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Using Response Surface Method for Optimizing Dilute Acid Hydrolysis of Walnut Green Skin

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ABSTRACT

The major pretreatment variables influences on fermentable sugar production from walnut green skin is considered by using response surface method based on dilute acid hydrolysis. According to previous results levels for retreatment were temperature (116, 124, 132 and 140^{o}C), process time (20,30,40 and 50 minute and sulfuric acid concentration (0, 1, 2, 3%). Glucose was analyzed by HPLC and modeled by a quadratic equation. Mathematical model was validated by independent experiment. Optimization based on mathematical model show that maximum Glucose concentration was 7.5% in 140^{o}C, 3% acid concentration, and 40 min process time.

KEYWORD: walnut green skin, fermentable sugar, hydrolysis, pretreatment, bioethanol

INTRODUCTION

Finding new biomass for producing ethanol is not stopped, because this material is the most plentiful resource in many countries for bioethanol production and it does not compete with animal feed and food industry. One of this biomass is green Walnut skin.

Walnut is one of the most important nuts that culture widely around the entire world. In the year 2007, total production of this nut was forecast at a record of 1700000 tons. China (503000 tons), USA (209000 tons), Turkey (184000 tons) and Iran (170000 tons) are its important producers. Walnut consists of 3 main parts, meat, woody skin and green skin.

Green skin consists of cellulose, hemicelluloses and lignin. Before fermentation, these materials need to be converted to simple sugars by saccharification. This process converts the hemicelluloses and cellulose fraction into their sugar components, pentose and hexose [1]. The reaction can be catalyzed by concentration acid. But it should be stopped in suitable process time. Because if decomposition continued, during this process other unexpected compounds such as Furfural from pentose and Acetic acid from acetyl groups in hemicellulose can be produced. These materials can delay or prevent a fermentation step that convert simple sugar to bioethanol.

Time, acid concentration and temperature are 3 variables that effect on sugars and inhibitor production. The effect of pretreatment on hydrolysate composition was modeled by response surface methodology by some authors for optimizing of acid pretreatment. Castru [2] used this model to optimize dilute acid pretreatment of rapeseed straw. Similar optimizing was used by Jeong [3] for extraction of hemicelluloses. Zhou [4] used similar investigate for efficient hydrolysis of steam exploded of corn Stover. Optimization of H_2SO_4- catalyzed hydrothermal pretreatment of rapeseed straw was other research that was done by Xuebin lu and his colleague [5]. This model can be used to find the optimal conditions [6].

For using a surface modeling a quadratic equation was used to evaluate the effect of these 3 variables. A large number of experimental designs adapted to various types' problems are available such as factorial designs [6], Centriod composite matrices [8] or doehlert shells [9,10]. Here experiments were designed based on L-16 matrix of Taqushi methods.

2. METHODS

2.1. Raw material

Walnut green skin (WGS) was provided by peeling of walnuts from Spidan village North Khorasan in Iran, in September of 2013. It was washed by distillated water, air dried, milled using vibratory disc mill (Retsch RS 100) to particle size smaller than 50 micrometers. The chemical composition of the WGS determined according to TAPPI T 257 om (1985) standard for preparation of the test specimens. Ash contents, lignin and extracted materials were determined according to TAPPI standards T 211 om (1988), T 222 om (1988), T 204 om (1988) standards, respectively. The hemicellulose and cellulose contents were determined according to WiseÕs chlorite and K.rschner-Hoffner nitric acid methods. The resulted composition of is shown in Table 1.

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Table 1. WGS's composition

Composition	%
Cellulose	21.4
Hemicellulose	13.24
Extractive M	18.25
Lignin	26.08
Ash	20.92

2.2. Experimental design

The influence of acid concentration, temperature and reaction time on fermentable sugars production by dilute acid hydrolysis was formulated by a quadratic equation:

$Y = A_0 + A_1.C + A_2.T + A_3.t + A_4.C^2 + A_5.T^2 + A_6.t^2 + A_7.C.T + A_8.C.t + A_9.T.t$ (1)

This equation determined influence of these factors and interactions among factors on products. This equation has 10 constant coefficients and at least 10 equations were needed to determine these coefficients by least square methods. Based on previous experience with acid hydrolysis to ensure a broad range of response, 4 levels for each factor were considered and walnut green skin was pretreated at 16 different operational conditions according to L-16 Taguchi matrix. Selected conditions were shown in Table 2. Fourteen experiments were used to determine A_n and other two experiments were used to verify the model validity. Every experiment was performed for three times and results was averaged.

Table 2. Experimental design, Experimental factor and code levels

Run	Acid concentrate. (code)	Temper-ature (code)	Time (code)	Acid concentrat. (%)	Tempera-ture (°C)	Time (min)	Glucose (%)
1	1	1	1	0	116	20	3.87
2	1	2	2	0	124	30	4.76
3	1	3	3	0	132	40	4.46
4	1	4	4	0	140	50	4.61
5	2	1	2	1	116	30	5.14
6	2	2	1	1	124	20	4.28
7	2	3	4	1	132	50	3.79
8	2	4	3	1	140	40	5.04
9	3	1	3	2	116	40	5.05
10	3	2	4	2	124	50	5.29
11	3	3	1	2	132	20	5.19
12	3	4	2	2	140	30	5.27
13	4	1	4	3	116	50	5.88
14	4	2	3	3	124	40	6.01
15	4	3	2	3	132	30	7.5
16	4	4	1	3	140	20	7.0
Sum	36	36	36	----	----	-----	

2.3. Dilute acid hydrolysis

Ten grams of Dried WGS in 490 cc water was treated with 0, 1, 2 and 3 wt% sulfuric acid in aluminum covered Pyrex bottles in Autoclave with temperature controller at 116, 124, 132 and 140 °C for 2, 3, 4 hour. Once the temperature of reaction mixture reached to designed point, pretreatment time was started. At the end of each run the bottle was removed from Autoclave and put in a cool water bath. Its PH reached around 7.0 by sodium hydroxide (NaOH) and then solids were separated by filter paper and Buchner funnel, solids washed with distilled water and final solution reached to 1000 ml. A 200 ml sample of solution was used to analyze by HPLC.

2.4. Analytical methods

An HPLC model JASCO with Bio-Rad column Aminex HPX-87P and RI detector were used to determine the composition of the glucose. Glucose was analyzed at 40°C.

3. RESULTS AND DISCUSSION

The composition of hydrolysates in terms of fermentable sugars is summarized in Table 1. Eq. 2 shows the model constant coefficients obtained from ANOVA table for glucose. Fig. 1 shows a good agreement between experimental values and predicted value obtained by model.

$y=12.3125+0.000576T^2-0.159936T+0.314375c^2-0.542216c+0.007798Tc-0.002069t^2+0.171847t-0.0000241447Tt-0.019602ct;$ (2)

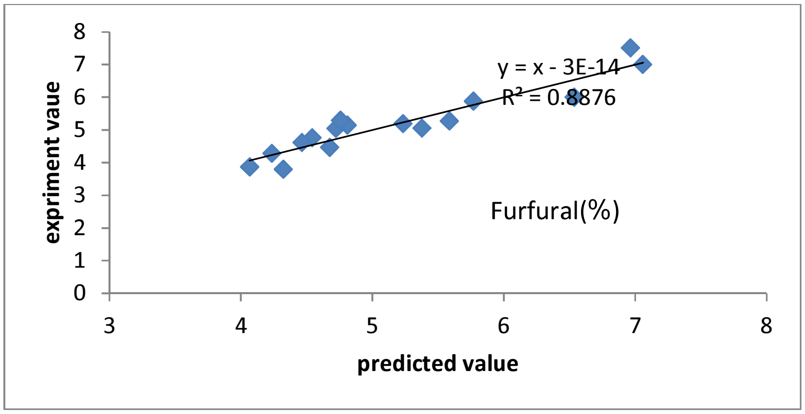

Figure 1. Predicted versus experimental values for liquid phase after pretreatment

3.4. Using the model to interpret the effect of hydrolysis conditions

The influence of acid sulfuric concentration (C) and temperature (T) in glucose yield is depicted in fig. 2. As can be seen in this figure the influence of acid concentration differs from the influence of temperature on glucose production. Fig. 2 shows that the maximum point is outside of the experimental region. While acid concentration was a determining factor for glucose production, glucose concentration increases with temperature very slightly in studied range. WGS remained almost untreated at low levels of both temperature and acid. Glucose concentration rise with acid concentration. Glucose concentration in 15^{th} run was the maximum value 7.5% and in first run was the minimum (3.87%).

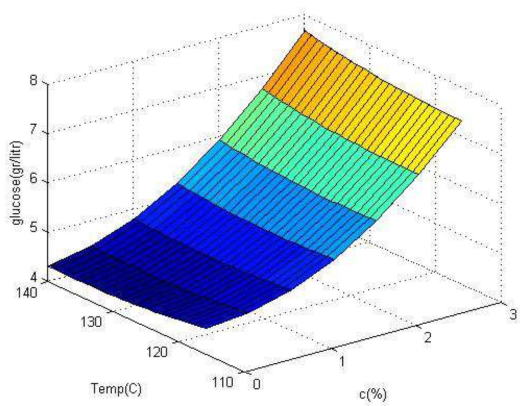

Figure 2. Glucose in liquid phase as a function of acid concentration and temperature

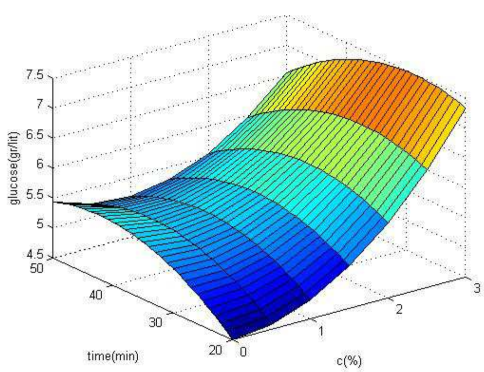

Figure 3. Glucose in liquid phase as a function of acid concentration and time

The surface shown in Fig. 3 presents a saddle point as a critical point. The saddle point is an inflexion point between a relative maximum and a relative minimum .As can be conducted from fig. 3, in studied reaction time in constant condition from 20 min to 40 min, glucose concentration increase but in next step, from 40 min to 50 min decrease. It means that glucose degraded during time.

4.3. Evaluation model validity

To evaluate model validity, two different experiment was designed. Experiment and results were shown in table 3. As can be seen in this table, the model could be a good model when error was less than 5% except one for furfural.

Table 3. Result of model check

Acid concentration (%)	Temperature (°C)	Time (min)	Comparison	Glucose (%)
3	140	40	Model	7.59
			Real	7.5
0	140	20	Model	4.3
			Real	4.15

4.4. Best condition for optimum glucose production

It is possible to calculate the optimal point through the first derivate of the mathematical function. It is necessary to solve the three first grade system formed to find best condition. Table 4 summarizes these conditions. Best condition was maximum glucose with minimum inhibitors. In optimize condition, mathematical model calculate condition to reach maximum glucose. Other extractive material was calculated in these conditions.

Table 4. Best condition for optimum glucose production

Acid concentration (%)	Temperature (°C)	Reaction time (min)	Glucose (%)
3	140	40	7.5

4. Conclusion

This work confirm that walnut green skin can be considered as a suitable feed stock for fermentable sugar production. Dilute acid hydrolysis helps us to reach the fermentable sugar in sever conditions. This process could be model by a 3 variable quadratic equation. These 3 variables were temperature, acid concentration, and process time. Model allows adjusting these variables to reaches optimum condition for maximum glucose concentrations. This conditions base on model was acid concentration 3%, temperature 140°C and process time 40 minute. In this condition glucose concentration reached to 7.5%.

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