Auto-hydrolysis of Lignocellulosics Under Extremely Low Sulphuric Acid and High Temperature Conditions in Batch Reactor

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Abstract Batch reactors were employed to investigate the kinetics of cellulose hydrolysis under extremely low acid (ELA) and high temperature condition. The sawdust was pretreated by Auto-hydrolysis prior to the batch reaction. The maximum yield of glucose obtained from the batch reactor experiment was about 70% for the pretreated sawdust, this occurred at 210 and 220°C. The maximum glucose yield from the untreated sawdust was much lower at these temperatures, about 55%. The maximum yields of glucose from the lignocellulosics were obtained between 15th and 20th minutes after which gradual decrease was observed.

Keywords: auto-hydrolysis, lignocellulosics, kinetics, cellulose hydrolysis

INTRODUCTION

Acid based hydrolysis of biomass is not uncommon process of saccharification that is been employed in the industries. There have been numerous literatures on hydrolysis of cellulose and lignocellulose [1-3]; Solomon *et al.* [4] reported acid and enzymatic hydrolytic process of sawdust where the kinetic were studied, Ojumu *et al.* [5] reported cellulase enzyme production from sawdust, corncob and bagasse using *Aspergillus flavus* Badmus [6] produced glucose from palm tree trunk via acid hydrolysis using auto hydrolysis prior to the acid hydrolysis obtaining 70% glucose yield at 2.0% Sulphuric acid. Jeffries and Lee [7] also reported auto-hydrolysis (steam explosion) as an effective pretreatment method for lignocellulosic materials for hydrolysis. In fact Boussaid *et al.* [1] reported an increasing glucose concentration in the hydrolysate as the severity of stem explosion increases.

Effort has been geared towards achieving hydrolysis of cellulosic materials under very extremely low acid (< 0.1%) and high temperature, thereby obtaining improved yield of glucose [8]. Although the extremely low acid condition are beyond the region normally explored in the convectional acid hydrolysis process, there are distinct advantages of using extremely low acid (ELA) conditions for hydrolysis of lignocellulosics biomass.

The corrosion characteristics of ELA are very close to a neutral aqueous reaction, thus standard grade stainless steel equipment can be used instead of high nickel alloy. ELA also gives a significant cost advantage in the equipment; According to Kim *et al.* [8] the advancement made in ELA has brought the hydrolysis to a position where it can favorably compete with enzymatic hydrolysis in the overall process economics. The process of using ELA could be regarded has being environmental friendly because it has a minimal environmental effect. Recent findings have proven that yields in the region of 61% are attainable with pure cellulose hydrolysis under the ELA conditions using batch reactor.

The present study was undertaken to investigate the effect of auto hydrolysis prior to hydrolysis under ELA and high temperature conditions, and to provide kinetic data on the reactions taking place under this condition.

MATERIALS AND METHODS

Materials

The sawdust was obtained from sawmill around Obafemi Awolowo University (OAU) vicinity in Ile-Ife town, it was derived from softwood tree *Triplochiton scleroxylon*. It was milled to pass through a 12-mesh screen (1.44 mm) and this was used as the standard substrate. The composition of *T. scleroxylon* was 69.5-80% cellulose and hemicellulose and 25-30% lignin [9].

Auto-hydrolysis (Steam Cracking) Procedure

Kedjahl flask was filled with water to about ¼ volume and heated steadily at about 250°C to obtain superheated steam. The superheated steam was injected through a glass tubing into a round bottom flask containing about 5 g wood samples for 60 min. Care must be

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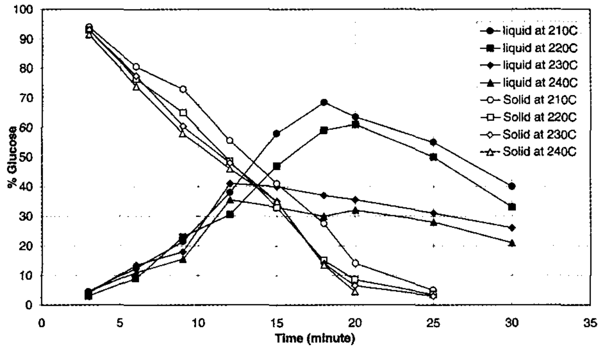

Fig. 1. Semilog plot of glucose remaining and glucose yield in batch reaction of pretreated sawdust.

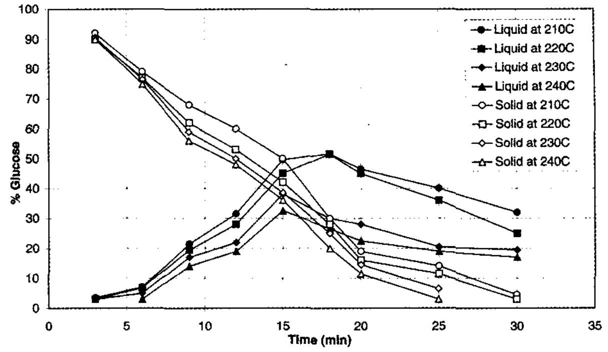

Fig. 2. Semilog plot of glucose remaining and glucose yield in batch reaction of untreated sawdust.

taken to avoid explosion by using plastic cork with two opening for glass tubing, the other opening vents the system of pressure build-up.

Batch Experiments

All the batch reactor experiments were carried out using sealed tubular reactors. The reactors each of 15 cm^3 internal volume were constructed with Hastelloy C-276 tubing (1.25). Both ends of the reactor were capped with Swagelok end caps measuring 1.27 cm wide 15.5 cm long. The reactors were packed with 1.0 g of solid substrate and 0.07%wt Sulphuric acid to achieve solid-to-liquid ratio of 1 : 10. The reaction temperatures were controlled in sand baths. The reactors were first submerged into a sand bath set at 50°C above the desired reaction temperature for rapid preheating and latter transferred quickly into another sand bath of desired temperature. The reaction temperature of 210, 220, 230 and 240°C were used for the experiment, the reactor temperature was monitored by means of a thermocouple inserted in the reactor. The reaction was quenched in an ice bath after the desired reaction time and the content of the reactor wee separated by filtration into solid and liquid which were subjected to analyses.

Analytical Methods

The sugars were determined using High performance liquid chromatograph using Bio-Rad Aminex HPX-87P column [8]. A refractive index detector was used. The compositional analysis of the solid biomass samples was carried out using the standard method recommended by Vinzant *et al.* [10]. The sugars in the liquid sample were determined after being subject to a secondary hydrolysis as prescribed by Kim *et al.* [8].

RESULTS AND DISCUSSION

ELA conditions have been applied for pure cellulose hydrolysis and it has produced remarkable results in that unusually high glucose have been achieved [8] ~61% in a batch reactor, a lower yield was achieved when applied on lignocellulosics. In this experiment, series of runs were conducted for the lignocellulosic sample (sawdust) - pretreated by auto-hydrolysis by using 0.07 wt.% Sulphuric acid at varying temperatures of 210, 220, 230 and 240°C. The progress of the reaction is summarized in Figs. 1 and 2

The results are shown in term of the percentage of glucan remaining in solid and the percentage glucose released in the liquid. The maximum yield of glucose obtained from the auto-hydrolyzed sawdust was about 70% for 210 and 220°C. However, at 240°C the maximum yield was less than 40%. The same experiments were conducted using the sawdust without auto-hydrolysis pretreatment. The overall reaction profiles shown in Fig.2 were similar to those of pretreated samples (Fig.1) only that the maximum yield of glucose was much lower at same temperature range being about 55%. Lower glucose yields were obtained at higher temperatures in both cases; this is contrary to the conventional concept of cellulose hydrolysis because the activation energy for hydrolysis is higher than that of the decomposition reaction as reported by Kim *et al.* [8].

Although the reaction profiles of untreated sawdust were similar to those auto-hydrolyzed, the batch yields obtained with auto-hydrolyzed sawdust were substantially higher than those of the untreated sawdust for all temperatures. This not a unique property of ELA but that of auto-hydrolysis. The auto-hydrolysis process weakens the bonds in the lignocellulosics, thus exposing these bonds for ELA penetration, this enhances reaction and thereby increasing the glucose yield. This was supported by the report of Boussaid *et al.* [1] and Badmus [6]. An increase in yield of glucose was reported by Boussaid *et al.* [1] as the severity of auto-hydrolysis increases from 175-215°C.

Another interesting point seen from the batch hydrolysis experiment is that at about 15 and 20 min of the experiment where the maximum yield was obtained, the glucose released into the liquid decrease steadily with time. This according to some workers could be attributed to the fact that; the released glucose decompose to furfural and hydroxymethylfurfural (HMF) [2,11]. Zerbe and Baker [2] reported an increase in decomposition rate to furfural as the reaction time increases; also some of it recondense with remaining cellulose or lignin, and some may repolymerize as suggested by Conner *et al.* [11]. However according to Kim *et al.* [8] the decreasing glucose yield was primarily due to the interaction of the released glucose with the non-glucosidic compound (lignin) in the liquid.

Acknowledgements The authors wish to thank the Management of Central Science Laboratory, Obafemi Awolowo University, Ile-Ife, for their support. Ojumu and AttahDaniel wish to the Management of Engineering Materials Development Institute, Akure, for their assistance, cooperation and support during the course of this research.

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[Received May 12, 2003; accepted July 19, 2003]