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Optimization on the Hydrolysis Process of Cellulose from Corn Husk to Glucose with Activated Carbon Catalyst Sulfonated

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Abstract – The purpose of this research was to determine the optimization from the hydrolysis process using an activated carbon catalyst to convert cellulose to glucose. The design of this research consisted of four stages that is manufacture of catalysts, cellulose hydrolysis process, glucose yield test and optimization process. The research data is plotted in a mathematical model that is optimized using software of Statistica 10 with *Response Surface Methodology* (RSM) and ANOVA methods. From the RSM method was obtained mathematical equation model for the relationship of the combination of temperature, time and amount of catalyst to glucose levels, that is: $Y = 25{,}0457 + 0{,}579x_1 - 0{,}111x_1^2 + 6{,}471x_2 + 2{,}798x_2^2 + 4{,}697x_3 + 2{,}965x_3^2 + 1{,}241x_1x_2 + 0{,}996x_1x_3 + 0{,}675x_2x_3$. ANOVA method produces a value of determination coefficient (R^2) as big 0.91545. In this research, the optimum temperature is at 70°C, the optimum time is at 2 hours, and the optimum amount of catalyst is at 11 grams. Results of Glucose yield obtained from the optimal operating conditions is 31%.

Index Terms – RSM Method; ANOVA Method, Cellulose, Activated Carbon Catalyst, Glucose.

1. INTRODUCTION

During this time corn husk waste is not utilized maximally, So that it disturbs the surrounding environment. Usually unused corn husk waste is immediately burned. The consequence is air pollution everywhere which can interfere with breathing. So the corn waste, especially the husk should be used to reduce environmental pollution. Based on BPS data for 1993 - 2018, the average corn production in Indonesia reaches 15 million tons per year [1].

In this research, corn husk will be hydrolyzed cellulose to get glucose. Cellulose is an organic compound which is a straight chain polysaccharide of 1,4β-glycosidic which binds in a D-glucose unit [2]. This cellulose can replace fossil sources used as fuel, because cellulose is a renewable source of biomass [3].

Corn husk has a high cellulose fiber content, so it is suitable for conversion to glucose by hydrolysis. Cellulose is the main element needed in making glucose. The results of Prasetyawati's study (2015) stated that the chemical composition of corn husk included 19,05% lignin; 6,47% ash; 5,80% hemicellulose; and 68,68% cellulose. Dried corn husks can be hydrolyzed using solid acid catalysts that are environmentally friendly [4].

The following table 1 contains the composition of the skin content of corn:

Chemical Composition	Corn Husk (%)
Cellulose	68,68
Hemicellulose	5,80
Lignin	19,05
Ash	6,47

Table 1 Chemical Composition of Corn Husk

Source: Prasetyawati's study (2015)

The generally, reaction of cellulose hydrolysis can be expressed as follows:

$$(C_6H_{10}O_5)n + nH_2O \rightarrow nC_6H_{12}O_6$$

The degree of cellulose polymerization is indicated by the length of the polymer chain, which is n. Decreasing 1 mole of cellulose will produce n moles of glucose. Based on this reaction equation, cellulose hydrolysis can actually be done using only water, but hydrolysis like this requires a very long time. To speed up the reaction, a catalyst needs to be added, which can be done using a catalyst of sulfonated activated carbon [5].Cellulose molecules are microfibils of glucose which are bound to one another to form very long polymer chains [6].

Mechanism of cellulose hydrolysis reaction that begins with the reaction of protons from acids that interact with hydrogen bonds in cellulose. Oxygen that connects two glucose molecules and forms a conjugate acid. Breaking the C-O bond and breaking the conjugate acid into a carbonium ion ring. Adding water (H_2O) will release glucose and proton molecules [7].

The technology used in hydrolyzing cellulose is acid hydrolysis and enzyme hydrolysis. Both have drawbacks in the process of hydrolysis which the drawbacks that generate waste which is very dangerous and also make use of acid and enzyme costs are very expensive. Hydrolysis technology using sulfonated activated carbon catalyst is the right solution, because it does not cause hazardous waste and in terms of cost is also very relatively cheap [8].

Based on research of Rispiandi (2015), Explain that the results of the sulfonated activated carbon catalyst performance test from a coconut shell have a very significant effect on the reaction of cellulose into glucose. This is due to the more catalysts, the more protons that play a role in chemical reactions. In accordance with Xiang et al (2005) who concluded that the higher the concentration of acid, the faster the reaction time because more and more available H + groups. Thus, so many catalysts are used in this variable, resulting in% yield and cellulose conversion to glucose also increases.

Based on the research of Ashadi (2013), glucose levels produced from the hydrolysis process are influenced by the hydrolysis temperature, hydrolysis time and the addition of the amount of catalyst. Increasing the reaction temperature in the hydrolysis process would lower glucose levels resulting from glucose that is formed will be degraded further [12]. Therefore an optimization is needed to determine the optimum conditions of hydrolysis which includes hydrolysis temperature, hydrolysis time and the addition of the amount of catalyst [6]. Determination of optimization in the process of cellulose hydrolysis from corn husk using the Response Surface Methodology (RSM) method with the help of software statistica 10.

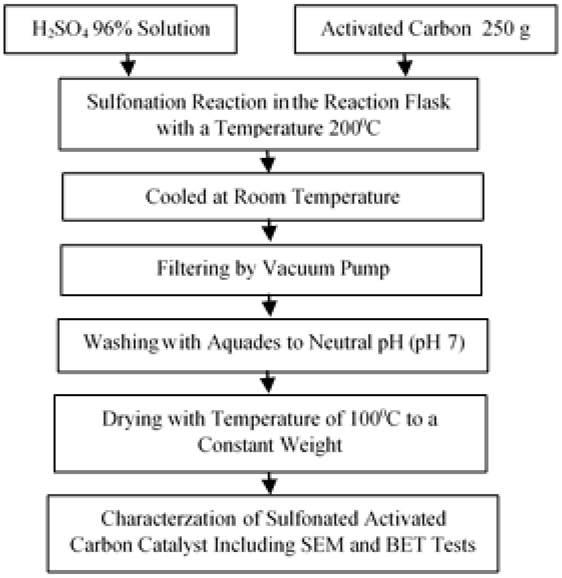

Figure 1 Flow Chart of Catalyst Making

2. METHODOLOGY

2.1. Materials

The materials used in this study are as follows: solution of technical H_2SO_4 96%, dried corn husk, aquades, benedict solution, activated carbon from coconut shell

2.2. Experimental Procedure

In this research, three variables are used to be tested. These variables are the hydrolysis temperature, hydrolysis time, and the addition of the amount of catalyst. The hydrolysis temperature is given a lower limit, a middle limit, an upper limit of 50^0C, 70^0C and 90^0C. Hydrolysis time is given a limit of 1 hour, 2 hours and 3 hours. While the amount of catalyst is 3 grams, 6 grams and 9 grams. After that it was run using software of statistica 10 and obtained 16 running as a benchmark experiment. After carrying out the hydrolysis process, glucose results from the hydrolysis filtrate were tested qualitatively using benedict solution and quantitatively using a spectrophotometer. Glucose test results were optimized by the Response Surface Methodology (RSM) method with the help software of Statistica 10 so that the optimum conditions of cellulose hydrolysis from corn husk obtained in the form of temperature, time and the addition of catalysts.

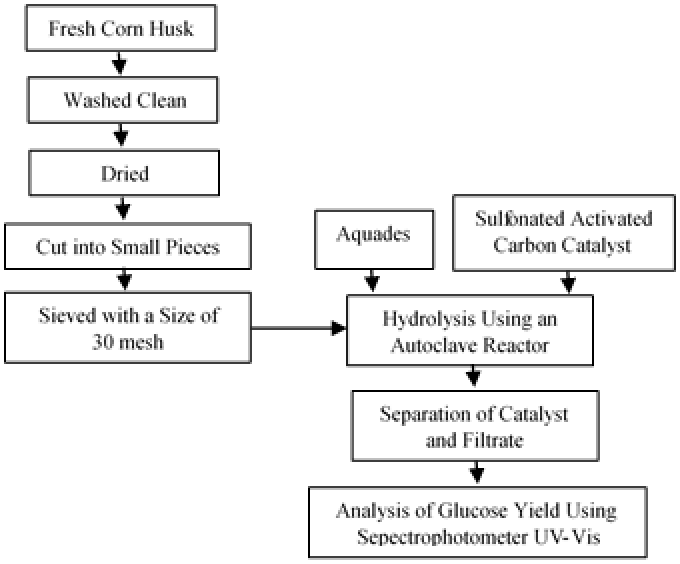

Figure 2 Flow Chart of Hydrolysis Process

3. RESULTS AND DISCUSSIONS

3.1. Experimental Results

The results of this research are listed in table 2 which shows that the highest glucose yield were obtained 31%. The relationships between the three independent variables (temperature of hydrolysis, time of hydrolysis and additional amount of catalyst) and glucose yield were research [13].

3.2. Characteristics of Activated Carbon Sulfonated

The surface of activated carbon can be seen using a Scanning Electron Microscope (SEM) to determine the presence of large pores on the surface of activated carbon. Test results of SEM that appear and shape of the catalyst surface morphology are amorphous so that the chance for a reaction is even greater. The shape of the catalyst surface influences the interaction of the reaction process [14]. From the SEM test results for 3000x magnification obtained the following results:

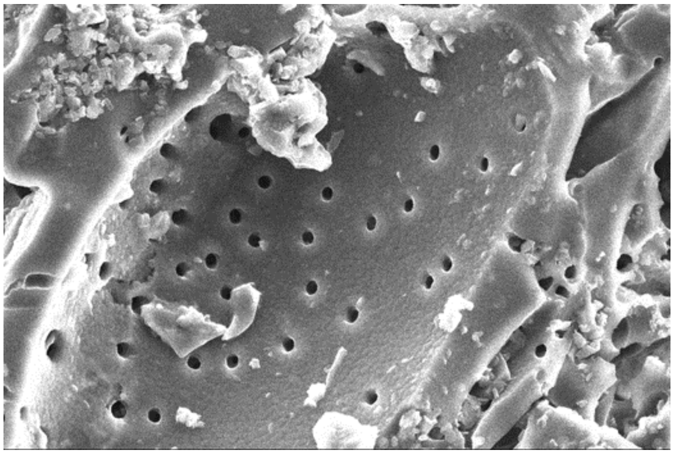

Figure 3 Result Test of Sulfonated Actived Carbon Catalyst with SEM

The SEM test results show that the surface morphology of the catalyst is amorphous (arranged irregularly) so that the chance The SEM test results show that the surface morphology of the catalyst is amorphous (arranged irregularly) so that the chance of a reaction is even greater (Figure 1). The shape of the catalyst surface influences the interaction of the reaction process. For SEM sulfonated activated carbon the surface structure appears more open compared to activated carbon before disulfonation [9].

With the same magnification of 3.000x it is seen that the morphological structure of the activated sulfonated carbon is more open, so that reactants (cellulose) more easily enter the surface of the catalyst so that it is possible to interact more easily with H + groups that are bound to the surface and form glucose [9].

In the field of nanomaterial BET can be used to measure surface area. The purpose of BET testing is to determine the surface area of the active side on the sulfonated activated carbon catalyst. Surface area is the number of pores in each unit area of the sample. Surface area is influenced by particle size, pore size, pore shape and pore arrangement in particles. Identification of surface area of sulfonated activated carbon was carried out by a BET (Brunaur Emmet Teller) test. Based on the analysis of these test results it is known that activated carbon from coconut shell has a surface area of 51.372 m^2/g.

3.3. Test of Catalyst Performances

From this table 2 the results of the glucose yield test using this spectrophotometer can be seen that the highest glucose yield values were obtained with variables with operating conditions at a temperature of 70^0C, 2hours time and the amount of catalyst 11 grams glucose yield reached 31%. This is because there is a saturation point during the process of cellulose hydrolysis, so that at excessive temperatures can cause glucose yield to be damaged. The excess catalyst will also interfere with the hydrolysis process cellulose. This is also influenced by the temperature treatment, the amount of catalyst and different time, so that the glucose yields obtained are also different. This is due to the increase in reaction temperature, the length of reaction time and the addition of excess catalysts which can accelerate the hydrolysis process which results in breaking the lignin and cellulose bonds [13]. Other than that, In addition, increasing the temperature, time and amount of catalyst can increase the rate of hydrolysis reaction. An increase in the rate of this reaction can affect the operation of the hydrolysis process. If the operating conditions are made in excess, then the glucose yield will be degraded, thereby causing glucose yield can be decreased [16]. Therefore, look for the value of the most optimum conditions, so that the glucose yield can be obtained results the most. Research data shows that the most glucose yield is produced under optimal conditions is not excessive (Number of Experimental Run 13).

The highest glucose yield can be achieved by adding a sulfonated activated carbon catalyst. This is due in the hydrolysis process, the H^+ group from the acid will change the group of cellulose fibers present in the husk of corn into free radical groups. A free radical group of cellulose fibers which then binds to the OH^- group of aquades and reacts with hydrogen bonds on cellulose, thus forming a large amount of reducing sugars. When a large acid concentration results from the addition of a solid acid catalyst, the need for H^+ ions is very fulfilled, so that free radical groups formed from cellulose and glucose are formed very maximal. The more H^+ groups as binding of free radicals that are formed, the more glucose is formed. This is because the H^+ group which makes the cellulose fiber group binds to OH^-.

Experimental Run	**Temperature of hydrolysis (^{0}C)**	**Additional amount of catalyst (grams)**	**Time of hydrolysis (hours)**	**Glucose yield (%)**
1	50	3	1	11
2	90	3	1	14

3	50	9	1	17
4	90	9	1	20
5	50	3	3	23
6	90	3	3	25
7	50	9	3	27
8	90	9	3	28
9	70	6	1	16
10	70	6	0,5	15
11	70	6	4	28
12	70	1	2	15
13	**70**	**11**	**2**	**31**
14	35	6	2	9
15	105	6	2	29
16	70	6	2	25

Table 2 Test Results for Glucose Yield

Effect	SS	Df	MS	F	P	R^2
x_1	15,9730	2	15,9730	1,7588	0,4330	0,91545
x_1^2	50,1514	2	50,1514	7,3481	0,0551	
x_2	55,8993	2	55,8993	9,0455	0,0112	
x_2^2	53,1018	2	53,1018	7,2393	0,0560	
x_3	0,5534	2	0,5534	0,0621	0,9836	
x_3^2	57,8076	2	57,8076	8,2020	0,0865	
x_1x_2	5,0957	2	5,0957	0,5923	0,5945	
x_1x_3	20,1526	2	20,1526	3,8995	0,3911	
x_2x_3	18,7354	2	18,7354	5,1217	0,2554	
Error	42,5262	6	6,887			
Total SS	303,3013	24				

Table 3 Variant Analysis with ANOVA Method

3.4. Optimization Using RSM Method

The results of the research were analyzed by the RSM method with the help software of statistical 10 to find out the most optimal conditions. The results of the optimization process obtained matamatis equation 1 is a model that shows the relationship between the hydrolysis temperature, hydrolysis time and the weight of activated carbon catalyst of the glucose content is expressed as the following equation:

$$Y = 25{,}0457 + 0{,}579x_1 - 0{,}111x_1^2 + 6{,}471x_2 + 2{,}798x_2^2 + 4{,}697x_3 + 2{,}965x_3^2 + 1{,}241x_1x_2 + 0{,}996x_1x_3 + 0{,}675x_2x_3.$$

Description: Y = Yield of glucose (%)

x_1 = Temperature of hydrolysis (^{0}C)

x_2 = Time of hydrolysis (hours)

x_3 = amount of catalyst (grams)

The accuracy of the mathematical model can be analyzed with ANOVA which is shown in table 3. The accuracy of this method can be seen from the coefficient of determination (R2), which reached 0.91545. Value of R2 The closer it is to number 1, the better the ANOVA analysis results related to the results of research conducted [17]. This indicates that 91.545 % of the total variation in the results obtained is represented in the model. The accuracy of this model can also be seen from the results of the calculation of the F (ratio of mean square) value is greater than the value of P (probability) [18]. The values of F (ratio of mean square) showed statistically significant regression results at the level of 5%. For a value of P (probability) less than 0.05, then the variable is very influential in getting the yield [19]. Analysis of variants obtained from software of Statistica 10 can be seen in table 3.

Analysis of the optimum operating conditions can use that response surface analysis using charts and graphs of 3-dimensional optimization surface contours. Graph 3 dimensional optimization consists of two independent variables and one dependent variable, so that one other variable is a constant number [20]. The axis of x and y are the independent variable and the dependent variable z axis shows. In the contour graph of surface areas of color, so that it can be seen from this graph the point - the point of interaction of two variables results in a clear, where by the most optimal interaction is located in the oldest red area [21] .The graph can be seen in the Figure 4.

Figure 4 shows that the most optimum glucose level is in the temperature range of 70^0C to 90^0C and the optimum time on the range of 2 to 4 hours. Whereas in Figure 5 shows that the addition of amount the most optimum on catalyst is in the range of 10 grams - 12 grams.

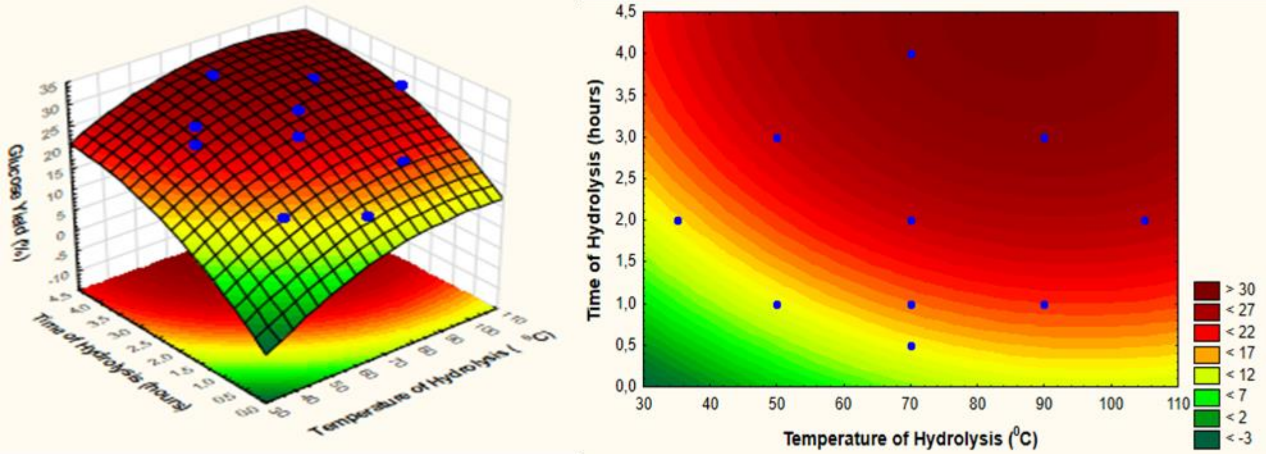

Figure 4. Graph Contour of Hydrolysis Temperature vs. Time Hydrolysis Reaction

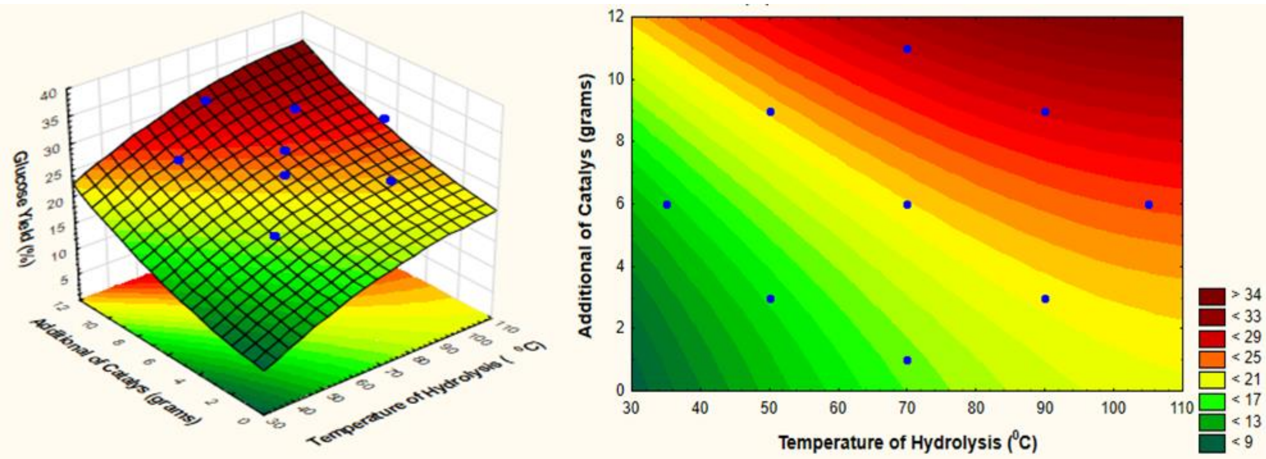

Figure 5. Graph Contour of Temperature Hydrolysis Reaction vs. Addition Amount of Catalyst

4. CONCLUSION

The process of cellulose hydrolysis reaction from corn husk using sulfonated activated carbon catalyst resulted in optimum operating conditions at 70^0C, 2 hours and 11 grams of catalyst. In that optimum conditions, glucose levels reached 31% with mathematical equations $Y = 25{,}0457 + 0{,}579x_1 - 0{,}111x_1^2 + 6{,}471x_2 + 2{,}798x_2^2 + 4{,}697x_3 + 2{,}965x_3^2 + 1{,}241x_1x_2 + 0{,}996x_1x_3 + 0{,}675x_2x_3$. Values of R^2 predicted with the model can approach the values obtained from the results of experimental which is 0,91545.

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