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Dilute acid hydrolysis of lignocellulosic biomass

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ABSTRACT

The overall aim of this work was to establish the optimum conditions for acid hydrolysis of hemicellulosic biomass in the form of potato peel. The hydrolysis reaction was undertaken in a 1l high pressure pilot batch reactor using dilute phosphoric acid. Analysis of the decomposition rate of hemicellulosic biomass (namely Cellulose, Hemicellulose and lignin) was undertaken using HPLC of the reaction products namely, 5 and 6 carbon sugars. Process parameters investigated included, reactor temperature (from 135 °C to 200 °C) and acid concentration (from 2.5% (w/w) to 10% (w/w)). Analysis of the reactor products indicated that high conversion of cellulose to glucose was apparent although arabinose conversion was quite low due to thermally un-stability. However, an overall sugar yield is 82.5% was achieved under optimum conditions. This optimum yield was obtained at 135 °C and 10% (w/w) acid concentration. 55.2 g sugar/100 g dry potato peel is produced after a time of 8 min. The work indicates that the use of potato peel may be a feasible option as a feed material for the production of sugars for biofuel synthesis, due its low cost and high sugar yields.

1. Introduction

1.1. Dilute acid hydrolysis

Dilute or concentrated acids break down the cellulose and hemicellulose polymers in lignocellulosic biomass to form individual sugar molecules which can be fermented into ethanol [1]. It is important to note that hemicellulose is more easily hydrolysed than cellulose [2].

The advantages of acid hydrolysis are that the acid can penetrate lignin without pretreatment, the rate of acid hydrolysis is faster than enzyme hydrolysis, but glucose also degrades rapidly under acidic conditions [3]. The acid hydrolysis process employs usually sulphuric acid and hydrochloric acid at concentrations of 1–10% using a moderate temperature (in the range of 100–150 °C) [4]. But in these relatively moderate operational conditions, it proves less effective in the formation of hexoses [5]. This is mainly due to the decomposition of the monosaccharides into less desirable compounds during hydrolysis. These compounds include furfural, a product of dehydration of pentoses and hydroxymethylfurfural-HMF, a product of the dehydration of hexoses. These compounds along with acetic acid which forms during initial decomposition of the hemicelluloses, as a result of hydrolysis of acetyl groups linked to the sugar, inhibit the later fermentation, leading to reduced ethanol yields [6]. The production of these inhibitors increases when hydrolysis takes place at higher temperatures and higher acid concentrations [7].

Sulphuric and hydrochloric acids are the most commonly used catalysts for hydrolysis of lignocellulosic residues. In contrast to these acids, phosphoric acid can be more advantageous for hydrolysis. Phosphoric acid is less aggressive than other acids which give solutions with higher concentrations of growth inhibitors of microorganisms such as furfural or acetic acid [6].

Dilute phosphoric acid, on hydrolysates from sugarcane bagasse, has shown fermentable sugars with 21.4 g of sugar L^{-1} with less than 4 g L^{-1} of inhibitors at operating conditions of 6% acid concentration at 100 °C for 300 min [8]. Similarly on hydrolysates from olive tree pruning, have shown hemicelluloses conversion rates of 77% with glucose and reducing sugar concentrations being observed as 89% of the hemicellulosic sugars contained in the raw material at conditions of 8% acid concentration at 90 °C for 240 min [6].

These hydrolysates obtained after the acid hydrolysis need to be processed if they are going to be used as fermentation media. In general the following operations are needed (in this sequence): concentration, detoxification, neutralisation and supplementation with nutrients. This process is illustrated in Fig. 1. The concentration of hydrolysates by evaporation is usual to increase the sugar concentration. In this operation, besides water, small amounts of growth inhibitors such as acetic acid, furfural and HMF are removed [8]. A detoxification operation by adsorption on active carbon in the form of charcoal can remove the growth inhibitors cited. In this operation, phenolic compounds proceeding from lignin can also be removed [8]. In the operation of neutralisation, it is usual to add

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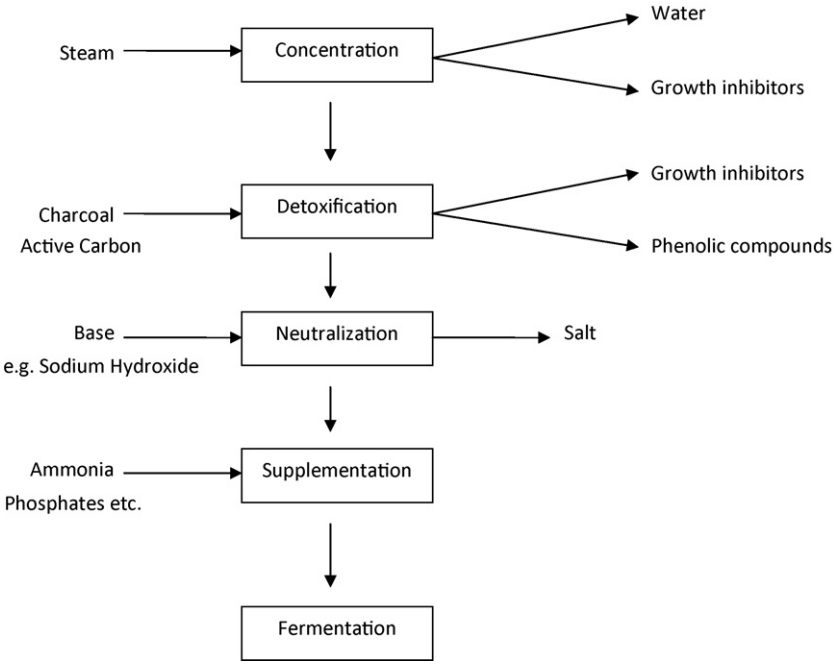

Fig. 1. General operations required after hydrolysis prior to fermentation.

chemicals that neutralise the acids of the hydrolysates, forming salts [9].

These salts have low solubility and are normally removed by filtration. For example, hydrolysates containing sulphuric acid are neutralised with calcium carbonate, forming calcium sulphate [5]. Finally, the processed hydrolysates are supplemented with several nutrients to be a favorable fermentation medium. These nutrients contribute the nitrogen and micronutrients needed for the growth of the microorganisms [10].

The interest in the use of H_3PO_4 is that after neutralisation of hydrolysates with NaOH, the salt formed is sodium phosphate. This salt can remain in the hydrolysates because it is used as nutrient by microorganisms. Therefore, an operation of filtration is not needed with the consequent advantage: improve the economics of the process (avoid the filtration to remove the salts and decrease the amount of nutrient needed for fermentation) and is friendly with the environment (the salt formed is not a waste) [5].

1.2. Kinetics of acid hydrolysis of cellulose

The hydrolysis reactions using dilute acid are very complex, mainly because the substrate is in a solid phase and the catalyst in a liquid phase. The reaction rate of hydrolysis depends on a number of variables, such as: temperature, acid concentration, time, substrate concentration and substrate composition. The practical objective of studying the kinetic model is, on a first level, to optimise the process and, on a second level, to obtain equations useful for economical estimations [8]. The models usually associated with dilute acid hydrolysis were first proposed by Saeman [11], for the hydrolysis of Douglas fir wood using sulphuric acid. The models proposed in the literature use irreversible pseudo-homogeneous first-order reactions [12–14]. They proposed that hydrolysis of cellulose involves the polymer glucan of cellulose being degraded to monomer glucose which is subsequently converted to decomposition products. This is represented below:

$$\text{glucan(s)} \xrightarrow{K_1} \text{glucose} \xrightarrow{K_2} \text{decomposition products} \quad (1)$$

where K_1 is the rate of conversion of glucan to glucose and K_2 is the rate of decomposition of glucose. Both have units of the reciprocal of time (min^{-1}). Both reactions were considered to be first order and irreversible. Saeman's model could also be applied to the hydrolysis of hemicellulosic fraction. Therefore this reaction was generalised to:

$$\text{Polymer} \xrightarrow{K_1} \text{Monomer} \xrightarrow{K_2} \text{decomposition products} \quad (2)$$

where the polymer can be glucose, xylose or araban.

From this reaction model and solving differential equations, monomer concentration (M) as a function of time (t) can be represented by [15]:

$$M = \left[\frac{k_1 P_0}{k_2 - k_1}\right](e^{-k_1 t} - e^{-k_2 t}) + M_0 e^{-k_2 t} \quad (3)$$

where M is the monomer concentration, g L^{-1}; P the polymer concentration, g L^{-1}; M_0 is the initial monomer concentration, g L^{-1}.

Assuming that the initial monomer concentration to be approximately equal to 0, then Eq. (1) can be simplified to [15]:

$$M = \left[\frac{k_1 P_0}{k_2 - k_1}\right](e^{-k_1 t} - e^{-k_2 t}) \quad (4)$$

An alternative model called the two fraction model is often used to describe the reaction kinetics and is tested against the Saeman's model to provide accuracy. This model considers that only a fraction of the polymer reacts. This is called the fast fraction, and the fraction that does not react or reacts slowly is called the slow fraction. The ratio between them is the parameter α. In the case that the slow fraction does not react, the following equation is used [8]:

$$M = \alpha\left[\frac{k_1 P_0}{k_2 - k_1}\right](e^{-k_1 t} - e^{-k_2 t}) \quad (5)$$

When determining kinetic parameters it is more thorough to apply both models to see if there is deviation of results. If both results returned do not match then it can be concluded that the two fraction model is more accurate. If on the other hand the kinetics reveal similar results, it can be concluded that the reaction is 100% fast fraction with $\alpha = 1\ \text{g g}^{-1}$.

Table 1
The chemical composition of potato peel.

Composition	Proportion
Cellulose	55.25%
Hemicellulose	11.71%
Lignin	14.24%
Moisture	10.0%
Ash	8.8%

The use of both models has been demonstrated by Gámez et al. [8] in their efforts to hydrolyze sugarcane bagasse into fermentable sugars. The hemicelluloses of sugarcane are primarily xylan. The primary sugar obtained from this process is xylose however there are concentrations of glucose arbinose and furfural obtained also. By carrying out phosphoric acid hydrolysis on the sugarcane bagasse at 100 °C at different acid concentrations and reaction times it was found that an optimum yield of 38.6% conversion was obtained at 2% phosphoric acid concentration for 300 min. Both the two fraction and the Saeman's model where used to derive reaction constants for the xylose kinetic model and it was found that both were approximately the same showing that the fast reaction was 100%.

Kinetic studies on the hydrolysis of various cellulosic materials (e.g. paper, sawdust, urban refuse and agricultural wastes) are reported in the literature and they are characterised by acid and solids concentrations, temperature and reaction time [13].

It was found that hemicellulose hydrolysis kinetic parameters were strongly dependent on the substrate material. Differences observed in kinetic behaviour are attributed to the different hemicellulosic structures of the agricultural residues [16]. Furthermore, as a consequence of the sugar degradation, the amount of sugars recovered from the raw material is dependent on the reaction time, temperature and acid concentration [17]. Therefore, the hydrolysis kinetics constants must be determined empirically for each biomass material, acid catalyst, and set of reaction conditions [18].

2. Experimental

2.1. Experimental aim

For the purposes of this research the conditions to be varied are temperature and acid concentration. The raw material will be hydrolysed at 135 °C, 150 °C, 175 °C and 200 °C using phosphoric acid at 2.5, 5, 7.5 and 10% (w/w) acid concentrations. The raw material substrate being studied is potato skins.

2.2. Materials

2.2.1. Potato peelings

The potato peelings used for this work were obtained from a potato crisp manufacturer, Tayto (NI) Ltd., with a typical composition detailed in Table 1.

2.2.2. Cellulose and hemicellulose analysis

The potato peels are first ground to pass a 16 mesh screen. Three 0.3 g samples are weighed into three test tubes and to each is added 3 ml of 85% sulphuric acid that has been cooled to 15 °C. The samples are stirred thoroughly before being placed in a water bath at 30 °C. This temperature is maintained for 2 h, stirring the samples every 10 min. After a total time of 2 h the mixture is washed from the vial into an Erlenmeyer flask and made up to 89.11 g with distilled water. The dilute solution is autoclaved at 1.5 bar steam pressure and 121 °C for 1 h. At the end of this time the sample is cooled and vacuum filtered to remove unreacted lignin. The filtrate is then syringed through a 0.45 μm filter, before being analysed by HPLC. With 100% conversion assumed the composition of glucose is recognised as cellulose and that of arabinose can be recognised as hemicellulose. It is noted however, that the hemicellulose fraction is actually composed of a number of shorter chain of polysaccharides such as hexoses (D-galactose, D-mannose, L-rhamnose, L-fucose), pentoses (D-xylose, L-arabinose), and uronic acids (D-glucuronic acid).

2.2.3. Other analyses

Due to the robust and complex nature of lignin, it is only decomposable through enzyme action, therefore making it virtually insoluble in mineral acids. Having hydrolysed the cellulose and hemicellulose components of the biomass the composition of lignin can be determined quite easily. The process of vacuum filtering the samples results in the separation of the hydrolysate and the remaining solid deposit. This deposit is made up of mainly lignin and ash components. The glass filter crucibles which have been used in the vacuum filter are dried over night in an oven at 110 °C before having their weight recorded. They are then placed in a muffle furnace at 550 °C for 3 h to burn off the remaining organic deposits. The weight is then recorded again. The proportion of acid-insoluble residue mainly lignin can be calculate using Eq. (6) as per the *Standard Test Method for Determination of Acid-Insoluble Residue in Biomass – E1721 - 95*:

$$\text{Percentage of lignin} = \frac{W_2 - W_3}{W_1 \times T_{110}} \times 100 \quad (6)$$

where W_1 = weight of potato peel sample (g); W_2 = weight of filter crucible after ignition in muffle furnace – Ash sample (g); W_3 = weight of filter crucible after vacuum filtration – Lignin and Ash (g); T_{110} = As received sample conversion factor.

2.2.3.1. Moisture analysis. Moisture content of a sample of potato peel is measured by weighing out a recorded amount of sample and placing it in an oven at 110 °C until the dry weight of the sample is constant over a 2 h period. The sample is then cooled and its weight is recorded. Moisture content is determined by dividing the dry weight by the initial weight.

2.2.3.2. Ash analysis. The ash content is calculated by dividing the weight of the filter crucible, after it has been ignited in the muffle furnace W_2, by the initial weight of the sample W_1 times the conversion factor T_{110}.

2.3. Experimental procedure

2.3.1. Equipment

A 1 L continuously stirred pilot batch reactor (Parr reactor) was employed for the experimental programme. The reactor operates at a temperature range of −10 to 350 °C up to 130 bar pressure. Operating conditions are modulated by a 4843 controller unit.

The total contents of the reactor constitute 700 g of which 5% (w/w) will be the raw material potato peels. The potato peels are dried and milled to 16 mesh or 1 mm diameter particles. The remaining 95% (w/w) content of the reactor is made up of the dilute acid concentration. The acid concentration is not initially added to the reactor but instead is delivered through the acid reservoir during the initialisation of the reaction. For acid concentrations 2.5, 5 and 7.5% (w/w) this is made by preparing a 70 g sample made up of the 85% phosphoric acid required to achieve the desired acid concentration for the reaction and distilled water. The remaining distilled water required to achieve this dilution is mixed with the potato peel and charged to the Parr reactor vessel.

The sample tube is then fitted with a gauze mesh to restrict the solid sample from blocking it. The reactor is secured tightly by 6 bolts to maintain the operating pressure within the vessel during

the reaction. The vessel is then attached with the heating jacket and the agitator impellor is connected to begin mixing.

The sample line and acid reservoir are bolted tightly to the reactor. The nitrogen line is then attached to the acid reservoir. Finally the thermocouple which provides feedback to the 4843 controller is inserted and the temperature setpoint is entered. The 4843 controller will then ramp up the jacket heating to achieve and maintain the required operating temperature setpoint. Depending on the whether the temperature output required is 135 °C, 150 °C, 175 °C or 200 °C it will take between 30 and 60 min to reach the desired temperature. The impellor is initiated at the same point as the jacket heating element and remains constant for all experiments at the 4843 controller maximum RPM rate of 632. This will ensure that by the time the reaction commences the concentration of potato peels will be constant throughout the vessel. Once the desired temperature setpoint is at steady state the reaction can commence.

2.3.2. Reaction procedure

To initialise the reaction the phosphoric acid must be delivered to the reaction vessel from the acid reservoir. The reservoir is first pressurised by opening the nitrogen valve, thus pressurising it to 20 bar. The acid inlet valve is then opened, causing a pressure differential between the reservoir and the reaction vessel which will allow the acid to be delivered to the vessel. The pressure gauge of the vessel is monitored for any increase in pressure, once this is observed it indicates that all the acid has been delivered. At this point the inlet valve is closed and the stop watch is started simultaneously.

Sampling occurs at time intervals of 2, 4, 8, 15, 30, 45, 60, 75 and 90 min. A sample tube is secured to the sample line; the sample outlet valve is then opened allowing a maximum of 5 ml of solution to be collected. The sampling procedure is assisted by the elevated pressure within the vessel allowing it to take the briefest amount of time possible. This helps to reduce further reactions of the solution which would spoil the results. The sample tube is coiled through a jug of cold water to further reduce the reaction rate of the solution by rapid cooling. The sample tube must then be cleared using compressed air to prevent contamination of the next sample. Once this has been completed the sample tube is removed sealed and placed in ice to completely cease any possible further reacting. Finally the nitrogen line is opened and the vessel is pressurised slightly to stabilise the reaction vessel, maintain a constant pressure and to clear any blockages in the sample line.

Although contamination of the solution by potato peel particles is severely reduced by the presence of a gauze mesh it is not eliminated, therefore purification by vacuum and syringe filtration must be done in preparation for analysis. On completion of this the samples are sent for analysis in a HPLC.

Sugars in the hydrolysate were measured using a column Supelcosil LC-NH_2 for the separation of the sugars and an ELSD 'Sedex 55'. Degassed acetonitrile:water 85:15 (v/v) was used as mobile phase at a flow rate of 0.8 ml/min. The sample of the hydrolysate was prepared as described in [12], 20 μl of the sample was loaded and injected manually. The ELS detector was operated at 40 °C and nitrogen was used as nebulising gas at 2 bar.

The data was recorded using a data logger, 'Picolog ADC – 10' from Pico Technology. It was connected to a computer that had the 'PicoLog' data acquisition software installed. The quantification of the sugars was carried out using 'Origin Pro 7.5 SR' 5 software for calculating the peak areas and the respective calibration curve for each sugar. The sugars produced in the hydrolysis reactions were identified using the retention times of standards sugars such as D-Xylose (Alfa Aesar), D-Galactose (Sigma), L-Arabinose (Sigma), D-Mannose (Alfa Aesar), D-Glucose (BDH AnalaR) and, D-Cellobiose (Sigma).

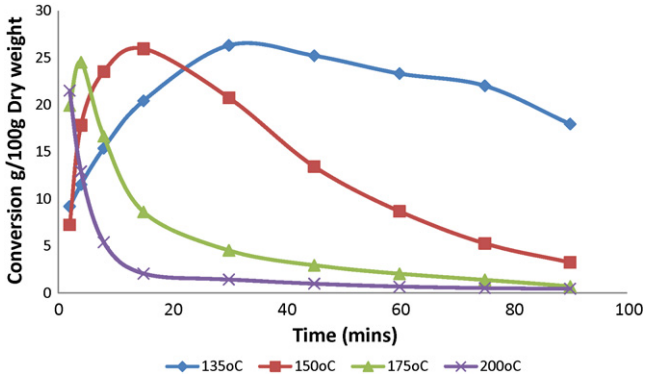

Fig. 2. The effect of temperature on total sugar yield at 5% (w/w) acid concentration. The "total sugar" is the sum of the individual sugars determined by HPLC.

3. Results and discussion

3.1. The effect of temperature on total sugar yield

Fig. 2 shows the various yields of sugars produced at different temperatures when the acid concentration is 5.0% (w/w). At 135 °C the rate of sugar generation is slower to reach its peak that at other temperatures; however sugar preservation is sustained for a longer period of time due to a low level of sugar decomposition which is occurring simultaneously. At this temperature the maximum yield of 26.32 g of sugar/100 g of dry potato peels is obtained after 30 min reaction time before the decomposition reactions begin to surpass sugar production. The rate of decomposition is moderate with 6.36 g of sugar being degraded in the final 60 min period of the reaction.

At 150 °C the rate of sugar generation peaks much earlier at a time of 15 min, at a slightly lower level of 25.97 g sugar/100 g dry potato peel. The reaction is more aggressive at reaching its optimum output; however it begins to decompose rapidly resulting at a low yield of 3.25 g sugar/100 g dry potato peel by the reactions end meaning that approximately 87% of the sugar has reacted irreversibly to produce waste products.

The rate of reaction is found to further increase when the temperature is raised to 175 °C. After 4 min the yield of sugar has been maximised, about 24.52 g per 100 g of dry potato peel. However the reaction quickly produces a negative sugar output rate as degradation is evident. By the end of the reaction only 2.8% of this sugar yield has been retained.

As is expected the sugar generation at 200 °C has the highest reaction rate peaking at 21.51 g sugar/100 g dry potato peel after only 2 min. As this is the first sample which has been taken during the course of the reaction, it is quite possible that a higher sugar yield is obtained in the intermittent time between the start of the reaction and the first sample period but due to the nature of the sampling process it is difficult to reduce the time taken to set up and carry out sampling. What can be established is that an aggressive sugar decomposition reaction begins with approximately 93% of the entire sugar yield being lost after 30 min of reaction time.

Through observing these reactions it is quite clear that the both the sugar production and decomposition reaction rates increase dramatically with rising temperature. The reaction takes less and less time to reach its maximum yield as temperature increases however this leads to a rapid rate of sugar degradation.

Within this range of temperature at 5% (w/w) phosphoric acid, glucose overwhelmingly constitutes the majority of the total sugar produced with between 95.2 and 100% of the total sugar yield. The remainder is made up of arabinose.

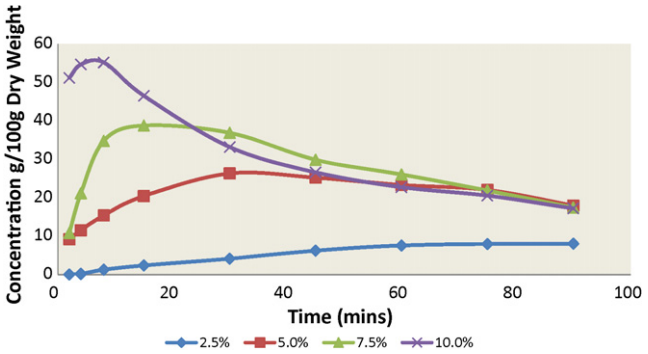

Fig. 3. The effect of Acid concentration on total sugar yield at 135 °C. The "total sugar" is the sum of the individual sugars determined by HPLC.

3.2. The effect of acid concentration on total sugar yield

It is evident from observing Fig. 3 that increasing acid concentration will dramatically increase the reaction rate at a temperature of 135 °C. At 2.5% (w/w) phosphoric acid concentration the rate of sugar production is low, and over the course of the reaction only increases slightly. The maximum yield obtained is a modest 8.01 g per 100 g of dry potato peel. However, it must be taken into account that, by the end of the reaction time the sugar yield is still steadily rising which indicates that the total possible total yield at these conditions will be at a higher level. One advantage of using less aggressive conditions is the negligible rate of sugar decomposition which can be seen.

As the acid concentration starts to rise the reactions rates begin to increase rapidly. A noticeable shift in the sugar production rate is evident when the acid concentration is increased from 2.5 to 5.0% (w/w). The reaction takes place at a moderate rate at first increasing to its maximum yield of 26.32 g sugar/100 g dry potato peel at a reaction time of 30 min. The reaction rate begins to decrease slowly however over 75% of the maximum sugar yield is retained by the end of the reaction.

Further increases in the reaction rate occur as the acid concentration is increased to a level of 7.5% (w/w). The rate of sugar production increases rapidly initially before reaching a maximum level of 38.78 g sugar/100 g of dry potato peel 15 min after the reaction starts. This level is diminished by the degradation of sugars as only 44% of this sugar remains at the end of the reaction or 17.41 g sugar/100 g of dry potato peel.

The optimum yield obtained at 135 °C is seen at 10% (w/w) acid concentration. 55.2 g sugar/100 g dry potato peel is produced after a time of 8 min. It must also be noted that due to the timing of sampling that between 4 and 8 min this level may have been higher than that level. This yield is also found to be the maximum experimental yield obtained across all the variable conditions of temperature and acid concentration carried out as part of this research into acid hydrolysis of biomass. As the reaction continues a high rate of sugar decomposition ensues resulting in a greatly diminished final yield of sugars by the end of the reaction period with only 17.27 g sugar/100 g dry potato peel remaining. The proportion of glucose which contributes to the total sugar yield for acid concentration vs. time at 135 °C is between 84.2 and 100% of the total yield.

From Fig. 3 it can be concluded that the acid concentration has an important relationship with the rate of reaction for both sugar production and decomposition. As the acid concentration increases the rate for both becomes more rapid however it is noticeable that the decomposition rate is only excessive once the acid concentration is increased to 10% (w/w). If this is compared to the effect of temperature on the reaction rate then it can be concluded that temperature has a stronger relationship with the net rate of sugar production compared to the acid concentration. Therefore it can be concluded that increasing the acid concentration is a more effective means of maximising sugar yields than increasing the operating temperature.

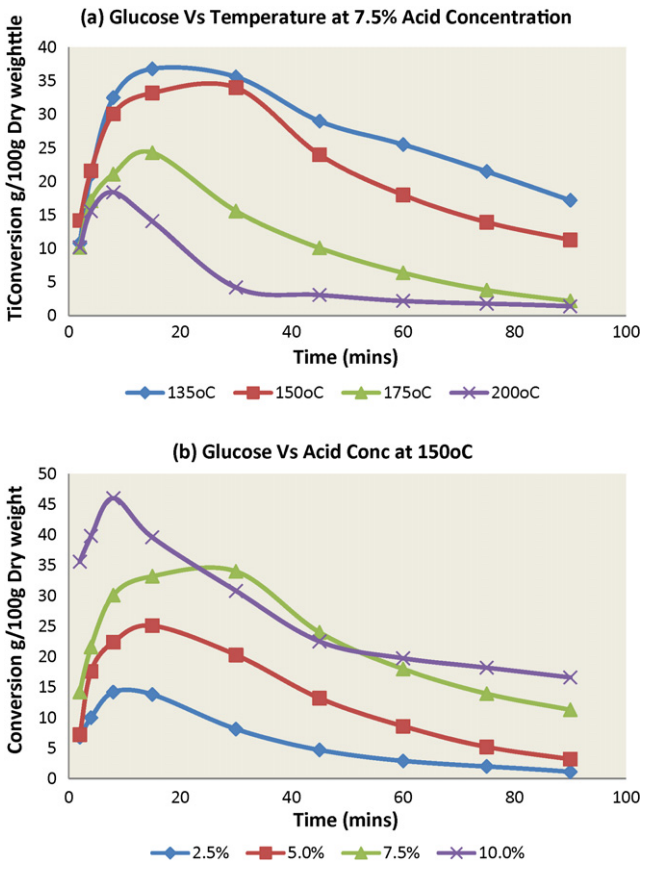

Fig. 4. The effect of acid concentration and temperature on glucose yield.

3.3. Effects of temperature and acid concentration on sugar yields

3.3.1. Glucose production

As mentioned previously the majority of the potato peel's composition is made up of hexosans, in the form of cellulose, therefore it not surprising that the majority of the sugar yield which is derived from acid hydrolysis is comprised of glucose. Over the range of temperatures and acid concentration, for which this experiment was carried out, it was found that the percentage of glucose in the total sugar yield varied from between 84.1% to 100%. As this is the primary product of the reaction it must be noted that the results for total sugars and glucose produced are strikingly similar. The yield obtained for glucose was 53.8 g sugar/100 g dry potato peel at the optimum operating condition of 135 °C and 10% (w/w) acid concentration after 4 min reacting. This constitutes 98.02% of the maximum total yield of sugar for the reaction thus emphasising its importance as the primary product.

Fig. 4 illustrates the overall effect acid concentration and temperature has on the glucose yields obtained. At a moderate temperature of 150 °C it can be seen that glucose production peaks at 46.02 g sugar/100 g potato peel at 10% (w/w) after 8 min. By comparing the effect of acid concentration with that of the temperature it can clearly be seen that increasing the temperature will have a detrimental effect on the net rate of sugar production.

In Fig. 4(a) it is observed that at a low temperature of 135 °C at 7.5% (w/w) acid concentration a maximum yield of 36.8 g glucose/100 g dry potato peal is obtained after 15 min. As the tem-

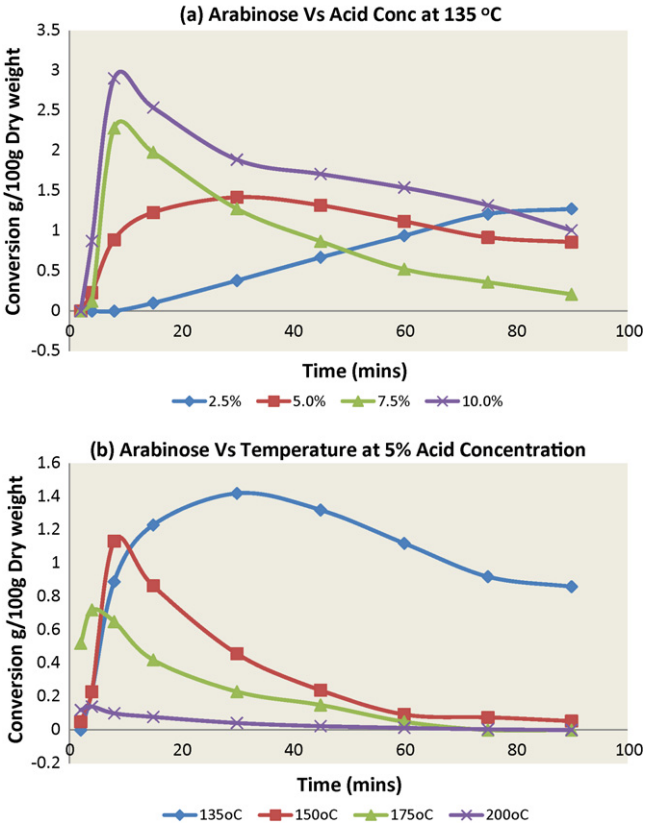

Fig. 5. The effect of acid concentration and temperature on arabinose yield.

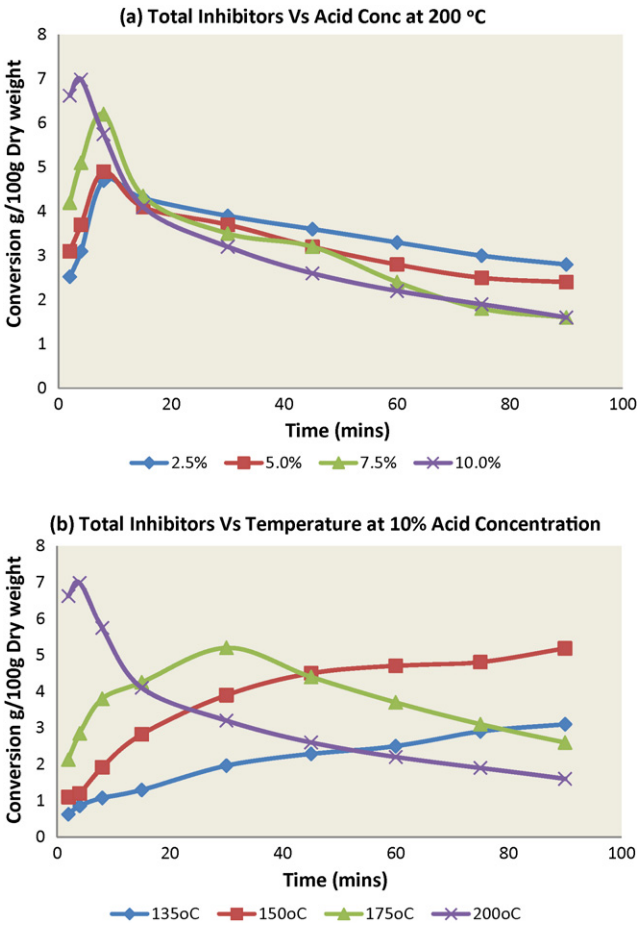

Fig. 6. The effect of acid concentration and temperature on total inhibitor yield (HMF, furfural, and acetic acid).

perature is increased to 150 °C, 175 °C and finally to 200 °C the maximum yield obtained falls to 33.2, 24.2 and 14.1 g glucose/100 g dry potato peel respectively. This illustrates the inverse relationship which the net rate of glucose production has with temperature. This action can be explained by the high glucan concentration in the feed. As the lignocellulosic structure is rapidly broken down into its components and further broken down into glucose, the reactor becomes saturated with glucose. The glucose is quickly converted into the unwanted by-products, due to increased collisions of the suspended particles within the reactor brought on by the increased temperature.

Conversely increasing the acid concentration will have a positive effect on total glucose yields. As can be seen in Fig. 4(b) when potato peels are reacted at 150 °C at varying acid concentrations it can be seen that the lowest glucose yield is obtained at 2.5% (w/w) acid concentration. The maximum yield for this output was found to be 14.2 g glucose/100 g dry potato peel after 8 min after which it begins to degrade. As the acid concentration is increased to 5.0, 7.5 and 10.0% (w/w) the maximum yield obtained increases according to 25.1, 34, and 46.02 g/100 g dry potato peel respectively. This is more than a threefold increase in output which is significant rise, while degradation is maintained along the model of temperature increase. This leads to the conclusion that decomposition of sugars is mainly a function of temperature.

3.3.2. Arabinose production

Arabinose is a minor product of acid hydrolysis of potato peels. The maximum yield obtained during the experimental research was found to be 2.9 g of arabinose/100 g dry potato peel at operating conditions of 135 °C and 10% (w/w) acid concentration after 8 min of the reaction as can be seen in Fig. 5(a). After this point it can be seen that degradation of sugars begins relatively quickly and the rate of decomposition outweighs that of arabinose production leading to an overall yield at the end of the reaction of 1 g arabinose/100 g dry potato peel. The experimental data which was obtained for arabinose production as a function of acid concentration is a similar model to that of glucose at higher temperatures. At the lowest temperature of 135 °C sugar degradation is seen to be negligible. The net yield of arabinose continues to rise and will likely rise beyond the time frame of the reaction. An arabinose yield of 1.27 g arabinose/100 g dry potato peel is obtained by the end of the reaction which is higher than that of all the other acid concentrations; however this rate of production is seen to be unfeasible as the cost of running the reaction would significantly outweigh any benefits gained from increased productivity.

Increasing acid concentration will increase the reaction rate significantly so that the optimum production rate can be obtained within the first 15 min of the reaction as can be seen from the experimental data obtained for 7.5 and 10.0% (w/w) acid concentration. Acid concentration seems to have little effect on the rate of degradation as the reaction would appear to be stable; however it does assist, to an extent, the generation of by-products as can be seen in Fig. 5(b). It is also noted that the time to reach the optimum production is reduced significantly: at first from 90 min for 2.5% (w/w) acid concentration; to 30 min for 5.0% then to 10 min for 7.5%; and finally its impact on time is diminished as it decreases to 8 min for 10.0% (w/w) acid concentration. From this it can be concluded that regardless of acid concentration there is a period of time required to break the robust hemicellulosic component of the feed material before conversion of araban can begin.

The effect temperature on arabinose production is immediately apparent from observing the trends in Fig. 5(a). It can be seen that

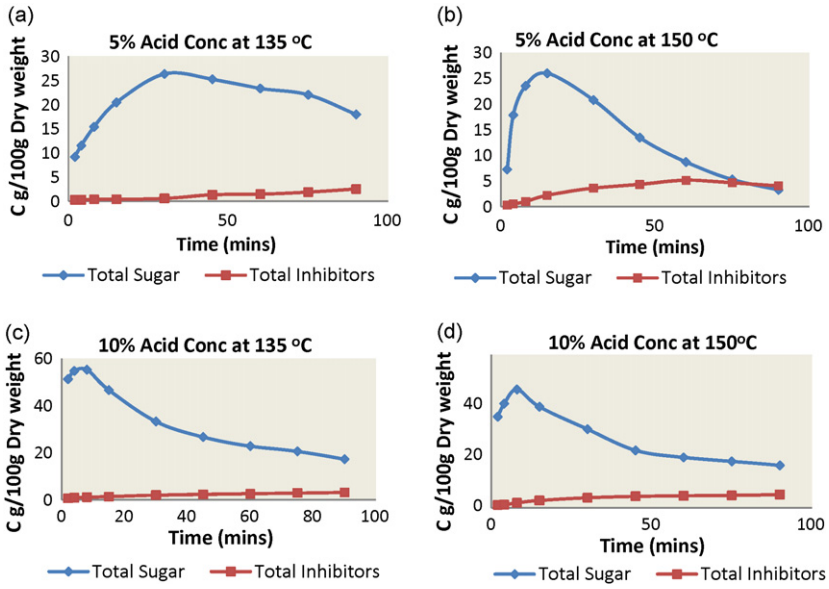

Fig. 7. Comparison of the yield of total inhibitors and sugars.

when reacting dry potato peel with a 5.0% acid concentration, temperature increase will have an adverse affect on the total arabinose yield, which mirrors the overall effect temperature has on glucose yields. The maximum yield obtained at this acid concentration was found to be 1.42 g arabinose/100 g dry potato peel at 135 °C after 30 min. After this, relatively low levels of arabinose degradation are noted, with 61% of the sugar preserved by the end of the reaction. The dramatic effect which temperature has on arabinose production only becomes evident when this is compared to the effect of increasing temperature on the production rate. As the temperature increases the reaction time, that the maximum yield is obtained, diminishes rapidly until the point where the arabinose is decomposing as soon as it is formed (as can be seen at 200 °C), this was expected as arabinose is much less robust to hydrolysis than cellulose and lignin. At temperatures 150, 175 and 200 °C it was found that by the end of the reaction between 96 and 100% of all arabinose produced had been degraded.

The thermal instability of arabinose is a leading factor contributing to the high reaction rates and low yields observed. Such a negative net production rate of arabinose indicates that as a function of temperature the decomposition rate overwhelms that of the production rate. From this data it can be concluded that: $k_1 < k_2$. As explained earlier arabinose constitutes a minor amount of the total sugar yield and therefore its formation and degradation is of negligible concern when overall yield and optimum conditions are taken into account.

3.4. Inhibitors produced in the hydrolysate

During acid hydrolysis, sugar degradation is a prominent feature. 5-Hydroxymethlyfurfural, or HMF, is formed from the dehydration of hexoses and furfural is formed from the dehydration of pentoses. These by-products have an inhibiting effect on the rate of reaction during the fermentation process, which is required to convert these low value sugars into high value biofuel products. The compounds damage the yeast and other microorganisms by slowing down their metabolism and reducing enzymatic activity. They enter the cell's nucleus and attaching to replicating DNA and severely hinder reproduction and growth of the cell culture. Obtaining high yields of sugar during hydrolysis can be offset by the concentration of inhibitors within the sugar slurry. These along with acetic acid, formed during a number of secondary reactions, retard the fermentation of hydrolysates and may require further processing to remove or, possibly, dilute to reduce their effect on the efficiency of fermentation.

3.5. Effects of temperature and acid concentration on inhibitor production

Fig. 6 shows the effects which temperature and acid concentration of the production of total inhibitors. Inhibitor production and degradation occurs in a similar fashion to that of sugar. It is evident from Fig. 6(a), that temperature has a profound influence in inhibitor reaction kinetics. As temperature increases the rate of inhibitor production increases rapidly. Peak yields of inhibitors are observed during the early stages of the reaction for all temperatures, i.e. between 2 and 8 min from the start of the reaction. As the reaction continues these inhibitors are broken down further into various degradation products, many of which are also inhibitors. The inhibitors studied in this experiment have been reduced to focus on the main contributors which include: HMF, furfural and acetic acid, of which HMF constitutes the majority (between 62 and 84%) of total inhibitors. The degradation reaction which occurs during this reaction reduces HMF to levulinic acid, which is itself an inhibitor. Therefore, although it appears as though the total inhibitors have been diminished as the reaction nears completion. It must be noted that the inhibitors degraded are almost entirely converted to other less potent inhibitors which have not been studied as they fall outside the scope of this work. It can be seen that although the higher temperatures of 175 and 200 °C, produce a higher yield of inhibitors initially, they are net yield of major inhibitors degrade below the final levels of inhibitors which are produced from lower temperatures of 135 and 150 °C.

From Fig. 6(b) it can be seen that acid concentration has less of an effect on the production rate of inhibitors. As the reaction rate rises with acid concentration, it can be seen that high yields of inhibitors are obtained, this is followed by a negative net production rate in the aforementioned inhibitors, which is relatively constant across all acid concentrations.

3.6. Comparison of the yield of total inhibitors and sugars

In order to fully realise the efficiency of a set operating condition the total yield of sugars must be offset by the total inhibitor yield

Table 2
Comparison of experimental yield with theoretical yield through quantitative saccharification.

	Maximum recorded yield, dry mass basis (g/100 g)	Quantitative saccharification of cellulose, dry mass basis (g/100 g)
Glucose	53.813	55.252
Arabinose	2.904	11.712
Total	55.217	66.96

to find the true optimum conditions. Due to the negative impact inhibitors have on the fermentation process, a valid comparison of their relationship with each other must be conducted to establish whether the advantages of high sugar yields from a set of operating conditions is outweighed by the disadvantages of high inhibitor yields.

As concluded previously, a high acid concentration coupled with a low temperature will lead to a high yield of total sugar; the comparison will mostly focus on the conditions of 5.0 and 10% (w/w) acid concentration in conjunction with the temperatures of 135 and 150 °C, see Fig. 7.

From Fig. 7(a) the maximum sugar yield is 26.32 g sugar/100 g dry potato peel after 30 min reaction time, whereas inhibitor concentration is about 0.6 g inhibitor/100 g dry potato peel. The ratio of inhibitors to sugar produced is 2.25%. When the temperature increases to 150 °C as shown in Fig. 7(b), the maximum sugar yield is 25.97 g sugar/100 g dry potato peel after 15 min of reaction time compared with 2.2 g inhibitor/100 g dry potato peel. The ratio of inhibitors to sugar produced is 8.4%.

Fig. 7(c) shows the condition with 10.0% (w/w) acid concentration at 135 °C. The sugar yield from this reaction constituted 55.2 g sugar/100 g dry potato peel after 8 min reaction time, this coincides with 1.1 g inhibitor/100 g dry potato peel. The inhibitor to sugar produced ratio is 1.9%. When the temperature increases to 150 °C as shown in Fig. 7(d), the maximum sugar yield is 46.4 g sugar/100 g dry potato peel, also after 8 min of reaction time compared with 1.91 g inhibitor/100 g dry potato peel. The ratio of inhibitors to sugar produced is 4.1%.

From Fig. 7 with the lower acid concentration of 5.0% (w/w), when the temperature is increased from 135 to 150 °C, the ratio of inhibitors to sugars produced at the optimum conditions increases from 2.25 to 8.4%, an increase by a factor of almost 4. However, at the higher acid concentration of 10.0% (w/w) the ratio of inhibitors to sugars over the same temperature change increases from 1.9 to 4.1%, an increase by a factor of just over 2. This demonstrates that at a higher acid concentration, an increase in the reaction rate of sugar generation due to temperature coincides with a smaller increase in the rate of inhibitor production than that of an increase in temperature with a lower acid concentration. It is also noted that at the operating conditions of 150 °C and 5.0% (w/w) acid concentration, the rate of degradation of sugars and production of inhibitors are both at such a high level that there is net yield of inhibitors by the end of the reaction. Both these observation reaffirm the conclusion that high acid concentration and low temperature provide the optimum operating condition for acid hydrolysis of potato peels.

It can be seen from Table 2 that a level of 97% glucose conversion has been obtained when compared to the theoretical yield. However, an un-quantified proportion of this yield is likely to be attributed to residual starch which is present in the feed stock prior to reacting. Starch is a mixture of both aourlose and amlyopectin (usually in 20:80 or 30:70 ratios) which are complex carbohydrate polysaccharides of glucose. Starch readily hydrolyses to form glucose monomers and experimental yields have been found to reach 111% that of the theoretical yield [19]. However the presence of starch should not be considered a contamination of the results as it is common place for a percentage of residual starch to be present after potatoes have been processed therefore it will only increase the attractive quality of potato peels to companies interested in utilising it as a feed material for biofuel production.

4. Conclusions

Although the high conversion of cellulose to glucose is apparent the low level of arabinose conversion is a concern. As mentioned previously arabinose is quite thermally unstable. When reacted at 135 °C and 2.5% (w/w) acid concentration the production rate is quite high and continues to rise until the reaction ends at 90 min. If this reaction where to continue unabated the conversion rate for arabinose may reach a more acceptable level. However in an industrial context allowing such a slow reaction is uneconomical but if the temperature is increased by any significant amount, even to 150 °C, the thermal instability becomes an issue and degradation of arabinose sets in rapidly thus rendering it a negligible side reaction to the dominant glucose reaction. Having said that even with the low arabinose conversion, overall sugar yield is 82.5% of the theoretical yield. The work indicates that the use of potato peel may be a feasible option as a feed material for the production of sugars for biofuel synthesis, due its low cost and high sugar yields.

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References

[1] C.E. Wyman, Ethanol from lignocellulosic biomass: technology, economics, and opportunities, Bioresource Technology 50 (1) (1994) 3–15.
[2] J Zaldivar, J. Nielsen, L. Olsson, Fuel ethanol production from lignocellulose: a challenge for metabolic engineering and process integration, Applied Microbiology and Biotechnology 56 (1–2) (2001) 17–34.
[3] S. Cheung, B. Anderson, Ethanol production from wastewater solids, Water Environment and Technology 8 (5) (1996) 55–60.
[4] A. Wingren, M. Galbe, G. Zacchi, Techno-economic evaluation of producing ethanol from softwood: comparison of SSF and SHF and identification of bottlenecks, Biotechnology Progress 19 (4) (2003) 1109–1117.
[5] S. Gámez, J.J. González-Cabriales, J.A. Ramírez, G. Garrote, M. Vázquez, Study of the hydrolysis of sugar cane bagasse using phosphoric acid, Journal of Food Engineering 74 (1) (2006) 78–88.
[6] I. Romero, M. Moya, S. Sánchez, E. Ruiz, E. Castro, V. Bravo, Ethanolic fermentation of phosphoric acid hydrolysates from olive tree pruning, Industrial Crops and Products 25 (2) (2007) 160–168.
[7] C.N. Hamelinck, G. van Hooijdonk, A. Faaijm, Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term, Biomass and Bioenergy 28 (4) (2005) 384–410.
[8] S. Gámez, J.A. Ramírez, G. Garrote, M. Vázquez, Manufacture of Fermentable Sugar Solutions from Sugar Cane Bagasse Hydrolyzed with Phosphoric Acid at atmospheric Pressure 74 (2004) 4172–4177.
[9] L.A. Alves, M. Vitolo, M.G.A. Felipe, J.B.A. Silva, Xylose reductase and xylitol dehydrogenase activities of Candida guilliermondii as a function of different treatments of sugarcane bagasse hydrolysate employing experimental design, Applied Biochemistry and Biotechnology 98–100 (2002) 403–413.
[10] R. Aguilar, J.A. Ramírez, G. Garrote, M. Vázquez, Kinetic study of the acid hydrolysis of sugar cane bagasse, Journal of Food Engineering 55 (4) (2002) 309–318.
[11] J.F. Saeman, Kinetics of wood saccharification. Hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature, Industrial and Engineering Chemistry 37 (43–52) (1945).
[12] A. Orozco, M. Ahmad, D. Rooney, G.M. Walker, Dilute acid hydrolysis of cellulose and cellulosic bio-waste using a microwave reactor system, Process Safety and Environmental Protection Trans IChemE, Part B 85 (B5) (2007) 446–449.
[13] A.I. Malester, M. Green, S. Kimchie, G. Shelef, Effect of the neutralizing capacity of cellulosic materials on the kinetics of cellulose dilute acid hydrolysis, Biological Wastes 26 (2) (1988) 115–124.
[14] I.A. Malester, M. Green, G. Shelef, Kinetics of dilute acid hydrolysis of cellulose originating from municipal solid wastes, Industrial & Engineering Chemistry Research 31 (8) (1992) 1998–2003.
[15] S.H.A. Rahman, J.P. Choudhury, A.L. Ahmad, Production of xylose from oil palm empty fruit bunch fiber using sulfuric acid, Biochemical Engineering Journal 30 (1) (2006) 97–103.

[16] N. Eken-Saracoglu, S.F. Mutlu, G. Dilmac, H. Cavusoglu, Comparative kinetic study of acidic hemicellulose hydrolysis in corn cob and sunflower seed hull, Bioresource Technology 65 (1–2) (1998) 29–33.
[17] I.C. Roberto, S.I. Mussatto, R.C.L.B. Rodrigues, Dilute-acid hydrolysis for optimization of xylose recovery from rice straw in a semi-pilot reactor, Industrial Crops and Products 17 (May (3)) (2003) 171–176.
[18] N. Mosier, C. Wyman, B. Dale, R. Elander, Y.Y. Lee, M. Holtzapple, M. Ladisch, Features of promising technologies for pretreatment of lignocellulosic biomass, Bioresource Technology 96 (6) (2005) 673–686.
[19] L. Kunlan, X. Lixin, L. Jun, P. Jun, P. Guoying, X. Zuwei, Salt-assisted acid hydrolysis of starch to D-glucose under microwave irradiation, Carbohydrate Research 331 (1) (2001) 9–12.