Comparative Modelling and Optimization of Different Pretreatment Technologies for Bioethanol Production

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Abstract

Bioethanol production from lignocellulose biomass is becoming of increasing importance because of its low-cost, widely available, non-food competence and high sugar content. However, lignocellulose is more difficult to convert than sugars, starches and oils because it consists of a complex mixture of cellulose, hemicellulose and lignin. To break down its complex structure, a pretreatment step is required. For that purpose physical, physico-chemical, chemical, biological or a combination of pretreatment steps have been proposed to process the raw materials [23]. Pretreatment is essential for the economic success of the entire system because the pretreatment may represent up to one-third of the overall processing cost [14].

The impact of the pretreatment step on the overall process motivates the development of models suitable for process design and optimization. This study presents the modelling and optimization of the pretreatment of sugarcane bagasse for bioethanol production. Alternative pretreatment steps are considered, including dilute-acid hydrolysis (with different acids) and processing with liquid hot water.

Models for each pretreatment step are derived from experimental data from the literature, based on an understanding of the kinetics involved in the different reactions and incorporating the kinetics into mass balances models to quantify the consumption and generation of the different components. The models are implemented in the Jacaranda system for process design and optimisation [8] to identify the optimal process conditions for each pretreatment. Results show the interaction between design variables (i.e. residence time, operating temperature or acid concentration) and optimal conditions.

Keywords: lignocellulose, biomass, ethanol, model, optimisation, design.

Resumen

La producción de bioetanol a partir de biomasa lignocelulósica está adquiriendo cada vez más relevancia debido a su bajo costo, amplia disponibilidad, alto contenido de azúcar y que no compite con los alimentos. Sin embargo, la lignocelulosa es más difícil de convertir que los azúcares, almidones y aceites, ya que consiste en una mezcla compleja de celulosa, hemicelulosa y lignina. Para poder romper su estructura, se requiere un tratamiento previo. Para esto diferentes metodos se han propuesto, entre ellos físico, físico-químicos, químicos, biológicos o una combinación de estos para pretratar la materia prima [23]. El pretratamiento es una parte esencial para el éxito económico de todo el sistema, debido a que puede representar hasta un tercio del costo de todo el proceso [14].

El impacto que tien el pretratamiento en el resto del proceso motiva el desarrollo de modelos adecuados para el diseño y optimización de procesos. Este estudio presenta la modelización y optimización del pretratamiento del bagazo de caña de azúcar para la producción de bioetanol. Diferentes pretratamiento son considerados, que incluyen pretratamiento con acido diluido (tres diferentes ácidos) y el pretratamiento con agua caliente.

Los modelos para el pretratamiento se derivan de datos experimentales extraidos de la literatura, y basados en el estudio de la cinética que participa en las diferentes reacciones y la incorporación de esta a los balances de masa para cuantificar el consumo y la generación de los distintos componentes. Los modelos se implementaron en Jacaranda, un sistema para el diseño y optimización de procesos [8], para determinar las condiciones óptimas para cada pretratamiento. Los resultados muestran la interacción entre las variables de diseño (tales como tiempo de residencia, temperatura, o concentración de ácido) y las condiciones óptimas.

Palabras claves: lignocelulosa, biomasa, etanol, modelación, optimización, diseño.

Introduction

Fuels derived from lignocellulosic biomass are essential in order to overcome our excessive dependence on petroleum for liquid fuel and also address the built-up of greenhouse gases that cause global climate change. Lignocellulosic biomass, including agricultural and forestry residues instead of traditional feedstocks (starch crops), could prove to be an ideally
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inexpensive and abundantly available source of sugar for fermentation into transportation fuels. However, lignocellu- losic biomass conversion to ethanol is not a simple process because of its complex structure. The cellulose crystallinity, protection by lignin and sheathing by hemicellulose contribute to the resistance of lignocellulosics to hydrolysis.

Pretreatment is the key cost element in the conversion that still require low-cost sugars to be cost competitive. In addition, pretreatment technology choice have heavily impacts on the performance and cost of virtually all the other operations. Thus, pretreatment must be advance and carefully integrated with the rest of the process to realize the full potential of lignocellulosic to bioethanol.

Over the years, many technologies have been considered in the quest for low-cost pretreatment approaches that release high sugars yields from both cellulose and hemicellulose. These technologies can be categorised as physical, physical- chemical, chemical and biological. The ideal pretreatment process would produce reactive fibre; yield pentoses in non-degrade form; exhibit no significant inhibition of fermentation; require little or no feedstock size reduction; entail reactors of reasonable size (high solids loading), built of materials with a moderate cost; not produce solid residues; and have a high degree of simplicity [13].

The effect of the pretreatment is however very dependent on the biomass composition and operating conditions. This variability depends on factors as the type of plant from which the biomass is obtained, crop age, method of harvesting, etc. This makes that so far no one of the pretreatment methods could be applied in a generic way for many different feedstocks. Sugarcane bagasse is a potential lignocellulosic feed-

stock for bioethanol production since it is consider a rich energy reservoir, with high production yields (80 t/ha) with an annual regeneration capacity, low-cost, readily available and with high carbohydrate content [18].

Hydrolysis with dilute sulphuric acid has been successfully developed, high reaction rates can be achieved improving significantly the subsequent process of cellulose hydrolysis, however, the costs of dilute acid pretreatment are still too high. The main advantage of dilute acid pretreatment is the higher recovery of sugars from hemicelluloses, but the formation of furan derivatives and other toxic products and the need of an additional concentration step are their main desadvantages. Liquid hot water and steam explosion seem as a promising technologies leading to a good solubilisation of sugars in the pretreatment steps, non inhibitors formation and its non corrosive nature. But the amount of water involved and the high temperatures and pressures are limitants to their industrial application.

This study present kinetic models for dilute-acid hydrolysis and liquid hot water pretreatment based on first-order re- actions through a statistical analysis, based on experimental data to obtain the kinetic parameters thorough non-linear regression analysis. The mathematical models, suitable for optimisation within a design framework, were implemented in the Jacaranda system for process design and optimisation [8] and the optimal conditions for the design variables are presented for each pretreatment.

Kinetic Models for the Pretreatment

Kinetic modelling studies of the pretreatment stage present two different approaches [11]: studies based on the severity factor; and studies based on formal kinetic models. Severity factors utilise approximations that make it possible to predict in a simple fashion the kinetics of simple irreversible reactions, but they are not applicable to more complex cases of reactions in series, such as those that take place in hydrothermal processes. Formal kinetics are based on the formulation of conventional kinetic models, normally through the use of pseudo-homogeneous, first-order, irreversible reactions, that allow us to obtain a more complete description of the process [4]. In this study the

use of kinetic models are considered as appropriate for the development of the optimisation analysis, owing to their superior ability for the interpretation of the effect of the pretreatment in hemicelluloses. The kinetic models selected are as simple as possible to enable them to explain in a satisfactory way the overall pretreatment process. Below we will describe in a brief way the models selected for the pretreatment of sugarcane bagasse with liquid hot water and with different acids.

2.1   Simplified reaction model

The modelling of the hydrolysis of a polysaccharide like hemicellulose, is complex and involves many factors related with the lignocellulosic material and the reaction medium [9]; other factors can also interfere in the determination of the reaction, such as the amount of wet in the raw material, interference of other compounds, presence of different kind of bonds (sugar-sugar, sugar-acetyl groups, etc.), protector effect of the structured of the intact cell, etc. An analysis of the factors that can interfere is reported by Gamez et al. [10].

The acid hydrolysis of cellulose was studied first by Saeman [21] in the middle of the past century, the main difficulty of this lineal homo-polymer is the presence of two fractions, one is crystalline and the other is amorphous, with different susceptibility to acid hydrolysis. The study of hemicellulose is even more difficult than cellulose, due to the presence of

a heterogenic nature with several sugar monomers (xylose, arabinose, glucose, etc.) and other compounds such as acetyl groups and uronic acids. All these compounds are linked forming a ramified polymer with an unknown structure [9].

Using the work of Saeman [21] on the hydrolysis of wood using sulphuric acid, we can describe the hydrolysis of cellulose and hemicellulose by pseudo-homogeneous models based on sequential, irreversible and first-order reactions:

$$\text{Cellulose} \xrightarrow{k_1} \text{Glucose} \xrightarrow{k_2} \text{Decomposition products} \qquad (1)$$

$$\text{Hemicellulose} \xrightarrow{k_1} \text{Monomers} \xrightarrow{k_2} \text{Decomposition products} \qquad (2)$$
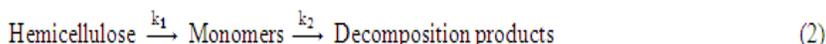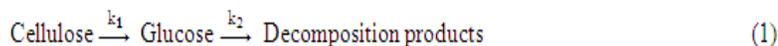
In a general way, the Saeman model can be applied to other polysaccharides:

$$\text{Polymer (P)} \xrightarrow{k_1} \text{Monomer (M)} \xrightarrow{k_2} \text{Decomposition products (Dp)} \qquad (3)$$
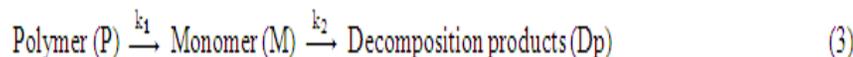
where the polymer (P) fractions (such as glucan, xylan, araban or galactan) contained in the raw material are converted into monomers (M) (such as glucose, xylose, arabinose or galactose), which are further converted into degradation prod- ucts (Dp) (such as HMF from glucose or galactose, and furfural from xylose or arabinose), in g/L. k_1 and k_2, different for each reaction, are the kinetic coefficients of the reactions of monomer release and decomposition (h—l), respectively.

Considering the reactions involved, the final amount of each species from solving the differential equations is defined by the set of the following equations:

$$\frac{dP}{dt} = -k_1 P \qquad\qquad P = P_0 \, e^{-k_1 t} \qquad (4)$$

$$\frac{dM}{dt} = k_1 P - k_2 M \qquad\qquad M = P_0 \frac{k_1}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right] \qquad (5)$$

$$\frac{dDp}{dt} = k_2 M \qquad\qquad Dp = \frac{P_0}{k_2 - k_1} \left[k_2 (1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t}) \right] \qquad (6)$$

2.2 Two-fraction reaction model

The existence of two hemicellulosic fractions, reported in the literature [14, 6, 15], leads to a two-fraction model which considers the susceptible or fast fraction easy to hydrolyse and a less susceptible fraction more difficult to hydrolyse. Kobayashi and Sakai [16] proposed the inclusion of the two fractions in the kinetic models. Therefore, the kinetic model is modified to include the presence of two fractions in the polymer. A more realistic kinetic model for the hemicellulose reaction is:
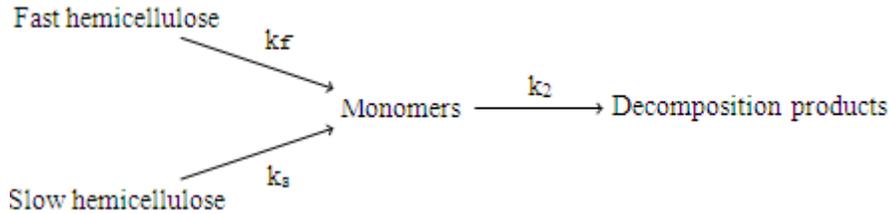
The susceptible fraction is measured by the parameter á (0 < á < 1) described as the mass ratio between the fractions (g of susceptible fraction/ g of total fraction) in the raw material. Rodriguez-Chong et al. [20] define the main reasons for using two fraction model:

• Transport limitation of mass and energy in the reactive mass, which are more important the bigger the particle size and the lower the WSR (water solid ratio).

• Presence of different fractions of hemicelluloses with different intrinsic reactivity due to differences in structure, accessibility, etc.

• Presence of uronic acid with lower reactivity than xylose that decreases the rate of hemicelluloses solubilisation.
• Different reaction rate of the fraction linked with lignin.
• Variations in the surface of the inter-phase water-hemicelluloses along the reaction.

 Therefore Eq. 5 was modified to include c:

$$M = c \ P_v \ \frac{k_i}{k_2 - k_i} \ (e^{-k_1 t} - e^{-k_2 \ t}) \tag{7}$$

where M is the concentration (g/l) of the monomer at time t and P0 is the initial polymer concentration (g/l). The value of P0 assumes a total conversion of polymer to monomer without degradation and is determined by the following equation:

$$P_v = f \ \frac{P_{n,0}}{W \ SR} \ \rho \tag{8}$$

i s the fraction of the polymer Pn in the raw material, on a dry basis (g/g), W SR is the water solid ratio (g water/ g raw material in dry basis) and ñ is the density of hydrolysates (g/l).

$$k_i = A_i \ e^{(-E_{ai} /RT \ )} \tag{9}$$

where Eai is the activation energy (kJ/mol); Ai is the pre-exponential factor (h—i); R is the universal gas constant
(8.3143 × 10—3 kJ/mol K); and T is the reaction temperature (K).
The pre-exponential factor Ai is a function of acid concentration, but the activation energy Eai is consider independent of temperature and acid concentration [17]. The pre-exponential factor Ai can be rewritten to explicitly include the effect of acid concentration:

$$A_i = A_{0,i} \, C_a^n \tag{10}$$

in which, Ca is the acid concentration in percent (w/w) added prior to hydrolysis, and n is an arbitrary constant that varies with the type of biomass being pretreated. Equations 9 and 10 can be combined to give:

$$k_i = A_{0,i} \, C_a^n \, e^{(-E\,ai/RT)} \tag{11}$$

In the next section, we are going to generate and evaluate the parameters for the models discussed above for the pretreat-
ment of sugarcane bagasse with liquid hot water (LHW) and different acids.

Kinetic Parameter estimates
Experimental data obtained from literature were used to fit the main function in each case and obtain the different kinetic parameters. For the simplified model the main function is the Equation 5 and for the two-fraction model it is Equation 7.

Nonlinear regression analyses were performed (due to the nonlinearity of the equations to fit), with an optimisation routine using the statistical computing program "R" (http://www.r-project.org/). R's nonlinear optimisation routines are optim(), nlm() and nls().

The parameter estimates are determined as the parameters providing the best fit to the mean function (M) to the obser- vations yi , ..., yn , that correspond to the concentration in g/l of the different components after the pretreatment. The parameters are obtained by minimisation of the residual sums of squares (RSS) with respect to a set of unknown parame- ters (c, ki , k2)

$$RSS = \sum_{i=i}^{n} [y_i - M(t, c, k_i, k_2)]^2 \tag{12}$$

The minimisation of RSS is often referred to as minimising the least-squares criterion or least-squares estimation, and the solution to the minimisation problem is the least-squares parameter estimates. In contrast to linear regression, the
minimisation of RSS will in general be a nonlinear problem, and therefore numerical optimisation methods are needed. These methods are iterative procedures that will ideally approach the optimal parameter values in a stepwise manner. At each step, the algorithms determine the new parameter values based on the data, the model and the current parameter values. By far the most common algorithm for estimation in nonlinear regression is the Gauss-Newton method, which relies on linear approximations to the nonlinear mean function at each step. Once the parameter estimates are found, the
estimate of the residual variance ó2 is obtained as the minimum value of RSS divided by the degrees of
.... RSS . The residual standard error is then s. The next subsec-
tions will present the results of this

n—p analysis.

3.1   Liquid hot water

The studies on the pretreatment of sugarcane bagasse with liquid hot water (LHW) in literature are scarce. Only the study of Boussarsar, Roge and Mathlouthi [2] presents enough data results to make an analysis and comparison for this study. The raw composition of the sugarcane bagasse used to calculate the potential concentration of the sugars P0 (equation 8) is shown in the Table 1.

Components	Percentage dry weight	Potential concentration of the sugars P_0
Glucan	45.0	50.00
Xylan	24.0	27.27
Araban	1.5	1.71
Galactan	0.5	0.56
Klason lignin	20.0	-
Others	9.0	-

Table 1: Main components of sugarcane bagasse used for the pretreatment with liquid hot water

R's nonlinear least squares routine nls() was used to fit the simplified reaction model, for this purpouse equations 5 and
9 were used. To fit the two-fraction model, equations 7 and 9 were used with the R's optimisation routines nlm() and
optim() due to the non-convergence on satisfactory estimates of nls().

Kinetic parameters values for the pretreatment of sugarcane bagasse with liquid hot water had not been reported in the literature so far. Table 2 shows the estimate values for the pre-exponential factors, activation energies and the minimum value of RSS that result from the fitting.

The comparison between the experimental and the calculated values for the simplified model and the two-fraction model, are shown in the Figure 1 for xylose, glucose, arabinose and galactose, respectively.

In the figures a degree of agreement can be observed between the calculated and the experimental values confirming the validity of the models employed. For comparison of the data from Table 2, it can be seen that there is practically no difference between the values of the simplified model and the two-fractions model for the pre-exponential factors and activaton energies for glucose and arabinose; however for xylose and galactose the differences are more pronounced between the values, as can be seen in Figure 1.

The value obtain from the susceptible fraction for xylan $c = 0.82$ is similar to that obtained for eucalyptus, 0.84 [11]; corncobs, 0.86-0.89 [12]; or brewery's spent grain, 0.80 [5]. The activation energy of xylan degradation is 90 kJ mol^{-i} which is lower than the reported range 103-143 kJ mol^{-i} for the degradation of hardwood xylan during autohydrolysis [12]. Whereas the activation energy of xylan hydrolysis is 122 kJ mol^{-i}, which is comparable to the reported value of 112 kJ mol^{-i} [11]. The difference in reported values of the activation energies has been attribute to the different composition of the raw material and the different experimental conditions. For these reasons a unique optimisation model can not be apply to the different lignocellulosic materials, for each species the kinetics have to be calculated with experimental data for further use in process modeling.

The comparison of kinetic parameters for the other hemicellulosic fractions is complex owing to the lack of information in the literature. The value for the susceptible fraction for glucan $c = 1.00$, means that all glucan is susceptible to hydrolysis, but as a result of the low pre-exponential factor and activation energy the

glucan fraction is expected to remain without further degradation. Almost all araban is susceptible to hydrolysis (c = 0.98) and part of the Galactan (c = 0.63), and on the contrary to glucan a major degradation is expected for these two polymers as the higer pre-exponential factors and activation energies indicate

(a)

(b)

(c)

(d)
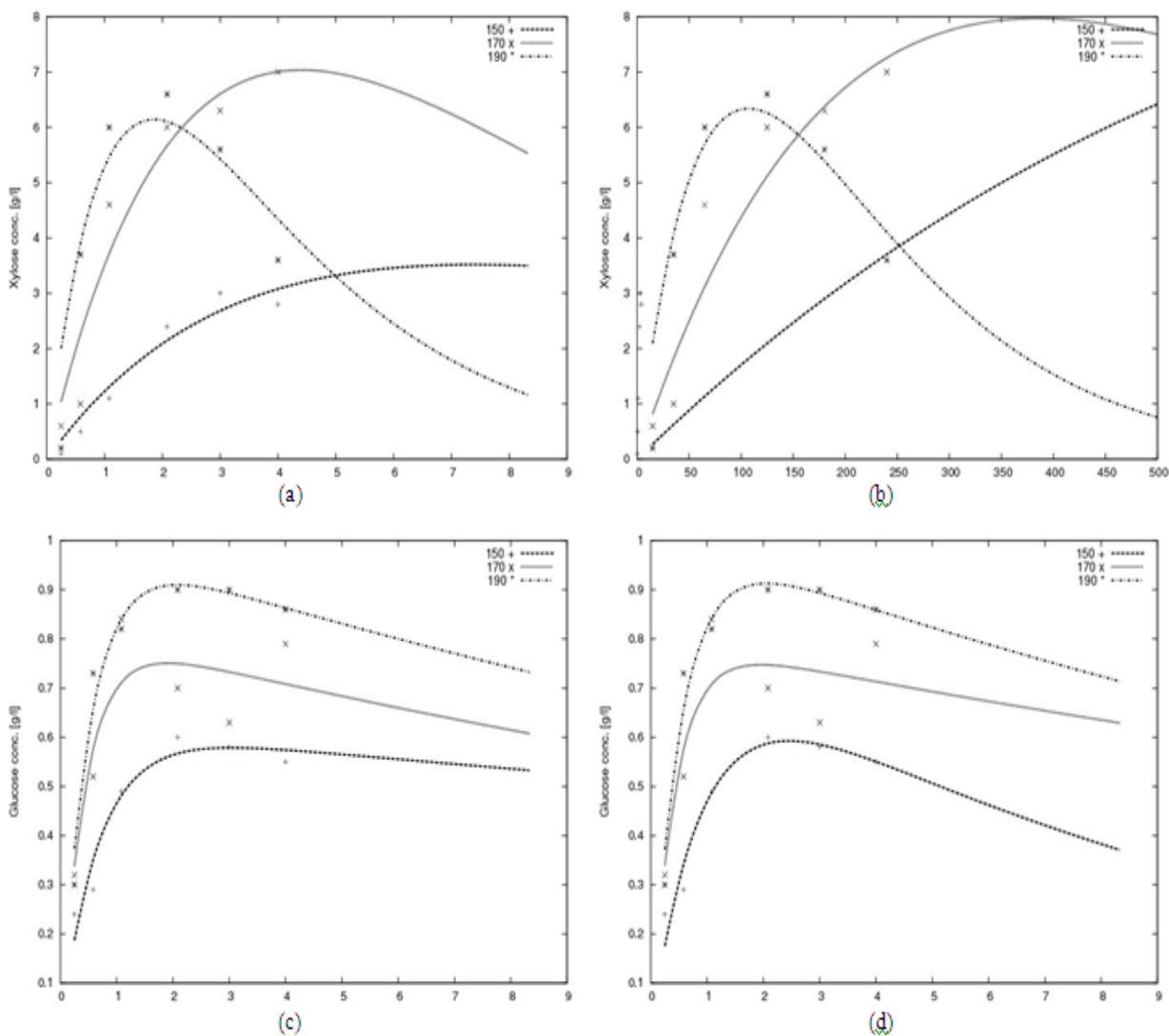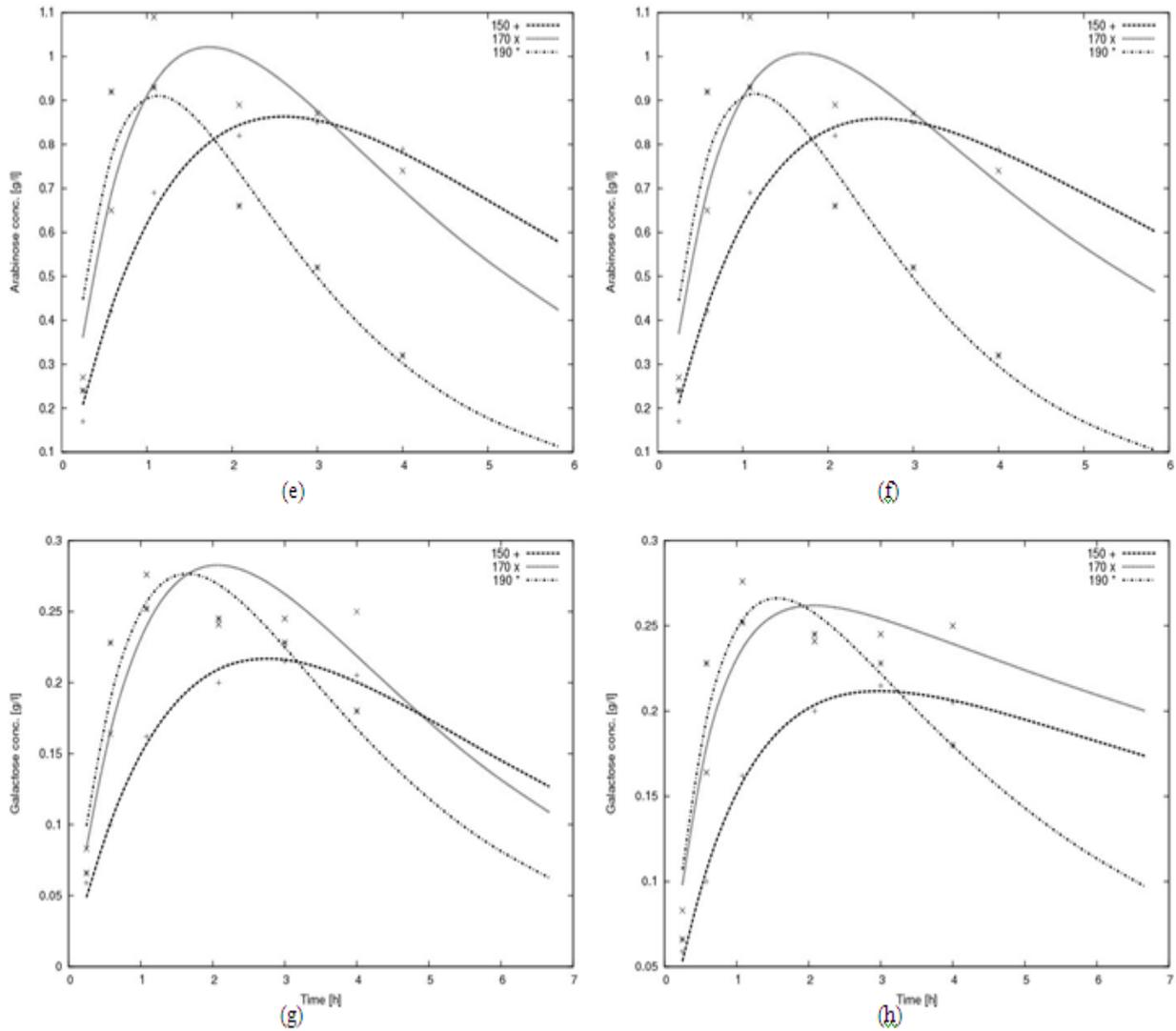
Figure 1: Experimental (symbols) and calculated (lines) time courses of the concentration of xylose (a,b), glucose (c,d), arabinose(e,f) and galactose(g,h) using the simplified model (a,c,e,g) and the two-fraction model (b,d,f,h) at different temperatures for the pretreatment of sugarcane bagasse with liquid hot water

Table 2: Kinetic parameters for the pretreatment of sugarcane bagasse with liquid hot water

Estimates		Xylan	Glucan	Araban	Galactan
			Simplified Reaction Model		
k_1	$\ln A_{0,i}$	22.38	3.78	10.97	8.57
	$E_{a,i}$	90.09	26.92	40.85	55.45
k_2	$\ln A_{0,i}$	31.52	2.63	8.49	1.89
	$E_{a,i}$	122.12	7.59	35.21	10.09
	RSS	9.24	7.09×10^{-2}	1.76×10^{-1}	1.10×10^{-2}
			Two-fractions Model		
k_1	$\ln A_{0,i}$	22.42	3.78	11.04	10.59
	$E_{a,i}$	88.52	20.95	41.00	58.70
k_2	$\ln A_{0,i}$	33.57	2.65	8.57	0.08
	$E_{a,i}$	151.50	7.45	35.01	0.90
	α	0.82	1.00	0.98	0.63
	RSS	8.97	7.09×10^{-2}	1.75×10^{-1}	9.51×10^{-3}

$A_{0,i}$: Pre-exponential Factors $[h^{-1}]$
$E_{a,i}$: Activation Energies [kJ/mol]
α : Susceptible fraction [dimensionless]

3.2   Acid-dilute hydrolysis

Three studies were selected to studied the pretreatment of sugarcane bagasse with acid-dilute. The studies selected were the work of Aguilar et al. [1] who studied the hydrolysis of sugarcane bagasse with sulphuric acid (H_2SO_4), the study of Bustos et al. [3] who use hydrochloric acid (HCL) and the study of Rodriguez-Chong et al. [20] who use nitric acid (HNO_3), all three works pre-treated sugarcane bagasse at 2%, 4% and 6% of acid concentration, at different temperatures (100æ% C, 122æ% C and 128æ% C).

The raw composition of the sugarcane bagasse, used in the three studies to calculate the potential concentration of the sugars (P0) is as shown in Table 3.

Components	Percentage dry weight	Potential concentration of the sugars P_0
Glucan	38.9 ± 1.0	43.22
Xylan	20.6 ± 1.6	23.40
Araban	5.56 ± 0.7	6.32
Klason lignin	23.9 ± 1.7	-
Others	11.0 ± 1.0	-

Table 3: Main components of sugarcane bagasse used for the pretreatment with dilute-acids

Table 4 shows the estimates values for the n constant, pre-exponential factors, activation energies and the susceptible fraction c from the fitting for the diferent acids and components. The comparison between the experimental values and the calculated values for the two-fraction model are shown in the Figures 2 and 3 for xylose and glucose, respectively, for the three acids.

The graphs show a good correspondence between the experimental and calculated values, that confirm the certainty of the models developed. For comparison of the data from Table 4, it can be seen that the values of the parameters for xylan, glucan and araban for the different acids varied, indicating that each acid has a particular effect over the polymers in the raw material and for this reason an individual analysis is needed.

The values of the parameters for k_i, for all acids, are consistent with those reported for dilute-acid hydrolysis in the literature [12, 1, 3, 20]. In general, values of kinetic coefficients increased with temperature and acid concentration. For xylan, it can be observed that the values for the parameters, for both, k_i and k_2 are similar for HCL and H_2SO_4, so that decomposition products and xylose are generated at similar rates. For HNO_3 the parameters for k_i are lower than k_2, suggesting that the amount of xylose generated is higher than its decomposition product. The ideal case is generate the maximum amount of xylose with the minimum convertion to its decomposition product. The value of the parameter

Acid	Component	Parameters					
		k_i		k_2		c	$\frac{E_a}{R}$
		n	ln A	n	ln A		
	Xylan	1.2	28.9	1.2	23.6	0.90	
HCl [3]	Glucose	0.8	26.2	4.3	18.3	0.12	12 299
	Araban	0.5	27.0	13.1	16.2	0.40	
	Xylan	3.8	39.4	7.6	4.2	0.78	
HNO_3 [20]	Glucose	1.1	27.8	20	4.3	0.09	12 509
	Araban	0.8	40.0	9.5	26.4	0.32	
H_2SO_4 [1]	Xylose	0.7	31.6	0.7	25.7	0.80	13 080
	Glucan	1.9	32.3	3.3	19.1	0.13	

Table 4: Kinetic parameters for acid hydrolysis of sugar cane bagasse for different acids with reference to source of experimental data noted

c for xylan was in the range of 0.78-0.9, close to others reported for acid hydrolysis for lignocellulosic materials. For example, values of c in the range 0.58-0.80 for hydrolysis of oak [15], 0.84 for corn and 0.86 for sunflower seeds [19]. This suggests that the polymer is highly susceptible to acid-hydrolysis.

In the case of glucan and araban the decomposition reaction proceeds at a lower rate than the main product reaction, therefore if some degradation occurs, the amount of inhibitors expected will be low, which is a benefit for the process.
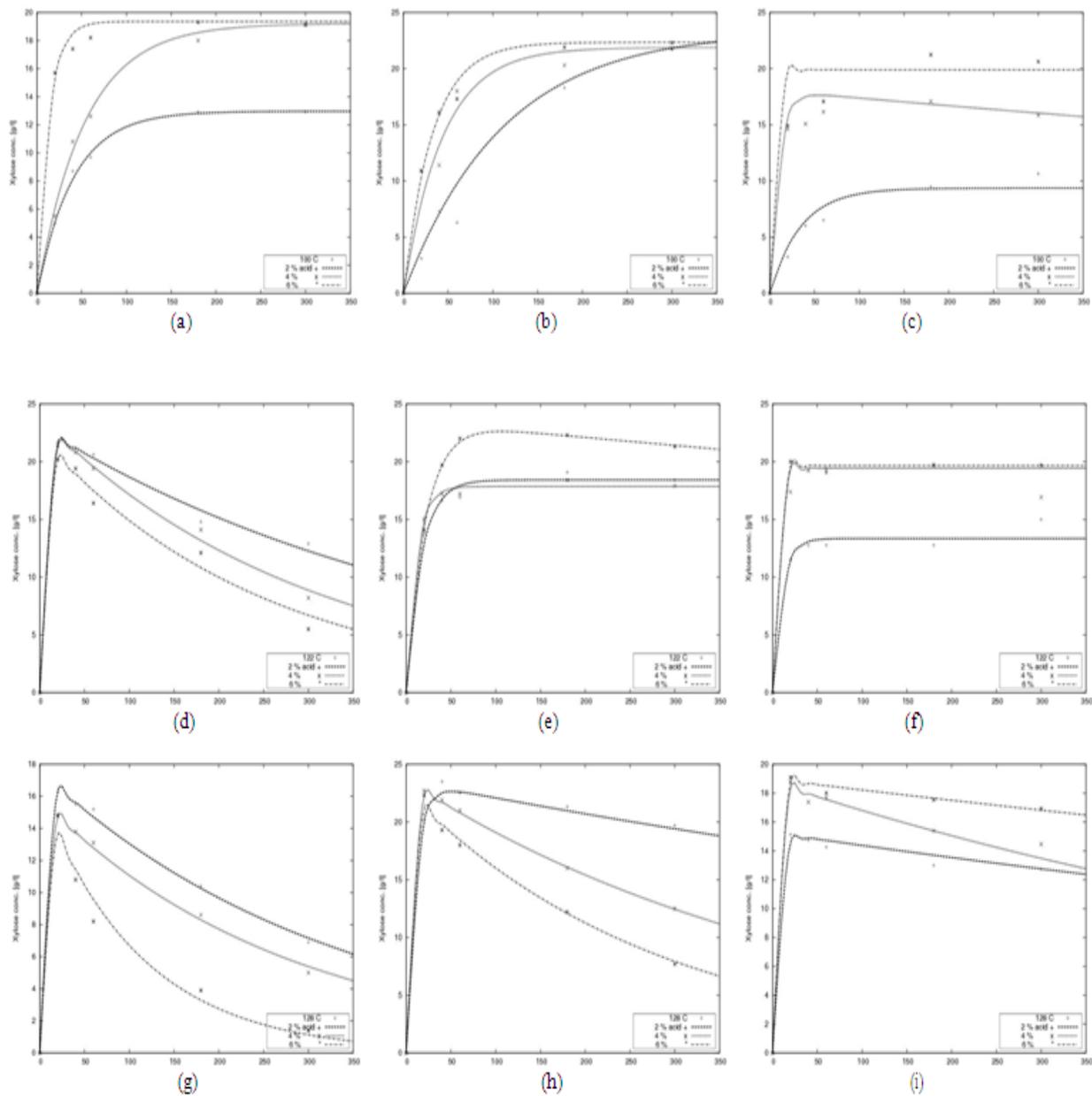
Figure 2: Experimental (symbols) and calculated (lines) time courses of the concentration of xylose at 100æ% C (a,b,c),
122æ% C (d,e,f) and 128æ% C (g,h,i) for the pretreatment of sugarcane bagasse with sulphuric acid (a,d,g), hydrochloric acid
(b.e,h) and nitric acid (c,f,i)
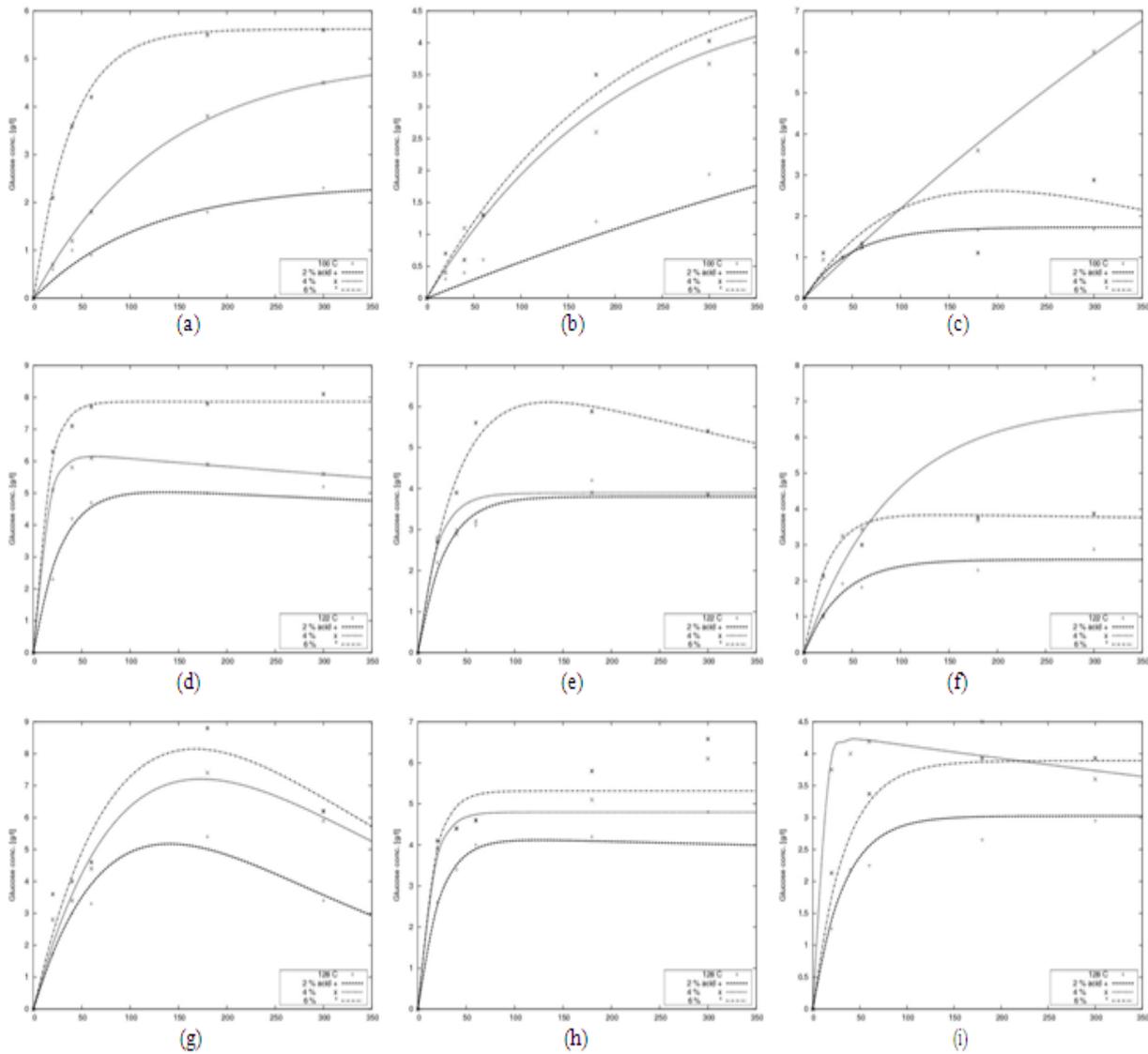
Figure 3: Experimental (symbols) and calculated (lines) time courses of the concentration of glucose at 100æ% C (a,b,c),
122æ% C (d,e,f) and 128æ% C (g,h,i) for the pretreatment of sugarcane bagasse with sulphuric acid (a,d,g), hydrochloric acid
(b.e,h) and nitric acid (c,f,i)

The values of ln A and n for k2 usually are not shown in the literature, but we consider these values in this study as they do impact on mass balances.

4   Optimisation of the pretreatment

The mass balance models incorporate the equation described in the sections above to quantify the consumption and generation terms for each species. After the pretreatment a liquid and solid fraction are considered independently. The liquid fraction of the pretreatment unit will be constituted by pentoses sugars (such as xylose, glucose, arabinose and galactose), products of decomposition of the hemicelluloses (such as acetic acid generated from the hydrolysis of acetyl groups linked to sugars) and the decomposition of the monosaccharides released (such as furfural, product of dehydration of pentoses). The solid fraction will be constituted by the remaining cellulose and lignin, assuming that the lignin has not been modified. For the pretreatment with dilute-acids we assume that the acid is consumed totally in the reaction.

The mass balance models have been implemented in the Jacaranda system for process design and optimisation [8]

and have been applied to the pretreatment of sugar cane bagasse. The pretreatment with different acids and liquid hot water (for the two models) have been considered and, for each case, the design variables shown in the Table 5 have been defined in Jacaranda.

The objective is to maximise the generation of xylose, z (g/l). A genetic algorithm (GA) procedure, in Jacaranda, was used for the optimisation. As a GA is stochastic, each solution attempt may potentially identify a different solution. For this reason, we attempted each problem 100 times and the results described include a statistical analysis. For each acid, the same objective function value was obtained (to within less than 0.1%) each time. The design variables, however, did vary. These results are summarised in Table 6 where, for each design variable, we present the average value obtained as well as the standard deviation in parentheses

Table 5: Design variables for the pretreatment of sugarcane bagasse with different acids and liquid hot water (LHW)

Design Variables	Pretreatment with acids			Pretreatment with LHW		
Water to solid ratio	W SR	$\in$	$[8, 10]$ $\frac{\text{g water}}{\text{g solid}}$	W SR	$\in$	$[8, 10]$ $\frac{\text{g water}}{\text{g solid}}$
Residence time	t	$\in$	$[0, 300]$ min	t	$\in$	$[0, 300]$ min
Temperature	T	$\in$	$[100, 128]$ °C	T	$\in$	$[100, 200]$ °C
Acid Concentration	C_a	$\in$	$[2, 6]$%	-		

Table 6: Design variables and objective function mean values and standard deviation (in parentheses) for different acids obtained solving each case 100 times in Jacaranda.

Acid	WSR	C_a	t (m)	T (K)	z (g/l)
H Cl	9.2 (0.55)	5.5 (0.45)	83 (38)	108 (6)	17.7
HNO_3	9.0 (0.58)	4.8 (0.81)	18 (73)	118 (7)	13.1
H_2SO_4	9.1 (0.54)	2.7 (0.82)	23 (11)	107 (7)	13.6
LH W [a]	9.0 (0.57)	-	294 (5)	171 (0.9)	7.7
LH W [b]	8.9 (0.59)	-	295 (6)	171 (1)	7.7

[a] Simplified model
[b] Two-fraction model

The results obtained demonstrate that the choice of the pretreatment has a direct impact not only on how much xylose we can produce but also on the values of the design variables. From the table, we can conclude that H C l leads to best per- formance for the objective used. When cost considerations are included, of course, this conclusion could change because, for instance, the residence time is significantly larger than for the other acids and, hence, the size of the pretreatment unit may be larger as well.

The behaviour of the design variables is presented in Figure 4 for acids and for liquid hot water cases. The graphs use a parallel co-ordinate system representation to show the values, normalised based on their upper and lower bounds, of the design variables and the objective function. Each solution obtained by Jacaranda is represented by a poly-line connecting each variable to an objective function value. The initial point for the search, the same in every case, is shown graphically using a dashed line.

The graphs show that, in all cases, the water to solid ratio design variable appears to have no impact. For the pretreatment with acids a lower value of temperature is desirable, opposite than for the pretreatment with only water

where we need high temperatures. The best concentration of the acid used varies from acid to acid: for H_2SO_4, a lower acid concentration is beneficial. For the residence time, for HCl a low to medium value is needed; for HNO_3 most of the domain allowed is possible; for H_2SO_4 only small residence times are suitable; and for liquid hot water a high residence time are needed. These results indicate that the type of acid does affect the design and the performance of the pre-treatment stages, in contrast to the findings of previous studies [20].

Conclusions

Liquid fuels produced from biomass sources may be a potentially valuable and necessary source of energy in the future. The use of lignocellulosic materials, to avoid using crops destined for food production, is appealing but poses challenges. Such lignocellulosics are difficult to process directly for the production of ethanol, for instance a pretreatment steps are required.

This study presents kinetics models of dilute-acid hydrolysis pretreatment based on first-order reactions and modified to take into account the two fractions of the polymer (hemicellulose). Additionally we present a statistical analysis, based on experimental data extracted from literature, to obtain the kinetic parameters through non-linear regression analysis. Finally we implement mathematical models, suitable for optimisation within a design framework, which allow us to compare the effect of different pretreatments.

The optimal design of the pre-treatment stage, using mathematical models of an acid and water based pretreatments, has demonstrated that the choice of the pretreatment has an impact on the effectiveness of this step. The results also provide some insight into the trade-offs between the different design variables. Developing kinetic models provide us with mathematical equations which describe the time-temperature courses of the different compounds, and those equations wi

(a) HCl

(b) HNO_3

(c) H_2SO_4

(d) LHW Simplified model

(e) LH W Two-fraction model
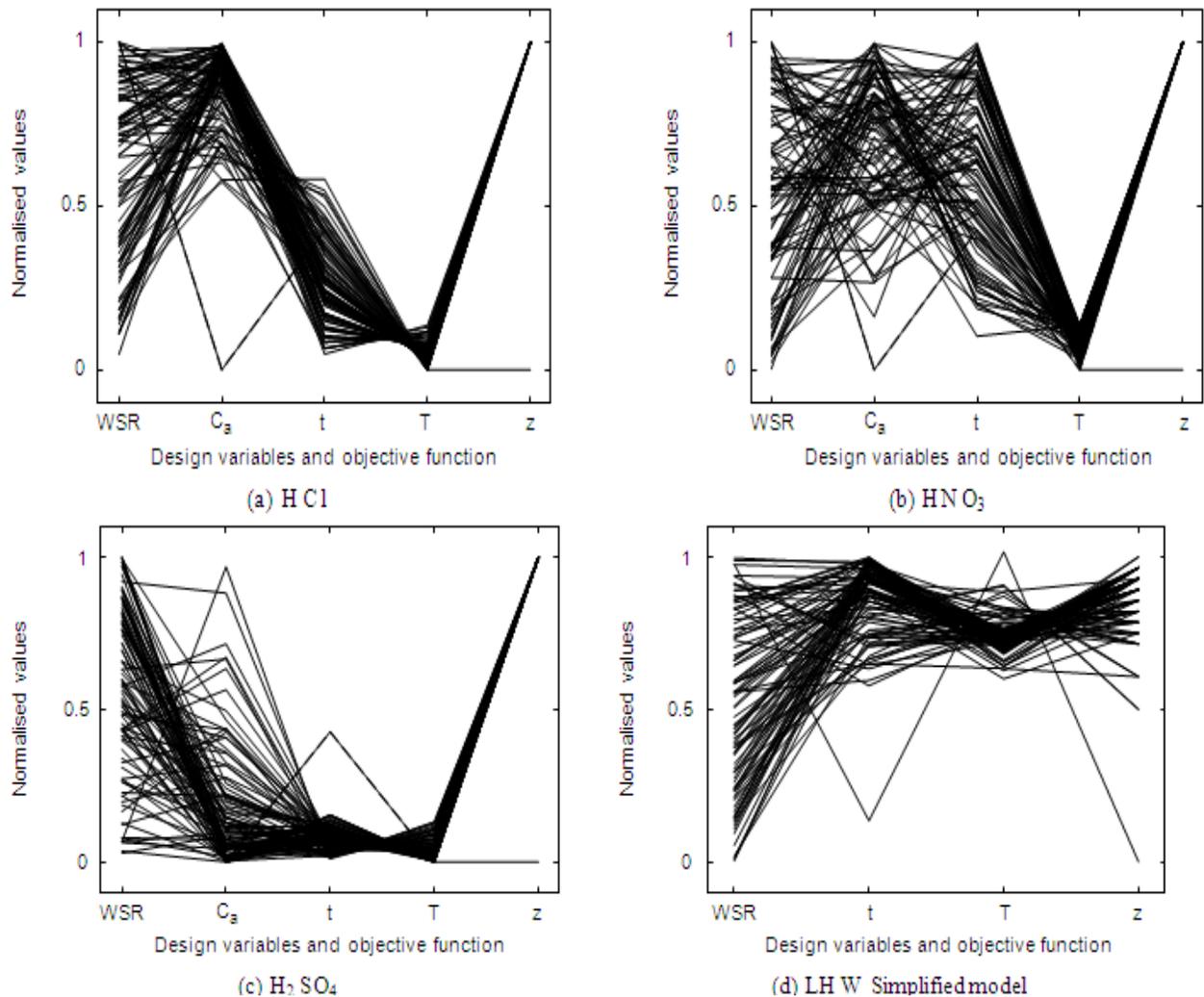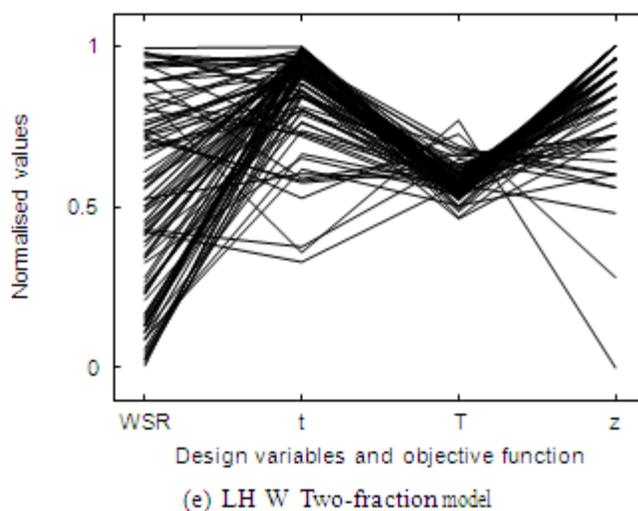
Figure 4: A parallel co-ordinate presentation of the solutions obtained from 100 runs of Jacaranda for each acid and the models for liquid hot water considered. The dashed line represents the same initial guess for the optimisation. form the basis for subsequent technoeconomic optimisation studies [4].

Although this initial investigation has used a simple objective function, the longer term aim is to incorporate multiple objective functions, such as detailed economics and various measures of the sustainability of the process; as well as incorporate the models developed into a larger framework that will consider the impact of pretreatment on the subsequent steps in the production of ethanol. This will be achieved by combining this effort with the models developed in a previous work [22].

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