Acid-catalysed hydrolysis kinetics of sugar cane bagasse to glucose and xylose in selected ionic liquid media

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Abstract. The process of converting lignocellulosic biomass to fuels (such as ethanol) is considered a potential method for supplanting current fossil fuels with renewable sources. A significant inhibitor to such processes is the lack of an efficient and economical means by which hemicellulose and cellulose may be hydrolysed to their constituent monosaccharides as precursors for ethanol fermentation. This research details experiments conducted by which sugar cane bagasse (SCB) immersed in ionic liquids (either 1-butyl-3-methylimidazolium chloride or 1-ethyl-3-methylimidazolium chloride – BmimCl and EmimCl respectively) were catalysed to glucose and xylose by adding variable amounts of hydrochloric acid (3.5 – 10.5wt%) at temperatures between 100°C to 140°C. Experiments were conducted over 5 hours and in all experiments the monosaccharide concentrations increased to a maximum then decreased as the monosaccharides were degraded to other products. Maximum yields of glucose and xylose of 133mg/g bagasse and 125mg/g bagasse respectively were achieved although under different reaction conditions. The kinetics of the process was modelled as a simple set of first order reactions for the conversion of biomass to sugars then the degradation of sugars to other products.

1. Introduction

The development of an economically viable process by which waste lignocellulosic materials (e.g. sugar cane bagasse (SCB), wheat straw, forest wood residue) may be upgraded to fuels has, in most cases, been fruitless. Despite instances where these waste materials may be used directly by an industry close to the waste source (for example, the combustion of SCB in furnaces to power a sugar mill) the vast majority of waste material is disposed of by either burning, landfill or allowing to rot in the fields.

Cellulose constitutes more than 50% of the carbon content of the plant sector. As a polymer of glucose, a process whereby cellulose may be easily digested to the constituent monosaccharides is a key step for the conversion of lignocellulosic waste material to ethanol, a readily accepted transport fuel. However, cellulose in plant matter is substantially in the crystalline state which is compact and inhibits chemical or biological hydrolysis. If present in a dissolved or amorphous state, cellulose hydrolysis is kinetically more favourable [1].

To improve the dissolution of lignocellulosic materials, ionic liquid (IL) pretreatment of biomass has shown great promise to decrystallise cellulose [2] under mild conditions after which the cellulose may be isolated from the other biomass components [3]. Research on the hydrolysis of the recovered cellulose is substantially focussed on the use of enzymes despite the poor economics of such a proposed scheme [4]. An alternative scheme for hydrolysis of the cellulose (and hemicellulose) is acid-catalysed hydrolysis of the biomass while dissolved in an IL medium with downstream separation
of the sugars from the mixture [5,6]. Previous studies by Li et al. [7] reports 68% yields of total reducing sugars (TRS) from SCB dissolved in 1-butyl-3-methylimidazolium chloride (BmimCl) with the addition of hydrochloric (HCl) at 100°C. Kassaye et al. [8] reported a 92% yield of TRS from micro-crystalline cellulose (MCC) when dissolved in BmimCl with the addition of sulphuric acid catalyst at 180°C. They also noted that the yield was enhanced by first dissolving the MCC in the IL before addition of the catalyst. Other more complex acid catalysts have also been shown to produce high yields of TRS when used to hydrolyse lignocellulosic biomass to TRS in IL media [9, 10]. Despite the high achievable TRS yields, the work by Li et al [7] is the only one that has sought to model the kinetics of the process. In their work, they modelled the process of corn stalk hydrolysis as a simple series reaction of degradation of the biomass to TRS followed by degradation of the TRS to other products. They performed their analysis of TRS yield versus time for a single set of conditions without seeking to discriminate between the types of sugars produced.

The purpose of the research reported here was to study the acid-catalysed hydrolysis of SCB to sugars when contained in an IL medium and, furthermore, to model the kinetics of the process over a wider range of variables (i.e. acid concentration, temperature) than previously reported.

2. Materials and methods
SCB was sourced from Bunnings Pty Ltd. Samples were washed, then dried over night at 70°C before being crushed and mechanically sieved using 1–2 mm sieve mesh. The moisture content of the SCB was measured at 5.4%. Glucose and xylose (purity>99%), 1-ethyl-3-methylimidazolium chloride (EmimCl) and BmimCl (assay >98%) were purchased from Sigma-Aldrich, Sydney, Australia.

Hydrolysis experiments were based on the methods reported in Li et al. [7]. A pre-weighed sample of SCB (0.4g) was added to a preheated mixture of IL (8g) and water (0.06g) at the desired temperature (100, 110, 120, 130 or 140°C) contained in a stirred test tube within a heated oil bath. An appropriate amount of concentrated HCl (37wt%) was then added so that the concentration of HCl was either 3.5, 7 or 10.5% (weight ratio of HCl to bagasse). At desired times (15, 20, 45, 60, 120, 150, 180, 240 or 300min), samples were withdrawn (0.25mL) and quenched using an ice-water bath and then neutralised with an appropriate amount of 0.25M NaOH followed by a small addition of water to make up a total volume of 5mL. The sample was then filtered using Grade 4 (20-25µm) Whatman filter paper. The filtrate was stored in a fridge at 4°C before proceeding to sugar analysis.

The concentrations of the sugars in the filtrate were measured using a Shimadzu HPLC with a refractive index (RI) detector (RID-10A). The column used was 300 x 7.8 mm Rezex RPM-Monosaccharide Pb+2 (8%) from Phenomenex, Australia. The column parameters are given in Table 1

| Table 1. Column Operating Parameters |
|--------------------------------------|
| Maximum pressure | 1000psi |
| Temperature | 85°C |
| Flow rate | 0.6 ml min⁻¹ |
| Detection | Refractive index |
| Mobile phase | Degassed Milli-Q water |
| Injection volume | 10µl |

The HPLC was calibrated to measure the concentrations of the sugars arabinose, cellobiose, fructose, galactose, glucose, mannose, sucrose and xylose.

3. Results and discussion
In all trials conducted, only the monosacchardies glucose and xylose were measured to any significant extent in the hydrolysate. Peaks for the sugars cellobiose, galactose and arabinose were detected by HPLC but in negligible quantities. In all further discussion only the results for glucose and xylose concentrations will be given.

Figure 1 shows a typical set of experimental data of the yield of glucose, xylose and total reducing sugars (TRS – the sum of the glucose and xylose yields) in IL hydrolysate for, in this instance, ionic...
liquid composed of BmimCl, temperature of 120°C and HCl concentration (i.e. mass ratio of HCl to bagasse) of 7%.

The yield of each sugar increased over time as the hemicellulose and cellulose were hydrolysed to, chiefly, xylose and glucose respectively, reaching a maximum before declining as the dissolved sugars were degraded to other products. Although the shapes of the curves for the yield were similar, there is enough difference to question the accuracy of modelling the hydrolysis process based on the TRS yield.

It is noted that the initial yields of glucose from the reaction is higher than that for xylose. This is in stark contrast to what occurs if the hydrolysis were conducted in an aqueous media. Under those conditions, xylose would appear first as the hemicellulose is more easily hydrolysed from the solid biomass. The hydrolysis of cellulose, which is a far more refractory component, occurs later if at all [11]. The effect of the IL in dispersing the SCB within the liquid media has clearly aided in the hydrolysis of the cellulose component. The maximum sugar yields, however, were relatively low compared to that reported in the literature.

It is noted also that the maximum yield of xylose is higher than that achieved for glucose despite the amount of cellulose in the biomass being significantly higher than that of hemicellulose. In all experiments the dissolution of the biomass within the IL was not total, i.e. solids were still apparent and samples taken for HPLC needed to be filtered to remove insoluble particles. The solubility of cellulose in IL is strongly influenced by the presence of water so the relatively low amounts of glucose formed may be a result of incomplete dissolution of the cellulose in the IL. Figures 2 and 3 shows the yield of glucose and xylose, respectively, at varying acid concentrations. As can be seen from the figures, the initial rate at which the monosaccharides are produced is rapid and relatively unaffected by the HCl concentration used. However, at the lowest acid concentration the rate of degradation is significantly reduced hence the maximum sugar yields are significantly higher than that at the higher acid concentrations. It is clear from these results that lower acid concentrations would preference optimum sugar yields.

Figure 4 shows the yield of sugars when two different ILs (EmimCl and BmimCl) are used. It is readily apparent that the alkyl chain length on the imidazolium ion has a significant effect on the sugar yields. The shorter alkyl-chain length of EmimCl leads to a reduction of the maximum sugar yield. This is despite reports that EmimCl is a more powerful solvent for cellulose [13] so should enable
more rapid hydrolysis of the cellulose fraction of the biomass. The effect of the chemical structure of an IL on hydrolysis kinetics clearly warrants a more thorough study to understand this phenomena.

![Graph showing glucose yield from the acid hydrolysis of SCB in BmimCl](image1)

**Figure 2.** Glucose yield from the acid hydrolysis of SCB in BmimCl

![Graph showing xylose yield from the acid hydrolysis of SCB in BmimCl](image2)

**Figure 3.** Xylose yield from the acid hydrolysis of SCB in BmimCl

To model the kinetics of the hydrolysis of cellulose/hemicellulose to glucose and then degradation of glucose to other products, Li et.al assumed a simple series of two consecutive first order reactions:

$$\text{cellulose} \xrightarrow{k_1} \text{glucose} \xrightarrow{k_2} \text{decomposition products of glucose}$$

where $k_1$ is the rate constant for the cellulose hydrolysis and $k_2$ is the rate constant for glucose degradation. The approach used here is the same other than the hydrolysis of hemicellulose to xylose is also modelled:
hemicellulose $\rightarrow$ xylose $\rightarrow$ decomposition products of xylose

where $k_3$ is the rate constant for the hemicellulose hydrolysis and $k_4$ is the rate constant for xylose degradation. For an experiment conducted at a single, constant temperature the rate of formation of products is given by the equation:

$$C_i = C_{i,0} \left( \frac{k_j}{k_{j+1} - k_j} \right) \left( e^{-k_{j+1}t} - e^{-k_jt} \right) \quad (1)$$

where $C_i$ is the concentration of ‘i’ (glucose or xylose and $j=1$ for glucose and $j=3$ for xylose) in the liquid, $C_{i,0}$ is the maximum concentration of glucose or xylose that can be produced if all the cellulose/hemicellulose were converted to glucose/xylose, and $t$ is time of reaction.

The rate constants $k_1$ to $k_4$ are modelled via the Arrhenius equation:

$$k_i = A_i e^{-E_i/RT} \quad (2)$$

where $A_i$ is the pre-exponential constant for reaction $i$, $E_i$ is the activation energy for reaction $i$.

The parameters $A_i$, $E_i$ and $C_{i,0}$ were calculated using a Marquardt-Levenberg curve fitting routine available in Sigmaplot version 5.0.

Figures 5 and 6 show the yields (shown as data points) of glucose and xylose, respectively, at temperatures between 110°C and 140°C. It can be seen that that the rate of sugar yield is quite different between the two monosaccharides. As the temperature increases, the rate at which glucose and xylose are produced increases. However, the maximum yield decreases with increasing temperature for glucose, whereas the maximum yield increases with temperature for xylose. Overlaying the experimental points are lines for the model fits obtained from the curve fitting assuming consecutive first order reactions for the formation and degradation on glucose and xylose. The curve fits are quite poor, with correlation coefficients $R^2 = 0.74$ and 0.53 for the glucose and experimental results respectively. In all sets of model curves the maximum yield is underestimated by a large margin.
The parameters extracted from the model fit to the experimental data were: i) For glucose, $C_{\text{max}} = 147$ mg/g bagasse, $A_1 = 6.04 \times 10^6$ min$^{-1}$, $E_1 = 65.6$ kJ/mol, $A_2 = 4.71 \times 10^6$ min$^{-1}$, $E_2 = 88.1$ kJ/mol, and; ii) for xylose, $C_{\text{max}} = 147$ mg/g bagasse, $A_3 = 8.82 \times 10^5$ min$^{-1}$, $E_3 = 58.8$ kJ/mol, $A_4 = 2.16 \times 10^4$ min$^{-1}$, $E_4 = 46.4$ kJ/mol.

It is clear that the modelling of the data assuming consecutive first order equations provides poor accuracy to the experimental data. This was especially true when inspecting the peak yields of sugars – the model fit has much lower values than that measured. However, both model fit and experimental data do agree that the maximum yield of the xylose and glucose are significantly lower than the potential yields if all cellulose and hemicellulose were hydrolysed to their constituent sugars. Clearly an investigation of different hydrolysis mechanisms and kinetics is warranted.
Conclusions

The hydrolysis of SCB to the monosaccharides glucose and xylose was conducted using HCl as a catalyst in the IL BmimCl or EmimCl at temperatures between 100°C and 140°C over a time period of 5 hours. In all experiments the yield of sugars increased to a maximum then declined as the sugars were degraded to other products. The maximum yield was affected by the temperature of reaction, the acid concentration and the IL used. The reaction kinetics were modelled by assuming two, consecutive, first order reactions for the formation of the sugars from the cellulose/hemicellulose followed by degradation to other products. However, the ‘line of best fits’ found from the models were only a poor approximation to the experimental data indicating that a different set of models needs to be investigated.

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