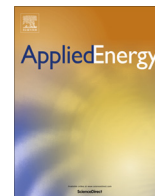




Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Desirability function for optimization of Dilute Acid pretreatment of sugarcane straw for ethanol production and preliminary economic analysis based in three fermentation configurations

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HIGHLIGHTS

- A 2³ experimental design was applied for the pretreatment of sugarcane straw.
- Desirability function was used to find the optimum conditions for pretreatment.
- PSSF process was successfully carried out using the pretreated sugarcane straw.
- Ethanol yield of 187 L/tonne was obtained from the biomass using C-6 sugars.
- PSSF process presented the lower total production cost.

ARTICLE INFO

Article history:

Received 14 December 2016

Received in revised form 18 February 2017

Accepted 4 March 2017

Available online xxxx

Keywords:

Sugarcane straw

Dilute acid pretreatment

Desirability function

Ethanol

Economic parameters

ABSTRACT

Sugarcane straw is a lignocellulosic residue accumulated during the harvest of sugarcane and is a potential feedstock for second generation biofuel. This work covers the optimization of pretreatment step in the ethanol production using a complete factorial design (2³), where the analyzed factors were temperature, acid concentration and time in the Dilute Acid pretreatment. Desirability function was applied in this stage to maximize sugar yields and minimize inhibitor concentrations, resulting in overall sugars yield ~60% and furfural concentration of 0.5 g/L. An enzymatic hydrolysis stage was done to increase sugar release. The fermentation stage was studied through three different configurations, such as Separate Hydrolysis and Fermentation (SHF), Simultaneous Saccharification and Fermentation (SSF) and Presaccharification and Simultaneous Saccharification and Fermentation (PSSF). The most promising alternative turned out to be PSSF due its higher ethanol concentration, with a value of 14.8 g/100 g dry weight (DW) biomass, equivalent to 187 L/tonne DW using C6-sugars. The economic analysis revealed that the integration between enzymatic hydrolysis and fermentation in the ethanol production affected the total capital cost. The cost of raw materials (sugarcane straw and enzymes) had the most significant impact on the total production cost and accounted between 35.66 and 25.88% of the total cost of the ethanol plant from sugarcane straw.

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1. Introduction

Significant efforts have been made to implement sustainability through the use of renewable resources, such as lignocellulosic biomass, enabling the reduction of fossil fuel consumption and satisfying its demand. Ethanol and by-product production from alter-

native feedstocks has been considered as a potential way to solve energy crisis and environmental pollution problems in the next decade, when the conversion costs are expected to be lower and product yields increase [1,2].

Sugarcane is one of the major cultures in Latin America, so its processing resulting in large quantities of waste after harvesting, including sugarcane bagasse and straw [3,4]. However, sugarcane straw has been studied in lesser extension than sugarcane bagasse due to the lack of long term experience with collection, storage and

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processing costs [5]. Generally, this residue is collected in large areas and its final destination is mostly to be burned.

The valorization of sugarcane straw as a raw material for ethanol production in the biorefinery concept depends on several factors like transport distance and load density, straw recovery fraction and system, sugarcane productivity, among others which may have to take into consideration in order to optimize the sustainability impacts [6]. But overcoming these aspects, the use of sugarcane straw for second generation biofuels will give an excellent opportunity to improve the economics and sustainability of ethanol production [5].

The sugarcane straw is composed by cellulose, hemicellulose, lignin, extractives and small amounts of minerals. Its particle size has to be reduced before pretreatment to increase the dry weight material ratio per reactor capacity, on large scale pretreatment. A pretreatment stage is necessary to transform polysaccharides into simple sugars such as glucose and xylose because it breaks the complex cellulose-hemicellulose-lignin making the cellulose more accessible to further enzymatic attack [5].

Pretreatment processes are a crucial technological step in the fractionation of lignocellulosic materials [7,8]. Various studies were carried out to optimize the pretreatment process to sugarcane straw: steam explosion [5], microwave irradiation in aqueous and acid glycerol solutions [9], combined process (hydrothermal and delignification) [10], wet disk milling and ozonolysis [11], alkali process [12,13], dilute acid [14] and organosolv fractionation [15].

Dilute acid hydrolysis (DAH) is one of pretreatment most studied in all types of biomass [7,16,17]. DAH pretreatment process has the lowest value ethanol production cost in comparison with other process scenarios (2-stage dilute-acid, hot water, and ammonia fiber explosion) [18,19]. Also, inside the advantages of the use this pretreatment process are the obtained good results when applying on different biomasses such as hard woods and residues crops [20–23]. This condition allows the possibility to mixture different types of biomass, ex. sugarcane straw with sugarcane bagasse as a unique raw material for bioethanol production.

With DAH pretreatment is possible to obtain xylose-rich hydrolysate. According to temperature applied to the process, sugars and lignin degradation may occur and obtaining hydrolysates with high content of inhibitors like furfural and HMF [24,25], and this condition affect the microorganism metabolism in the fermentation step and then it would be necessary to incorporate a step of detoxification of the hydrolysate [26]. The control of the severity of pretreatment is a way to find better results, since have been demonstrated that acid hydrolysis has higher sugars released and smaller amounts of inhibitory compounds at moderate temperatures [27].

Study of bioethanol production from sugarcane lignocellulosic residues has gained significant attention in terms of pretreatment and enzymatic conditions, flowsheet development and techno economic evaluation. Among the published research, a few have focused on overall process of ethanol production from sugarcane straw. Although most of these studies are based only on evaluating the effect of pretreatment on enzymatic hydrolysis and, eventually, analyzing some fermentation alternatives.

Among the fermentation alternatives can be mentioned Separate Hydrolysis and Fermentation (SHF), Simultaneous Saccharification and Fermentation (SSF), and Presaccharification and Simultaneous Saccharification and Fermentation (PSSF). Each one have advantages and disadvantages over the rest. The characteristics of SHF allow to develop each stage under their specific optimal conditions and there is a chance of recycling the cellulase, but can exist cellulase inhibition by the final product. On the other hand, in the SSF the hydrolysis and fermentation coexist at the same time, disappearing the inhibition by product, higher yields are obtained

and decrease the amount of enzymes to use and the investment costs, but there has to be a commitment between the variables of the process. The PSSF is a combination of both previous explained configurations. During a designated time there is only an enzymatic hydrolysis at its optimal conditions, and after the addition of the microorganism it turns to be a SSF. To explore all those configurations experimentally could lead us to find out the most feasible option.

To optimize the pretreatment step is crucial because it plays a key role in the success of the process since critically influences the subsequent stages of bioethanol production. In general, some of the premises of the ideal pretreatment is to ensure highest enzyme susceptibility, greater recovery of hemicellulose sugars (mainly xylose) and fewer inhibitors [27]. The present work differs from previous studies [9–15], in the optimization of DAH pretreatment through the desirability function that allows to choose the value of the independent variables to obtain those characteristics above mentioned. This method of optimization generates an enzymatically-accessible solid and a high quality hydrolysate after pretreatment. Also, this study evaluates three alternatives of enzymatic hydrolysis and fermentation and provides the data required for a preliminary economic evaluation.

Whereby the aim of this work is to optimize the DAH pretreatment for subsequently determining the most promising option of several fermentative alternatives from technical and economic perspective to obtain ethanol from sugarcane straw.

2. Experimental section

The research methodology consisted of two parts; the first one describes the experimental procedures for Dilute Acid pretreatment optimization and different alternatives of enzymatic hydrolysis and fermentation. The second part analyzes an approach to technical economic analysis of the described alternatives in order to establishing criteria for selecting the best alternative.

2.1. Raw material

Sugarcane straw was supplied by the sugar mill “Amancio Rodríguez” in Las Tunas, Cuba. The leaves were taken directly from the collection center, without washed or minced. This material had a moisture content of 10% (w/w).

2.2. Pretreatment

The pretreatments were performed in a 1-L continuously stirred batch reactor (Berghof reactor) under different conditions of temperature, with addition or not of H₂SO₄, and reaction time (Table 1). For the experiments, the reactor was fed with 15 g of sugarcane straw (straw was manually cut to a size approximately 1 cm) and mixed with the reaction medium (with or without acid) in a solid-to-liquid ratio of 1/10 (g/mL). The reaction media were heated until reaching the desired temperature, which was maintained during the selected time. After the reaction, the obtained solid residue was separated by filtration, washed with water until neutral pH, dried at 40 °C to attain around 5% moisture content, and chemically characterized to determine the contents of sugars contents and lignin. The liquid fraction was used to determine the concentrations of furfural and sugars present. Sugars (xylose) from initial raw material in the hydrolysate were calculated according to Eq. (1), where C is the concentration of sugars (xylose) in liquid fraction, V is the volume of liquid fraction and RM is the initial raw material.

$$\text{Yield (g/100gRM)} = C(\text{g/L}) * V(\text{L})/\text{RM}(\text{g}) * 100 \quad (1)$$

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