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Research article

Use of trace elements addition for anaerobic digestion of brewer's spent grains

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ABSTRACT

The brewery industry generates a large amount of by-products and notably Brewer's Spent Grain (BSG) which seems an attractive substrate for anaerobic digestion. Nevertheless, previous studies have shown risk of inhibition in the mono-digestion of lignocellulosic substrates. One way to stabilize the reaction is the addition of trace elements. The current study evaluates and compares the stability of BSG anaerobic mono-digestion with and without addition of trace elements for several BSG samples. Based on the average composition of the BSG, two levels of nutrients addition were defined and tested on 4 different BSG samples. Control reactors, without addition of nutrients, showed signs of instability after 3 months or less of operation, with a decrease in performance and even collapse. On the contrary, supplemented reactors led to a COD removal rate of 60–65% and a methane production ranged between 220 and 350 NL $CH_4.kg^{-1}$ VS_{added}, depending on the sample. According to these results, guidelines for nutrients solution addition adapted to BSG degradation were defined.

1. Introduction

Anaerobic digestion of breweries residues could be a good option to reduce fossil fuel and disposal costs while reducing carbon foot-print (Panjičko et al., 2017). Three main by-products are found on breweries: wastewater, yeast and spent grains. Brewery spent grains (BSG) is a by-product consisting of crushed husks of malted barley grains obtained after the extraction of fermentable starch and polypeptides (Mussatto, 2014). The worldwide annual production of BSG has been estimated to 38.6×10^6 tons (Mussatto, 2014). Therefore, the possibility of producing energy from this by-product could have an economic interest. Actually, BSG is mainly valorized as food supplement and cattle feed (Panjičko et al., 2017). Anaerobic digestion seems to be a promising option to convert BSG into energy, but Sežun et al. (2011) have shown that it is difficult to achieve long-term stable anaerobic digestion process, even using thermal, chemical or mechanical pre-treatment of ligno-cellulose. They have shown an inhibition with p-cresol occurring after 120 days of operation.

Other lignocellulosic agricultural feedstocks, like maize silage, are anaerobically digested with the addition of trace elements. The supplementation of reactors compensates the lack of these elements, ensures an adequate distribution in order to answer to micro-organisms requirement, allows stabilization of anaerobic reactions and avoid reduction of performance (Nges et al., 2012; Thamsiriroj et al., 2012). One approach to optimize nutrients requirement is to consider the concentration of the different elements present in the micro-organisms. Based on the works of Scherer et al. (1983), several authors have studied the composition of methanogens in order to define minimum nutrients requirement for anaerobic metabolism (Deublein and Steinhauser, 2008; Oleszkiewick and Sharma, 1990; Speece, 1996). Chemicals elements (C, H, O, N, S and P) are essential for the synthesis of carbohydrates, lipids and proteins whereas trace elements (Fe, Ni, Co especially) are important in metabolic pathways and enzymatic reactions. They are part of cofactors of enzymes or coenzymes involved in the synthesis of methane and the growth of microorganisms (Beraki, 2007). A deficit causes problems in anaerobic degradation whereas supplementation leads to stabilization or improved performance (Nges et al., 2012; Pobeheim et al., 2010). Nowadays, the necessity to have adequate chemical and trace elements repartition in anaerobic digestion has been established, however the exact role of each component and quantities required are still under discussion (Choong et al., 2016).

In the present work, we studied the impact of trace elements addition on the anaerobic digestion of BSG. Three levels of solutions were tested on four different BSG samples.

2. Materials and methods

2.1. Brewer's spent grains as substrate

Four BSG samples were used for this experiment. Samples were

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Table 1
Operational conditions for reactors.

Reactor	BSG sample	HRT (d)	θ (°C)	TS in feeding (%)	OLR (g VS.L^{-1}.d^{-1})	Nutrients Solution
BSG1-CTL	BSG1	40	35	9.4%	2.28	/
BSG1-LC	BSG1	40	35	9.4%	2.28	LC
BSG1-HC	BSG1	40	35	9.4%	2.28	HC
BSG2-CTL	BSG2	40	35	8.5%	2.03	/
BSG2-HC	BSG2	40	35	8.5%	2.03	HC
BSG3-CTL	BSG3	40	35	6.9%	1.68	/
BSG3-LC	BSG3	40	35	6.9%	1.68	LC
BSG3-HC	BSG3	40	35	6.9%	1.68	HC
BSG4-CTL	BSG4	40	35	9.4%	2.23	/
BSG4-LC	BSG4	40	35	9.4%	2.23	LC
BSG4-HC	BSG4	40	35	9.4%	2.23	HC

collected from 4 industrial breweries, with a beer production of more than 300 000 hL for the BSG1 sample, 1.6 million hL per year for the BSG2 sample, 2.8 million hL per year for the BSG3 sample and almost 8 million hL per year for the BSG4 sample. All four BSG samples were characterized in terms of dry and organic matter, biochemical composition and trace elements content in order to define the operational parameters and the trace elements solutions composition.

BSG samples were stored at 4 °C during the experiments.

2.2. Experimental set-up

Eleven 5 L glass reactors (operational volume of 4 L) were used. Temperature in the reactors was maintained constant at 35 °C (mesophilic range) by water recirculation through a double envelope. Each reactor was mixed using a shaft with 3 paddles. The start-up inoculum was obtained from a municipal wastewater treatment plant (Cergy, France). Table 1 presents the experimental set-up for these trials.

Average Total Solid (TS) content of BSG was around 25%. Therefore, in order to fit wet process recommendations BSG were diluted by a 2.5-fold factor with addition of tap water. Semi-continuous reactors were fed manually. Hydraulic retention time (HRT) was fixed to 40 days to ensure complete degradation and organic loading rate ranged between 1.63 and 2.25 kg VS.m^{-3}.d^{-1} depending on the sample. The feeding volume was equivalent to 100 mL per day but as BSG is a solid substrate, feeding was realized 3 times a week: on Monday (2 days dose: 200 mL), Wednesday (2 days dose: 200 mL) and Friday (3 days dose: 300 mL). BSG was diluted with tap water in order to obtain a TS content in the feed lower than 11%, suitable with mixing.

2.3. Definition of the nutrients solutions

Two levels of supplementation were used based on BSG composition and the literature review: the Low Concentration (LC), which concentration was calculated considering the low range of concentrations found in the literature and that only 50% of nutrients and trace elements originally contained in BSG were bioavailable and the High Concentration (HC), which concentration was defined according the highest values of the literature and that nutrients in BSG were not bioavailable. Table 2 presents nutrients and trace elements content in nutritive solutions. Elements added have been chosen according their importance in the literature review (Thanh et al., 2016; Chen et al., 2008; Deublein and Steinhauser, 2008; Beraki, 2007; Speece, 1996).

Nutrients solution addition was 0.02 mL g^{-1} BSG whereas trace elements solution was only 0.01 mL g^{-1} BSG. Solutions were added with each feeding. Due to lack of material, the BSG2 sample was not tested with the addition of the LC solution: only BSG2-CTL and BSG2-HC reactors were tested.

Table 2
Nutrients and trace elements solutions added.

Nutrients	LC (g.L^{-1})	HC (g.L^{-1})	Trace elements	LC (g.L^{-1})	HC (g.L^{-1})
NH_4Cl	–	1.86	$FeCl_2$ $4H_2O$	0.71	3.56
K_2HPO_4	1.19	5.94	$CuSO_4$ $5H_2O$	0.04	0.06
KH_2PO_4	0.93	4.64	$MnCl_2$ $4H_2O$	0.72	1.44
Na_2SO_4	–	0.66	$NiCl_2$ $6H_2O$	0.06	0.24
$NaHCO_3$	7.28	13.80	$CoCl_2$ $6H_2O$	0.06	0.48
$CaCl_2$, $2H_2O$	–	7.34			
$MgCl_2$, $6H_2O$	–	16.73			
Quantity added	0.02 mL g^{-1} BSG			0.01 mL g^{-1} BSG	

2.4. Analytical methods

The performance of the process was evaluated by the follow-up of different parameters. pH was measured 3 times a week, before each feeding. Biogas production was measured daily, using a milligascounter (Ritter). Biogas yield is reported on weekly basis and normalized to the weekly amount of feed. Biogas composition was measured once a week using gas chromatography with thermal conductivity detector (7890 A GC System, Agilent) equipped with polarplot Q and molar sieve columns (HP-PLOT/Q and HP-MOLESIEVE, J&W Scientific).

For digestate characterization, phase separation was realized by centrifugation at 9.000*g* during 10 min (Centrifuge 5804, Eppendorf). Soluble fraction was then filtered (0.45 µm) before measurement. Measurements were conducted according to APHA recommendations (APHA, 2005). Total Solids (TS) and Volatile Solids (VS) were measured by weight determination after drying (24 h at 105 °C) and calcination (4 h at 550 °C). Total and soluble Chemical Oxygen Demand (COD), Alkalinity, total and soluble Total Kjeldahl Nitrogen (measured as total N since nitrites and nitrates contents were zero), ammoniacal nitrogen and also total and soluble phosphorous were measured using Hach-Lange kits (spectrophotometric method), according to manufacturer's protocols (LCK514, LCK362, LCK338, LCK302 and LCK350 kits respectively). Volatile Fatty Acids (VFA) content was determined using gas chromatography with flame ionization detector (7890 A GC System, Agilent) equipped with polyethylene glycol capillary column (HP-FFAPP, J&W Scientific). Acids measured were acetic, propionic, *n*-butyric, *iso*-butyric, *n*-valeric, *iso*-valeric, hexanoic and heptanoic acids. Nutrients and trace elements contents were determined on a monthly basis by an external laboratory, on both total and soluble phase of the digestate, using inductively coupled plasma technology coupled with the atomic emission spectrometry (ICP-AES).

For BSG samples and for digestate, TS and VS measurement were conducted after drying and calcination respectively. A slurry of the BSG sample was prepared and homogenized (crushed mixing + ultraturrax) in order to measure COD and N concentrations using Hach-Lange kits. Biochemical Methane Potential (BMP) was measured 3 times during experiments using AMPTS II Device (Bioprocess Control) and following Cresson et al. (2015) and Angelidaki et al. (2009) recommendations. For biochemical characterization and trace elements content, samples were sent to external laboratories at the beginning of experiments. Proteins content was calculated from N content using a 6.25 factor (N content measure using Dumas method). Lipids were measured by weight after hexane extraction. Fibers were estimated considering lignin like, hemicellulose like and cellulose like fractions according to Van Soest and Wine (1967). Carbohydrates were measured according EU legislation n°152/2009 according Luff-Schoorl method.