

Response Surface Optimization Studies of the Acid-Catalysed Hydrolysis of Hazelnut Shells

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ABSTRACT

The utilization of hazelnut shells as a renewable and low cost lignocellulosic biomass for bioethanol production requires the optimization of hydrolysis step. A comprehensive, experimental and modeling study on the acid hydrolysis of hazelnut shells is reported at variable sulfuric acid concentrations (0.1-0.7 M) and temperatures (100-120 °C) where a solid to liquid ratio is 1/7. The influence of the acid concentration, the temperature and reaction time on reducing sugar as well as the degradation product furan levels were evaluated by performing a 3³ full factorial experimental design. The analysis of the optimum combinations of independent variables indicates that a high acid concentration and a moderate temperature may provide the optimum acid hydrolysis conditions for hazelnut shells.

Key words: Hazelnut shells, hemicellulose, acid hydrolysis, factorial experimental design

1. INTRODUCTION

In recent years demands for biofuels and efforts towards a more efficient utilization of renewable sources in biofuel production have increased. Bioethanol is the important biofuel for transportation with an annual world production increasing from 28.5 billion liters in 2004 to 87.2 billion liters in 2013 (Nair et al., 2015). In contrast to first generation bioethanol which is derived from starch or sucrose, cellulosic ethanol may be produced from agricultural residues or other lignocellulosic raw materials (Larsson et al., 1999). The lignocellulosic raw materials are the most abundant, renewable materials and generally considered to be sustainable (Orozco, 2013). For the conversion of lignocellulosic biomass to ethanol, polysaccharides (cellulose and hemicelluloses) must be broken down into their corresponding monosaccharides (D-glucose, D-xylose, L-arabinose, etc.) (Saleh et al., 2014). This may be achieved using either acid or enzyme hydrolysis. Hydrolysis process have an important effect on the design and efficiency of the bioconversion process and

the overall profitability (Ertaş et al., 2014). Lignocellulosic biomass is made up principally of lignin, hemicellulose and cellulose. Cellulose is a linear, crystalline homopolymer with a repeating unit of glucose strung together with beta-glycosidic linkages. The structure is rigid so harsh treatment is required to break it down (Gray et al., 2006). Hemicellulose consists of short, linear and highly branched chains of sugars. In contrast to cellulose, hemicellulose is a heteropolymer of D-xylose, D-glucose, D-mannose and L-arabinose (Saha et al., 2003). The composition of holocellulose (cellulose + hemicellulose) varies with the origin of the lignocellulosic material (Chandel et al., 2007). The hemicellulosic fraction of lignocellulosic material can also be reduced to monomeric sugars, xylose and glucose by the usage of acids under mild conditions and then, the resulting fermentable sugars are converted into ethanol by yeasts (Wyman, 1994). Naturally occurring yeasts such as *Pichia stipitis* is able to ferment both xylose, glucose and cellobiose to ethanol. The acid hydrolysis is a relatively cheap and fast method for the hydrolysis of lignocellulosic

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materials in comparison with enzymatic hydrolysis (Lenihan et al., 2010). Sulphuric and hydrochloric acids are the most commonly used catalysts for hydrolysis of lignocellulosic residues. However, some of the sugar degradation products unavoidably formed during hydrolysis such as furans (furfural and hydroxymethylfurfural), inhibit the metabolism of fermentative microorganisms and be detoxified if they are going to be used as fermentation media to remove inhibitors. negatively affect the efficiency of fermentation (Carvalho et al., 2004).

Previous research has indicated that the yield of sugar recovered and the formation of the sugar degradation products in hydrolysates depend on the process conditions of the acid hydrolysis such as temperature, acid concentration, time, substrate concentration and composition (Lenihan et al., 2009; Canettieri et al., 2007). That's why the optimization of hydrolysis condition is one of the most important stages in the preparation of an appropriate hydrolysate as substrate for further fermentation process.

The conventional technique for the optimization of a multivariable system usually defines one-factor at a time. This method is time consuming and requires a number of experiments to determine optimum levels, which are unreliable. Experimental design technique is a very useful tool for this purpose as it provides statistical models, which help in understanding the interactions among the parameters that have been optimized. Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions. Response surface methodology is an effective statistical procedure using a minimum set of experiments to determine the coefficients of a mathematical model and the optimum conditions (Bian et al., 2014, Yemis and Mazza, 2012).

The utility of various agricultural residues such as corn stover (Chen, 2015), pine sawdust (Stoffel et al., 2014), sugarcane bagasse (Vallejos et al., 2015), olive tree (Romero et al., 2010) for the production of organic fuels and chemicals has an enormous potential for commercial applications (Saha et al., 2015).

Turkey is an ideal country for hazelnut production. Hazelnut shells are solid by-products from the hazelnut and the amount of hazelnut shells is estimated to be about 3×10^5 tons per year in Turkey (Demirbaş, 2006). The average structured analysis of hazelnut shell is as follows: hemicelluloses 30.4%, celluloses 26.8%, lignin 42.9% and extractive matter 3.3% (Demirbaş, 2006). Although the conversion of hazelnut shells into useful chemicals such as acetic acid, methanol (Aşık et al., 1977) and ammonia (Corlett, 1975) has been reported, its main utilization still remains as a boiler fuel. Recently very few efforts have been made to utilize hazelnut shells as a renewable and low cost lignocellulosic biomass for ethanol production (Arslan and Eken-Saraçoğlu, 2010). Utilization of hazelnut shells for bioethanol production gives an added value

for this material and a solution for the removal of this abundant waste.

The objective of this work is to study the hydrolysis of hazelnut shells with sulfuric acid at different temperatures and acid concentrations. Response surface methodology with 3^3 full factorial experimental design was adapted to optimize sulfuric acid-catalyzed hydrolysis in respect to acid concentration, temperature and reaction time to obtain high sugar concentration coupled with a low furan concentration (acting as growth inhibitor) in the hydrolysate.

2. MATERIALS AND METHODS

2.1. Raw material

Hazelnut shells used as raw materials were obtained from a local plant in Düzce a province in Turkey. Hazelnut shells were milled into fine particles and screened into fractions between 1.4 and 0.63 mm for easy reaction with acid. To reduce the water content, hazelnut shells were dried in an oven at 105 °C for 16 hours and a 5.24% moisture content was measured.

2.2. Dilute sulfuric acid hydrolysis

Acid hydrolysis reactions were performed in cylindrical stainless-steel reactors under isothermal conditions. Each reactor was 45x105 mm in dimensions and each reactor inside was lined with PTFE. The reaction vessels were placed in an oven at desired temperatures. The temperature inside the reactor was controlled using a thermocouple probe and digital temperature indicator system. Zero time was taken when the temperature inside the reactor reached to the experimental temperature. Acid concentrations of 0.1, 0.4, and 0.7 M; and temperatures of 100, 110 and 120 °C were used in the experiments. The hydrolysis was conducted with the solid/liquid ratio of 1/7. Samples drawn from the reactor at several reaction times were analyzed to follow reducing sugars and total furan concentrations.

2.3 Analytical methods

According to the Standard TAPPI method (Tappi, 1978), the pentosan content in hazelnut shells was found on dry base to be 29.26% (w/w). Total reducing sugars was determined colorimetrically using dinitrosalicylic acid reagent (Miller, 1959). Total furans in hydrolysate samples were estimated by a spectrophotometric method based on the difference in absorbance at 284 nm and 320 nm using a Hach DR/4000 spectrophotometer (Martinez et al., 2000). All experiments and analyses were carried out in duplicate. The range of the duplicate values was within 10%.

3. FACTORIAL DESIGN

The factorial design is a useful tool to characterize a multivariable process and to find the optimal responses within specific ranges of pre-established factors (Paterakis et al., 2002). The influence of acid concentration (A), temperature (B), and time (C) on two responses, namely reducing sugar concentration and

furan (growth inhibitor) concentration, was investigated according to the 3³ full factorial design. The low, intermediate and high levels of each operating parameters are summarized in Table 1 and different operational conditions applied are shown in Table 2. This kind of design provides sufficient degrees of freedom to resolve the main effects well as any possible interactions between them. The regression analysis of the results led to equations that describe responses in terms of independent variables and the statistical evaluation of the results by analysis of variance

(ANOVA) were carried out using a commercially available statistical software package (DESIGN EXPERT v7.0.0, Minneapolis U.S.A). The quadratic model was selected for this analysis. Finally, the desirability was used with DESIGN EXPERT for the optimization process. During the optimization process, two responses were combined in order to ensure multicriteria, which maintain a maximum in reducing sugar concentration and a minimum in furan level simultaneously.

Table 1. Experimental range and levels of independent process variables

Natural variables	Coded variables X ₁ , X ₂ , X ₃		
	-1 (Low Level)	0 (Medium Level)	1 (High Level)
A = Acid concentration (M)	0.1	0.4	0.7
B = Temperature (°C)	100	110	120
C = Time (min)	0	60	120

Table 2. The results obtained for a 3³ full factorial experimental design for the hydrolysis of hazelnut shells with sulfuric acid

Run	Variables			Responses	
	Acid (M)	Temperature (°C)	Time (min)	Reducing Sugar (g/l)	Furan (g/l)
	X ₁ (A)	X ₂ (B)	X ₃ (C)		
1	-1(0.1)	-1(100)	-1(0)	0.10	0.01
2	0(0.4)	-1(100)	-1(0)	1.28	0.02
3	1(0.7)	-1(100)	-1(0)	2.41	0.02
4	-1(0.1)	0(110)	-1(0)	0.14	0.01
5	0(0.4)	0(110)	-1(0)	3.28	0.05
6	1(0.7)	0(110)	-1(0)	12.12	0.07
7	-1(0.1)	1(120)	-1(0)	0.67	0.01
8	0(0.4)	1(120)	-1(0)	6.17	0.18
9	1(0.7)	1(120)	-1(0)	28.5	0.33
10	-1(0.1)	-1(100)	0(60)	0.86	0.02
11	0(0.4)	-1(100)	0(60)	10.77	0.04
12	1(0.7)	-1(100)	0(60)	14.4	0.11
13	-1(0.1)	0(110)	0(60)	2.69	0.01
14	0(0.4)	0(110)	0(60)	15.75	0.14
15	1(0.7)	0(110)	0(60)	30.86	0.29
16	-1(0.1)	1(120)	0(60)	7.93	0.05
17	0(0.4)	1(120)	0(60)	19.74	0.23
18	1(0.7)	1(120)	0(60)	36	1.50
19	-1(0.1)	-1(100)	1(120)	2.3	0.03
20	0(0.4)	-1(100)	1(120)	16.1	0.10
21	1(0.7)	-1(100)	1(120)	23	0.24
22	-1(0.1)	0(110)	1(120)	7.1	0.05
23	0(0.4)	0(110)	1(120)	11.53	0.27
24	1(0.7)	0(110)	1(120)	28.6	0.70
25	-1(0.1)	1(120)	1(120)	13.5	0.11
26	0(0.4)	1(120)	1(120)	10.1	1.48
27	1(0.7)	1(120)	1(120)	31	2.80
28	0(0.4)	0(110)	0(60)	15.8	0.14
29	0(0.4)	0(110)	0(60)	16.2	0.13
30	0(0.4)	0(110)	0(60)	15.5	0.11
31	0(0.4)	0(110)	0(60)	16.5	0.12

4. RESULTS AND DISCUSSIONS

During acid hydrolysis, sugar degradation is inevitable. The degradation by-products (furans) have inhibiting effects on the fermentation process. These compounds damage yeasts and other microorganisms by slowing down their metabolisms. To avoid high furan concentrations in the sugar-to-ethanol formation, the final sugar and furan containing hydrolysate preparation must be optimized by means of operating conditions. In the present work, the difficulty associated with developing a kinetic model for furan concentration due to the complex nature of hazelnut shell hydrolysate medium did not enable the optimization of the hydrolysis condition by using only kinetic model equations for sugar formation. Therefore, the response surface statistical technique was used for this purpose. The results obtained for a 3³ full factorial experimental design for the hydrolysis of hazelnut shells with sulfuric acid are given in Table 2, where reducing sugar concentration varies between 30.9-0.14 g/l while furan levels generated from decomposition of sugars ranges between 2.8-0.01 g/l. A regression analysis was performed to develop correlations between the process variables and the two responses. The quadratic models were selected as suggested by software to describe the influence of independent variables on the selected responses. When RSM is applied, the experimental responses are usually fitted to quadratic functions by least-squares (Giordano et.al., 2013). The models expressed by Eqs. (1) and (2), where variables take their

coded values, represent the reducing sugar concentration and furan concentration, respectively, during hydrolysis as a function of acid concentration (X₁), temperature (X₂) and time (X₃).

$$\begin{aligned} \text{Reducing Sugar (g/l)} = & +14.83 + 9.53 * X_1 + 4.58 * X_2 + 4.92 * X_3 + 3.07 * X_1 * X_2 + 1.47 * X_1 * X_3 - 1.53 * X_2 * X_3 + 2.35 * X_1^2 + 0.21 * X_2^2 - 5.03 * X_3^2 \\ \text{Furan (g/l)} = & +0.11 + 0.32 * X_1 + 0.34 * X_2 + 0.28 * X_3 + 0.34 * X_1 * X_2 + 0.26 * X_1 * X_3 + 0.30 * X_2 * X_3 + 0.058 * X_1^2 - 0.55 * X_2^2 + 0.076 * X_3^2 \end{aligned} \quad (1)$$

(2)

The statistical evaluation of the results was carried out by an analysis of variance (Tables 3 and 4). It is evident from F-values and very low probability values (p) for both models that both regression equations (Eqs. 1 and 2) are statistically significant. The values of the coefficients of determination R², which is 0.887 for reducing sugar and 0.8766 for furan ensure a satisfactory adjustment of the models of experimental data. The actual and the predicted reducing sugar and furan concentrations are shown in Figs. 1 and 2, respectively. The effects of the variables on reducing sugar and furan concentrations are also shown in Tables 3 and 4 respectively.

Table 3. ANOVA analysis for reducing sugar concentration

Source	SS ^a	DF ^b	MS ^c	F-value	Prob>F p-value	Remarks
Model	2821.92	9	313.55	19.20	<0.0001	Significant
X ₁	1635.81	1	1635.81	100.16	<0.0001	Significant
X ₂	377	1	377.01	23.08	<0.0001	Significant
X ₃	435	1	435.62	26.67	<0.0001	Significant
X ₁ X ₂	11.32	1	113.22	6.93	0.0152	Significant
X ₁ X ₃	25.77	1	25.77	1.58	0.2222	
X ₂ X ₃	28.03	1	28.03	1.72	0.2037	
X ₁ ²	39.38	1	39.38	2.41	0.1347	
X ₂ ²	2.13	1	2.13	0.13	0.7215	
X ₃ ²	181.30	1	181.30	11.10	0.003	Significant
Residual	359.31	22	16.33			
Lack of fit	359.17	17	21.13	743.5	<0.0001	Significant
Pure error	0.14	5	0.028			
Total	3181.24	31				

SS^a: Sum of squares

DF^b: Degree of freedom

MS^c: Mean square

Table 4. ANOVA analysis for furan concentration

Source	SS ^a	DF ^b	MS ^c	F-value	Prob>F p-value	Remarks
Model	9.18	9	1.02	17.37	<0.0001	Significant
X ₁	1.84	1	1.84	31.26	<0.0001	Significant
X ₂	2.06	1	2.06	35.11	<0.0001	Significant
X ₃	1.42	1	1.42	24.18	<0.0001	Significant
X ₁ X ₂	1.43	1	1.43	24.30	<0.0001	Significant
X ₁ X ₃	0.84	1	0.84	14.33	0.0010	Significant
X ₂ X ₃	1.06	1	1.06	18.00	0.0003	Significant
X ₁ ²	0.024	1	0.024	0.42	0.529	
X ₂ ²	0.31	1	0.31	5.32	0.0309	Significant
X ₃ ²	0.041	1	0.041	0.70	0.4117	
Residual	1.29	22	0.059			
Lack of fit	1.29	17	0.076	4699.11	<0.0001	Significant
Pure error	8.083E-005	5	1.617E-005			
Total	10.47	31				

SS^a : Sum of squares

DF^b: Degree of freedom

MS^c: Mean square

Design-Expert® Software
Reducing Sugar (g/l)

Color points by value of
Reducing Sugar (g/l):

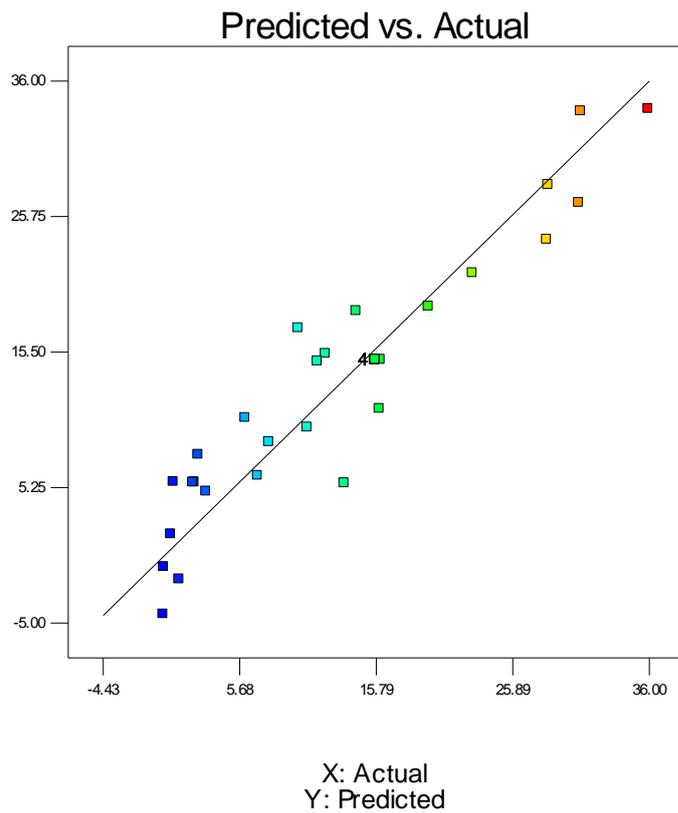


Figure 1. The actual and predicted plot of reducing sugar concentration.

Design-Expert® Software
Furan (g/l)

Color points by value of
Furan (g/l):

2.80
0.01

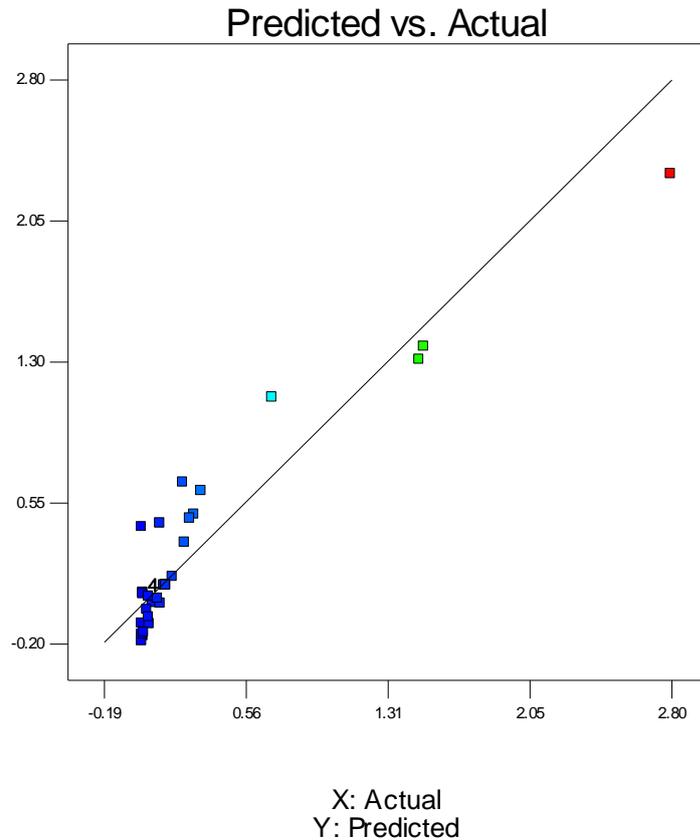


Figure 2. The actual and predicted plot of furan concentration.

Based on the ANOVA analysis, obtained acid concentration (X_1), temperature (X_2) and time (X_3) were found to have a very significant effect ($p < 0.0001$) on reducing sugar concentration (Table 3). The interaction effect between X_1 X_2 ($p = 0.0152$) and the quadratic effect of time X_3^2 ($p = 0.003$) imposed a moderate influence on reducing sugar. On the other side, Table 4 indicates that furan formation is strongly dependent on main effects such as acid concentration (X_1), temperature (X_2) and time (X_3) ($p < 0.0001$). Besides, the combined action of acid concentration and time X_1X_2 ($p < 0.0001$) is very significant. The combined

effects of acid concentration and time X_1X_3 ($p = 0.001$) as well as temperature and time X_2X_3 ($p = 0.0003$) significantly influenced furan production. The quadratic effect of temperature (X_2^2) was considered moderate. Bian et al., 2014 and Stoffel et al., 2014 have found that temperature, acid concentration and time produced significant effects on the acid hydrolysis process. The fitted response surfaces for the reducing sugar concentration and furan level were generated by DESIGN-EXPERT program and given in Figs. 3 and 4, respectively.

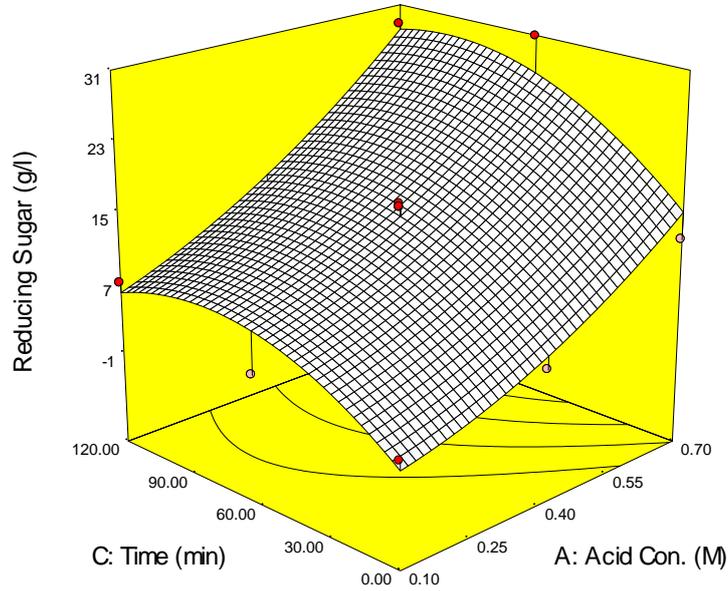
Design-Expert® Software

Reducing Sugar (g/l)



X1 = A: Acid Con. (M)
X2 = C: Time (min)

Actual Factor
B: Temperature (C) = 110.00



(a)

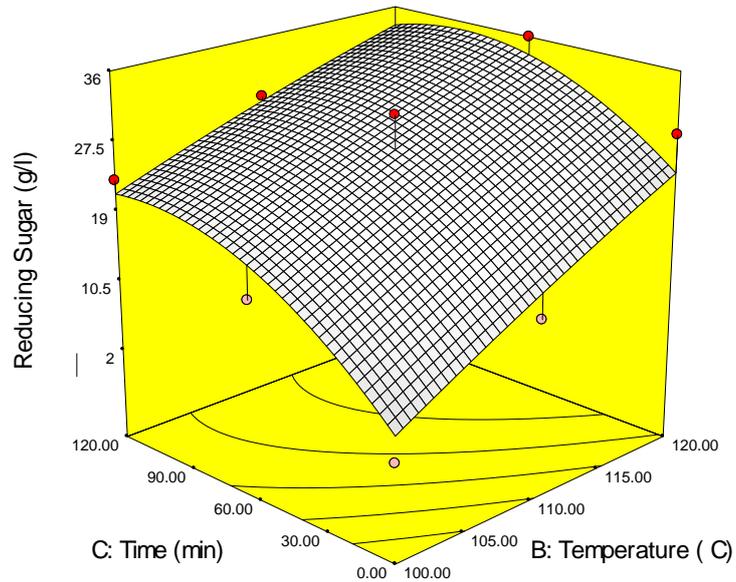
Design-Expert® Software

Reducing Sugar (g/l)



X1 = B: Temperature (C)
X2 = C: Time (min)

Actual Factor
A: Acid Con. (M) = 0.70



(b)

Figure 3. Response surfaces for reducing sugar formation (a) Effect of sulfuric acid concentration and time at 110 °C reaction temperature (b) Effect of temperature and time at 0.7 M sulfuric acid concentration.

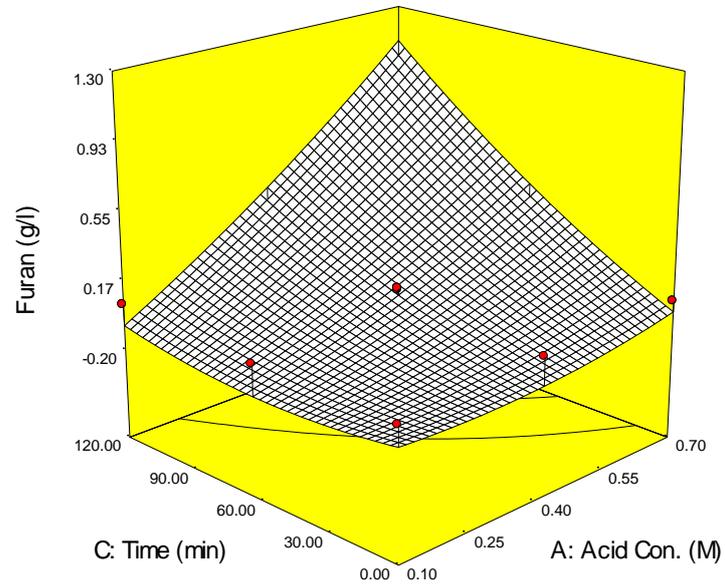
Design-Expert® Software

Furan (g/l)



X1 = A: Acid Con. (M)
X2 = C: Time (min)

Actual Factor
B: Temperature (C) = 110.00



(a)

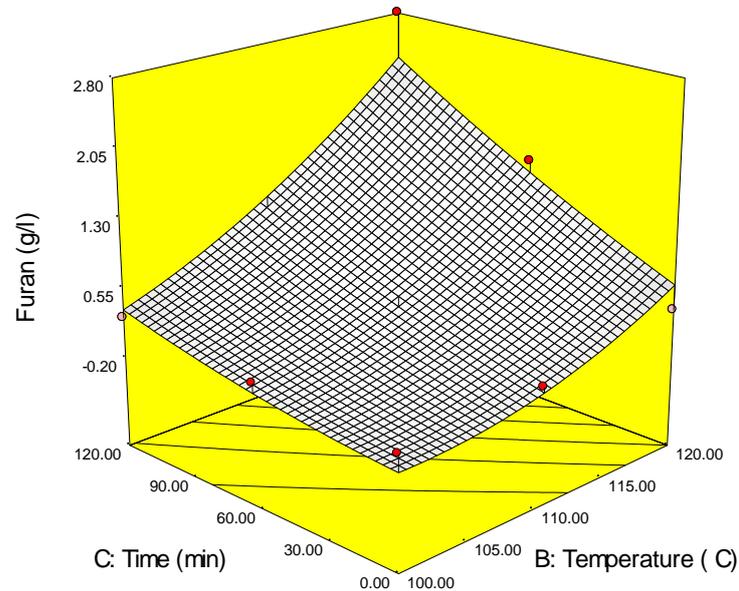
Design-Expert® Software

Furan (g/l)



X1 = B: Temperature (C)
X2 = C: Time (min)

Actual Factor
A: Acid Con. (M) = 0.70



(b)

Figure 4. Response surfaces for furan formation (a) Effect of acid concentration and time at 110 °C reaction temperature (b) Effect of temperature and time at 0.7 M sulfuric acid concentration.

It is evident, from observing Figs. 3 a and b as the acid concentration and temperature start rising, sugar formation begins to increase rapidly. It continues to increase with time well beyond the point where degradation reaction becomes significant. It is expected that total reducing sugar will diminish with time after reaching a maximum as a result of degradation reactions. The behaviors of Figs. 4a and b indicate that a displacement in the hydrolysis reaction in the direction of high process conditions (high acid concentration, high temperature and long reaction time) initiated sugar decomposition reactions and furan formation, which have a very negative effect on fermentation. The optimum conditions found in literature for dilute acid hydrolysis of lignocellulosic materials were very different. These were attributed to the type of equipment used and the composition of the biomass (Canettieri et al., 2007). Figs. 3a-4a and 3b-4b bring information about the intervals of optimum reaction conditions which is very important from a practical point of view regarding the preparation of hazelnut hydrolysate as a substrate for fermentation. It

appears that the process conditions which produce high sugar outputs are also associated with high inhibitor levels due to the nature of process. Based on the models developed Eqs. (1) and (2), a numerical optimization was carried out with the help of DESIGN-EXPERT. The constraints used are high and low levels of each factor where the objective used is to maximize the reducing sugar concentration and minimize the furan (inhibitor) level. The DESIGN-EXPERT provides optimal designs with using the combined overall desirability function. The alternative solutions are also shown in Table 5. The considered optimal conditions for the hydrolysis of hazelnut shells were sulfuric acid concentration of 0.7 M, temperature of 110 °C with a reaction time of 62 minutes. Under these conditions 26.55 g/l reducing sugar may be achieved with 0.47 g/l furan which corresponds to 68% sugar yield based on hemicellulose content in biomass. The optimal process conditions almost resemble Run 15 in Experimental Design, which provided 30.86 g/l reducing sugar (13% difference with model) along with 0.29 g/l furan (62% difference with model).

Table 5. Optimal solutions

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Constraints						
Acid Conc. (M)	is in range	0.1	0.7	1	1	5
Temperature(°C)	is in range	100	120	1	1	5
Time (min)	is in range	0	120	1	1	5
Reducing Sugar (g/l)	maximize	0.106	36	1	1	5
Furan (g/l)	minimize	0.013	2.8	1	1	5
Solutions						
Number	Acid Conc. (M)	Temperature (°C)	Time (min)	Reducing Sugar (g/l)	Furan (g/l)	Desirability
1	0.70	109.49	62.30	26.55	0.47	0.785(Selected)
2	0.70	109.59	61.94	26.60	0.47	0.785
3	0.70	109.72	61.36	26.64	0.48	0.785
4	0.70	109.58	61.20	26.52	0.47	0.785

5. CONCLUSION

To date, no reports are available in the literature regarding optimization of acid hydrolysis of hazelnut shells. In the present work, A 3³ full factorial experimental design for the hydrolysis of hazelnut shells with sulfuric acid was adopted in the designing of the experiments in order to optimize the hydrolysis process. The quadratic models were developed to describe the two responses: reducing sugar and furan concentrations. The optimization provided an optimal design by using the combined overall desirability function. Sulfuric concentration of 0.7 M, a temperature of 110 °C with a reaction time of 62 minutes were to be the considered optimal conditions for hydrolysis of hazelnut shells. Under these conditions 26.55 g/l reducing sugar may be achieved besides 0.47 g/l furan which corresponds to 68% sugar yield based on hemicellulose content in biomass.

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