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Multiple response optimization analysis for pretreatments of Tequila's stillages for VFAs and hydrogen production

Froylán M. Espinoza-Escalante [a], Carlos Pelayo-Ortiz [a], Humberto Gutiérrez-Pulido [b], Víctor González-Álvarez [a], Víctor Alcaraz-González [a], André Bories [c,*]

[a] University of Guadalajara, Department of Chemical Engineering, Guadalajara, Mexico
[b] University of Guadalajara, Department of Mathematics, Guadalajara, Mexico
[c] INRA-Unité Expérimentale de Pech-Rouge, 11430 Gruissan, France

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Abstract

The objective of this work was study the effect of three pretreatments (alkalinization, thermical treatment, and sonication) on Tequila's stillages hydrolysis process in acidogenesis stage, through the following response variables: soluble chemical oxygen demand (CODs), total sugar and volatile fatty acids profile and the hydrogen production at the time. The stillages were subject to these pretreatments (according to a 2^3 factorial design); afterward they were transferred to a batch reactor at 35 °C and inoculated with an anaerobic digestor sludge. Multiple response optimization (MRO) analysis was done to find the global optimum for the response variables described above. This optimum is able to maximize simultaneously all these variables. It was found adequate to be useful hydrolyzing the organic matter present in Tequila's stillages. Mathematical models were fitted to observe the estimated effects of pretreatments on each response variable, then the MRO was applied.

Keywords: Multiple response optimization; Tequila's stillage; Hydrolysis; Volatile fatty acids; Hydrogen

1. Introduction

Wastewaters from food industries present generally high organic load and therefore the anaerobic digestion is considered as the best available technology for their treatment (Angenent et al., 2004). Alcohol producing industries affront real problems cause of their high strength stillages. Of special interest for this study are the Tequila's stillages, given the proximal organic load of 60 g/l as chemical oxygen demand due to remaining organic suspended solids and the dissolved organic compounds (Espinoza-Escalante et al., 2006). In Mexico, the Bureau for the Regulation of Tequila, reported a production of 253,000 m^3 of Tequila during 2006 (http://www.crt.og.mx), and it is known that when producing Tequila, 10 l of stillages are produced for each liter of this beverage, and then 2.5 million m^3 of Tequila's stillages were generated for this year. Considering the high organic load of the wastewater and the high volume generated per year, this becomes a real problem of pollution for Mexico.

Given the complex composition of Tequila's stillages, the hydrolysis is the rate limiting step in the anaerobic digestion process. Pretretaments are often required to promote solubilization of organic matter, such as: chemical addition, thermal pretreatment, disintegration or mechanical or ultrasonic oxidation, enzymatic or microbial pretreatment (Carballa et al., 2004; Benabdallah et al., 2007).

Thermal hydrolysis is referred as the process where wastes are heated in a range varying from 130 to 180 °C during 30 to 60 min at the corresponding vapor pressure, however, according to several authors optimal temperature is around 170–200 °C (Gosh, 1991; Tanaka et al., 1997).

* Corresponding author. Tel.: +33 (0) 468494400; fax: +33 (0) 468494402.
E-mail address: bories@supagro.inra.fr (A. Bories).

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This process yields a partially solubilized waste and biological cells are broken (Bougrier et al., 2004; Carballa et al., 2004). Even when thermal hydrolysis is energetically demanding, electrical needs are actually low. The energy consumed during heating can be optimized in such way that the energetic balance becomes positive compared to the conventional treatment of wastes.

In chemical hydrolysis (alcalinization), the waste pH is increased up to 12, and this process may be used to hydrolyze and decompose lipids, hydrocarbons and proteins into smaller soluble substances such as aliphatic acids, polysaccharides and aminoacids (Carballa et al., 2004; Chiu et al., 1997; Luo et al., 2002).

In ultrasonic treatment, cavitational collapse produces intense local heating and high pressure on liquid–gas interface, turbulence and high shearing phenomena in the liquid phase, but also formation of OH^-, HO_2 and H^+ (Bougrier et al., 2004).

The physical process occurring during cavitation is almost the same as boiling. The major difference between these two processes is how is affected the phase change. In boiling, the vapor pressure of the liquid is increased over the local pressure to cause a change to gas phase, meanwhile cavitation is caused by a local pressure decrement under the vapor pressure of the liquid.

This offer the possibility of analyze the effect of pretreatments in solubilizing the complex compounds (mainly polymeric sugars) present in Tequila's stillages, and also to study their aid in the acidogenic process known already as the first stage of the anaerobic digestion process in which hydrogen is produced. It has been shown by several studies that the response surface methodology (RSM) is a suitable tool to investigate the acidogenic process (Hwang et al., 2001; Hu et al., 2006; Wang et al., 2005). However, as we have several response variables, besides of use RSM it is necessary to use MRO. Which gives the opportunity of optimize multiple process variables at once and facilitates the process of taking decisions at same time that offers a general view of the anaerobic digestion process of this novel wastewater.

The MRO methodology is oriented to the industrial processes depending on multiple variables $(X_1, X_2, \ldots, X_p)$, which have to been controlled in order to achieve a final goal; this statistical tool leads to achieve a global optimum for each the individual variables of interest. In this technique two or more variables are evaluated at once, these are correlated to generate the global optimum that satisfies as much as possible the individual optimum of each variable considering acceptable all those values of the variable inside of the "desired" limits.

The desirability function approach is one of the most widely used methods for the optimization of multiple response processes. It is based on the idea that the "quality" of a product or process that has multiple quality characteristics, with one of them outside of some "desired" limits, is completely unacceptable. The method finds operating conditions x that provide the "most desirable" response values (http://www.itl.nist.gov/div898/handbook/, 2006).

The objective of this work was determine the effect of three pretreatment factors (thermical treatment, alkalinization and sonication) on the Tequila's stillages hydrolysis process in the acidogenesis stage, through the following response variables: soluble chemical oxygen demand (CODs), total sugar and volatile fatty acids profile and the hydrogen production at the time.

2. Methods

2.1. Tequila's stillage

Stillages coming from a Tequila distillery of Jalisco, Mexico, processing Tequila 100% Agave, were frozen at −20 °C until their utilization. The Tequila's stillage used in this study has a total COD of 64,000 mg/l, a sugars content of 19 g/l and a VFAs concentration of 3 g/l.

2.2. Analytical methods

The pH was measured using a potentiometer (Orion 520A+). For VFAs analysis, samples were centrifuged to 10,000 rpm for 10 min, a 1 ml supernatant aliquot was taken into a clean 2 ml vial then 1 μl of extern standard (2-ethyl butyric acid) was added. Samples were thoroughly mixed with vortex; 1 μl of sample was used for chromatography. VFAs were detected and quantified with a Perkin–Elmer Autosystem XL chromatographer using a capillary column (WCOT Fused Silica 25 m × 0.32 mm ID Coating CP-Wax 25CB DF 0.2) with nitrogen as carrier gas; the temperature of the injector was 205 °C, flame ionization detector (FID) temperature was 250 °C. The soluble COD was measured according to the colorimetrical method of Knetchel (1978), samples were centrifuged to 10,000 rpm for 10 min, a 20 μl aliquot of supernatant was taken for CODs analysis. Total reducing sugars were measured with the Phenol–Sulphuric method (Dubois et al., 1956) and total solids and volatile soluble solids were analyzed according to the APHA (1998). Gases were measured using a Perkin–Elmer Autosystem XL with a thermal conductivity detector (TCD) chromatographer using molesieve 13X column with nitrogen as carrier gas.

2.3. Fermentation tests

A 1 l glass vessel was used as model reactor with a working volume of 540 ml. A 90% vinasse:10% inoculum mixture was added to the reactor and then purged with gaseous nitrogen for 15 min and then sealed. A tedlar bag was used for gas capture. Temperature was controlled with a water bath to 35 °C. The pH was adjusted manually twice a day, keeping it into a pH range varying from 6.5 to 7.5.

2.4. Inoculum

A digested sludge (14,158 mgVSS/l and 1.74 mgCOD/mgVSS) from a mesophilic reactor from a brewing plant was used as inoculum.