12

Kinetic Modelling of Dilute Acid Hydrolysis of Lignocellulosic Biomass

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1. Introduction

1.1 Dilute acid hydrolysis

Dilute Acid hydrolysis refers to the hydrolysis of hemicellulosic material by acids (typically sulphuric, hydrochloric or phosphoric acid) at concentrations of 1-10% using a moderate temperature (in the range of 100-150^{0}C). But in these relatively moderate operational conditions, it proves less effective in the formation of hexoses[1]. 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 hydroxymethilfurfural-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[2]. The production of these inhibitors increases when hydrolysis takes place at higher temperatures and higher acid concentrations[3].

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[2].

Dilute Phosphoric acid, on hydrolysates from sugar cane 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^{0}C for 300 mins[4]. 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^{0}C for 240 mins[2].

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, neutralization and supplementation with nutrients. This process is illustrated in Figure 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[1]. 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[1]. In the operation of neutralization, it is usual to add chemicals that neutralize the acids of the hydrolysates, forming salts[5]. These salts have low solubility and are normally removed by filtration. For example, hydrolysates containing sulphuric acid are neutralized with calcium carbonate, forming calcium sulphate[1]. 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[6].

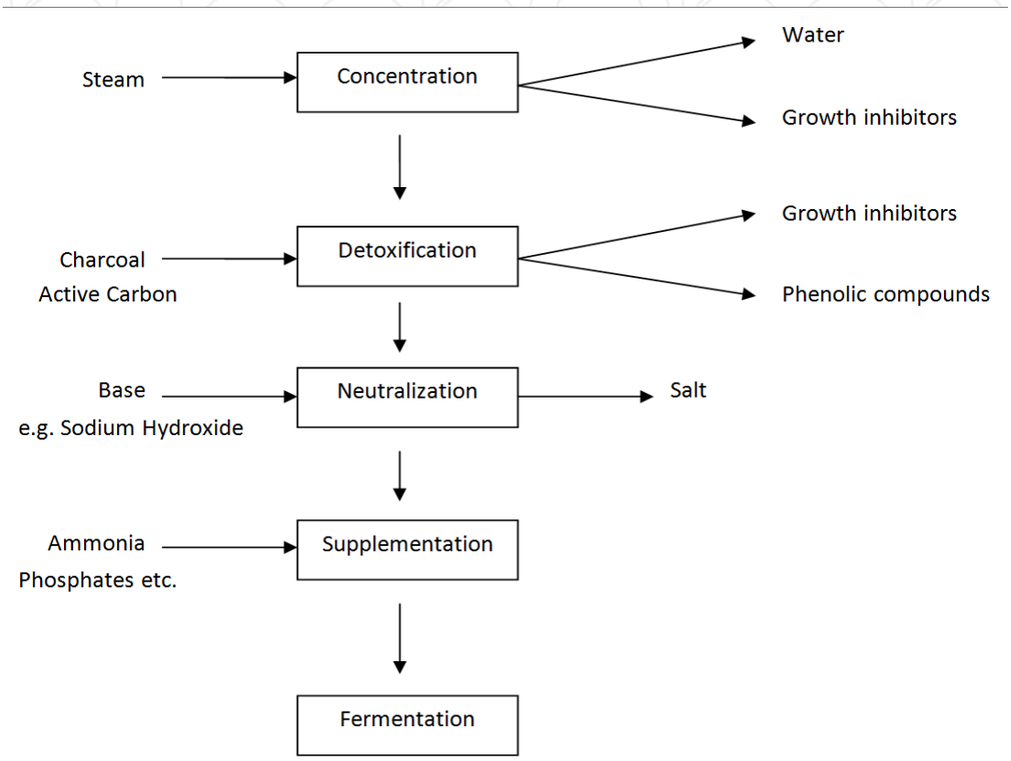


Fig. 1. General operations required after hydrolysis prior to fermentation.

The interest in the use of H_3PO_4 is that after neutralization 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)[1].

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 optimize the process and, on a second level, to obtain Equations useful for economical estimations[4]. The models usually associated with dilute acid hydrolysis were first proposed by Saeman[7], for the hydrolysis of Douglas fir wood using

sulphuric acid. The models proposed in the literature use irreversible pseudo-homogeneous first-order reactions. 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[8]:

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

Where:

M = Monomer Concentration, g L^{-1}

P = Polymer Concentration, g L^{-1}

M_0 = Initial Monomer concentration, g L^{-1}

Assuming that the initial monomer concentration to be approximately equal to 0, then Equation (1) can be simplified to[8]:

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

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[4]:

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

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 α=1 g g^{-1}.

The use of both models has been demonstrated by Gámez et al.[4] in their efforts to hydrolyze sugar cane bagasse into fermentable sugars. The hemicelluloses of sugar cane are primarily xylan. The primary sugar obtained from this process is xylose however there are concentrations of glucose arabinose and furfural obtained also. By carrying out phosphoric acid hydrolysis on the sugar cane bagasse at 100^0C 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 mins. 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%. Therefore the latter model was used because it's simplicity.

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^{0}C, 150^{0}C, 175^{0}C and 200^{0}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.

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

Table 1. The chemical composition of Potato Peel

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^{0}C. The samples are stirred thoroughly before being placed in a water bath at 30^{0}C. This temperature is maintained for 2 hours, stirring the samples every 10 minutes. After a total time of 2 hours the mixture is washed from the vial into an Erlenmeyer flask and made up to 89.11g with distilled water. The dilute solution is autoclaved at 15 pounds steam pressure and 121 ^{0}C for 1 hour. 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 recognized as cellulose and that of arabinose can be recognized as hemicellulose.

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^{0}C before having their weight recorded. They are then placed in a muffle furnace at 550^{0}C for 3 hours 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 Equation 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

- 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^{0}C until the dry weight of the sample is constant over a 2 hour period. The sample is then cooled and its weight is recorded. Moisture content is determined by dividing the dry weight by the initial weight.

- 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 Litre continuously stirred pilot batch reactor (Parr reactor) was employed for the experimental programme. The reactor operates at a temperature range of -10 to 350^{0}C up to 130 bar pressure. Operating conditions are modulated by a 4843 controller unit. The total contents of the reactor constitute 700g of which 5% w/w will be the raw material potato peels. The potato peels are dried and milled to 16 mesh or 1mm 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 70g 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.[10]

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^{0}C, 150^{0}C, 175^{0}C or 200^{0}C it will take between 30-60 minutes 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.[10]

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 minutes. 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.[10]

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.

3. Results and discussion

3.1 Reaction kinetics

As mentioned previously the reaction which illustrates the production and decomposition of sugars is demonstrated below in Equation (1).

$$\text{Polymer} \xrightarrow{K_1} \text{Monomer} \xrightarrow{K_2} \text{decomposition products} \tag{1}$$

The polymer can be cellulose (glucan) or hemicellulose (araban). Saeman[7] found that a simple two-step reaction model adequately described the production of sugars from hydrolysis. This model assumes an irreversible first-order type reaction. If the reaction is studied in terms of concentration it can be represented by the following Equation (7).

$$\text{Glucan (A)} \xrightarrow{K_1} \text{Glucose (B)} \xrightarrow{K_2} \text{HMF (C)} \tag{7}$$

The formation rate of the product glucose (B) with respet to time is represented by Equation (8):

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \tag{8}$$

By integrating this Equation with respect to time gives an Equation representing the concentration of sugar as a function of time. The Equation (9) below is derived:

$$C_B = k_1 C_{A0} \left(\frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1} \right) \quad (9)$$

Using this Equation it will be possible to accurately model the reactions kinetics at each of the operating conditions of temperature and acid concentration and therefore determine the reaction constants.

3.2 Modelling

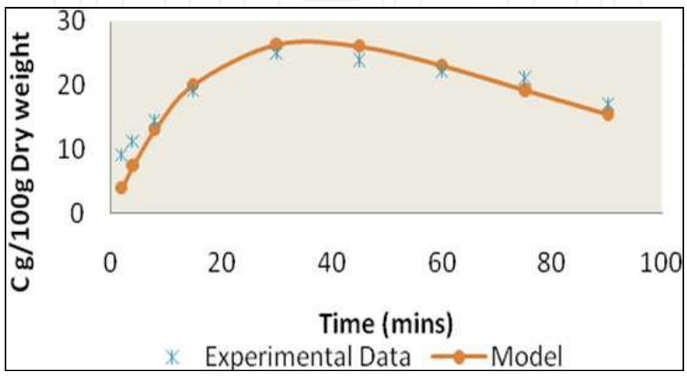
The reaction constants k_1 and k_2 are determined through using the solver function on Microsoft Excel. By minimising the sum of the square of the error between the experimental data and the model data obtained accurate reaction parameters can be found. The solver function operates by attempting to acquire a value of zero error through changing of the k_1 and k_2 values.

As this is a solid-liquid reaction the initial concentration of A is difficult to determine without going into mass transfer and shrinking particle theory, which is based on the average size of the particles used. On this basis quantitative saccharification is used to determine the concentration of the reactants. By taking into account the solid liquid ratio, the initial concentrations C_{A0} can be established by determining the concentration of their products in an assumed 100% conversion reaction. Through quantitative saccharification the hexosans (glucan) and pentosan (araban) are hydrolysed completely to form hexose (glucose) and pentose (arabinose) respectively. The concentrations, of the sugars produced, which are obtained from analysing the chromatograms are fixed as the initial concentrations of the cellulose and hemicellulose. Therefore the concentration of glucose is assumed that of the C_{A0} of glucan or cellulose, and the concentration of arabinose is assumed that of the C_{A0} of araban or hemicellulose. These values will satisfy the respective parameters within the mathematical model.

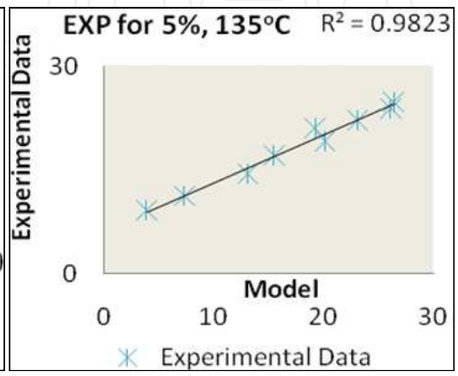
The reaction was modelled to determine the kinetics for phosphoric acid concentrations of 2.5, 5.0, 7.5, 10.0% (w/w) and operating temperatures of 135, 150, 175 and 200 ^{o}C.

3.3 Glucose production

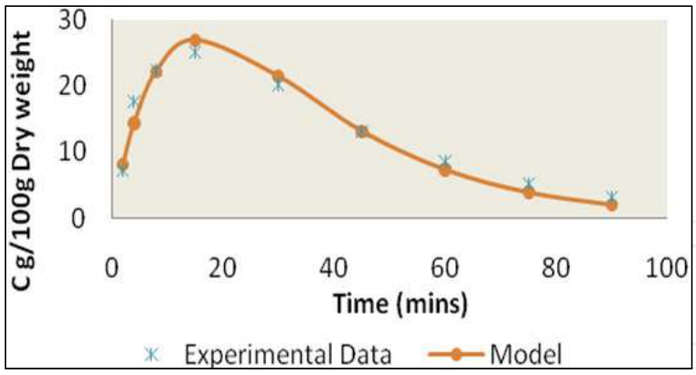
Figure 2 shows the results of the kinetic model constructed to represent glucose at temperatures 135, 150, 175 and 200^{o}C at an acid concentration of 5.0% w/w. The model was constructed through calculating best fit reaction coefficients for k_1 and k_2.

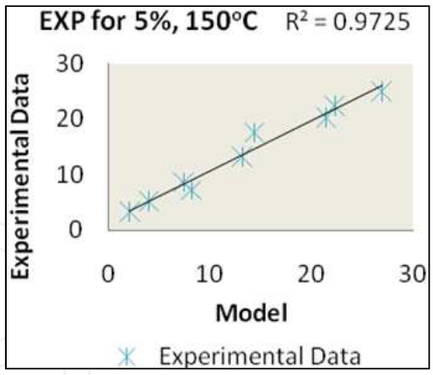


(a.1) Glucose model at 135^{o}C, acid conc. 5.0%

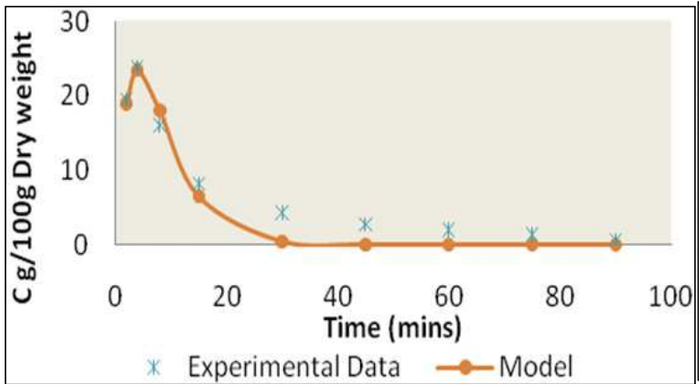


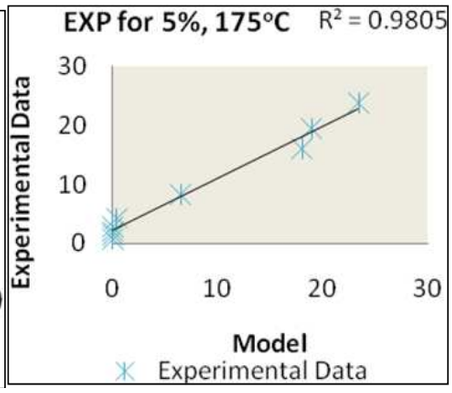
(a.2) Fitting Test



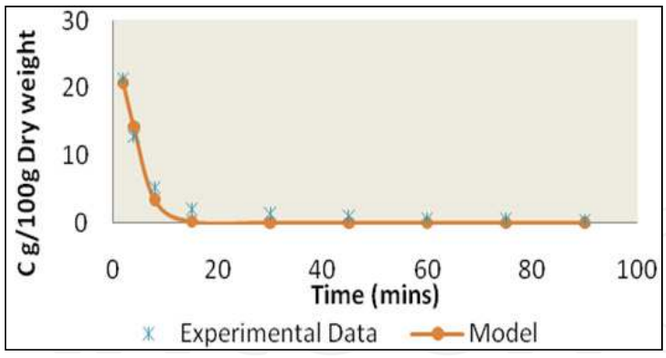


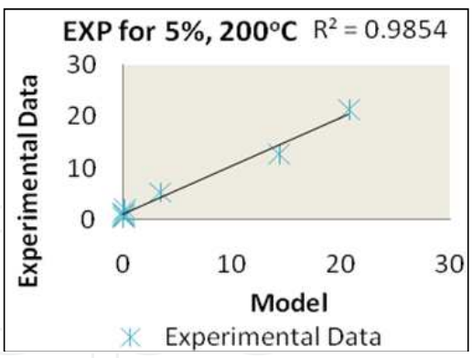
(b.1) Glucose model at 150°C, acid conc. 5.0% (b.2) Fitting Test





(c.1) Glucose model at 175°C, acid conc. 5.0% (c.2) Fitting Test





(d.1) Glucose model at 200°C, acid conc. 5.0% (d.2) Fitting Test

Fig. 2. Glucose model with variation in acid concentration

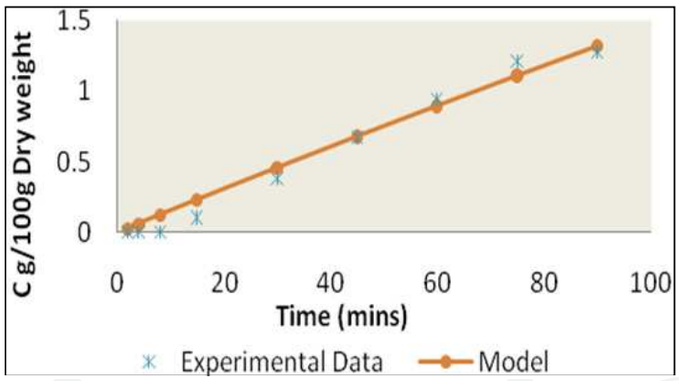
From observing these graphs it can be seen that the models generated for glucose production at 5.0% w/w acid concentration are highly accurate. Along with the model for the reaction, the experimental values against the model values are constructed to determine if the data fits. The correlations represented by R^2 are seen to be well above 0.9 which indicates the high level of accuracy achieved from the model. The kinetic model is of first order principles further demonstrating that the glucose generation reaction is a first order reaction as has been noted in numerous studies.

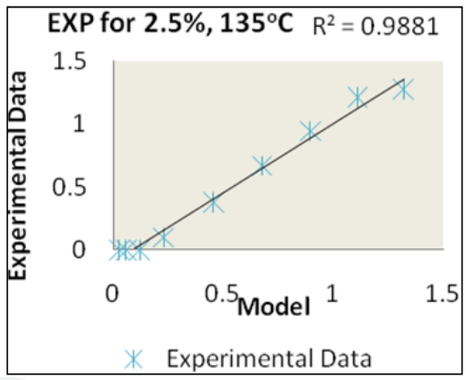
3.4 Arabinose production

Figure 3 shows the results of the kinetic model constructed to represent arabinose at temperatures 135, 150, 175 and 200 °C at an acid concentration of 2.5% w/w. The model was constructed through calculating best fit reaction coefficients for k_1 and k_2.

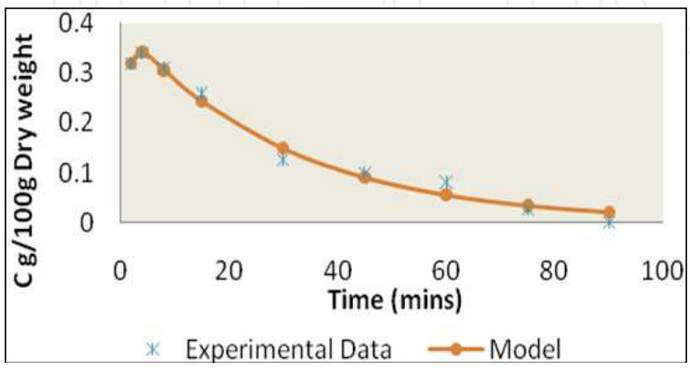
From observing these graphs it can be seen that the models generated for arabinose production at 2.5% w/w acid concentration are highly accurate. Along with the model for the reaction the experimental values against the model values are constructed to test that the data fits. The correlations represented by R^2 are seen to be well above 0.9 which indicates the high level of accuracy achieved from the model. The kinetic model is of first order principles further demonstrating that the arabinose generation reaction is a first order reaction as has been noted in numerous studies. Due to the relatively low level of arabinose being formed in this hydrolysis reaction there were a number of experiments which registered little or no arabinose formation and therefore could not be modelled accurately. These models were under operating conditions of 7.5 and 10.0% w/w acid concentration at 175 and 200°C. The reasons for these failed models are likely as a result of low concentrations formed which led to indecipherable chromatogram readings from the HPLC.

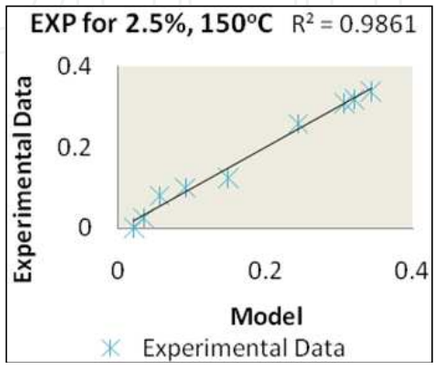
It can be concluded that the first order models of Glucose and Arabinose, where there was reasonable experimental data, are accurate. Glucose was modelled entirely with all R^2 correlations exceeding 0.95, which is acceptable. Due to discrepancies in the data points for a small number of more aggressive reactions, four models of arabinose generation where



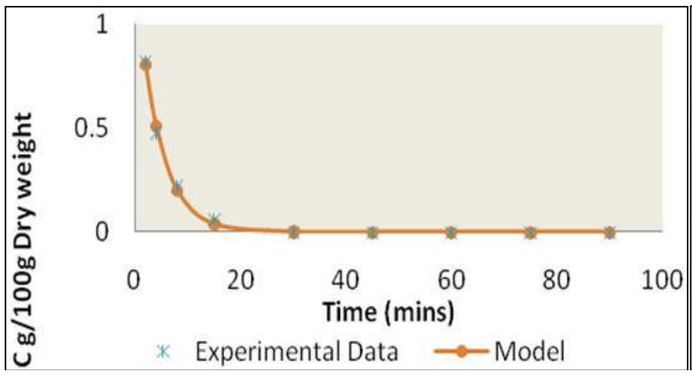


(a.1) Arabinose model at 135°C, acid conc. 2.5% (a.2) Fitting Test

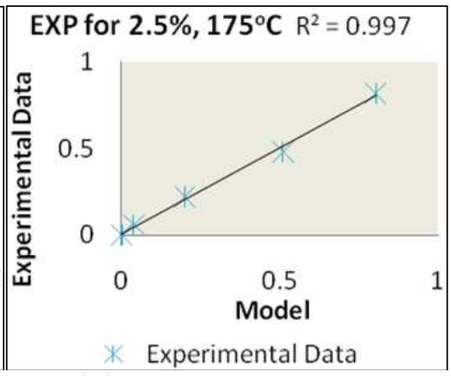




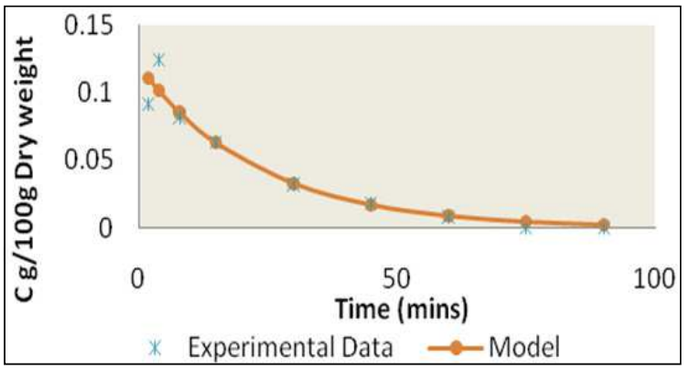
(b.1) Arabinose model at 150°C, acid conc. 2.5% (b.2) Fitting Test



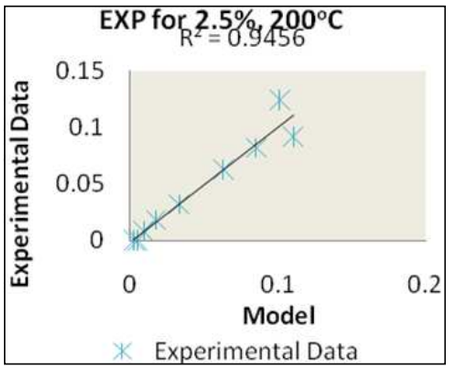
(c.1) Arabinose model at 175°C, acid conc. 2.5%



(c.2) Fitting Test



(d.1) Arabinose model at 200°C, acid conc. 2.5%



(d.2) Fitting Test

Fig. 3. Arabinose model with variation in reaction temperature

unachievable however the remainder attained R^2 correlations exceeding 0.95. To improve the models certain data points were ignored (one or two entries per reaction) when it was judged to be upsetting the model. In all cases this improved the overall yield.

3.5 Reaction constants

Having successfully determined the accurate k values for the reactions through the mathematical models, a number of other important kinetic information can be derived. These kinetic coefficients can be correlated with temperature by applying the Arrhenius Equation, and from that additional information, such as the activation energy and the pre-exponential factor, can be obtained. This correlation is demonstrated below[4]:

$$k_i = k_{i0} e^{\frac{-E_a}{RT}} \tag{10}$$

Where,

k_i = Kinetic coefficient (i = 1 or 2) (min^{-1})
k_{i0} = Pre-exponential factor (i = 1 or 2) (min^{-1})
E_a = Activation Energy (kJ mol^{-1})
R = Gas Constant, 8.314 (kJ mol^{-1} K^{-1})
T = Temperature (K)

The pre-exponential factor is the link between the temperature and acid concentration variables in the reaction. As can be seen above from the Arrhenius Equation the reaction constant k_i increases exponentially with temperature, to coincide with this the acid concentration affects the kinetic model as per the following Equation 10[4]:

$$k_{i0} = a_i[Ac]^{n_i} \tag{11}$$

Where
a_i, n_i = Regression Parameters
Ac = Acid Concentration (% w/w)
Therefore once k_i has been determined, it is possible to derive all the reaction constants associated with the variables of temperature and H_3PO_4 concentration. The k_{10} values are unique to the potato peel raw material source and vary greatly between raw materials. These differences can be due to the structure and composition of the material which may neutralize the acid. In order to extract these additional kinetic parameters, both Equations must be rearranged into the form of a linear function; $y = mx + c$, whereby the reaction coefficients are represented by the linear constants m and c. Equation 10 and Equation 11 are therefore rearranged as follows[4]:

$$ln\ k_i = -\frac{E_a}{R}\frac{1}{T} + ln\ k_{i0} \tag{12}$$

$$ln\ k_{i0} = n_i ln\ [Ac] + \ln a_i \tag{13}$$

Figure 4 illustrates the linear relationship between the log values of the k coefficients and the inverse of temperature at 5.0% w/w acid concentration. The R^2 correlation shows good agreement between the k values, this indicates that the model accurately follows the theoretical Equation (12).

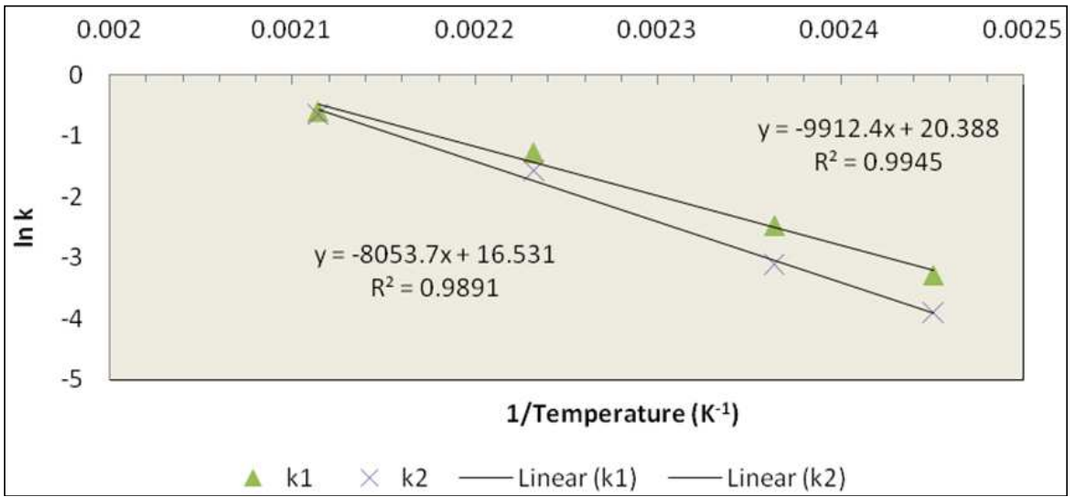


Fig. 4. Relationship between the calculated k values and the temperature of glucose, at 5.0% w/w acid concentration

Similarly with Glucose, Arabinose demonstrates good agreement between the experimental and modelling data. The data extracted from the linear Equation is then used to obtain values for activation energy, E_a, while $ln\ k_{i0}$ is used later to establish the mathematical

relationship between acid concentration and the rate of reaction. Table 2 shows the reaction constants obtained for hydrolysis of potato peels at temperatures 135, 150, 175 and 200 °C at 5.0% w/w acid concentration. The reaction constants for all other acid concentration reactions are also generated. Having calculated all the k_{i0} values for the reaction constants k_i it is now possible to introduce acid concentration into the reaction model as per the empirical Equation 12. Figure 5 shows that the log values of k_{i0} vary linearly with the log of acid concentration for glucose generation.

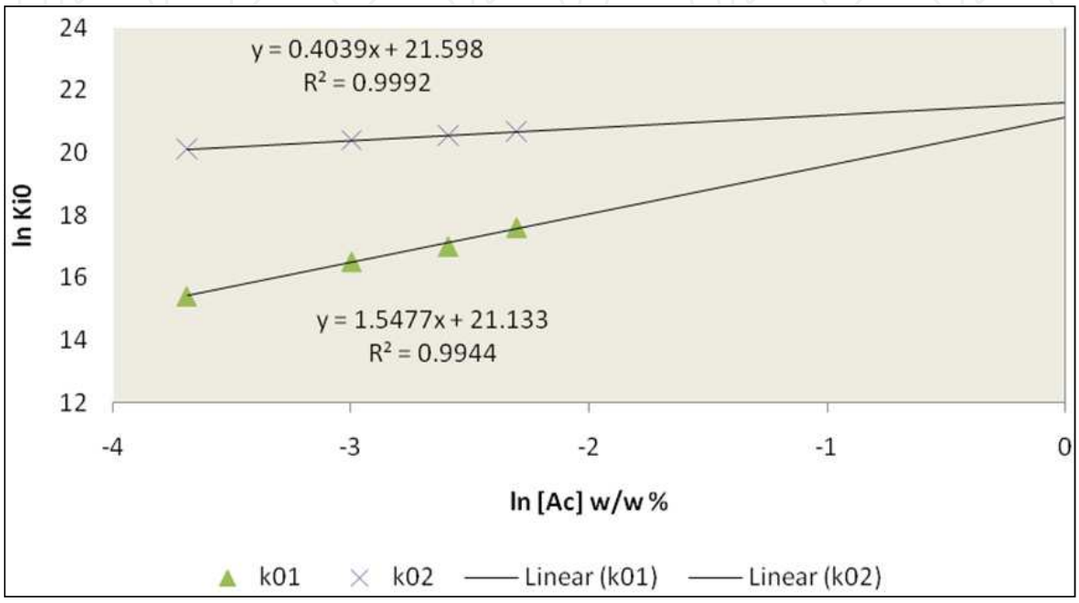


Fig. 5. The relationship between the calculated k_{i0} values and acid concentration for glucose

The model for glucose was found to be more accurate than that of Arabinose due to issues with reliability of Arabinose experimental data obtained brought on by experimental/human error. The linear fit has a high accuracy level, indicated by the R^2 correlations obtained. This illustrates a strong agreement between acid concentration and the k_{i0} parameters. Table 3 shows the reaction constants obtained from Equation 12 for both sugars investigated.

	135°C	150°C	175°C	200°C
(a) Glucose				
k_1 (min^{-1})	0.03731	0.0841	0.2772	0.5438
k_2 (min^{-1})	0.02002	0.0444	0.2054	0.5213
Reaction constants	k_1	E_a = 66.958 kJ,	k_{10} = 1.51x10^7,	R^2 = 0.9945
	k_2	E_a = 82.411 kJ,	k_{20} = 7.15x10^8,	R^2 = 0.9891
(a) Arabinose				
k_1 (min^{-1})	0.0116	0.0225	0.03903	0.041
k_2 (min^{-1})	0.0683	0.2777	0.5517	3.3665
Reaction constants	k_1	E_a = 30.939 kJ,	k_{10} = 127.84,	R^2 = 0.9127
	k_2	E_a = 89.226 kJ,	k_{20} = 2.05x10^{10},	R^2 = 0.961

Table 2. Reaction constants of sugars released in 5.0% w/w H_3PO_4 hydrolysis of Potato Peels

One notable conclusion can be drawn from these results is that the value of *n* for sugar formation of glucose is markedly higher than that for sugar degradation. This parameter justifies the conclusion that increasing the acid concentration will increase net yield of sugars as the k_1 would increase by a magnitude faster than the rate of degradation.

A generalised model for the prediction of sugar production rate from hydrolysis by H_3PO_4 has been developed. The kinetic parameters k_1 and k_2 can be determined at any given temperature and acid concentration, by substituting Equation 10 and Equation 11 to give Equation 14.

$$k_i = a_i e^{\left(\frac{-E_{aj}}{RT}\right)}[Ac]^{n_i} \quad (14)$$

Where,

i = 1 or 2 (depending on whether reaction is sugar formation or degradation)

	k_{10}	k_{20}
(a) Glucose		
a_i	1.51×10^{9}	2.40×10^{9}
R^2	0.9944	0.9992
n_i	1.5477	0.4039
(a) Arabinose		
a_i	5.54×10^{-18}	4.12×10^{21}
R^2	0.99	0.988
n_i	-14.89	8.733

Table 3. Reaction constants of sugars released for varying H_3PO_4 concentrations during hydrolysis of Potato Peels

3.6 Process optimisation

With a theoretical model in place consisting of accurately determined reaction parameters, the optimum conditions can be examined more closely.

When taking into account the reaction kinetics involved in the formation of sugars through hydrolysis, it is seen that the larger the value of k_1 the higher the rate of sugar formation and therefore the lower the cycle time required to maximise yield. In contrast to this the larger the value of k_2 the higher the rate of sugar degradation. Hence, the most desirable operating conditions will result in a high value of k_1 and a low value of k_2.

In practice this scenario is difficult to achieve so the optimum conditions available at the current operating conditions must be investigated. The value of k_1 and k_2 both increase exponentially with temperature as per the Arrhenius Equation. To increase the temperature would serve to increase the sugar production rate but a rapid decline due to sugar degradation would render the process highly inefficient as was seen earlier. Therefore, to preserve sugars, it is best to limit the temperature of the reaction and to try and manipulate the k values through varying the acid concentration.

As mentioned previously, through detailed analysis of the reaction kinetics it was found that the acid concentration had affected the k_1 value by a magnitude greater than it affects k_2. By studying the theoretical results of the Arrhenius Equation it can be seen that the values of k_2 vary only slightly compared to the variance of k_1. This will allow the rate of production to increase at the expense of the rate of degradation allowing for high yields to

be achieved in a shorter time span. One such example is sugar generation at 135°C and 10.0% w/w acid concentration whereby a maximum yield of 55.2g sugar/ 100g dry potato peel is achieved after a short residence time of between 4-8 minutes. As acid degradation is primarily a function of temperature, almost negligible sugar degradation occurs during this period. However using more concentrated acid reactants will require acid recovery techniques which can prove both tricky and expensive to operate.

Baring this in mind a more attractive proposition would be to run the reaction at a more moderate temperature and acid concentration. One possible set of operating condition is 175°C and 7.5% w/w acid concentration. A maximum yield of 38.78 g sugar/ 100g potato peel is observed after 15 minutes residence time and the degradation of this sugar is at a more manageable rate with over 44% sugar retained after 90 minutes. This reaction would be considered easier to control.

If the cost of the process is introduced to the model it will have an effect on the selection of operating conditions. The main aim of a major energy providing company is to maximise profit, therefore the cycle time and throughput of the reaction is paramount. The maximum yield residence time becomes a significant factor in this situation. If a company opts to use a more controllable cost effective reaction model to hydrolyse their feed material such as 135°C and 5.0% w/w acid concentration then a maximum yield of 26.32g sugar/ 100g dry potato peel is achieved after 30 minutes reaction time. However if the reaction conditions are modified slightly to 150°C at the same acid concentration then a maximum yield of 25.97g sugar/ 100g dry potato peel is achieved after 15 minutes. Although the yields are similar the retention time for the reaction is halved by increasing the temperature by 25 deg C. The outcome of this sort of comparison will ultimately be determined by the energy input costs and the costs of treating process wastes related to the reaction.

The limitations of a batch system for this type of reaction are apparent when examining the results. Preparation and cleaning of the reactor are cumbersome processes taking between 2-3 hours to complete from start to finish. Therefore, to achieve and maintain the optimum conditions for this hydrolysis reaction a continuous process with an average retention time is a more desirable option. This is currently the case in bulk manufacturing of biofuel where plug-flow reactors are a viable option.

A summary of the optimum conditions for both glucose and arabinose at each concentration is presented in Table 4.

Conc. H_3PO_4 (% w/w)	Temperature (°C)	Time (min)	Glucose g/ 100g dry Potato Peel
2.5	150	8	14.2
5.0	150	15	25.1
7.5	135	15	36.8
10.0	135	4	53.8

Table 4. (a) Summary of the conditions required for optimum glucose yield at 2.5, 5.0, 7.5 and 10% w/w acid concentration

4. Conclusions

It can be seen from Table 5 that a level of 97% glucose conversion has been obtained when compared to the theoretical yield. However an unquantified 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[9]. 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.

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

Table 5. Comparing yields with total theoretical yields through Quantitative Saccharification

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^{o}C and 2.5% w/w acid concentration the production rate is quite high and continues to rise until the reaction ends at 90 minutes. 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^{o}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 unimpressive arabinose conversion, overall sugar yield is 82.5% of the theoretical yield which would be considered quite an acceptable return in the circumstances.

Another conclusion drawn from this study is the difference between the effect of temperature and acid concentration on conversion rates. Both variables have the effect of increasing the overall reaction rate however the production and degradation of sugars is more sensitive to fluctuations in temperature. By increasing either condition the reaction rate increases allowing for a maximum yield to be obtained in a far shorter period of time, however it was found that by increasing the temperature had an overall detrimental effect on the net sugar yield during the reaction. It was found in all cases that as temperature increased the decomposition reaction began to drastically outpace the formation rate which led to rapid declines in the net sugar yield. In contrast to this increases in acid concentration had a less dramatic effect on the production and decomposition rate of sugar. As acid concentrations raised so did the production rate of sugars, but it was seen to affect the sugars in a more stable manner. Although degradation of sugars also increased with increasing acid concentration it was less rapid than was seen with increasing temperature. In conclusion, to run this reaction in the most effective manner temperature should be kept at a reduced level while acid concentration should be the primary reaction dependency.

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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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