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Microwave-assisted carboxymethylation of cellulose extracted from brewer's spent grain

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ABSTRACT

Cellulose was extracted from brewer's spent grain (BSG) by alkaline and bleaching treatments. The extracted cellulose was used in the preparation of carboxymethyl cellulose (CMC) by reaction with monochloroacetic acid in alkaline medium with the use of a microwave reactor. A full-factorial 2^3 central composite design was applied in order to evaluate how parameters of carboxymethylation process such as reaction time, amount of monochloroacetic acid and reaction temperature affect the average degree of substitution ($\overline{DS}$) of the cellulose derivative. An optimization strategy based on response surface methodology has been used for this process. The optimized conditions to yield CMC with the highest $\overline{DS}$ of 1.46 follow: 5 g of monochloroacetic acid per gram of cellulose, reaction time of 7.5 min and temperature of 70 °C. This work demonstrated the feasibility of a fast and efficient microwave-assisted method to synthesize carboxymethyl cellulose from cellulose isolated of brewer's spent grain.

1. Introduction

Carboxylmethylcellulose is the most widely used cellulose ether today, with applications in paper, textile, pharmaceutical, food exploration and paint industries (Singh & Khatri, 2012). Production of carboxymethyl cellulose is carried out commercially on a large scale, by the slurry process and includes two steps; first, cellulose fibers are swollen in concentrated NaOH solution then, still under conditions, the hydroxyl groups of cellulose react with the monochloroacetic acid (MCA) (Bhandari, Jones, & Hanna, 2012; Heinze & Koschella, 2005).

The etherification processes commonly employed for the production of carboxymethyl cellulose require temperature between 40 and 80° C and long reaction time (1–6 h) (Cheng & Biswas, 2011; Heinze & Koschella, 2005; Singh & Khatri, 2012). Under these conditions, the occurrence of side reactions, such as depolymerization of cellulose and the formation of sodium glycolate, negatively affect both the yield of the process and the characteristics of the derivatives obtained, and the development of conversion processes that minimize the occurrence of side reactions, the reaction time and amount of reagents employed and energy is very important.

In recent years, microwave chemistry has become increasingly popular within the organic synthesis (Gawande, Shelke, Zboril, & Varma, 2014; Moseley & Kappe, 2011). Compared with conventional heating, microwave-assisted heating, under controlled conditions, has been shown to be an advanced technology in reducing reaction time besides increasing product yield and purity (Caddick & Fitzmaurice, 2009; Nuchter, Ondruschka, Bonrath, & Gum, 2004; Zhu & Chen, 2014). Microwave irradiation–assisted synthesis and modification has been widely used in chemical functionalization of polymer materials. It has been developed for cellulose modification processes including acetylation (Li et al., 2009) and carboxymethylation (Biswas, Kim, Selling, & Cheng, 2014). Therefore, microwave irradiation is a promising method to modify the physical–chemical properties of cellulose.

Most of the sources of cellulose that were modified to carboxymethyl cellulose are wood and cotton (Singh & Singh, 2013). However, many others resources could be used such as corn cobs (Singh & Singh, 2013), rice straw (Ragheb, Nassar, Abd El-Thalouth, Ibrahim, & Shahin, 2012), cotton by-products (Cheng & Biswas, 2011), cavendish banana pseudo stem (Adinugraha, Marseno, & H, 2005), however none of them uses the brewer's spent grain (BSG) as a cellulose source.

Brewer's spent grain is the main solid by-product generated in the brewing process. Approximately 15–20 kg of BSG is produced

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per every hectolitre of beer, which corresponds to an annual production of more than 34 million tons of wet BSG (8.5 million tons of dry BSG) (Mussatto, Dragone, & Roberto, 2006; Xiros & Christakopoulos, 2012). This material is composed of the barley malt residual constituents and includes the barley grain husk in the greatest proportion, and also minor fractions of pericarp and fragments of endosperm (Forssell et al., 2008).

BSG is rich in cellulose (16–21%), hemicellulose (15–29%), lignin (19–28%) and proteins (24–39%) (Meneses, Martins, Teixeira, & Mussatto, 2013; Mussatto, Rocha, & Roberto, 2008; Pires, Ruiz, Teixeira, & Vicente, 2012). Some recent studies suggest the possibility of reusing this material for industrial applications such as the production of activated carbon (Poerschmann et al., 2014), ethanol (Forssell et al., 2008) and xylitol (Mussatto & Roberto, 2008), but BSG is still traditionally used as a relatively low value cattle feed (Niemi, Martins, Buchert, & Faulds, 2013). So, there is a need to find new value-added end-uses for this by-product.

The aim of this work was to increase the economic value of brewer's spent grain by the extraction of the cellulosic component from this by-product through chemical methods. The obtained cellulose was used in the preparation of carboxymethyl cellulose, which has many important industrial applications. Carboxymethyl cellulose was obtained through reaction of the extracted cellulose with monochloroacetic acid in alkaline medium employing microwave reactor.

2. Materials and methods

2.1. Materials

Brewer's spent grains (BSG) were supplied by Ambev, S.A. (Anápolis, Goiás, Brazil). As soon as obtained, the material (approx. 80% moisture content) was dried at 105 °C to 94% dry matter. Then the dried BSG was milled using a knife mill fitted with a 1 mm-sized grating and used in all experiments. Sodium chlorite ($NaClO_2$), monochloroacetic acid (MCA), sodium hydroxide and isopropanol were obtained from Sigma-Aldrich. All of the other reagents were analytical grade and were used without further purification.

2.2. Cellulose extraction from Brewer's spent grains (BSG)

2.2.1. Alkaline treatment

Initially, the dried BSG was treated with a 2% (w/w) sodium hydroxide aqueous solution in a solid:liquid ratio of 1:20 (w:v) for 2 h at 90 °C, as reported by Mussatto et al. (2006b) with some modifications. The obtained black slurry was filtered and the solid material was washed several times with distilled water until the alkali was completely removed, and dried at 50 °C for 12 h in an air-circulating oven. The yield was calculated based on the dried solid product weight and the starting weight.

2.2.2. Bleaching process

After the alkali treatment, the fibers were treated with a solution made up of equal parts (v:v) of acetate buffer and aqueous sodium chlorite (2 wt% $NaClO_2$ in water) in a solid:liquid ratio of 1:50 (w:v) for 4 h at 80 °C. Then the mixture was allowed to cool and was filtered using excess distilled water until the pH of the fibers became neutral. The bleached fibers were dried at 50 °C for 12 h in an air-circulating oven. The bleaching process was carried out in a single step. The yield was calculated based on the dried solid product weight and the starting weight.

2.3. Preparation of carboxymethyl cellulose (CMC)

Synthesis of CMC was carried out in two steps i.e., alkalization and etherification under heterogeneous conditions. Alkalization was conducted into glass reaction vessels with an internal volume 35 mL as follows: bleached cellulose (0.5 g) was suspended in isopropanol (2 mL) and 2 mL of 40% (w/v) aqueous NaOH was added dropwise under magnetic stirring at room temperature over a period of 15 min.

The etherification was carried out in a monomode microwave reactor (Discover-SP DC-7196, CEM, USA). The desired amount of monochloroacetic acid (MCA) was dissolved in 2 mL of isopropanol. The mixture was subjected to microwave irradiation at 200 W up to the desired temperature (70–90 °C) and stirred at that temperature for the desired duration (2.5–7.5 min). When the irradiation was complete, the slurry was neutralized with glacial acetic acid and then filtrated. The solid obtained as CMC was washed with 70% ethanol for four times to remove undesirable by-products. The obtained cellulose derivative (CMC) was dried at 60 °C in an oven.

For the purification of these derivatives, 1.5 g of the sample was dissolved in 750 mL of aqueous 0.4 mol L^{-1} NaCl. The resulting solution was submitted to positive filtration through 0.45 μm membrane (Millipore®) and the carboxymethyl cellulose was precipitated upon addition of ethanol. Subsequently, the carboxymethyl cellulose was sequentially washed with ethanol/water mixtures of increasing ethanol content (70%, 80%, and 90%), with absolute ethanol and then it was dried at room temperature. This procedure resulted in purified sodium carboxymethyl cellulose samples.

Table 1
Uncoded and coded levels of the independent variables of the carboxymethylation process.

Independent variables	Symbol	Levels		
		−1	0	1
Time (min.)	X_1	2.5	5	7.5
MCA/celullose (g/g)	X_2	2	3.5	5
Temperature (°C)	X_3	70	80	90

2.4. Experimental design

A full-factorial 2^3 central composite design was employed to analyze the main effects and interactions of the following variables: reaction time, amount of monochloroacetic acid (MCA) per gram of cellulose and reaction temperature on the average degree of substitution ($\overline{DS}$). The independent variables and their levels are shown in Table 1. Maximum and minimum treatment levels were chosen by carrying out preliminary screening tests. Each experiment was performed in triplicate.

2.5. Characterization of brewer's spent grain fibers and carboxymethyl cellulose

2.5.1. Chemical composition of brewer's spent grain fibers

The chemical composition of the BSG at each stage of treatment was measured as follows: the holocellulose (α-cellulose + hemicellulose) and cellulose content were estimated according to standard methods (Browning, 1967). The α-cellulose content was determined treating the holocellulose with potassium hydroxide solutions (Browning, 1967). The hemicellulose content was found by subtracting the α-cellulose part from the holocellulose content. The lignin content was determined according to a standard method of Technical Association of Pulp and Paper Industry TAPPI T222 om-88. The viscosity of pulp (cP) dissolved in a cupriethylene-diamine solution was determined according to Tappi standard (T230 om-99). An average of three measurements was calculated for each sample.