problems if their proper disposal is not given. In this research, BSG and BSY were used as a novel precursor for the production of bio-oil and a low-cost granular activated carbon (GAC) via pyrolysis and CO_2 activation in one-step and two-step. The effects of the production variables, such as BSG:BSY mass ratio and activation time on yield and the some textural properties were investigated. Pyrolysis of briquettes yielded 19%, 56% and 25% charcoal, liquid and gas, respectively. The liquid product showed two phases: aqueous and organic (bio-oil). The bio-oil was similar to other biomass-derived bio-oils, but with a pH of 7.45 and a calorific value of 31.26 kJ g^{-1}. Surface area and pore volume of GAC increased as activation time increased. Six hours of activation produced GAC with a specific surface area of 617.4 m^2 g^{-1}, a total pore volume of 0.2316 cm^3 g^{-1} and good adsorption of iodine and methylene blue. The GAC and bio-oil produced by one-step and two-step processes were similar. Thus, the reuse of BSG and BSY can provide an important advantages and benefits as the generation of value-added products (GAC and bio-oil), more jobs and solutions to pollution problems.

1. Introduction

Beer is the most commonly consumed alcoholic beverage in the world, and a total volume of 188.64 billion litres was produced in 2015. The largest beer producers are China (42.99 billion litres), the United States (22.28 billion litres) and Brazil (13.86 billion litres) (Kirin Holdings, 2016). Beer production generates large quantities of residue and by-products due to the large production volume (Ferreira et al., 2010). Brewer's spend grain (BSG), or malt bagasse, the barley malt residue that remains after preparation of the wort, is the main by-product of breweries; approximately 20 kg are generated for every 100 L of beer produced (Mathias et al., 2014). Residual yeast (brewer's surplus yeast, BSY), *Saccharomyces* sp., is the second largest by-product of the brewing industry; in the process, between 1.5 and 3 kg of yeast cells (with 85–90% moisture) are generated per 100 L of beer produced (Mathias et al., 2014). The

disposal of these by-products often presents environmental problems, and the by-products are primarily reused as animal feed. BSG and BSY are available year-round at a relatively low cost and can serve as raw materials for the production of other value-added products (Mussatto et al., 2006). Several studies have shown that these by-products can be used in food and animal feed, in energy production, for products of industrial interest, and in the development of biotechnological processes (Mussatto et al., 2006; Mussatto, 2014; Klímek et al., 2017).

However, the thermochemical conversion of these by-products has received little attention. Thermochemical biomass conversion processes, including pyrolysis, combustion, gasification and liquefaction, are used to generate energy and produce biofuels, chemicals and char (Miranda et al., 2012). According to Özçimen (2013), bio-oil produced by biomass pyrolysis is renewable and can be used as a source for production of high-quality chemicals, or as an alternative fuel following purification and improvement. Char, the solid residue of pyrolysis, can be used as a solid fuel for energy generation (Mahmood et al., 2013). In addition, char can be activated using physical or chemical agents for production of activated carbon. Activated carbon is an adsorbent used by various industries

in multiple processes for the separation and purification of products and for the treatment of liquid effluents and gaseous emissions (Montané et al., 2005).

The reuse of these two main by-products using pyrolysis can contribute to cleaner production by reduce the environmental impact of brewery industry, as well as by reducing the final disposal costs and by adding value via conversion into bio-oil and activated carbon (Amaya et al., 2007). However, production of bio-oil and activated carbon from brewery by-products has not been reported in the literature.

In this study, the brewery residues BSG and BSY were used as a novel precursor for the production of a low-cost granular activated carbon (GAC) and bio-oil from an innovative and sustainable approach.

2. Material and methods

2.1. Raw materials

The moist BSG and BSY used in the pyrolysis and activation experiments were provided by a brewery in the western region of Paraná, Brazil. To extend the shelf life of the raw materials, the BSG was oven-dried at 105 °C with air circulation (Solab - model SL. 102/125) until its moisture content was <10%, and then placed in plastic recipient for storage. The BSY was homogenised, packed in plastic bags and then stored in a vertical freezer (Bosch - model IF 32) at a temperature of −5 °C ± 2 °C.

The moisture content of the biomass was determined according to the ASTM D3173. The samples were oven-dried (Solab - model SL. 102/125) at 105 °C until they reached a constant weight, and their moisture content was calculated from the mass loss of the samples. The ash content was determined according to the ASTM D3174. The samples were subjected to calcination at 750 °C in a muffle furnace (Fornitec - model HW1000), and the mass of the residue obtained represents the percentage of ash. The fixed carbon and volatile contents were determined according to the ASTM D3175 and ASTM D3172, respectively. All experiments were performed in triplicate.

2.2. Pyrolysis/activation equipment

A schematic representation of the experimental module used to perform pyrolysis and activation of BSG and BSY briquettes is presented in Fig. 1.

The module consisted of an electric muffle furnace with temperature control, a stainless steel reactor (75 mm in diameter and 300 mm in height) within which the BSG and BSY briquettes or the charcoal to be activated were placed, and a system for injecting and controlling gas flow (N_2 and CO_2) composed of gas cylinders, pressure regulating valves and a flowmeter. Temperature was controlled via the type K thermocouple placed together with the sample. Kitasatos flasks and a condenser cooled with room-temperature tap water were used for cooling and collection of condensed gases (bio-oil).

2.3. Preparation of BSG and BSY briquettes

The BSY was thawed until it reached room temperature and then centrifuged for 5 min in a centrifuge (ITR - model simplex II), with a rotation speed of 1100 rpm to separate the aqueous fraction.

The briquettes were produced using various mass ratios of BSG:BSY (1:0, 1:0.5, 1:1 and 1:1.5). BSG and BSY were mixed and press-molded in a stainless-steel cylinder (1.5 cm in diameter and 5.0 cm in length) using a laboratory press (Specac - model GS15011). A pressure of 566 $kg_f \cdot cm^{-2}$ was applied to the cylinder contents for 1.0 min to form briquettes with 1.5 cm in diameter and 1.5 cm in length.

The high moisture content of the mixture BSG and BSY 1:1 and 1:1.5 made briquette formation difficult; thus, the samples were pre-dried for 2–3 h at 105 °C for production of briquettes.

2.4. Two-step production of bio-oil and activated carbon using various proportions of BSG and BSY

In the two-step process, the first step involved pyrolysis of briquettes, which were prepared using various mass ratios of BSG:BSY (1:0, 1:0.5, 1:1 and 1:1.5). Approximately 100 g of moist briquettes were placed in the reactor and inserted into the oven. N_2 was injected into the reactor at a flow rate of 150 mL min^{-1} to produce an inert atmosphere. Samples were heated at a rate of 10 °C·min^{-1} until a temperature of 850 °C was reached, and samples were held at this temperature for 1 h. The mixture of condensed gases produced was cooled and collected in two Kitasatos flasks. Following pyrolysis, the reactor was removed from the oven and the charcoal briquettes were cooled with a flow of N_2 (150 mL min^{-1}) until the interior of the reactor reached a temperature below 100 °C. The reactor and charcoal briquettes were then weighed. The percentage yields of charcoal, pyrolytic liquid and uncondensed gases were determined according to equations (1)–(3), respectively.

$$Charcoal\ Yield\ (\%) = \left(\frac{m_{charcoal}}{m_{briquettes}} \right) * 100 \qquad (1)$$

$$Liquid\ Yield\ (\%) = \left(\frac{m_{liquid}}{m_{briquettes}} \right) * 100 \qquad (2)$$

$$Gases\ Yield\ (\%) = 100 - Charcoal\ Yield\ - Liquid\ Yield \qquad (3)$$

For the second step, activation, approximately 50 g of charcoal briquettes, which had previously been oven-dried at 105 °C for 12 h, were transferred to the reactor and heated at a rate of 10 °C·min^{-1}, under 150 mL min^{-1} N_2 flow, until it reached a temperature of 850 °C. At this point, the gas flow was changed to CO_2 (100 mL min^{-1}) and the samples were subjected to 2 h of activation. After the activation time, the gas flow was returned to N_2 (150 mL min^{-1}), and the samples were cooled until the interior of the reactor reached a temperature below 100 °C. The percentage of mass loss of the samples due to activation (burn-off grade) and the yield of activated carbon were calculated according to equations (4) and (5), respectively.

$$Burn - off\ (\%) = \left(\frac{m_{charcoal} - m_{activated\ carbon}}{m_{charcoal}} \right) * 100 \qquad (4)$$

$$Activated\ Carbon\ Yield\ (\%) = \left(\frac{m_{activated\ carbon}}{m_{briquettes}} \right) * 100 \qquad (5)$$

The activated carbon briquettes were ground and sieved to produce granules of 0.6 mm–2.0 mm. The GAC samples produced from the various ratios of BSG:BSY are referred to as CA1:0; CA1:0.5; CA1:1 and CA1:1.5.

2.5. Two-step production of bio-oil and activated carbon using various activation times

Twelve batches of pyrolysis of briquettes (BSG:BSY mass ratio of 1:1) were realized using the equipment and pyrolysis parameters described in the previous section. The yields of charcoal, pyrolytic