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Process Optimization of Microwave Assisted Lime Pretreatment on Ramie Decortication Waste Using Response Surface Methodology

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Abstract: Abstract-Lignocellulosic materials are promising alternative feedstocks for production of bioethanol. One of the lignocellulosic material that can be used for bioethanol production is ramie decortication waste (RDW). This study investigated pretreatment of RDW using microwave assisted alkaline. Calcium hydroxyde was used as the alkaline agent. Response Surface Methodology was used for the optimization of pretreatment. A 2^3Central Composite Design (CCD) was used to develop statistical model and analyze the effect of each variables, which are pretreatment time (10-30 min), solid liquid rasio(0,1-0,3) and alkaline/lime concentration (3-7%). Data abtained from RSM were subjected for analysis of variance (ANOVA) and analysis using second order polynomial equation. The isoresponse contour plot were used to study the interaction between three variables. The optimal condition resulted was 28,8 minutes pretreatment time, solid liquid rasio 0,28 and lime concentration 5,65% with percentage of lignin removal was 38,8%.
Keywords : bioethanol, optimization, pretreatment, ramie decortication waste, microwave assisted alkaline.

I. Introduction

Bioethanol is a potential biofuel which is suitable for liquid transportation fuel. It is an attractive biofuel since it is renewable and oxygenated, thereby has potential to reduce particulate emissions in engine[1]. Bioethanol also can be blended with fossil petrol or used as neat alcohol in dedicated engine[2]. Bioethanol can be produced from any material that contain simple/fermentable sugar or can be changed into simple sugar. Lignocellulosic materials are composed from component that can be changed into simple sugar, hence could be sources for bioethanol production. Nowadays, lignocellulosic materials seem to be a potential source of bioethanol. These materials are abundant, plentiful, cheap and renewable[3-4]. Lignocellulosic materials are reported comprise about 50% of world's biomass and the annual production was estimated around $1x10^{10}$ metric ton[5].

One lignocellulosic material that can be an alternative of bioethanol feedstock is ramie decortication waste (RDW). This waste is produced from decortication process, a process to separate ramie fiber from its rod. The waste is coming from the rest of the rod and skin rod. Currently, this waste only used for animal feedstock. Ramie decortication waste contain high cellulose, 33,1%, therefore it is suitable for biethanol production. Besides cellulose, RDW also contain high lignin content[6].

Conversion of lignocellulosic materials to bioethanol consists of pretreatment, hydrolisis, fermentation and ethanol purification process. Among these steps, pretreatment is the first and also can be the most important and crucial step[7], which will liberate the cellulose from the lignin and at the same time will reduce the lignin content[2,8-9]. This process utilizes as much as 30% of the total ethanol production cost[5]. Pretreatment also will break the rigidity of fibers and making them easy for hydrolisis by altering the cellulose structure that make the enzym can access the carbohydrates polymer to convert them into fermentable sugar.

There are many pretreatment processes that are common for lignocellulosic materials, they are physical, chemical and biological process. All the pretreatment processes are reported effective for lignocellulose but the yield or percentage depends on the method selected[9]. Among many pretreatment process, the combination of using microwave and alkali agent have produced successful result[2,5]. The usage of microwave will give advantages, like no direct contact between the material and heating source, rapid heat and selective heating. More over, microwave pretreatment method is reported very effective in reducing the lignin ratio in biomass, thus increasing the proportion of cellulose[9]. The alkaline agents which are common to be used in pretreatment process are sodium hydroxyde, calsium hydroxyde/lime and ammonia.

This paper studied the optimization of microwave assisted lime pretreatment of rami decortication waste using central composite design for RSM (response surface methodology). Responce Surface Methodology is considered as more efficient approach to evaluate the experimental factors and observed results[10]. Moreover, RSM also can be used to study individual and interactive effects of the parameter observed[11]. The objective of the research was to identify the optimum process condition for the selected operating variables, namely time, solid liquid rasio and lime concentration.

II. Experimental

A. Materials

Ramie decortication waste (RDW) as lignocellulosic material was gained from ramie processing industry in Wonosobo, Central Java Indonesia. The waste choosen is the fresh waste that is obtained after the decortication process running. The waste is washed with distilled water and dried for 24 hours in 105^{0}C. Dried ramie decortication waste than mashed and sieved in 18 mesh. The fine grained waste is stored in sealed container in room temperature and called ‘sample’. The alkaline used for pretreatment is calcium hydroxide/lime.

B. Methods of Pretreatment

Ten gr of sample was added in $Ca(OH)_2$ solution with concentration of each alkaline and solid liquid ratio are based on experimental design. The solution is then pretreated using microwave (power 30% from the maximum power 399W) with the time also based on experimental design. After pretreatment, solution was filtered. The solid part is washed until pH 7 and dried for 4 hours. The sample was analyzed its lignin content.

C. Analysis of lignin content

The original and pretreated samples were analyzed its lignin and cellulose content using Chesson method[12]. One g of dried sample (a) was heated with 150 ml of aquadest at temperature of 100^{0}C for 1 h. The mixture was filtered and dried until the weight was constant (b). The residue was mixed with 150 ml of 0,5M sulfuric acid and heated at temperature 100^{0}C for 1 h. The mixture was filtered and the residue was dried (c). The residue was added with 10 ml of 72% $H2SO_4$ at room temperature for 4 h and then heated for 1 h. The solid was dried (d). Finally, the solid was heated until become ash and weighed (e). The lignin content was calculated as follows :

% lignin = (d-e)/a x 100% ....(1)

D. Experimental design and statistical analysis

Experimental design use Central Composite Design (CCD) to investigate the effects of different factors on RDW pretreatment. The software used was STATISTICA 8,0 to obtain the analysis of variance (ANOVA) and polynomial regression equation. The CCD contains 16 experiments with dependent variable is percentage of lignin removal, while the three independent variables are time, solid liquid ratio and alkaline concentration. The range and levels of variables optimized are given in Table 1. A mathematical model that describing relationship between dependent and independent variable will follow equation (2) below :

$$Y = b_o + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_1^2 + b_5X_2^2 + b_6X_3^2 + b_7X_1X_2 + b_8X_1X_3 + b_9X_2X_3 \text{ .... (2)}$$

Table 1. Range and levels of independent variables

Variable	Range and levels				
	Star point (-α/-1,682)	**Low level (-1)**	**Center level (0)**	**High level (+1)**	**Star point (+α/1,682)**
Time (minute)	3,18	10	20	30	36,82
Solid liquid rasio	0,32:10	1:10	2:10	3:10	3,7:10
Lime concentration (%b/v)	1,64	3	5	7	8,36

The quality of fit of the second order equation was expressed by the coefficient of determination R^2 and its statistical significance was determined by the F-test. The p value (probability value) were used as a tool to check the significance of the interaction effects[13].

III. Result and Discussion

The experimental results together with each independent variables are listed in Table 2, while Table 3 showed the analysis of variance (ANOVA). The regression equation is fitted to a second order polynomial equation, and can be expressed in the equation (3) below :

$$Y=35{,}04+12{,}84X_1+3{,}27X_2+3{,}49X_3-9{,}01X_1^2-3{,}51X_2^2-8{,}95X_3^2+2{,}8X_1X_2+2{,}38X_1X_3+0{,}3X_2X_3 \text{ .....(3)}$$

Table 2. Experimental Response

NO	X_1	X_2	X_3	Y
1	10	0,1	3	13,5
2	10	0,1	7	15,74
3	10	0,3	3	18,59
4	10	0,3	7	16,67
5	30	0,1	3	24,44
6	30	0,1	7	26,67
7	30	0,3	3	30,37
8	30	0,3	7	37,96
9	3,18	0,2	5	14,44
10	36,82	0,2	5	33,89
11	20	0,03	5	32,22
12	20	0,37	5	31,67
13	20	0,2	1,64	20,18
14	20	0,2	8,36	28,33
15	20	0,2	5	33,52
16	20	0,2	5	35,93

X_1 = time (minute)
X_2 = solid liquid rasio
X_3 = lime concentration (%)
Y = percentage of lignin removal (%0

Table 3. Analysis of ANOVA

Factor	SS	DF	Mean square	F	p
X_1	562,55	1	562,55	38,05	0,0008
X_2	36,46	1	36,46	2,46	0,1673
X_3	41,64	1	41,64	2,82	0,1443
X_1X_2	15,68	1	15,68	1,06	0,3427
X_1X_3	11,28	1	11,28	0,76	0,4159
X_2X_3	0,18	1	0,18	0,01	0,9157
X_1X_1	188,06	1	188,06	12,72	0,0118
X_2X_2	28,53	1	28,53	1,93	0,2141
X_3X_3	185,412	1	185,412	12,54	0,0121
Error	88,71	6	14,78		
Total SS	1029,45	15			

The regression equation obtained from ANOVA analysis showed the coefficient of determination R^2 was 91,4%. The number indicates fraction of overall variation in the data accounted by the model. For good statistical model, the value of R^2 will range between 0 and 1,0, and nearer to 1,0, the more fit the model. Normally, a regression model with an R^2 higher than 0,90 is considered to have a very high correlation[10]. The value of R^2 0,914 also means that 8,6% of the total variation is not explained by the model.

The value of p less than 0,05 show that the model was significant, while the value more than 0,1 show that model was not significant[14]. From the ANOVA analysis it showed that factor X_1, X_1^2 and X_3^2 are significant, while interaction between factors are not significant. We can also conclude that the most affecting factor of the pretreatment process was time, since the highest value of F.

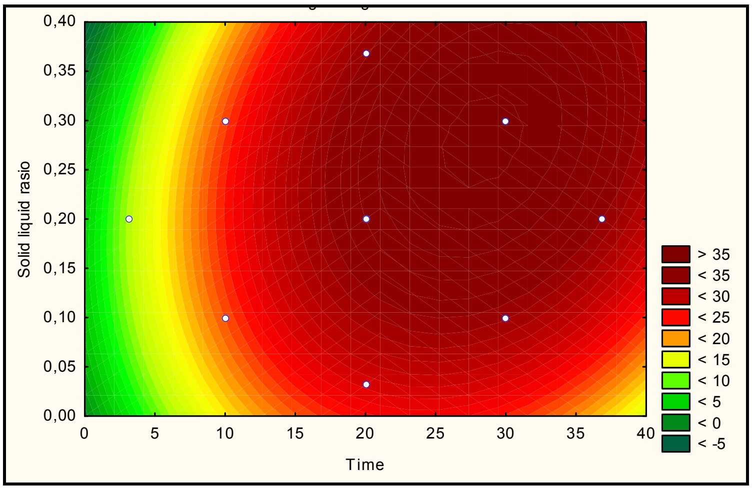

Figure 1. Contour plot of time and solid liquid rasio on lime concentration 5%

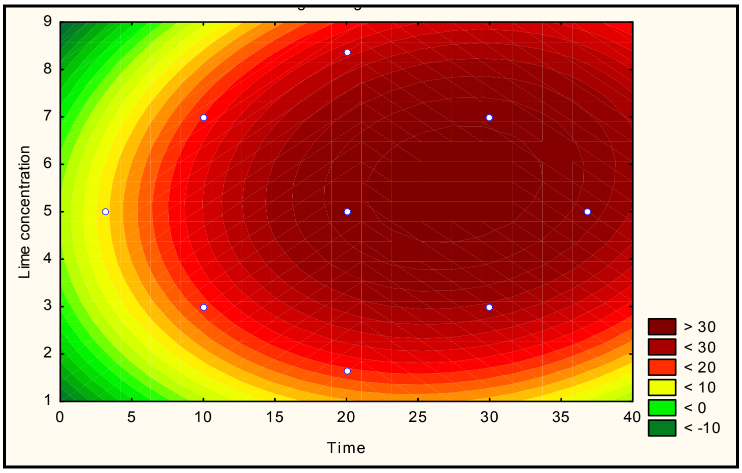

Figure 2. Contour plot time and lime concentration on solid liquid rasio 0,2

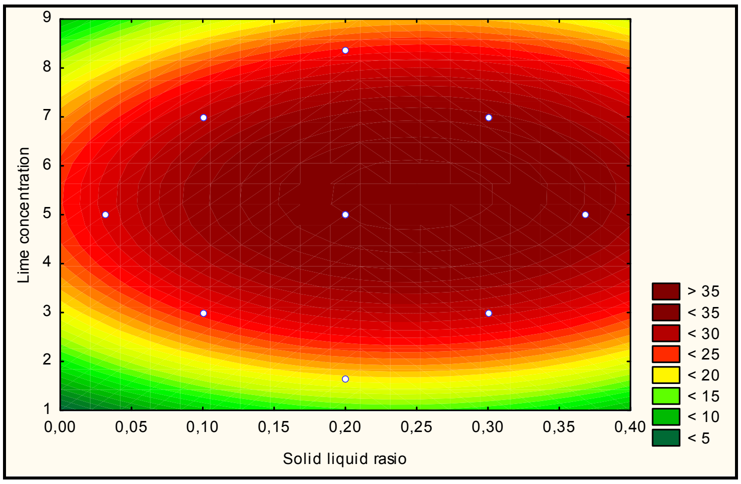

Figure 3. Contour plot of rasio solid liquid and lime concentration on time 20 minutes

Contour plot and response surface curves can be used to predict the optimum range of the variables and the interaction between the variables involved. This interaction can be seen from the circular or elliptical nature of contour. If the contour is circular, then the optimum condition can be easily obtained and the interaction between variables involved are not significant[13]. Figure 1 showed the contour plot of interaction between time and solid liquid ratio on alkaline (lime) concentration 5%. The response surfaces is circular, then there is no significant interaction between time and solid liquid rasio. The contour plot of interaction between time and lime concentration at solid liquid rasio 0,2 is given on Figure 2. This figure is similar with Figure 1, where the contour is circular. The different contour is resulted on contour plot of solid liquid rasio and lime concentration on time 20 minutes. The contour was elliptical and getting longer on x axis (solid liquid rasio). It means that little change on response will need the change on solid liquid rasio variable. The optimum condition obtained for the pretreatment of RDW was 28,8 minutes pretreatment time, solid liquid rasio 0,28 and alkaline concentration 5,65% with percentage of lignin removal was 38,8%. The percentage of lignin reduction got in this research was higher compared with lime peroxide oxidation pretreatment for sawdust which is 16%[11] but still lower than microwave assisted alkaline pretreatment for oil palm empty fruit which can reach 74%[2]. While another study for optimization of wheat straw pretreatment using combination of NaOH-$Ca(OH)_2$ got the percentage of lignin reduction between 8-60%[15].

Conclusion

Response Surface Methodology was suitable for opmitization process of microwave assisted lime pretreatment of ramie decortication waste. Three independent variables were choosen, time, solid liquid rasio and lime concentration, while the response was the percentage of lignin removal. The optimum condition from the research was 28,8 minutes pretreatment time,solid liquid rasio 0,28 and lime concentration 5,65% with percentage of lignin removal was 38,8%.

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