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Kinetic studies of two-stage sulphuric acid hydrolysis of sugarcane bagasse

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ABSTRACT

The present paper reports the two-stage hydrolysis of sugarcane bagasse to produce monomer sugars by using dilute and concentrated sulphuric acid. About 88% of the sugars present in bagasse could be recovered with a little formation of toxic compounds such as furfural/HMF. The sugar concentration in the first-stage of hydrolysis was obtained as xylose-rich solution of 49.7 g l^{-1} using 8% acid concentration at 100 °C and a solid to liquid ratio of 1:4, whereas, with the same solid to liquid ratio of 1:4, 73.4 g l^{-1} glucose-rich solution was obtained in the second-stage of hydrolysis by using 40% acid concentration at 80 °C. The acid hydrolysis of bagasse could be described by a first-order, two-step consecutive reaction model, where the polysaccharides first decompose into monomers through hydrolysis, and thereafter, decompose into various products in the second step. The proposed kinetic model correlates the experimental data satisfactorily.

1. Introduction

Fossil fuel reserves are limited and are depleting at a fast rate. Energy production from fossil fuels is also harmful to environment, and is an agent of global climate change to a large extent. Therefore, it is prudent to explore the possibility of exploitation of renewable energy sources such as biomass which is carbon-neutral, and has the potential of providing clean energy in a sustained manner. Biochemical conversion of biomass into liquid fuels is one such option which has attracted worldwide attention. Biomass-derived ethanol can be used as an alternative automotive fuel, preferably as a blend with gasoline. For countries like India, the use of ethanol-blended gasoline as a fuel in the transport vehicles is economical as it imports majority of crude oil for gasoline manufacture, and thus spends a large amount of foreign exchange on oil import [1]. The production of ethanol as a fuel from biomass-based feed-stocks is a closed carbon cycle process, and therefore, the use of ethanol reduces CO_2 emission to atmosphere proportionately.

The traditional feed-stocks for ethanol production such as corn, food grains, sugarcane juice, and cane molasses affect food security for human and live-stock population, particularly, the rural population in developing countries. Since lignocellulosic biomass, which includes forest residues such as wood; agricultural residues such as sugarcane bagasse, corncob, corn stover, wheat straw and rice straw; industrial residues such as pulp and paper processing waste and sugar mill press mud, and municipal solid wastes; and energy crops such as switch grass, etc., is

Abbreviations: A, Polymer; $A_{1,2}$, Pre-exponential factor, min^{-1}; C_A, Concentration of polymer, mol l^{-1}; C_{Acid}, Concentration of acid, % (w/w); C_D, Concentration of decomposition products, mol l^{-1}; C_M, Concentration of monomer, mol l^{-1}; D, Decomposition products; E, Activation energy, kJ mol^{-1}; k_1, First order reaction rate constant for step 1, min^{-1}; k_2, First order reaction rate constant for step 2, min^{-1}; k_o, Frequency factor, min^{-1}; k'_x, Pre-exponential factor, min^{-1}; M, Monomer; m_{Ao}, Initial mass concentration of the polymer, g l^{-1}; m_M, Mass concentration of the monomer, g l^{-1}; O, Oligomers; r, Rate of reaction, mol l^{-1} min^{-1}; R, Universal gas constant (8.3143 × 10^{-3} kJ mol^{-1} K^{-1}); T, Absolute temperature, K; X, Xylose; α, Ratio of molecular weight of polymer per unit sugar to molecular weight of monomer; β, Acid concentration exponent; η_{Hyd}, Hydrolysis efficiency, %.

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available in abundance, it can be used as an alternative feed-stock for bioethanol production [1–5]. The availability of such lignocellulosic biomass for exploitation as a feed-stock for ethanol production depends on geographical, climatic and anthropogenic factors, other environmental factors, particularly agricultural and forestry practices, and usage/consumption pattern of farm and forestry products.

Several biochemical routes are used to produce biofuels such as ethanol, butanol, etc. Biochemical routes for producing ethanol from lignocellulosic materials have four major unit processes/operations: (i) hydrolysis of the hemicellulose and the cellulose to monomeric sugars, (ii) separation and recovery of various sugars, (iii) fermentation of sugars, and (iv) product recovery and concentration by distillation [5–7].

For economical production of ethanol, both cellulose and hemicellulose present in a typical biomass need to be hydrolyzed. Biomass can be hydrolyzed with an acid or with an enzyme. The enzymatic hydrolysis generally produces hydrolysate which has less inhibitory impact on the fermentation step than the acid hydrolysate. However, low specific activity of enzymes on lignocellulosic biomass, requirement of one or more pretreatment steps, and the relatively slower rate of hydrolysis make the acid hydrolysis more competitive [5,6,8].

Hydrolysis of lignocellulosic biomass is a complex process. The complexity arises from the embedded structure of cellulose, hemicellulose and lignin in the biomass matrix. Cellulose is present in crystalline and amorphous forms which behave differently when treated with acids [9]. Hemicellulose is a complex of a large number of sugar monomers-glucose, xylose, arabinose, etc. and other compounds containing acetyl groups and uronic acids, etc. [10]. The linkages between these compounds make it a ramified polymer with an unknown structure [11].

Acid hydrolysis is generally of two types: dilute acid hydrolysis and concentrated acid hydrolysis. In dilute acid hydrolysis, the acid strength is generally $\leq$10% (w/w), whereas in the concentrated acid hydrolysis, the acid concentration is $\geq$10% (w/w) [12,13], although some investigators call dilute acid hydrolysis with acid concentration at $\leq$3% (w/w) and concentrated acid hydrolysis with acid concentration $\geq$3% (w/w). Dilute acid hydrolysis has been a preferred mode of hydrolysis so far due to its low acid consumption. However, some researchers reported higher sugar recovery, up to 90% of theoretical yield, for both glucose and xylose under mild operating conditions using concentrated acid hydrolysis [5,14].

Any of the acids, viz. sulphuric, hydrochloric, nitric, or phosphoric acid can be used for hydrolysis [15], although sulphuric acid has been used in most of the studies [2,3,5,6,8–10]. The biomass can be hydrolyzed with acid either in a single stage or in two stages. In two-stage hydrolysis, biomass is treated first with dilute acid and then with concentrated acid. In the first-stage, the dilute acid mainly hydrolyses the hemicelluloses that are solubilized at milder conditions than the cellulose. The residual cellulose is, thereafter, hydrolyzed by more concentrated acid [16]. The advantage of the dilute acid hydrolysis is that the process does not require acid recovery, whereas, the two-stage hydrolysis increases the total hydrolysis time, and the loss of acid is insignificant [6,10]. The majority of the acid hydrolysis studies reported in the literature were carried out in a single stage. However, a few studies dealt with two-stage acid hydrolysis too [5,10].

The present study deals with the two-stage acid hydrolysis of sugarcane bagasse using sulphuric acid as a catalyst at a relatively milder temperature. The study also reports on the kinetics of the two-stage acid hydrolysis, and the results of the various kinetic parameters that were estimated from the experimental data using the proposed kinetic model.

2. Materials and methods

2.1. Chemicals and raw material used

Sulphuric acid (H_2SO_4), LR grade was procured from Ranbaxy Fine Chemicals Ltd., New Delhi, India. Sugarcane bagasse (compositions of glucan 35% and xylan 26%) was collected from a sugar mill in Northern India. Amberlite (IRA-904 No. A-4275 chloride forming strongly basic anion exchanger, approximately 58% moisture) was procured from Sigma–Aldrich, USA. Alumina and acetonitrile for HPLC and spectroscopy, and furfuraldehyde (furfural), LR grade were procured from S.D. Fine-Chemicals Ltd., Mumbai, India.

2.2. Hydrolysis of sugarcane bagasse

The hydrolysis of bagasse using sulphuric acid was carried out in a high pressure stainless steel autoclave of 700 ml working volume (Ernst Haage, Germany) in two stages: dilute sulphuric acid used in the first stage and, thereafter, concentrated sulphuric acid in the second stage. The digested material was then taken out of the autoclave and filtered through a muslin cloth of pore size 0.7 mm. The residual material was washed twice by mixing with 50 ml of fresh water and filtered through the muslin cloth. The total filtrate, including the washings, was filtered again through a 0.2 μm Whatman GF/C filter paper using a vacuum filtration unit.

In the first-stage of hydrolysis, 35 g of crushed sugarcane bagasse (dry basis) was soaked in 350 g of dilute acid (i.e. a solid to liquid ratio of 1:10) with acid concentration in the range of 1.8%–5.4% (w/w). Initially, the hydrolysis was carried out for 120 min at a temperature of 121 °C. It was observed that the furfural concentration in the hydrolysate obtained from the first stage of hydrolysis was $\geq$1 g l^{-1}. Therefore, some hydrolysis experiments were conducted for 90 min duration at a temperature of 100 °C. In these experiments, 35 g of crushed bagasse (dry basis) was soaked in 280 g of dilute acid with varying acid concentration in the range of 2%–10% (w/w) in the autoclave. The solid to liquid ratio was also varied in the range of 1:8 − 1:4 for the selection of the optimum ratio.

In the second-stage of hydrolysis, the residual bagasse from the first-stage of hydrolysis was soaked in concentrated acid (18%–40% w/w), using a solid to liquid ratio of 1:4. The hydrolysis was carried out for 90 min at a temperature of 80 °C.

2.2.1. Recovery of sugars from hydrolysate

The sugars from the bagasse hydrolysate were recovered by ion-exchange chromatography using a mixture of amberlite IRA-904 and alumina as an anionic resin. About 700 g of the resin was packed in a 30 mm diameter and 1000 mm long glass column. The bagasse hydrolysate was passed through the column from the top to the bottom at a constant flow rate. The flow rates at the inlet and the outlet were maintained constant and same so as to maintain the level of hydrolysate in the column constant. The effect of the flow rate of the hydrolysate on the separation efficiency was studied in the flow rate range of 4–17 ml min^{-1}. The sulphuric acid was retained by the resin in the column and the sugars were eluted. In the regeneration step, the acid was recovered by passing distilled water through the column. The recovered acid solution was recycled back for the hydrolysis of fresh sugarcane bagasse. This ensured no acid loss in the process.

2.3. Analytical methods

Sugars (glucose and xylose) were analysed by a HPLC using