Chemical Engineering Journal 260 (2015) 178–187

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Influence of dual salt on the pretreatment of sugarcane bagasse with hydrogen peroxide for bioethanol production

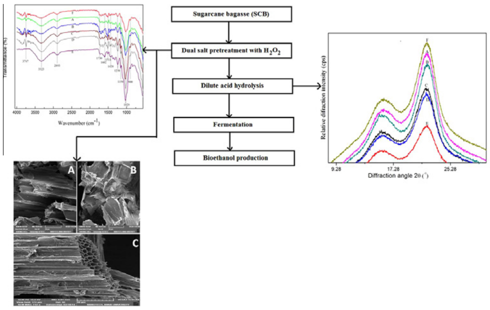
Govindarajan Ramadoss, Karuppan Muthukumar *

Department of Chemical Engineering, Alagappa College of Technology Campus, Anna University, Chennai, Chennai 600 025, India

HIGHLIGHTS

- Influence of dual salt on the pretreatment of SCB with H_2O_2 was carried out.
- Better performance was observed using H_2O_2 with $MnSO_4 \cdot H_2O$ and ZnO.
- The inhibitors formation was found to be less.
- The maximum theoretical ethanol yield of 84.32% was achieved during fermentation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 May 2014
Received in revised form 28 July 2014
Accepted 1 August 2014
Available online 23 August 2014

Keywords:
Sugarcane bagasse
Pretreatment
H_2O_2
Dual salt
Bioethanol

ABSTRACT

This study presents the influence of different dual salts on the pretreatment of sugarcane bagasse (SCB) with H_2O_2 for the production of bioethanol. The results showed better cellulose recovery and delignification for $MnSO_4 \cdot H_2O$ and ZnO system. At optimized conditions (1% H_2O_2, 1 g SCB, 30 min, 100 °C and 0.5:100 g/mL), the maximum cellulose recovery of 93.42 ± 1.74%, and delignification of 74.18 ± 1.51% were obtained. The SCB was subjected to dilute acid hydrolysis, and under optimized conditions, the maximum glucose, xylose and arabinose concentrations obtained were 15.26 ± 0.37 g/L, 11.62 ± 0.21 g/L and 3.58 ± 0.17 g/L, respectively. The results of SEM, FTIR and XRD analysis suggested that the proposed method effectively removed lignin and disrupted the crystal structure of cellulose for a better hydrolytic process. The fermentation of hydrolyzate with *Saccharomyces cerevisiae* showed maximum bioethanol production of 13.1 g/L at the end of 72 h and bioethanol yield of 0.184 g/g SCB.

1. Introduction

The depletion of fossil fuel reserves and increase in greenhouse gas emissions necessitated the production of economically feasible alternative fuels from biomass. Lignocellulosic biomass (LCB) is an attractive feedstock for the production of second generation biofuels since they are cheap and abundant in nature [1]. LCBs including corn stover, rice straw, sugarcane bagasse (SCB), garden wastes and forest residues, were successfully used for ethanol production.

SCB is mainly composed of cellulose, hemicellulose and lignin. The conversion of complex cellulose and hemicellulose present in SCB into fermentable sugar poses a technical and economic challenge. The crystalline nature of cellulose and the strong protective layer around the lignin and hemicellulose hinder the breaking of β-(1, 4) – glycosidic bonds of cellulose by acid/enzyme catalysts. In order to facilitate the hydrolytic reaction, a variety of pretreatment methods including alkali pretreatment, acid hydrolysis, steam explosion, liquid hot water process, wet oxidation, ammonia fiber explosion (AFEX), biological pretreatment and pretreatment with

---

* Corresponding author. Tel.: +91 44 22359153; fax: +91 44 22352642.
E-mail address: muthukumar@annauniv.edu (K. Muthukumar).

http://dx.doi.org/10.1016/j.cej.2014.08.006
1385-8947/© 2014 Elsevier B.V. All rights reserved.

hydrogen peroxide have been developed [2]. The pretreatment process disrupts the crystalline structure and reduces the degree of polymerization of cellulosic region. This makes cellulose and hemicellulose more suitable for hydrolytic process, which converts these polymers to fermentable sugars [3]. It should be noted that few pretreatment processes require high pressure, high temperature and chemicals like acid or alkali [4].

The performance of pretreatment can be improved by the addition of inorganic salts [5] and the main advantage of using inorganic salts is that it is recyclable and less corrosive than inorganic acids [6]; also it alters the structure and greatly affects the composition of biomass [5]. The combined effect of alkaline hydrogen peroxide with metal ions produces hydroxyl radicals and superoxide ions, which decompose the lignin [7]. The effective formation of phenoxy radicals is due to the action of hydroxyl radical and metal ions [8]. The usage of inorganic salts expected to increase the hydrolysis rate of pentose and hexose sugar and this result in higher sugar yields [9,10].

The aim of the present study was to maximize the cellulose recovery and delignification besides reducing the pretreatment time and inhibitors formation. The effect of various dual salts on the pretreatment of sugarcane bagasse with hydrogen peroxide was studied and the influence of operating parameters such as H_2O_2 concentration, SCB dosage, reaction rime, temperature and molar ratio of metal salts to H_2O_2 was also studied. The pretreatment was performed at moderately rigorous conditions in order to reduce the formation of inhibitory products.

2. Materials and methods

2.1. Materials

Sugarcane bagasse (SCB) was collected from the local sugarcane processing unit located at Chennai, Tamil Nadu. SCB was washed thoroughly with distilled water to remove the soluble sugars, and kept in a hot air oven at 60 °C for 24 h. The dried SCB was ground and screened to a particle size, below 1 mm (>18 mesh size, ASTM Standard) using a sieve shaker. The sieved biomass was stored in an air tight polyethylene bag, at room temperature for further use. The chemicals such as 3, 5-dinitrosalicylic acid, manganese sulfate, acetone were purchased from Sisco Research Laboratory Pvt., Ltd., Mumbai, India, sulfuric acid was purchased from Thermo Fischer Scientific India, Ltd., Mumbai, India, 30% hydrogen peroxide was purchased from Merck Specialties Private Ltd., Mumbai, India, and zinc oxide was purchased from Sigma–Aldrich chemicals Pvt., Ltd., Bangalore, India. The chemicals used in this investigation were analytical grade and used as such without any further treatment.

2.2. Pretreatment

The SCB was pretreated using hydrogen peroxide in the presence of dual salt. Metal salts such as manganese sulfate monohydrate ($MnSO_4{\cdot}H_2O$), zinc oxide (ZnO), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), ammonium molybdate ($(NH_4)_6Mo_7O_{24}$), cobalt chloride ($CoCl_2$), and titanium dioxide (TiO_2) were employed. The influence of operating parameters, such as H_2O_2 concentration (0.25, 0.50, 1 and 2% v/v), SCB dosage (1, 2, 3 and 4 g), reaction time (15, 30, 45 and 60 min), temperature (25, 50, 75 and 100 °C) and molar ratio of metal salts to H_2O_2 (0.5:100, 1:100, 2:100 and 4:100 g/mL) were investigated. The pretreated SCB was filtered, washed several times with distilled water, hot water and finally with acetone to remove metal salts. The filtered residue was dried at 60 °C until a constant weight was observed, and then it was subjected to dilute acid hydrolysis. The % cellulose recovery in the solid content was calculated using the following equation.

$$\%\ \text{Cellulose recovery} = \frac{R_{\text{PT-SCB}}}{R_{\text{SCB}}} \times 100 \tag{1}$$

where R_{SCB} is the amount of cellulose in native SCB and $R_{\text{PT-SCB}}$ is the amount of cellulose in pretreated SCB expressed in (g/g).

The % delignification was calculated using the following equation:

$$\%\ \text{Delignification} = \left(\frac{D_{\text{SCB}} - D_{\text{PT-SCB}}}{D_{\text{SCB}}}\right) \times 100 \tag{2}$$

where D_{SCB} is the amount of lignin present in the native SCB, and $D_{\text{PT-SCB}}$ is the amount of lignin in the pretreated SCB, measured in (g/g).

2.3. Hydroxyl radicals measurement

The hydroxyl radicals formed during the pretreatment of SCB using dual salt with H_2O_2, played a vital role in removing lignin. In the present study, hydroxyl radicals formed were measured by Fricke dosimetry [11]. The Fricke solution was prepared, using 1 mM $FeSO_4$, 0.4 M H_2SO_4 and 1 mM NaCl. The amount of hydroxyl radicals present was estimated based on the oxidation of Fe^{2+} to Fe^{3+}. Initially, Fricke solution was added with SCB, H_2O_2 and dual salt. Then, the reaction was carried out as per the pretreatment conditions. The samples were withdrawn at regular time intervals and Fe^{3+} formed was determined by observing the absorbance at 304 nm using Elico double beam SL210 UV–Visible spectrophotometer. The number of hydroxyl radicals formed in the Fricke solution is theoretically equal to one quarter the amount of Fe^{3+} produced [12]. The concentration of H_2O_2 was indirectly measured by the iodine method [13]. About 2 mL of liquid sample was mixed with 0.75 mL of iodine indicator (0.06 M sodium hydroxide, 0.2 mM ammonium molybdate and 0.4 M potassium iodide) and 1 mL of 0.1 M potassium biphthalate. The absorbance of the treated sample was measured at 351 nm in a UV–Visible spectrophotometer.

2.4. Dilute acid hydrolysis

Dilute acid hydrolysis was carried out in an Erlenmeyer flask (250 mL) containing SCB with maximum cellulose content. About 1 g of pretreated SCB was suspended in different concentrations (0.25, 0.5, 1 and 2% v/v) of sulfuric acid solutions and experiments were carried out at 121 °C and at a constant solid-to-liquid ratio of 1:20 g/mL for 15 min. After the hydrolysis, the mixture was cooled to room temperature. Then, the samples obtained were centrifuged at 8000 rpm for 10 min and the supernatant obtained was subjected to glucose, xylose, arabinose, acetic acid and furfural analysis [14]. The optimum concentration was selected based on the sugar yield. The hydrolyzate obtained was neutralized using sodium hydroxide (2 N) to obtain the neutral pH solution for fermentation. All the experiments were carried out in triplicate and the average values were reported. The catalytic efficiency [E] of dilute acid hydrolysis was calculated, using the following equation [15]:

$$[E] = \frac{\sum S}{1 + \sum I} \tag{3}$$

where $\sum S$ is the sum of the sugar concentrations in the hydrolyzate (glucose, xylose and arabinose) and $\sum I$ is the sum of the inhibitor concentration in the hydrolyzate (acetic acid and furfural).