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Effect of liquid hot water pre-treatment on sugarcane press mud methane yield

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HIGHLIGHTS

- Improved biomethanation by LHW pre-treatment compared with untreated press mud.
- A 33% COD solubilisation resulted in the best methane yield (>55% increase).
- Increase of methane yield by a maximum of 63% at 150 °C for 20 min.
- Highest furfural concentration of 1214.17 mg L^{-1} was found at 200 °C for 5 min.
- HAc release was influenced more by temperature than by pre-treatment severity.

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ABSTRACT

Sugarcane press mud was pretreated by liquid hot water (LHW) at different temperatures (140–210 °C) and pre-treatment times (5–20 min) in order to assess the effects on the chemical oxygen demand (COD) solubilisation, inhibitors formation and methane yield. The experimental results showed that a high degree of biomass solubilisation was possible using LHW. Higher methane yields were obtained at lower severities ($\log(R_o) = 2.17–2.77$) with (i) mild temperatures (140–150 °C) and long contact times (12.5 min, 20 min) or (ii) mild temperatures (175 °C) with short contact time (2 min). The highest increase in methane yield (up to 63%) compared to the untreated press mud was found at 150 °C for 20 min. At temperatures of 200 °C and 210 °C, low methane efficiency was attributed to the possible formation of refractory compounds through the Maillard reaction.

1. Introduction

Sugarcane cultivation has increased dramatically with a world production level of about 1.7 billion tons in 2011. The global expansion of sugarcane has been in response to a rising sugar demand for food consumption and as a feedstock for ethanol production (FAO, 2013). That increase leads to larger quantities of by-products and waste generated by sugar production. One of them is press mud, a solid residue obtained by the vacuum filtration of the settled cake in the clarification process of the cane sugar juice. Each ton of milled cane generates 28–45 kg of press mud (Velarde et al., 2004).

Press mud is a potential source for methane production. However, the presence of a resilient biomass matrix (9.03%, 21.67% and 17.23% on dry basis for lignin, hemicelluloses and cellulose, respectively) and a low COD solubilisation (around 21%) explains its low efficiency (40%) for bio-conversion processes (Lopez et al., 2013).

Previous pre-treatment studies have focused on improving the digestibility of lignocellulosic material by many different means: mechanical, thermal, chemical, and through combined measures (Hendriks and Zeeman, 2009; Taherzadeh and Karimi, 2008; Zheng et al., 2014). Among these methods, liquid hot water (LHW) pre-treatment utilises water at elevated temperatures as the only solvent (usually between 120 °C and 230 °C) and various

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pressures, conditions at which water exists in subcritical conditions (Nitsos et al., 2013). Water under high pressure and temperature can penetrate the biomass, hydrate cellulose, and remove hemicellulose and a share of lignin. LHW pre-treatment enhances the accessible and susceptible surface area of the cellulose and makes it more accessible to hydrolytic enzymes. The major advantages offered by this technique are: no additional chemicals needed and no corrosion resistant materials required for the hydrolysis reactors. Furthermore, since much less amounts of chemical are needed for hydrolysed neutralisation, lesser amounts of neutralisation residues are generated when compared to other processes (Taherzadeh and Karimi, 2008).

A significant drawback is the formation of phenolic compounds, as well as furfural and hydroxymethylfurfural (HMF). These by-products are commonly toxic and inhibit the growth of bacteria and archea (Hendriks and Zeeman, 2009). The optimisation of operating parameters is therefore required in order to reduce the formation of these inhibitory compounds, and obtain a pre-treated substrate that can be easily decomposed to biogas.

To our knowledge, LHW pretreatment on press mud have not been published yet. LHW pre-treatment has been studied as part of the biochemical conversion of lignocelluloses into biogas from a variety of feedstocks with positive results, including the solid and liquid cattle manure (Budde et al., 2014) and agricultural waste such as wheat straw (Chandra et al., 2012b; Menardo et al., 2012), rice straw (Chandra et al., 2012a; Menardo et al., 2012), oil palm empty fruit bunches (O-Thong et al., 2012), sunflower oil cake (Fernandez-Cegri et al., 2012), sunflower stalks and palm oil mesocarp fibre (Costa et al., 2013), sorghum bagasse and ensiled sorghum forage (Sambusiti et al., 2013), etc. Milder temperatures (120–170 °C) with times between 5 and 30 min, were most effective for substrates as wheat straw, solid cattle manure, liquid cattle manure and sunflower oil cake. On the contrary, LHW pre-treatments at higher temperatures (200–230 °C, 10–15 min) were needed in order to observe a higher methane yield when using rice straw and oil palm empty fruit bunches. As can be seen, depending on the chemical compositions and structural properties of the different biomass materials the effectiveness of LHW pre-treatment varies considerably.

The purpose of the present study is to evaluate the influence of time and temperature on the effectiveness of LHW pre-treatment of press mud for methane production, using a central composite design (CCD) statistical experimental design.

2. Methods

2.1. Substrate characterisation

Fresh press mud (2013 harvest) was provided from the Sugar Mill "Melanio Hernández" (Sancti Spiritus, Cuba). Press mud was air-dried and stored in plastic bags at 4 °C until use. Dry press mud contained 90.48% and 72.22% of total solids (TS) and volatile solids (VS), respectively. Furthermore, the compositional analysis resulted in 11.34% cellulose, 27.13% hemicellulose and 9.30% lignin on dry weight basis. Concentrations of sugar, protein and extractable material containing wax and fat of the press mud were determined as 8.14%, 11.05%, and 9.32% on dry weight basis, respectively. The fresh press mud also contains various micronutrients such as nitrogen, phosphorous, potassium, calcium, magnesium, manganese and zinc (Lopez et al., 2013).

2.2. Analytical methods

Total chemical oxygen demand (tCOD), TS, VS, ashes and pH were determined according to standard methods (APHA et al., 1995). Liquid samples were centrifuged for 30 min at 6000 rpm and further used for soluble COD (sCOD) and volatile fatty acids (VFA) analyses. COD analysis was carried out by standard closed reflux, colorimetric method 5220 D (APHA et al., 1995). VFA (acetic acid, propionic acid, butyric acid, valeric acid and iso-valeric acid) were determined by gas chromatography using a previously published methodology (Lopez et al., 2013).

Liquid aliquots were analysed for carbohydrates mono-and disaccharides (xylose, arabinose, fructose, galactose, mannose, glucose, sucrose, lactose, cellobiose and maltose). The sugars were determined by a gas chromatograph (GC Varian 3380) coupled to a FID: CP Sil-5CB column (25 m $L \times 0.32$ μm *internal diameter* × 0.25 μm *particle size*). Oven initial $T = 120$ °C, T ramp = 20 °C min^{-1} to a final temperature of 290 °C held for 3 min, split/splitless inlet at 280 °C. Hydrogen was the carrier gas, detector $T = 325$ °C.

Lignin and structural carbohydrates were determined according to the NREL procedure (Sluiter et al., 2008), using GC–FID as pointed out above.

Other organic compounds found in the liquid product of hydrothermally pre-treated biomass, such as gallic acid, hydroxymethylfurfural (HMF), furfural, vanillic acid, syringic acid, p-coumaric acid and ferulic acid were analysed by High Performance Liquid Chromatography (HPLC)-Agilent 1100 Series-equipped with a diode array detector-Agilent 1200 Series-. The analysis was done using an Inertsil-ODS column, 5 μl injection volume, 1 ml/min flow rate in a gradient run using 1% v/v acetic acid in distilled water and 1% v/v acetic acid in methanol as mobile phase.

Press mud Soxhlet extraction was performed with water followed by ethanol. The aqueous and ethanolic extracts were dried under vacuum in a rotary evaporator at 80 and 60 °C respectively. The obtained solids were further dried to a constant weight at 60 °C, and maintained under vacuum in a desiccator with tetraphosphorus decaoxide. Wax and fats were quantified as ethanol extracts. Proteins were calculated from the Total Kjeldahl nitrogen (TKN) content, using a conversion factor of 6.25.

2.3. Pre-treatment conditions

The LHW press mud pre-treatment assays were conducted in a 600 ml Mini Reactor System, Model number 4568 (Parr Instruments, Moline, USA) (Budde et al., 2014). A press mud sample of 100 g was mixed with 500 g of deionized water with a liquid to solid ratio of 5.5 and heated at varying temperatures (140–210 °C) under constant stirring (350 rpm) for different reaction times (2–23 min). The pressure values were equivalent to the temperature-specific saturated water vapour pressure. The heating rate was 3 °C/min. Table 1 shows detailed experimental conditions according to a CCD setup. Experiments were replicated two times for factorial and axial points, and four times for center points. In total, 29 trials were performed.

After completion of the pre-treatment time the heater was removed and the reactor was cooled down to less than 50 °C by immersing it into room temperature water. The pre-treated press mud slurry was taken out of the reactor and stored in containers at 4 °C for subsequent biochemical methane potential test. A subsample was used to separate liquid and solid fraction by centrifugation. The solid fraction was washed with hot deionized water at 60 °C several times until the filtrate had a neutral pH, dried in air and stored at 4 °C until used for further analysis. The liquid product was passed through a 0.2 μm filter and stored at −20 °C for further analysis. The COD solubilisation (S_{COD}) was calculated as sCOD/tCOD and expressed in %.

The severity factor R_o was determined for each experiment. This parameter quantifies the hydrothermal pre-treatment combined