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Bioethanol production from lignocellulosic biomass: Modeling of pretreatment step

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Abstract
Using bioethanol as a fuel is a growing trend all over the world. The economical and biological values or advantages have made it possible to consider the production technology and the utilization of bioethanol as an important fuel. Hydrolysis and fermentation are two important and major steps in bioethanol production from lignocellulosic materials. The most frequent methods to analyze the lignocellulosic materials and to hydrolyze wood in to sugar with capability of being fermented are acid hydrolysis (diluted and concentrated) and enzyme hydrolysis. In this article the effect of different factors on acid hydrolyzes of waste wood are investigated. Sulfuric acid with four different concentrations (15, 25, 30 and 35 (%w/w)) and in three different temperatures ($60^\circ C$, $70^\circ C$ and $80^\circ C$) was used .The experiments was carried out in 2, 3 and 4-hour times and the ratio of wood to acid solution was considered in three levels (5, 8.33 and 11.67(%w/w)). Based on the experimental results, a mathematical model was developed for prediction the amount of sugar produced in acid hydrolyzes of waste wood.

Key words: Acid Hydrolysis, Bioethanol, waste wood, modeling

1. Introduction

The need for energy has been growing yearly; however, the fossil fuel resources have been decreasing. It is predictable that by increasing the fossil fuel consumptions, they will not meet the people's need in less than fifty years [1, 2]. The preferences of biofuels to fossil fuels have made it possible to study hard and do more researches which lead us to their production technology. Accessibility to the first resources, decreasing the environmental pollution (decreasing the green house gases and disposing the waste), making job opportunities in rural areas and being independent from the countries producing fossil fuels are the important benefits and advantages of biofuel technology [3]. The raw materials used for bioethanol production are divided into three groups: Sugars [4-8], starch materials [9, 10] and lignocellulosic materials [11]. Waste wood, which has high percentage of cellulose and hemicellulose, is one of the most adequate and abundant resource for lignocellulosic materials. The process of bioethanol production from lignocellulosic materials includes hydrolysis and fermentation [6, 7]. In this article, the effects of different factors on hydrolyzing waste wood into sugar were studied and by using the statistical analysis, a mathematical model for hydrolysis of waste wood with concentrated acid was developed. The composition of a typical softwood and hardwood is shown in Table 1 [12].

Table 1. Composition of various lignocellulosic raw materials in a typical softwood and hardwood [12].

Components (wt%)	Populus tristis (hardwood)	Douglas fir (softwood)
Cellulose	45.0	42.0
Hemi-cellulose	30.0	27.0
Lignin	20.0	28.3
Ash	1.0	0.2
Carbohydrate (wt% of sugar equivalent)		
Glucose	40.0	50.0
Mannose	8.0	12.0
Galactose	NA	1.3
Xylose	13.0	3.4
Arabinose	2.0	1.1

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2. Acid hydrolysis

There are two main types of acid hydrolysis processes: dilute acid and concentrated acid. Dilute acid processes should be performed under high temperature and pressure, and have a short reaction time. Mostly, dilute acid hydrolysis limits the production of sugar to 50% because of the production of inhibiting chemical materials through unwanted reactions which delay the yeast growth in the fermentation stage. The most important advantage of dilute acid hydrolysis is its high rate of reaction which allows continuous processing. However, the low yield of sugar conversion is the main drawback of this process. Concentrated acid hydrolysis processes require mild operating conditions. The low temperature and pressure reduces the degradation of sugar materials. Therefore, the production of inhibiting chemical materials is minimized in this process. The first advantage of concentrated acid hydrolysis is the high yield of sugar production which is higher than 90% for both cellulose and hemicellulose sugars. In addition, the low operating temperature and pressure allows the utilization of low cost materials and equipments. However, the reaction is time consuming and the recovery of the concentrated acid imposes expensive operating conditions [13, 14]. In this study, various levels of concentrated acid are investigated.

3. Materials and Methods

The raw materials used in this study, are the waste wood of poplar tree with 5.33% moisture (dry basis) and mesh size of 30 to 70. In experiments, sulfuric acid with four different concentrations (15, 25, 30 and 35 (%w/w)) and at three different temperatures ($60^\circ C$, $70^\circ C$ and $80^\circ C$) was used. In addition the experiments were done in 2, 3 and 4-hour times and the ratio of wood percentage to acid solution were in three levels (5, 8.33, and 11.67(%w/w)). During the hydrolyzing step, the solution was agitated at the rate of 750 rpm. A schematic view of the experimental set up used for the hydrolysis process is shown in Fig. 1. After that, the solution was neutralized (with NaOH 2N) and filtered. Finally, a sample of the hydrolyzed solution was analyzed, using High performance liquid chromatography (HPLC).

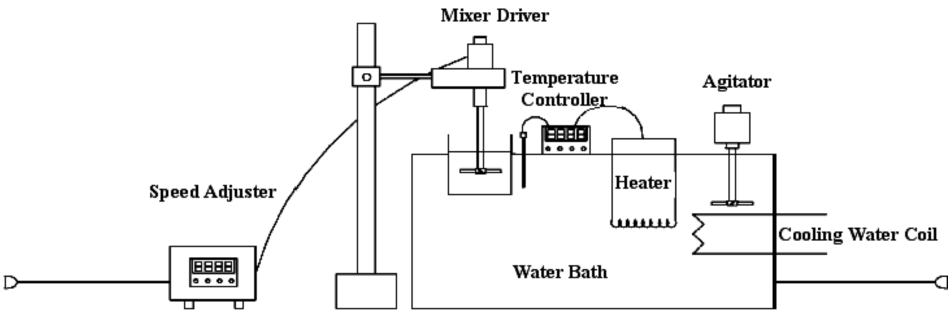

Fig. 1. A scheme of experimental set up

3.1. Analysis

The samples of hydrolyzed solutions were analyzed using an HPLC system (Jusco, Japan). The concentration of hexoses and pentoses in the sample, such as glucose, galactose, mannose, xylose and arabinose are reported as the total sugar. The detector used in HPLC system for analysis of sugar solution is the Refractive index in $40^\circ C$ with one Supelco-Pb column (mobile phase is distillated water in $80^\circ C$ with flow rate of 0.5 ml/min). The concentration of other produced materials such as furfural and acetic acid were detected spectrophotometrically (absorbance at 210nm wave length) equipped with an Aminex HPX-87H column (Bio-Rad; mobile phase is 5 mM H_2So_4; temperature is $60^\circ C$; flow rate is 0.6 ml/min and injection volume is 20 ml) [15].

3.2. Linear Regression Model

The design and planning of the experiments was carried out using Taguchi L_9 table. Considering the optimized predicted and doing some complementary experiments, a suitable mathematical model was developed for the hydrolysis process. The variables used in this model are acid concentration, temperature, time and the ratio of wood to acid solution which are shown in Table 2 (the dimensionless form of these variables are used in the model). The carried out experiments consist of 15 runs. The 14 runs are used for modeling and one run is used for validation. The selected model which has a linear form, is

$$Y_i = b_0 + \sum b_i x_i \tag{1}$$

where Y_i is the predicted response, x_i is the input variables, b_0 is the offset term and b_i is the linear coefficients. Model coefficients were calculated and analyzed using the SAS statistical software (version 9.0.1). Statistical analysis of the model was performed by the analysis of variance (ANOVA).

Table 2. Coded level of variables

Variables	Symbols (dimensionless)	Actual values of coded levels, X_i			
		1	2	3	4
Sulfuric acid (%w/w), X_1	$x_1 = X_1/50$	15	25	30	35
Temperature(^{o}C) , X_2	$x_2 = X_2/100$	60	70	80	-
Wood chips(gr), X_3	$x_3 = X_3/300$	15	25	35	-
Time (hr), X_4	$x_4 = X_4/4$	2	3	4	-

4. Results and discussion

The resulted mathematical model has the following form:

$$Y= -0.26552 + 0.21179\, x_1 + 0.32745\, x_2 -0.14671\, x_3 + 0.03996\, x_4 \quad (2)$$

The predicted and actual value of total produced sugar is shown in Table 3. The obtained regression equation explains the relationship between the total produced sugar and the test variables.

Table 3. Experimental plan and total sugar yield

Experiment	Coded levels				Total sugar (%w/w)		
no.	X_1	X_2	X_3	X_4	Predicted	Actual	Residual
1	1	1	1	2	0.7135	1.06	0.3485
2	1	2	2	2	3.50	2.93	-0.5655
3	1	3	3	2	6.28	6.36	0.0729
4	2	1	2	2	4.46	3.52	-0.9399
5	2	2	3	2	7.25	7.78	0.5296
6	2	3	1	2	11.50	11.91	0.4115
7	4	1	3	2	8.21	8.70	0.4885
8	4	2	1	2	12.46	12.70	0.2422
9	4	3	2	2	15.25	14.39	-0.8598
10	4	3	1	2	15.73	15.96	0.2257
11	4	3	1	3	16.73	16.21	-0.5274
12	3	3	3	3	13.64	13.73	0.0900
13	3	3	1	3	14.62	15.15	0.5305
14	3	3	1	4	15.61	15.57	-0.0466

The coefficient of determination (R^2), was calculated as 0.9901 for total produced sugar (Table 4), indicating that the statistical model can explain 99.01% of variability in the response. The closer the R^2 to 1.0, the stronger the model will be and also the better it will predict the response.

Table 4. ANOVA for model

Source	SS	DF	MS	F-Value	P-Value
Model	0.03614	4	0.00903	236.56	<.0001
Residual (error)	0.00034369	9	0.00003819		
Total	0.03648	13			

R^2 = 0.9901; adjusted R^2 = 0.9864; predicted R^2 = 0.9794; coefficient of variation (C.V.) = 5.93 %; SS, sum of squares; DF, degree of freedom; MS, mean square.

The predicted R^2 is 0.9794 which is in reasonable agreement with the adjusted R^2 of 0.9864. This indicated a good agreement between the experimental and predicted values for total sugar production. The model F-value of 236.56 indicated that the whole regression is meaningful and significant. Moreover, the coefficient of variation (C.V. = 5.93%) was low that is indicating a better and higher precision in experiments.

The interactive effect of these components on total sugar production was analysed by generating response surface plots (Fig. 2-4).

Table 5. Significance of the coefficients of regression

Model parameter	Parameter value	Standard error	Computed t-value	P-Value
b_0	-0.26552	0.01716	-15.48	<.0001
b_1	0.21179	0.01168	18.13	<.0001
b_2	0.32745	0.02334	14.03	<.0001
b_3	-0.14671	0.06034	-2.43	0.0379
b_4	0.03996	0.01261	3.17	0.0114

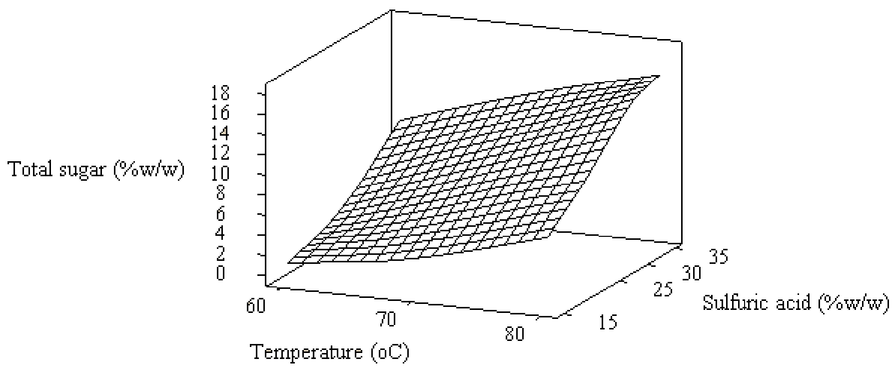

Fig.2. Response surface plot for the interaction of sulfuric acid with temperature on the production of total sugar

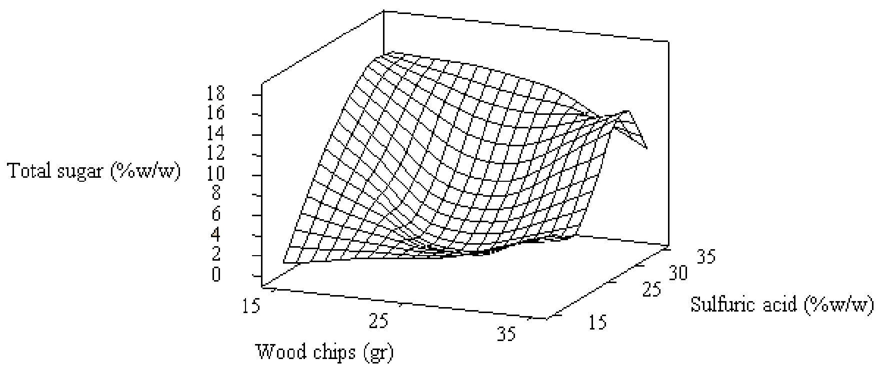

Fig.3. Response surface plot for the interaction of sulfuric acid with wood chips on the production of total sugar

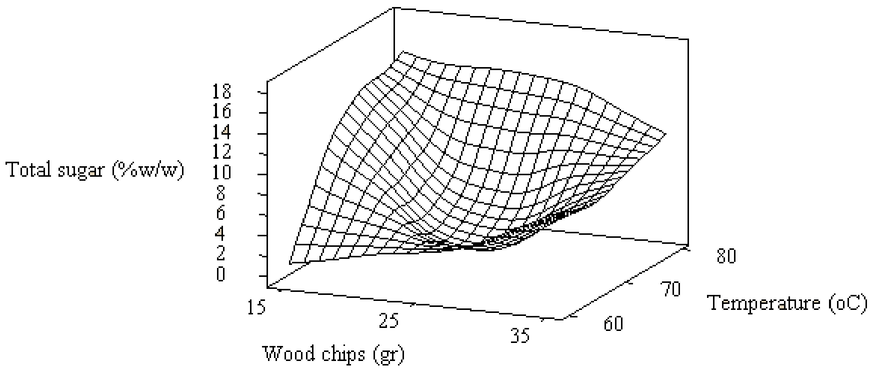

Fig.4. Response surface plot for the interaction of temperature with wood chips on the production of total sugar

The amount of t-test and p-values of coefficients of linear regression are listed in Table 5. According to the obtained P-values, it is indicated that each of the variables has direct effect on total sugar production (P-value< 0.05). The interactive effect of these components on total sugar production was analyzed by linear regression which is shown in Fig.5. It was determined that by increasing the acid concentration, temperature, and time of process, the amount of total produced sugar was increased as well, while by increasing the amount of each gram of wood in acid solution, the total amount of sugar decreased.

To make sure that the model in correct and acceptable, an experiment with acid sulfuric concentration of 35%, temperature of $80^\circ C$, process time of 4 hours and with the ratio of wood to acid solution of 5% was carried out in which 17.307% for real amount of total sugar was calculated which is similar in amount to the predicted values by the model (17.732%).

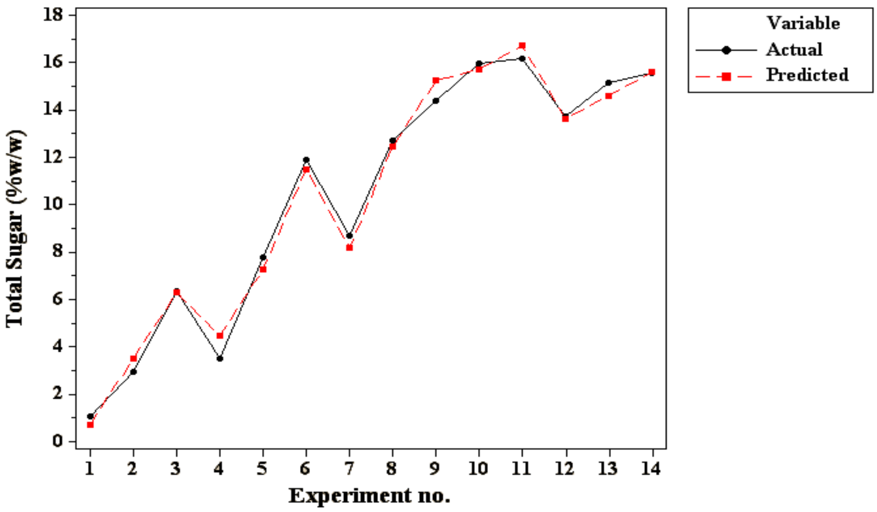

Fig.5. Actual and predicted values of total produced sugar

5. Conclusion

High acid concentration hydrolysis is one of the most common methods used to analyze lignocellulosic materials and to hydrolyze wood into sugar to be fermented. In this research, after studying the different bioethanol production methods and measuring the present situations, the effect of acid concentration, temperature, time and the ratio of wood to acid solution on hydrolyzing of Poplar wood using high concentration acid, was evaluated. Considering the optimal situation predicted by Taguchi software and doing some complementary experiment the linear regression model was offered to be used in hydrolysis process. The optimal and best results was obtained when the experiment was carried out with acid sulfuric concentration of 35% , temperature of $80^\circ C$ process time of 4 hours and the ratio of wood to acid solution of 5% , which is the same as conditions in the model experiment. The real amount of total sugar in this condition is 17.307% which is similar to the predicted value by the model (17.732%). This modeling can have a key role in choosing the best experimental conditions and reducing the economical risks and also to improve the results.

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