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STATISTICAL OPTIMIZATION AND MODELING OF DILUTE ACID HYDROLYSIS OF AQUATIC MACROPHYTES.

BHETALU A. D.[1], PATIL S. S.[2], THORAT P. V.[3]

1. Assistant Professor, Department of Engineering Chemistry, Dr. Rajendra Gode Institute of Technology and Research, Amravati, Maharashtra, India
2. Director, Adult Education and Continuous Learning, Sant Gadge Baba Amravati University, Amravati, Maharashtra, India
3. Professor and Head, Department of Chemical Technology, College of Engineering and Technology, Akola, Maharashtra, India

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Abstract: Dilute acid hydrolysis was applied for the pretreatment of three different biomass samples viz. water hyacinth, cattails and duckweeds. The effect of acid concentration, soaking time, hydrolysis temperature and treatment time on the fermentable sugar concentration was evaluated. The results obtained from the experimental runs carried out according to the central composite design are evaluated and the impact of the operating variables on the yield of fermentable sugars has been determined by using regression analysis. The regression coefficients were obtained by statistical analyses of the data. Significance of factors was determined by their P-value in the Analysis of variance (ANOVA). A second order polynomial was fitted to the data using multiple linear regressions to determine the optimum conditions for the dilute acid hydrolysis of various lignocellulosic biomasses.

Keywords: Acid Hydrolysis; Lignocellulosic Biomass; Optimization, Regression Analysis

Corresponding Author: MR. BHETALU A. D

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INTRODUCTION

All life forms on Earth need some kind of energy for its survival. It is the most basic of the factors which made life possible on this planet. About 200 years ago, all human needs for energy were fulfilled by non-renewable sources. Currently, more than 80 percent of world energy consumption comes from fossil fuels, a finite and non-renewable source. But, the over utilization of these resources have created a scarcity and now is the time to look beyond fossil fuels in order to meet the huge demand of energy.

Biofuels, in most recent times, have emerged as a substitute for fuel oil. One of the most important advantages of biofuels is that they are renewable, and are being seen as sustainable sources of energy. Moreover, Biofuels help to reduce environmental emissions, apart from addressing the problem of the rising import cost of fuel oil.

Biomass is highly diverse in nature and it is evident that, biofuels can be produced from a variety of materials. Some of these materials are of a great importance due to the value these bring about as food; while some are the by-products or wastes of a little or no use. Lignocellulosic biomass due to the composition can be a suitable option for the production of biofuels.

The three main components of lignocellulosic biomass are cellulose, hemicellulose, and lignin. The cellulose and hemicellulose are first converted to fermentable sugars, which then are fermented to produce ethanol. Hydrolysis of cellulose and hemicellulose to generate these sugars can be carried out by using either acids or enzymes. Pretreatments of the biomass are needed prior to hydrolysis.

In the present study, three aquatic macrophytes viz. Water hyacinth, Cattails and Duckweeds were investigated for their potential to serve as a possible source for bioethanol production.

However, a pretreatment is required to alter the biomass macroscopic and microscopic size and structure as well as its submicroscopic chemical composition and structure so that hydrolysis of carbohydrate fraction to sugars can be achieved more rapidly and with greater yields (Sun and Cheng, 2002; Moiser et al., 2005).

Pretreatment affects the structure of biomass by solubilizing hemicellulose, reducing crystallinity and increase the available surface area and pore volume of the substrate. Native lignocellulosic biomass is extremely recalcitrant to enzymatic digestion. Therefore, a number of thermochemical pretreatment methods have been developed to improve digestibility (Wyman et al., 2005). Recent studies have clearly proved that there is a direct correlation between the removal of lignin and hemicellulose on cellulose digestibility (Kim and Holtzapple, 2006).

Sun et al 2002 suggested a rough classification of pretreatment based on pH divides it into acidic, alkaline and neutral pretreatments. Whereas, Wyman 1996 classified the several methods that have been introduced for pretreatment of lignocellulosic materials prior to hydrolysis as Physical pretreatment, Physico-chemical pretreatment, Chemical pretreatment Biological pretreatment and Combinatorial or multiple pretreatments .

In combinatorial pretreatment methods, physical parameters such as temperature or pressure or a biological step are combined with chemical treatments and are termed physicochemical or biochemical pretreatment methods. Combinatorial pretreatment strategies are generally more effective in enhancing the biomass digestibility, and often employed in designing leading pretreatment technologies.

Wyman C.E 1996 describes that Dilute-acid pretreatment is probably the most commonly applied method among the chemical pretreatment methods. It can be used either as a pretreatment of lignocelluloses for enzymatic hydrolysis, or as the actual method of hydrolyzing to fermentable sugars.

During the present work, the effect of acid concentration, soaking time, hydrolysis temperature and treatment time on the total reducing sugar concentration was evaluated. The biomass was subjected to pretreatment with Sulphuric acid.

The purpose of this treatment is to select effective parameters which facilitate the maximum release of sugars from biomass.

MATERIALS AND METHODS

Sample preparation

The Water hyacinth and Cattail plants stems were cut near to root, whereas the whole Duckweed plants were used for the experiment. The plants were washed with tap water several times to remove any adhering dirt and were cut in to pieces of 2-3 cm size.

Dilute acid hydrolysis

The dilute acid pretreatment of biomass samples was carried out by treating 10 g biomass sample with dilute sulphuric acid using varied acid concentrations (0.5-5.0% v/v) and soaking time (0 to 60 min) at 1000-1600C temperature range for treatment time of 0-10 min. The hydrolyzate after treatment was separated by filtering the contents through double layered muslin cloth. The acid hydrolyzates obtained after acid treatment was analyzed for the amount of sugars using DNSA method (Miller 1959). The parameters were investigated for optimization studies .The effect of change of one parameter on the amount of sugars was studied by keeping other parameters constant.

Statistical analysis

The impact of the operating variables (Acid concentration, soaking time, and temperature and treatment time) on the yield of fermentable sugars has been determined in this section by using regression analysis. The regression coefficients were obtained by statistical analyses of the data. Significance of factors was determined by their P-value in the Analysis of variance (ANOVA). A factor was considered significant if the P-value was lower than 0.001, meaning that the probability of noise causing the correlation between a factor and the response is lower than 0.001. Insignificant factors were eliminated using backward elimination, and the significant factors were used to model the data.

A second order polynomial was fitted to the data using multiple linear regressions to determine the optimum conditions for the dilute acid hydrolysis of various lignocellulosic biomasses. The relationship between the total fermentable sugar concentrations produced during acid hydrolysis with the four process parameters i.e. acid concentration, soaking time, hydrolysis temperature and treatment time has been related by using various statistical analysis methods. The fit of the statistical model for the total reducing sugar concentration was assessed by carrying out analysis of variance (ANOVA).

RESUTS AND DISCUSSION

The chemical composition of the aquatic macrophytes under investigation was determined as per the NREL protocol. The analysis of structural carbohydrates in Water hyacinth indicates that it contains 10.02% lignin, 33.38% cellulose and 36.49% hemicellulose. Similarly, the compositional analysis of cattails reveal that it contains 89.72% moisture,9.78% ash, 24.12% lignin, 40.09% cellulose and 22.86% hemicellulose. Whereas, the duckweeds are found to contain 91.21% moisture, 6.89% ash, 7.28% lignin,12.88% cellulose and 12.98% hemicellulose.

Lignin is limiting factor during the hydrolysis of biomass which must be removed in order to attain the higher degree of saccharification of cellulose and hemicellulose.

The low content of lignin presents better opportunities for the maximum utilization of cellulose and hemicellulose in the hydrolysis process. Thus, it is evident that the cellulose and hemicellulose content of all the three aquatic macrophytes make them attractive as a source of ethanol in bioconversion processes.

Statistical analysis

Multiple regression method was applied to the experimental data for the amount of fermentable sugars released from raw Water hyacinth, Cattails and Duckeeds after dilute sulphuric acid hydrolysis to generate a statistical relationship between the four process parameters viz. acid concentration (X1), Soaking time (X2), Temperature (X3), Treatment time (X4) and amount of sugars obtained. The terms X1,X2,X3 and X4 are linear terms whereas terms X1X2,X3X4 and X12,X22 etc. are quadratic terms.

The following second degree polynomial was found to represent the relationship between the total sugar produced and acid concentration, soaking time, pretreatment time and pretreatment temperature adequately:

Sample	Variables (X)	Equation	R^2	P
Water hyacinth	All	$Y = 33.92 + 0.378 X_1 + 0.1456 X_2 + 0.0581 X_3 + 1.852 X_4 + 2.1683 X_1^2 - 0.0693 X_4^2 - 0.0511 X_1 * X_2 + 0.0583 X_1 * X_4 + 0.00528 X_3 * X_4$	58.25	<0.01
	Acid conc.	$Y=83.50+24.36X-45.42X^2$	21.36	<0.001
	Soaking Time	$Y=104.9+0.1551X-0.002071X^2$	0.32	0.029
	Temperature	$Y=88.36+0.1418X$	3.12	<0.001
	Treatment Time	$Y=90.00+3.919X-0.08007X^2$	30.33	<0.001
Cattails	All	$Y = 33.92 + 0.378 X_1 + 0.1456 X_2 + 0.0581 X_3 + 1.852 X_4 + 2.1683 X_1^2 - 0.0693 X_4^2 - 0.0511 X_1 * X_2 + 0.0583 X_1 * X_4 + 0.00528 X_3 * X_4$	61.20	<0.001
	Acid conc.	$Y=56.14+11.52X-21.68X^2$	19.05	<0.001
	Soaking Time	$Y=66.86+0.003197X$	0.01	0.727
	Temperature	$Y=5598+0.0445X$	4.29	<0.001
	Treatment Time	$Y=57.49+2.378X-0.06926X^2$	34.58	<0.001
Duckweeds	All	$Y = -0.73 + 13.588 X_1 + 0.0976 X_2 + 0.0277 X_3 + 2.004 X_4 + 2.1964 X_1^2 + 0.000773 X_2^2 - 0.0979 X_4^2 - 0.05613 X_1 * X_2 - 0.0545 X_1 * X_4 + 0.00296 X_3 * X_4$	65.36	<0.001
	Acid conc.	$Y=14.72+11.63X-2.196X^2$	28.99	<0.001
	Soaking Time	$Y=25.88-0.01041X$	0.09	0.166
	Temperature	$Y=20.68+0.03759X$	1.25	<0.001
	Treatment Time	$Y=17.79+2.239X-0.09790X^2$	29.51	<0.001

Water hyacinth

The coefficient of determination (R2) of the model was 58.25 which mean that 58.25% of the variability among the results was explained by the model and 41.75% was as a result of chance. Values of ‘‘Prob. > F’’ less than 0.001 indicate the model terms are significant.). Normally, a P-value of less than 0.05 will indicate that a model is statistically valid and acceptable. Values greater than 0.10 indicate the model terms are not significant. From the regression model of total reducing sugar concentration, the model terms X1, X2, X3, X4, X12, X22, X42 were significant with a probability of 95%. The terms X1X2 and X3X4 were also significant indicating that there was interaction between acid concentrations and soaking time as well as temperature and treatment time.

In this model, the high R2 value and also that of the adjusted R2 indicate a close agreement between the experimental results and the theoretical values predicted by the model, the model is capable of explaining 58.25% of the variation in the response. The high P-value for the lack of fit test indicates the high level of insignificance he error, and further confirms that the model fits suitably the data.

Cattails

The coefficient of determination (R2) of the model was 61.20, which indicated that the model adequately represented the real relationship between the variables under consideration. An R2 value of 61.20 means that 61.20% of the variability was explained by the model and 37.80% was as a result of chance.

Values of ‘‘Prob. > F’’ less than 0.001 indicate the model terms are significant. Values greater than 0.10 indicate the model terms are not significant. From the regression model of total reducing sugar concentration, the model terms X1, X2, X3, X4, X12, X22, X42 were significant with a probability of 95%. The terms X1X2 and X3X4 were also significant indicating that there was interaction between acid concentrations and soaking time as well as temperature and treatment time.

Duckweeds

The coefficient of determination (R2) of the model was 65.36, which indicated that the model adequately represented the real relationship between the variables under consideration.

An R2 value of 65.36 means that 65.36% of the variability was explained by the model and 34.64% was as a result of chance. Values of ‘‘Prob. > F’’ less than 0.001 indicate the model terms are significant. Values greater than 0.10 indicate the model terms are not significant. From the regression model of total reducing sugar concentration, the model terms X1, X2, X3, X4, X12, X22, X42 were significant with a probability of 95%. The terms X1X2, X1X4 and X3X4 were also significant indicating that there was interaction between acid concentration and soaking, concentration and treatment time as well as temperature and treatment time.

CONCLUSION

Three aquatic macrophytes were subjected to dilute sulphuric acid hydrolysis for the purpose of producing fermentable sugars. Results of chemical composition analysis indicate that cellulose, hemicellulose and lignin were the major constituents of theses macrophytes. The hydrolysis process was affected by the acid concentration, soaking time, temperature and treatment time. These variables were related to the total sugar concentration by a validated statistical model. The model was able to predict to a high level of confidence.

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