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Research article

Agave tequilana bagasse for methane production in batch and sequencing batch reactors: Acid catalyst effect, batch optimization and stability of the semi-continuous process

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ABSTRACT

Agave tequilana bagasse is the main solid waste of the tequila manufacturing and represents an environmental issue as well as a potential feedstock for biofuel production due to its lignocellulosic composition and abundance. In this contribution, this feedstock was subjected to pretreatments with HCl and H_2SO_4 for sugar recovery and methane was produced from the hydrolysates in batch and sequencing batch reactors (AnSBR). Sugar recovery was optimized by using central composite designs at different levels of temperature, acid concentration and hydrolysis time. Results showed that at optimal conditions, the HCl pretreatment induced higher sugar recoveries than the H_2SO_4 one, 0.39 *vs.* 0.26 g total sugars/g bagasse. Furthermore, the H_2SO_4 hydrolysate contained higher concentrations of potential inhibitory compounds (furans and acetic acid). Subsequent anaerobic batch assays demonstrated that the HCl hydrolysate is a more suitable substrate for methane production; a four-fold increase was found. A second optimization by using HCl as acid catalyst and methane production as the response variable demonstrated that softer hydrolysis conditions are required to optimize methane production as compared to sugar recovery (1.8% HCl, 119 °C and 103min *vs.* 1.9% HCl, 130 °C and 133min). This softer conditions were used to feed an AnSBR for 110 days and evaluate its stability at three different cycle times (5, 3 and 2 days). Results showed stable reactor performances at cycle times of 5 and 3 days, obtaining the highest methane yield and production at 3 days, 0.28 NL CH_4/g-COD and 1.04 NL CH_4/d respectively. Operation at shorter cycle times is not advised due to microbial imbalance.

1. Introduction

The current global energy supply is mainly based on fossil fuels, which are nonrenewable resources and the main cause for the accumulation of greenhouse gases in the atmosphere (Monlau et al., 2014). Several governments around the world have encouraged the introduction of alternative energy sources that are both environmentally friendly and renewable. In this context, due to its abundance, composition and renewability, lignocellulosic biomass is recognized as a promising energy source for the production of biofuels such as methane (Kumar et al., 2009).

Globally, large amounts of lignocellulosic biomass are generated as byproducts of agro-industrial processes. For instance, in México the tequila industry produces ~380,000 tons per year of *Agave tequilana* bagasse (CRT, 2016; Saucedo-Luna et al., 2010). Currently, most of this bagasse is disposed in agave fields causing environmental damage, such as pollution by leachates, odor generation and habitat for pest and diseases (Crespo et al., 2013).

The main limitation to use the *A. tequilana* bagasse as feedstock for methane production is the low conversion rate due to the lignocellulosic recalcitrance (Fig. S1), making necessary to apply pretreatments in order to release the sugars from the hemicellulose and cellulose fractions (Arreola-Vargas et al., 2015). In this context, dilute acid hydrolysis is the most reported method for depolimerization of lignocellulosic biomass because of its effectiveness and low cost (Kumar et al., 2009). This pretreatment can depolymerize the holocellulose to its main sugars: hexoses (glucose, mannose, and galactose) and pentoses (xylose and arabinose); which are suitable substrates for methane

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production via anaerobic digestion. However, the main disadvantage of dilute acid hydrolysis is the formation of by-products (furans, week acids and phenolics) that are considered inhibitory to microorganisms at high concentrations (Monlau et al., 2014). Thus, optimization of hydrolysis conditions is required to maximize sugar recovery and minimize the generation of potential inhibitory compounds.

Several studies have evaluated the acid pretreatment of different type of biomasses by mainly using hydrochloric (HCl) or sulfuric (H_2SO_4) acids as catalysts (Dussán et al., 2014; Kumar et al., 2009; Rodrigues et al., 2010). However, only few studies have aimed to compare the efficiency of these two acid catalysts over the same biomass (Hutomo et al., 2015; Meinita et al., 2015, 2012; Shi et al., 2012). Overall, these works suggest that H_2SO_4 is more effective than HCl for sugar recovery. For instance, Meinita et al. (2012) found higher sugar concentrations by pretreating marine algal biomass with H_2SO_4 as compared to HCl (38.45 *vs.* 22.68 g/L). Nonetheless, regarding *A. tequilana* bagasse, the results are inconclusive on this respect, since only individual efforts have been made to evaluate the acid hydrolysis of this feedstock under different conditions and type of acid. For instance, Saucedo-Luna et al. (2010) reported sugar concentrations up to 26.9 g/L by using H_2SO_4, while we previously reported sugar concentrations up to 27.9 g/L by using HCl (Arreola-Vargas et al., 2015).

Another aspect to consider on the selection of the acid catalyst is the downstream process. In the case of methane production, to the best of our knowledge there are no studies that compare the effect of HCl or H_2SO_4 hydrolysates over the anaerobic digestion process. This is relevant because chloride and sulphate ions present in the hydrolysates may cause negative effects during this process; for instance, by promoting the competence between methanogen archaea and sulphate reducing bacteria.

On the other hand, regarding the full scale application of the *A. tequilana* bagasse hydrolysates for methane production, it is clear that anaerobic digestion studies on continuous or semi-continuous operation modes need to be addressed. In the current literature, there is only one study that has evaluated the use of a semi-continuous system, an anaerobic sequencing batch reactor (AnSBR) (Arreola-Vargas et al., 2015). Nonetheless, such study lasted only 15 days, making clear that the stability of the process needs to be evaluated for longer periods of time. It is worth to highlight that high methane yields were obtained in such study regardless of the short AnSBR operation (average value of 0.26 NL CH_4/g COD). The latter is mainly due to the advantages of this reactor configuration, such as the high degree of process flexibility, the better control of the microbial population and the decoupling of the solids retention time (SRT) from the hydraulic retention time (HRT) (Arreola-Vargas et al., 2015; Mace and Mata-Alvarez, 2002).

Due to all the above, this work aimed i) to optimize the hydrolysis conditions for maximizing sugar recovery from *A. tequilana* bagasse by using HCl and H_2SO_4 as acid catalysts, ii) to compare the efficiency of both acid catalysts for sugar recovery and methane production in batch assays, iii) to optimize the hydrolysis conditions for maximizing the methane production and compare such conditions with those obtained for sugar recovery optimization, and iv) to evaluate the long-term stability of an AnSBR operated at different cycle times for the production of methane from the acid hydrolysates.

2. Materials and methods

2.1. A. tequilana bagasse

A. tequilana bagasse was provided by a local distillery and was composed of 10.86% hemicellulose, 56.44% cellulose, 15.24% lignin and 17.46% extractives. The composition was determined by using a semiautomatic ANKOM fiber analyzer (Macedon, NY, USA) (Arreola-Vargas et al., 2015). Prior to be subjected to any pretreatment, the fibers were dried at room temperature and reduced to an average length of 0.5 cm by using a blade mill.

Table 1
Natural and coded values in the central composite design for optimization of sugar and methane production.

Variable	Coded symbol	Coded level				
		-α[a]	−1	0	1	α[a]
Temperature (°C)	X1	83	100	125	150	167
Acid concentration (% w/w)	X2	0.3	1	2	3	3.7
Reaction time (min)	X3	19	60	120	180	221

[a] α (axial distance) = $4\sqrt{n_f}$ = 1.68, where n_f is the number of experiments of the factorial design.

2.2. Acid pretreatments

Acid pretreatments were carried out by dispersing the *A. tequilana* bagasse at 5% (w/v) in HCl or H_2SO_4 solutions at different concentrations. The reaction took place in 1 L corning® bottles that were introduced in an oven for certain periods of time at different temperatures. The acid concentration, temperature and hydrolysis time varied according to the experimental design presented in the following section. At the end of both treatments, the hydrolysates were filtered through a 0.45 mm membrane for further analyses.

2.3. Experimental design

The central composite design (CCD) is the most popular response surface design for optimization of desired variables. In this study, such design was employed to optimize the hydrolysis conditions (acid concentration, temperature and hydrolysis time) for maximizing the sugar recovery from *A. tequilana* bagasse by using HCl and H_2SO_4 as acid catalysts. Furthermore, the CCD was also employed to optimize the hydrolysis conditions for maximizing the methane production by using the best acid catalyst found in the former stage. Table 1 shows the natural and coded values of the independent variables for all the CCDs.

It is worth mentioning that the CCD arises through sequential experimentation, i.*e.* an orthogonal first order design (*e.g.* 2^k factorial design) is used to fit a first order model and once it exhibits lack of fit, axial points are added to complete the CCD and allow the quadratic terms to be incorporated into a second order model (Montgomery, 2013). The 2^k factorial design must be augmented with central points in order to allow estimation of the experimental error without altering the orthogonality property of the design (our design was augmented with 5 central points). The first order model is represented in equation (1), where B_0 is the constant coefficient, B_i is the linear coefficient; Y is the response variable, and X_i are the independent variables that have influence on the response variable.

$$Y = \beta_0 + \sum \beta_i X_i + \varepsilon \quad (1)$$

Once the first order model exhibited lack of fit, 6 axial points were added to the 2^k factorial design to complete the CCD. The method of steepest ascent was employed when the 2^k factorial design was well fitted to the first order model until no further increase on the response variable was observed. Then, a new 2^k factorial design augmented with 5 central points was applied and the procedure continued until lack of fit to the first order model was observed. The second order model is represented in equation (2), where B_0 is the constant coefficient, B_i is the linear coefficient, B_{ii} is the quadratic coefficient, B_{ij} is the interaction coefficient, Y is the response variable, and X are the independent variables that have influence on the response variable.

$$Y = \beta_\circ + \sum \beta_i x_i + \sum \beta ii x_i^2 + \sum \sum \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

Data analysis, response surface plots and analysis of variance (ANOVA) were performed by using the software Statgraphics centurion XV (Statpoint, Technologies, Inc. USA).