Modelling of the acid hydrolysis of potato (*Solanum tuberosum*) for fermentative purposes

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ABSTRACT

The hydrolysis of non-commercial potatoes to obtain glucose solutions has a double consequence, the elimination of a waste and the generation of a value-added product. Potato hydrolysates can be used to prepare growth media for fermentative processes. This work deals with the modelling of the acid hydrolysis of potato using sulphuric acid. The effect of temperature, time, acid concentration and liquid/solid ratio were evaluated. Considering the important effect and interactions of the variable involved, a statistical Box-Behnken design was conducted including the cited variables as operational variables and concentrations of glucose, fructose, arabinose, acetic acid, furfural and 5-(hydroxymethyl)-2-furaldehyde (HMF) released as dependent variables. Significant models were obtained. The maximum glucose concentration predicted was 85 kg m^{-3}. The conditions selected as optimal were: Temperature, 120ºC; time, 60 min;

acid concentration, 2.4 kg m^{-3} and liquid/solid ratio, 9.8 g g^{-1}. The acid hydrolysis of dried potatoes gave solutions with 58 kg m^{-3} of glucose and only 0.47 kg m^{-3} of HMF. These solutions are adequate for further fermentation process.

Keywords potato; acid hydrolysis; furfural; 5-(hydroxymethyl)-2-furaldehyde; Box-Behnken

1. Introduction

The main compound of potato (*Solanum tuberosum*) is starch. It is composed of two polysaccharides: the linear molecule amylose, which consists of polymers of glucose predominantly connected by α-1,4-linkages, and amylopectin, the major macromolecular component of starch and responsible for the structure of the starch granules [1].

Starch is a polysaccharide compound found in many plants. According to its origin, starch can be classified into cereal, legumes, palm and tuber or root starches. Potato is the main starch derived from tubers.

With increasing worldwide demand for potato, the discharge of potato pulp has increased each year and has become an environmental pollution problem that cannot be neglected [2].

As a consequence of the accumulation of high amounts of potato wastes on the environment, several studies have been carried out in order to demonstrate the harmful effect on animals caused by accumulation of the glucoalcaloids α-solanine, and α-chaconine which are naturally produced by potatoes [3]. Therefore it is needed to find an efficient way to dispose this waste or processing to convert it in an added-value product. The use of potato starch as poultry feed supplemented with protein of bacteria and yeast by solid state fermentation was proposed [4].

Regarding with biotechnology, potato is a good substrate for microorganisms, due to its starch, cellulose, hemicelluloses and fermentable sugars content [5-7].

In cases where microorganisms are not able to produce extracellular hydrolyzing starch enzymes, a hydrolysis step is required. Industrial production of starch hydrolysis products like glucose syrup is typically based on acid or enzymatic hydrolysis. Both hydrolyses can lead to the production of sugars solutions, which can be fermented to produce ethanol or other biotechnological products [8-10]. However, acid hydrolysis

has some advantages. The enzymatic hydrolysis needs a pre-treatment of gelatinization where starch is heated in water and after cooling the gelatinized starch forms a textural gel network that allows enzymes to penetrate easily into starch structures contributing to a more efficient reaction [1, 11]. A first advantage of acid hydrolysis is that the step of gelatinization is not needed.

Potato starch is an amylolytic resistant starch, as it undergoes an incomplete enzyme hydrolysis due to the fact that potato starch contains relatively high amounts of amylopectin and demonstrates a relatively high degree of crystallization [12]. A second advantage of the acid hydrolysis relies on the fact that low molecular weight substances pass through some alternating amorphous and crystalline regions with different densities. The internal defects at submolecular level affect the supramolecular granule organization promoting the penetration of protons within the granule and decreasing the resistance of the starch to the acid hydrolytic [13].

Additionally, the acid hydrolysis of starch has some other advantages over the enzymatic processes, such as the short reaction times and the simpler pre-treatment required. Therefore it is a good alternative for hydrolyzing potato starch for biotechnological aims.

The main drawback of acid hydrolysis is the generation of degradation products, such as furfural, 5-(hydroxymethyl)-2-furaldehyde (HMF) and acetic acid that remain in the glucose solutions. These by-products are microbial growth inhibitors and must be controlled under lethal concentrations to allow posterior fermentations [14]. Other drawbacks are the necessity of neutralize the acidic medium, dispose the calcium sulphate waste, the energy requirements, needs supplementary equipments for neutralization and filtration and part of the equipments must be acid-resistant.

In order to optimize the production of glucose from starch, mathematical models for the enzymatic hydrolysis of potato starch have been carried out using α-amylase and glucoamylase [15]. Other studies have been carried out using crude extract enzymes from *Trichoderma reesei* Rut C30 [16].

Studies on the acid hydrolysis of potato tuber mash using mineral acids have been carried out in order to have a process for the hydrolysis of potato starch aiming to use the glucose solutions as media for the biotechnological production of ethanol or other fermentation products [17]. However, no strategies to modelling and optimize acid hydrolysates of potato starch have been found in literature.

This work deals with the modelling and optimization of the operational conditions for the acid hydrolysis of potato starch, leading to the generation of fermentable glucose solutions with low concentration of microbial growth inhibitors.

2. Materials and methods

2.1. Raw material and powder characterization

Tuber samples of potato (*Solanum tuberosum*) were kindly supplied by a local company (Pitita´s farm, Dozón, Spain). They were harvest at the geo-coordinates 42.6039°N 8.0235°W. In order to avoid spoiling during storage, they were washed, sliced and dried. Then, the potato chips were milled to a particle size around 0.5 mm. The moisture extracted from potatoes was 801.0 g kg^{-1} of the fresh weight. The residual moisture content of dried potatoes was 81.5 g kg^{-1} of the final product.

The composition of the dried substrate was determined through a quantitative acid hydrolysis under standard conditions. Briefly, aliquots from the homogenized lot were taken and submitted to a treatment with a sulphuric acid mass fraction of 72 % at 30 °C during 1h and then, after dilution to a sulphuric acid mass fraction of 3 %, the reaction mixture was submitted to 121°C for 1 h [18].

2.2. Acid hydrolysis and experimental design

The sulphuric acid hydrolysis was performed in an autoclave capable to control the temperature (±1 °C). In order to allow all the mater to be wetted, and to obtain a good supernatant recovery, the liquid/solid ratio was selected in a range (Table 1) where the potato powder was well submerged in the reaction mixture. The experiments were performed in 250 mL bottles. The set of experiments followed a Box-Benkhen experimental design using four factors (independent variables) and three levels (see below the statistical section). The operational conditions were set as shown in Table 1.

Table 1 here

2.3. Analytical methods

Glucose, fructose, arabinose, acetic acid, furfural and HMF were determined in hydrolyzates by HPLC using a Rezex RHM (Phenomenex, Torrance, California, USA) column with isocratic elution (flow rate of 0.400 mL min^{-1} and mobile phase of 25 mol m^{-3} H_2SO_4), a column oven set at 45°C and a refractive index detector (LC 2000 plus, Jasco, Tokio, Japan).

2.4. Modelling and statistical analysis

The results were analysed by response surface methodology using Design Expert® 7.1 software (Stat-Ease, Inc., Mineapolis, MN, USA). Analysis of variance (ANOVA) test was used to statistically validate the model.

Box-Benkhen design was applied. This is a kind of response surface design formed by combining two-level factorial designs with incomplete block designs creating designs with desirable statistical properties but with only a fraction of the experiments required for a three-level factorial. It is specially made to require only 3 levels, coded as -1, 0, and +1 [19]. The variables studied were temperature in ºC (T), time of reaction in min (t), concentration of sulphuric acid as mass fraction in % (C) and liquid/solid ratio ($R_{L/S}$). To the computation requirements of the Box-Behnken design, the coded or normalized dimensionless variables were expressed as functions of real variables in the following form:

$$x_1 = \frac{T - 115}{15} \quad (1)$$

$$x_2 = \frac{t - 35}{25} \quad (2)$$

$$x_3 = \frac{C - 2}{1} \quad (3)$$

$$x_4 = \frac{R_{L/S} - 10}{2} \quad (4)$$

The interrelationship between operational and dependent variables can be established through an equation including linear, interaction and second-order terms. The mathematical model used as first approach was a polynomial model of quadratic order as shown in equation (5).

$$R = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + b_1{x_1}^2 + b_2{x_2}^2 + b_3{x_3}^2 + b_4{x_4}^2 + c_{12}x_1x_2 + c_{13}x_1x_3 + c_{14}x_1x_4 + c_{23}x_2x_3 + c_{24}x_2x_4 + c_{34}x_3x_4 \quad (5)$$

where R is the response (glucose, fructose, arabinose, furfural or HMF concentration, kg m^{-3}); x_i, are normalized dimensionless variables; a_i, b_i and c_{ij} are regression coefficients calculated from the experimental data. Partial models of the quadratic model were also fitted and analyzed by ANOVA.

3. Results

The composition on a dry matter base determined by quantitative acid hydrolysis in mass fraction was: starch expressed as glucan, 64.91 % ± 3.34 %; xylan, 2.81 % ± 0.24 %; arabinan, 0.47 % ± 0.36 %. As expected, Klasson lignin content was very low as (0.82 % ± 0.14 %). The low concentration of lignin confirms that all the glucan detected can proceed from the starch and not from cellulose which is linked with lignin and hemicelluloses. These results compare well with the analysis of previous lots of potatoes analyzed in our laboratory [15].

3.1. Overall process

The overall process studied in this work is shown in Figure 1 where 200 kg of potatoes were washed and sliced. Then they were dried at 60°C where 156.5 kg of moisture was removed, yielding a dry mass of 217.5 g kg^{-1} of fresh potato. The residual moisture in mass fraction was 8.15 %. Then, it was mixed with a sulphuric acid solution to start the hydrolysis reaction at the conditions assayed in this study (several temperature, time, acid concentration, liquid/solid ratio showed in Table 2). On the basis of the liquid/solid ratio used, the total reaction mass was in the range 320-480 kg.

At the end of the reaction, the hydrolysates were filtered and the liquid yielded 93.26 %, giving around 298.00-447.68 kg. The filtered solution was mainly composed by glucose that can be used as substrate for the growth of microorganism or other industrial purposes after neutralization. Obviously, the concentration of glucose depends on the hydrolysis conditions.

Figure 1 here

Table 2 here

Table 2 shows the operational conditions assayed in terms of dimensional and dimensionless operational variables. Table 3 shows the experimental results determined for glucose, fructose, arabinose, acetic acid, furfural and HMF concentrations in the hydrolysates obtained. The obtained solutions ranged 0.93-73.08 kg m^{-3} for glucose. With glucose the solutions contained also fructose and arabinose in low concentrations. Fructose ranged from 1.22 to 3.08 kg m^{-3} and arabinose ranged from 0.00 to 0.46 kg m^{-3}. Microbial growth inhibitors such as acetic acid, furfural and HMF were also detected.

The high glucose concentrations obtained in the hydrolysates and the production of microbial growth inhibitors during the process make interesting to model the hydrolysis in order to predict the best conditions for the acid hydrolysis with maximum glucose and minimal microbial growth inhibitors.

Table 3 here

3.2. Glucose modelling for the acid hydrolysis of dried potato pulp

The mathematical model was selected by analyzing the sequential model sum of squares for the partial and complete models. In this case, data fitted well to a two-factor-interaction (2FI) model since this is the highest order polynomial where the additional terms are significant (p-value < 0.05). The equation of this model is shown in equation (6).

$$G = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + c_{12}x_1x_2 + c_{13}x_1x_3 + c_{14}x_1x_4 + c_{23}x_2x_3 + c_{24}x_2x_4 + c_{34}x_3x_4 \quad (6)$$

where G is glucose concentration, kg m^{-3}; x_i, are normalized dimensionless variables; a_i and c_{ij} are regression coefficients calculated from the experimental data.

Table 4 shows the ANOVA for the 2FI model of equation 6. In an ANOVA test, "Model" and "Terms of the model" are significant if the value of "p-value probability > F" are less than 0.05". According with the criterion for ANOVA test, the F-value of 49.59 and the value of "p-value probability > F" less than 0.0001 for 2FI model implies that the model is significant.

The terms x_1, x_2, x_3, $x_1 \cdot x_2$, $x_1 \cdot x_3$, $x_2 \cdot x_3$ were significant model terms since their p-values were less than 0.05. Model reduction may improve the model if there are many not significant model terms (p-value Prob > F more than 0.05). In this case, x_4, $x_1 \cdot x_4$, $x_2 \cdot x_4$ and $x_3 \cdot x_4$ were not significant.

The value of r^2 for the regression was 0.9649. This statistical parameter is the relative predictive power of a model. However, this parameter does not give useful information about if this model can be used for all the population and not only for the samples.

Table 4 here

It is better to compare the values of adjusted r^2 and predicted r^2. Parameter adjusted r^2 is a measure of the amount of variation adjusted for the number of terms in the model. The adjusted r^2 decreases as the number of terms in the model increases if those additional terms do not add value to the model. On the other hand, the predicted r^2 is a measure of the amount of variation in new data explained by the model. The adjusted r^2 obtained (0.9455) is in reasonable agreement with the predicted r^2 obtained (0.8847) since not more than 0.2 units were between them. Another statistical measurement is the "Adequate precision", which relates the signal/noise. A ratio higher than 4 is desirable. The "Adequate precision" obtained (24.94) indicated an adequate signal. Considering the above analysis, a model reduction was carried out to improve the model fitting. Therefore, the non-significant terms were deleted from the equation (6) to improve the fitting.

The reduced mathematical model for the glucose concentration (C_G) as function of the actual or dimensional variables used for the new fitting was:

$$C_G = a_0 + a_1T + a_2t + a_3C + b_{12}Tt + b_{13}TC + b_{23}tc \qquad (7)$$

Table 5 shows the ANOVA for the reduced 2FI model. The model F-value of 93.70 implied the model was significant. In this case, all the terms were significant in the model (equation 7).

The value of r^2 was 0.9623, slightly lower than the value of r^2 for the model of the equation (6). However, the previous value of predicted r^2 (0.8847) was increased up to 0.9228, which is in reasonably agreement with the new value of adjusted r^2 of 0.9521. Moreover other improvement was the increase of the value of adequate precision (33.33) since it was higher in comparison with the value of 24.94 for the complete model. The mathematical model obtained for dimensional variables is showed in equation (8).

$$C_G = 163.85 - 1.45T - 3.52t - 107.75C + 0.03Tt + 0.97TC + 0.49tC \qquad (8)$$

Note that the effect of the liquid/solid ratio (8-12 g g^{-1}) was not significant in the range of the study.

Table 5 here

Figure 2 shows the good agreement between experimental values and predicted values of glucose concentration. Groups of points above or below the line could indicate areas of over or under prediction. It can be observed that the points were randomly scattered along the 45 degree line. To evaluate the predictive strength of the model also a residual test was performed. A graphical way to see how much the regression changes if a sample is deleted is the Cook's Distance measurement [20]. Relatively large values (2-3 times larger than the other points) are associated with cases with high leverage and large studentized residuals. Figure 3 shows the "Cook's Distances for the reduced model (equations 8). It allows to observe that it is not necessary to delete observed values to improve the fitting, since no case are over the discontinuous line (2-3 time

larger the mean). It confirms that the mathematical model predicts the glucose concentrations with a good precision.

Figure 2 here

Figure 3 here

Figure 4 shows the glucose concentration (C_G) predicted by the reduced 2FI model (equation 8) as function of the acid concentration and temperature. Values of time and liquid/solid ratio were fixed at their central levels used in the experiments design since time was the variable that showed a lower influence on the glucose concentration obtained and the liquid/solid ratio showed no influence. The highest response was found at the combination of parameters corresponding to the highest levels tested. This figure shows that the conditions to obtain the maximum glucose concentration are an acid mass fraction of 3% at a temperature of 130 °C. The maximum glucose concentration predicted was 85 kg m^{-3}. This value compare very well with the maximum obtained in the enzymatic hydrolysis of potato where a maximum of 38.9 kg m^{-3} was predicted [15]. This can be due to that sulphuric acid hydrolyzed the resistant starch and the enzymes used in the enzymatic hydrolysis did not hydrolyze it.

Figure 4 here

The fraction of resistant starch can be estimated knowing the mass fraction of starch expressed as glucan. The potential concentration of glucose can be calculated assuming a total conversion of starch to glucose without degradation. For comparative purposes and calculations, the maximum concentration for glucose was calculated using the equation (9) [21].

$$G_p = F \frac{CGn_0}{WSR} \rho \qquad (9)$$

where G_P is the maximum (potential) concentration of glucose (in kg m^{-3}), F is the stoichiometric factor due to the hydration of molecules during the hydrolysis ($F_{hexoses}$ is 180/162), CGn_0 is the mass fraction of starch (glucan as g g^{-1} of raw material, on dry

basis), WSR is the water/solid ratio used (8-12 g/g in this study) and ρ is the density of hydrolysates (1025 kg m^{-3}).

Applying Eq. (9), it was calculated G_p can reach up to 92.41 kg m^{-3}. The maximum glucose concentration obtained in the acid hydrolysis was 92% of G_p meanwhile the maximum glucose concentration obtained in the enzymatic hydrolysis [15] was 42% of G_p. This implies a 58% of resistant starch, considering resistant starch as the fraction that it is not hydrolyzed by enzymes. This is a mass fraction of resistant starch of 0.375 g g^{-1} of potato on dry basis. This value is in reasonable agreement with others found in the literature (in the range 0.186-0.674 g g^{-1}) [22].

3.3. Fructose Modelling for the acid hydrolysis of dried potato pulp

For modelling the fructose concentration, the same statistical analysis than that of glucose concentration was followed. The mathematical model selected was also a 2FI model. The equation of this model is shown in equation (10).

$$F = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + c_{12}x_1x_2 + c_{13}x_1x_3 + c_{14}x_1x_4 + c_{23}x_2x_3 + c_{24}x_2x_4 + c_{34}x_3x_4 \quad (10)$$

where F is fructose concentration, kg m^{-3}; x_i, are the normalized dimensionless variables; a_i and c_{ij} are the regression coefficients calculated from the experimental data.

Table 6 shows the ANOVA for the 2FI model. The F-value of 17.71 and the value of "p-value probability > F" less than 0.0001 for 2FI model implies that the model was significant. In this case, x_4 was significant but its interactions with the other variables $x_1 \cdot x_4$, $x_2 \cdot x_4$ and $x_3 \cdot x_4$ were not significant.

The value of r^2 for the regression was 0.9077. The adjusted r^2 obtained (0.8565) is in reasonable agreement with the predicted r^2 obtained (0.7148). The Adequate precision was 14.76. Considering the above analysis, a model reduction was carried out to improve the modelling.

Table 6 here

The non-significant terms were deleted from equation (9) to improve the fitting.

The reduced mathematical model for the fructose concentration (C_F) as function of the actual or dimensional variables used for the new fitting was:

$$C_F = a_0 + a_1T + a_2t + a_3C + a_4R_{L/S} + b_{12}Tt + b_{13}TC + b_{23}tC \quad (11)$$

Table 7 shows the ANOVA for the reduced 2FI model. The model F-value of 27.15 implied the model was significant. The value of r^2 and adjusted r^2 were similar than those of the whole model. However, the previous value of Predicted r^2 (0.7148) was increased to a value of 0.7980 and the value of Adequate precision was increased to 18.70. The mathematical model obtained for dimensional variables is showed in equation (12).

$$C_F = 8.34 - 0.05T - 0.09t - 3.47C - 0.11R_{LS} + 0.00Tt + 0.03TC + 0.01tC \quad (12)$$

Table 7 here

Figure 5 shows the fructose concentration (C_F) predicted by the reduced 2FI model (equation 11) as function of the acid concentration and temperature. Values of time and liquid/solid ratio were fixed at their central levels used in the experiments design. The highest response for fructose was reached at a border of the space of study. This figure showed that the conditions to obtain the maximum fructose concentration were 3% acid concentration at 130 °C. The maximum fructose concentration predicted was 3.4 kg m^{-3}.

Figure 5 here

3.4. Arabinose Modelling for the acid hydrolysis of dried potato pulp

The mathematical model selected was a linear model. The equation of this model is shown in equation (13).

$$A = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 \quad (13)$$

where A is arabinose concentration, kg m^{-3}; x_i, are normalized dimensionless variables; a_i are regression coefficients calculated from the experimental data.

Table 8 shows the ANOVA for the linear model. The F-value of 16.18 and the value of "p-value probability > F" less than 0.0001 implies that the model was significant. However, the value of r^2 obtained (0.7295) was lower than that obtained for glucose and fructose. The adjusted r^2 obtained (0.6844) is in reasonable agreement with the predicted r^2 obtained (0.4959). The adequate precision was 13.82. Considering these statistical parameters, the model can be used to predict but the results could be worse than those of glucose and fructose models. These can be due to the narrow range obtained for this compound (0.00-0.52 kg m^{-3}).

The mathematical model obtained for dimensional variables is showed in equation (14).

$$C_A = -0.674 + 0.007\mathrm{T} + 0.002\mathrm{t} + 0.101\mathrm{C} - 0.018\mathrm{R}_{\mathrm{LS}} \qquad (14)$$

The conditions to obtain the maximum arabinose concentration were an acid mass fraction of 3% at 130 °C. The maximum arabinose concentration predicted for this case was 0.50 kg m^{-3}.

Table 8 here

3.5. Modelling of growth microbial inhibitors in the acid hydrolysis of dried potato pulp

In the acid hydrolysis of potato, monosaccharides produced during the hydrolysis undergo further reactions towards degradation products like acetic acid, furfural and HMF.

In the case of acetic acid, a quadratic model was fitted. The statistical parameters showed a bad prediction of the model. The value of r^2 was 0.7233, adjusted r^2 was 0.4466 and predicted r^2 was -0.3245. Although the adequate precision was 7.33 (higher than 4), the negative predicted r^2 implies that the overall mean is a better predictor than the current model.

This can be explained due to there were no statistical differences between the assays for the values of acetic acid concentration obtained in the experiments. These

values were the range 0.00-0.44 kg m^{-3} and can be considered negligible. For example, in the hydrolysis of sorghum straw up to 1.20 kg m^{-3} was obtained [21] and in the acid hydrolysis of wheat straw up to 2.57 kg m^{-3} was obtained [14].

No statistical differences between furfural values (0.00-0.03 kg m^{-3}) were obtained and this did not allowed to obtain a good model. These low values agree with the fact that furfural is a decomposition product of pentoses, being these monosaccharides in low concentration in the potato.

HMF is a decomposition product from hexoses. Glucose was generated in high concentrations in the hydrolysis of starch from potato. It could be expected a potential high concentration of HMF. However, for the conditions of the hydrolysis studied, the concentrations were low, ranging from 0.01 to 1.03 kg m^{-3}. The modelling of HMF was possible. In this case, data fitted to a quadratic model. The statistical evaluation for the experimental data to the model was done by an ANOVA. The terms x_4, $x_1 \cdot x_4$, $x_2 \cdot x_4$, $x_3 \cdot x_4$ and x_2^2, x_3^2, x_4^2 were not significant. The non-significant terms were deleted from the model to improve the fitting. The reduced mathematical model for the HMF concentration (C_{HMF}) as function of the actual or dimensional variables used for the new fitting was:

$$C_{HMF} = a_0 + a_1 T + a_2 t + a_3 C + b_{12} Tt + b_{13} TC + b_{23} tC + b_{22} T^2 \qquad (15)$$

Table 9 shows the ANOVA for the reduced model. The model F-value of 53.10 implied the model was significant. The value of r^2 was 0.9465, adjusted r^2 was 0.9287 and predicted r^2 was 0.8349. The value of adequate precision was also good (26.27). The mathematical model obtained for dimensional variables is showed in equation (15).

$$C_{HFM} = 13.685 - 0.214T - 0.066t - 1.447C + 0.001Tt + 0.012TC + 0.003tC + 0.001T^2 \qquad (15)$$

Table 9 here

Figure 6 shows the HMF concentration (C_{MHF}) predicted by the reduced model (equation 15) as function of the acid concentration and temperature. Values of time and liquid solid/ratio were fixed at their central levels. The highest response was also reached at a border of the space of study. This figure showed that the conditions to

obtain the maximum HMF concentration were also acid mass fraction 3% at 130 °C. The maximum concentration predicted was 0.94 kg m^{-3}.

HMF is generated as a degradation product from glucose. Furfural is generated as a degradation product from pentose and acetic acid derives from the hydrolysis of the acetyl groups bound to the hemicellulosic monomers. The concentration of pentoses is very low in potato. The relationship between the low concentration of furfural and acetic acid obtained with the low content in pentoses is confirmed by the results.

Figure 6 here

3.6. Optimization of the process

An optimal condition was selected using the following constrains with an importance value from 1 to 5: The lower sulphuric acid concentration (importance 1), the maximum glucose concentration (importance 5) and the lower HMF concentration (importance 2). On the basis of these constrains the condition selected were: Temperature, 120ºC, time, 60 min; acid mass fraction, 2.4 % and liquid/solid ratio, 9.8 g g^{-1}. Using these conditions a solution with a glucose concentration of 66.1 kg m^{-3} and 0.56 kg m^{-3} of HMF was predicted.

A set of three confirmation experiments were performed to verify the optimum obtained. The results gave a mean of 58.75 ± 7.94 kg m^{-3} of glucose and only 0.47 kg m^{-3} of HMF.

These results compare very well with results using enzymatic hydrolysis, where only 38 kg m^{-3} of glucose were obtained in 60 min [15] or 32.62 kg m^{-3} of reducing sugar concentration was obtained in 180 min [23].

The hydrolysis of starchy materials compare also very well with the acid hydrolysis of lignocelullosic materials where glucose concentration obtained are usually in the range 11-12 kg m^{-3} [24-26]. This kind of hydrolysates contains also xylose in the range 17.4-18 kg m^{-3} [24-26]. Xylose is the main monosaccharide released in the acid hydrolysis of hemicelluses. However, xylose is not consumed by many microorganisms. The low concentration of sugars obtained in the acid hydrolysis of lignocellulosic material make necessary a step of concentration by evaporation to can use the

hydrolysates for fermentative purposes. This evaporation step is not needed in the acid hydrolysis of starchy materials. All these considerations make very interesting the acid hydrolysis of starchy materials.

4. Conclusions

Sulphuric acid was an adequate acid to hydrolysis dried potatoes. Mathematical models obtained for the predictions of the process showed that the main operational variables are temperature and acid concentration. The optimization gave as optimal conditions: Temperature, 120 ºC; time, 60 min; acid concentration, 2.4 kg m^{-3} and liquid/solid ratio, 9.8 g g^{-1}. The acid hydrolysis of dried potato was more efficient than enzymatic hydrolysis, allowing the generation of solutions containing 58.75 kg m^{-3} of glucose and only 0.47 kg m^{-3} of HMF.

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