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Integration of chlorogenic acid recovery and bioethanol production from spent coffee grounds

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ABSTRACT

Spent coffee grounds (SCG) are an abundant by-product of the coffee industry with a complex composition that makes them a promising feedstock for a biorefinery. The objective of this study was to evaluate SCG as a substrate for combined chlorogenic acid and bioethanol production after dilute acid hydrolysis. The effect of phenolics extraction on the downstream process was evaluated exhibiting no loss of sugars and an increase in the sugar release efficiency during the dilute acid hydrolysis. In order to suggest an economically feasible process, phenolics extraction and dilute acid hydrolysis prior to ethanol fermentation were optimised by means of experimental design. The responses of the designs were not only the efficiencies of the processes, but also a balance between product recovery and estimated costs. In both cases, decreased efficiencies obtained with low liquid-solid ratios were countervailed by increased products concentrations and higher economical performance. Under the optimised conditions, the purity of the phenolics extract (32%) could allow it to enter the market as a dietary supplement of chlorogenic acid, a product with high trade value. Moreover, a concentration of 3.9% (w/v) ethanol was reached upon fermentation of the hydrolysate of SCG after extraction and dilute acid hydrolysis.

1. Introduction

Around 8.6 million tonnes of coffee were produced in 2014 [1], making it a very important global commodity. Throughout the production of the coffee, several types of waste are generated including spent coffee grounds (SCG), obtained after brewing the coffee beans both for direct consumption and for production of instant coffee. Given that around 2 kg of wet SCG are generated per each Kg of coffee processed [2], the magnitude of this by-product is remarkable. Since the 1980s, combustion is the most common way to utilise spent coffee grounds, given its high calorific value [3]. However, the composition of SCG (Table 1), which is rich in carbohydrates, lipids and phenolic compounds, has motivated an increasing interest to develop processes in order to exploit the various fractions of this residue and add more value to the production chain [2,4].

Almost 50% of the SCG dry mass corresponds to carbohydrates and most of them are hexose sugars as part of the hemicellulosic material (mannose and galactose) (Table 1). This constitutes a great advantage over other lignocellulosic substrates given that most of the easily biodegradable sugars can be released in a single step using mild pre-treatments such as dilute acid hydrolysis. First attempts on testing spent coffee grounds as feedstock for bioethanol production have been recently documented [8,13–15].

Green coffee beans are an important source of phenolics compounds (Table 1), with chlorogenic acids being the most abundant family. Its main representative is 5-*O*-caffeoylquinic acid (5-CQA), which the denomination chlorogenic acid (CGA) generally refers to. This compound has potential applications as antioxidant, food preservative and various medical treatments [16]. Moreover, it has already a commercial application in the form of weight loss dietary supplements containing green coffee beans extract such as Svetol® [17].

Given that part of the phenolic compounds are still present in spent coffee grounds this residue has been suggested

Abbreviations: CGA, chlorogenic acid; CGA eq., chlorogenic acid equivalents; CQA, caffeoylquinic acid; HMF, hydroxymethylfurfural; HC_H, high concentrated hydrolysate; LC_H, low concentrated hydrolysate; HC_S, high concentrated slurry; LC_S, low concentrated slurry; L/S ratio, liquid-solid ratio; SCG, spent coffee grounds; SCG^{E}, spent coffee grounds after phenolics extraction; SCG^{H}, solid fraction of spent coffee grounds after phenolics extraction and dilute acid hydrolysis; TSS, total suspended solids; TS, total solids; VS, volatile solids; WIS, water insoluble solids.

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Table 1
Main reported components of green coffee beans and spent coffee grounds. References are provided in brackets.

(Dry matter%)	Green coffee bean	Spent coffee grounds
Carbohydrates	48–61 [5,6]	45–47 [7,8]
Cellulose	7.8 [6]	8.6–9.0 [7,8]
Hemicellulose	40 [6]	37–38 [7,8]
Mannose	22 [6]	23–26 [7,8]
Galactose	12 [6]	15 [7,8]
Arabinose	4 [6]	1.4–1.9 [7,8]
Lipids	10–16 [5]	9–16 [9]
Proteins	10 [5]	13–17 [7,9]
Total polyphenols	<14 [10]	1.7–3.5 [11]
Chlorogenic acids	4–14 [5,10,12]	0.1–0.8 [9,11]
Caffeine	1–2 [5,12]	0.5–1.2 [9,11]

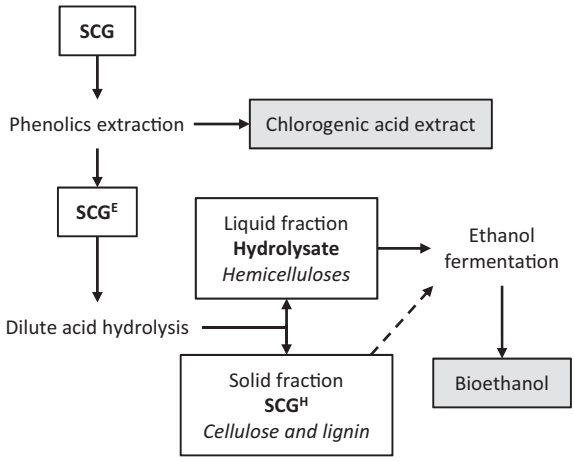

Fig. 1. Process scheme. Spent coffee grounds (SCG) were used for phenolics extraction obtaining a liquid chlorogenic acid extract. The solids (SCG^E) were then treated with dilute sulphuric acid hydrolysis and the liquid hydrolysate was used in ethanol fermentation. Solids after dilute acid hydrolysis (SCG^H) were incorporated in the fermentation in some of the experiments, denominated slurry fermentations.

as a sustainable alternative for phenolics extraction, already tested in laboratory scale using different methods [4] such as liquid-solid extraction [16,18–22], Soxhlet extraction [20] and microwave-assisted extraction [23]. From those methods, liquid-solid extraction arises as a simple and effective method [18,20], and was thus chosen herein.

This study investigates the possibility of producing chlorogenic acid and bioethanol in a biorefinery scheme (Fig. 1). After extraction of chlorogenic acid, the remaining solids underwent acid hydrolysis to release the hemicellulose sugars, which were further fermented into bioethanol. With this strategy, both the phenolics and the carbohydrate fraction would be exploited. Moreover, the inclusion of a high value product could contribute to the economic viability of bioethanol production from SCG.

First of all, the effect of the extraction process on the dilute acid hydrolysis was studied, focusing on the possible loss of sugars and the effect of the sugar release efficiency. Then, both the extraction and the dilute acid hydrolysis were studied using experimental design methodology. In both cases, the objective was not only to study the effect of the different parameters on the efficiency, but to suggest values that would be reasonable from an economic point of view. Special focus was put on the liquid-solid ratio, as a factor dramatically affecting the product concentration and the downstream costs. Thus, an additional response balancing the product recovery and the expected income with the estimated process costs was calculated and the model arising from it was used to choose the parameter values.

The recovery efficiency was validated with the chosen values of the parameters and the concentration and purity of the products (chlorogenic acid and ethanol) discussed.

2. Materials and methods

2.1. Biomass

Spent coffee grounds (SCG) were obtained from a coffee machine Wittenborg model 7100 B2C. The coffee was a mixture of Arabica roasted coffees provided by Frellsen Kaffe (Frellsen Rød). Noteworthy to say, two batches of SCG were utilised throughout the experiments. Characterisation of the first batch (used in Section 3.1) was the following: TS: 46.6% (w/w), total sugars: 42.0 g/100 g TS (% of the total sugars: glucose 17.0% and hemicelluloses 83.0%). For the second batch (used for Sections 3.2 and 3.3), the figures were: TS: 45.9% (w/w), total sugars: 50.1 g/100 g TS (% of the total sugars: glucose 17.5%, hemicelluloses 82.5%, mannose 57%, galactose 20% and arabinose 5%).

2.2. Analytical methods

Total solids (TS), volatile solids (VS) and total suspended solids (0.7 μm) (TSS) were determined as described in Sluiter et al. [24]. Total structural sugars of biomass were determined in duplicate with the protocol described in Sluiter et al. [25]. Soluble sugars content in the liquid fraction was assessed by dilute acid hydrolysis according to Bjerre et al. [26]. HPLC analysis of sugars, ethanol, furfural and hydroxymethylfurfural (HMF) was done as reported in Baroi et al. [27]. Noteworthy, peaks for mannose and galactose overlapped in the HPLC chromatogram and were discriminated using an independent assay (Megazymes K-ARGA).

Total phenolic content of the extracts was estimated by the Folin Ciocalteu method using the proportions described in Pinelo et al. [19], but with a total volume of 200 μL in 96 well plates. Readings were done at 765 nm after two hours of incubation and by mixing 200 μL of the reaction with 800 μL of water. In specific experiments, absorbance at 325 nm was also used as indicative of chlorogenic acid concentration [28]. Chlorogenic acid (5-*O*-caffeoylquinic acid) was used as standard for both assays. Samples were analysed using technical duplicates.

2.3. Effect of chlorogenic acid extraction on the downstream processes

The experimentation included three main steps: extraction, hydrolysis and fermentation. Extraction was carried out at 70 °C using 40 g of raw SCG with a liquid-solid (L/S) ratio of 25 mL solvent/g TS. Ethanol 60% (v/v) was used as a solvent. After extraction, solid-liquid separation was done by vacuum filtration (Whatman 1003-185) and the cake was washed with 150 mL of distilled water and dried overnight at 45 °C to remove residual solvent. Free and soluble sugars in the extracts were quantified to evaluate sugar loss during this step.

Hydrolysis was performed both on extracted SCG (SCG^E) (TS 95% w/w) and non-extracted SCG (TS 46.6% w/w) for comparison purposes. The procedure was done as optimised in Mussatto et al. [7] with some modifications: 1% H_2SO_4 (w/w) with a liquid-solid (L/S) ratio of 10 g liquid/g TS and 45 min at 140 °C in the autoclave.

The liquid hydrolysates obtained after solid-liquid separation (vacuum filtration Whatman 1003-185) were analysed for sugars concentration and total phenols (Folin Ciocalteu) and the sugar release efficiency was calculated as g sugar released per gram of dry SCG/SCG^E based on the sugar compositional analysis of both solids. The different moisture contained in the solids was taken into account for the calculations. As a clarification, the hydrolysate