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Green Chemistry

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Diponegoro University (UNDIP),

Semarang State University (UNNES), Sebelas Maret University (UNS) and

Jenderal Soedirman University (UNSOED)

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Green Chemistry

Editors

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Preface to The Conference Proceedings

We are very pleased to introduce The 9th Joint Conference on Chemistry (9th JCC) held by Diponegoro University (UNDIP) On behalf of the Chemistry Consortium in Central Java, Indonesia. The JCC is an annual conference organized by the consortium of Chemistry Department of four universities in Central Java: Diponegoro University (UNDIP), Semarang State University (UNNES), Sebelas Maret University (UNS) and Jenderal Soedirman University (UNSOED); since 2006. The growing of environmental problems that persist to escalate worldwide has compelled us to select **"Green Chemistry"** as the leading theme of the 9th JCC.

We had 10 plenary speakers, 10 invited speakers and over 120 suitable papers from 11 countries were submitted for presentation at the conference. This required the program to be organized in five parallel sessions, each on a specific theme, to provide each paper with sufficient time for presentation and to accommodate all of them within the overall time allocated. One of the five sessions contained analytical chemistry. A second session was devoted to the theme of biochemistry. The third and fourth session were dedicated to physical and material chemistry. The fifth session was concerned with chemical education. These were well represented in the program of the conference and were clearly topics which continue to stimulate a global interest. The programs were chaired in a professional and efficient way by the session chairmen who were selected for their international standing in the subject.

All the papers went through a peer-review procedure prior to being accepted for publication in this book. These Proceedings present the permanent documentation of what was presented. They indicated the state of advancement at the time of writing of all aspects of this theme and will be very useful to all people in the field.

As a final point, it is appropriate that we record our thanks to our fellow members of the steering committee, organizing committee, and scientific committee. We are also indebted to those who served as chairmen. Without their support, the conference could not have been the success that it was. We also would like to express our sincere gratitude to all authors for their valuable contributions. We are thankful to the students of Chemistry Department Faculty of Science and Mathematics Diponegoro University especially to Maya and Fuad for their support during preparation of the manuscript.

Dwi Hudiyanti

Agustina L.N. Aminin

Adi Darmawan

Yayuk Astuti

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Board of Reviewers

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Proceedings of The 9th Joint Conference on Chemistry

Diponegoro University

Green Chemistry Section 1:

Material Chemistry

Optimization Process of H-Zeolite Catalyst Preparation with Surface Response Methods

Widayat[a,b], H. Susanto[a], H. Satriadi[a]

Abstract

H-zeolite have been produced from natural zeolites by chemical and physical activation process. The producing process has been optimized by the response surface method with variables process: X_1 is a dimensionless number value for the concentration of NH_4Cl solvent, and X_2 is a dimensionless number value for the diameter of natural zeolite. The response in this experiment is a surface area and pore diameter that analysed by Brunauer, Emmet dan Teller. Regression analysis was obtained determination coefficient R^2=0.84425. The optimization process produces a saddle-shaped contour with the critical value at the saddle area is -1.0759for X_1 and 0.8159 for X_2.

Keywords: Catalyst, surface response method, optimization and natural zeolite

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Introduction

Zeolite is an inorganic polymer, which is composed of monomer units and form of tetrahedral SiO_4 and AlO_4 (Bekkum et al, 1991). Based on the manufacturing process, zeolite can be divided into synthetic zeolite and natural zeolite. Natural zeolite has various types, which is currently approximately 40 types. in Indonesia, natural zeolite deposits are large enough and high enough purity. Areas that have zeolite mine are; South Lampung, Bayah, Cikembar, Cipatujah, Nangapada West Java, NTT Ende, Malang Regency, and Gunung Kidul Regency. Silica concentration is approximately 60% [1,2]. Zeolites are widely used in industry for processes such as catalytic cracking, alkylation processes, the process of dehydration and hydration. As a catalyst natural zeolites require a process, to have the large activity.

Some research has used a lot of natural zeolite as a catalyst, either directly or through the activation process. Utilization of natural zeolite directly as a catalyst was in the cooking oil cracking process conducted by Widayat [3,4]which the natural zeolite has the ability to cracking process of cooking oil and produce diesel fuel types. Utilization of natural zeolite through the activation process was in the conversion ABE compound into hydrocarbon [5], impregnation of the Cr [6], impregnation of the Fe_2O_3 [7]. Results developing of the metals Cr and Fe_2O_3 can increase the acidity level of the natural zeolite. Widayat and workers [1,2] have done the activation process with some of the methods and the results showed that the chemical treatment and continued by physical treatmentthat catalysts have higher surface area than the reaction of the alcohol compound template and ion exchange. Widayat and workersalso have done the catalytic H-zeolite catalyst test for ethanol dehydration process. The results showed that the H-zeolite catalyst has the ability to convert ethanol into diethyl ether products, ethylene and methanol with capabilities that are not much different from alumina catalyst [8-10].

Takahara and workers (2005) have researched utilization of mordenite type zeolite catalyst to produce ethylene [11]. Dealuminated mordenite type zeolite catalysts process has also been conducted by Chung (2007). Mordenite type of zeolite catalysts were dealuminated by acetic acid solvent. The results obtained showed that acid treatment can increase the pore size to the meso although that is not significant. Catalyst results dealumination process used for alkylation process of cumene compound [12]. Both researchers use synthetic mordenite catalyst which has a surface area that is already quite high. Ferrierite type zeolite was dealuminated by various concentrations of hydrochloric acid solution [14]. The results showed that increasing the concentration will increase the surface area of the catalyst. The results of catalysts activation can be used for xylene compound isomerization process. Widayat and workers (2009) research showed that the process of dealumination using ammonium chloride solvent was obtained H-zeolite catalysts with

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ethanol conversion better than hydrochloric acid solvent and EDTA[9].

The objective of the research is to obtain optimum condition on H-zeolite catalyst preparation from natural zeolite byusing surface response method.

Methodology

Materials

Natural zeolite was obtained from Gunung Kidul District. Hydrochloric acid has technical grade. $AgNO_3$ has analytical specification (Merck) and used as indicator of chloride ion on washing processing. The equipment for catalyst preparation shown in Figure 1.

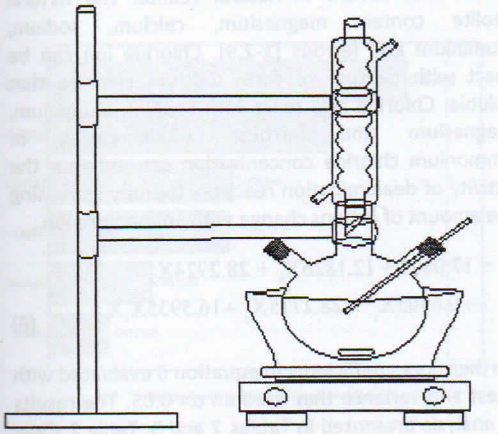

Figure 1. Catalyst preparation equipment

Catalyst Preparation

H-zeolite is produced from natural zeolite which is obtained from WonosariGunung Kidul district. H-zeolite was prepared with Widayat et.al. methods[8-10]. H-zeolite catalysts were produced with chemical and physical treatments include washing, drying and calcinations process. The chemical treatment was do in a three-neck flask which equipped with condenser, water heater, and magnetic stirrer.40 grams of natural zeolite added with ammonium chloride solution amounts 800 ml. The process was at reflux temperature for 10 hours. The washing process aims to remove the Cl^- ion. After the time is reached, the solution was filtered and washed with distilled water until chloride ions (Cl-) in the zeolite was zero. Then the solid zeolites dried in an oven at 110 °C temperature for 5 hours. Furthermore zeolite catalyst was calcined. The catalyst was placed in crucible and heated at a temperature of 500 °C which added by nitrogen gas flowing at a rate of 500 ml/min. The process was 5 hours. Once the time is reached, the furnace is cooled and the catalyst removed for analysis and testing of catalytic characteristics.

Catalyst Characteristic

The characterization of catalyst includes surface are, pore diameter and crystallography. Surface area and pore diameter were analysed in instrumentation laboratory Department of Chemical Engineering FTI Institute of Technology Bandung. The measurement of surface area and total pores volume was using *Quantachrome NOVA 1000 High Speed Gas Sorption Analyser* with P_o = 711.65 mmHg and nitrogen gas as adsorb gas/inert.

The crystals are characterized by X ray Diffraction (XRD) which analysed in Research Centre Institute of Technology Sepuluh Nopember Surabaya. The analysis crystallography used x-ray diffraction photographs a Philips 57.3 mm diameter camera, with Cu Kα radiation

Results and Discussion

The experiments data found include surface area and pore diameter. The data used calculated the increase in surface area of zeolite catalyst (Y_1) and the pore diameter decreases (Y_2). Y_1 and Y_2 was calculated with 1,2 equations.

$$Y_1 = \frac{A}{A_o} \tag{1}$$

$$Y_1 = \frac{D}{D_o} \tag{2}$$

Experiments Data

The experiment design used surface response methods with 2 variable processes. X_1 is coding of ammonium chloride concentration and X_2 is coding of initial diameter natural zeolite. The value for ammonium chloride concentration and initial diameter natural zeolite that used on experiment can be calculated with equation 3-4. The experiments data and variable presented in Table 1. The data analysed with Statistica software.

$$X_1 = \frac{C_{Am} - 3}{1} \tag{3}$$

$$X_2 = \frac{D_{in} - 0.425}{0.175} \tag{4}$$

Table 1. The result and experiments design of SRM

Variable		Real value		Y_1 (m^2/gr)/ (m^2/gr)	Y_2 A/A
X_1	X_2	M	D		
0	0	3	0.425	26.735	33.987
-1	1	2	0.25	40.003	94.993
0	0	3	0.425	7.444	95.098
1	1	4	0.6	101.943	31.641
1	-1	4	0.25	24.163	94.346
1.41	0	4.41	0.425	18.290	125.285
-1	-1	2	0.25	28.597	33.897
0	-1.41	3	0.178	11.274	122.070
-1.41	0	1.59	0.425	12.746	121.049
0	1.41	3	0.672	130.657	34.023

Where X_1 : (-1) 2 (0) 3 and (+1) 4
X_2 : (-1) 0.25 (0) 0.425 and (+1) 0.6
(-1) : below value (bv)
(0) : central value (cv)
(+) : upper value (uv)

Statistics Analysis

The results of statistical analysis include mathematical model, t test, analysis of variance, paretto analysis and validation of mathematical model. Polynomial equations to mathematical model the surface response methods follow:

$$Y = X_o + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \quad (5)$$

Where:
Y = predicted response
β_1, β_2: linear coefficient for 1, 2 variable
β_{11}, β_{22} : squared term coefficient for 1,2 variable
β_{12}: interactions variable coefficient
X_1:, X_2 .non dimensional number of independent variables

The results of analysis regression for equation 5 like presented in equation 6. Data that used for this analysis presented in table 1. in the mathematical model shows that the coefficient of linear variable, the variables X_2 more influencing than X_1. Variables X_2 and X_1 are positive which means increasing value of this variable can be increasing of Y variable. Increasing of ammonium chloride concentration can be increasing solubility chloride ion. Chloride ion reacts with cations in natural zeolite. The natural zeolite contain magnesium, calcium, sodium, aluminium and ferrous [1-2,9]. Chloride ion can be react with calcium to form Calcium chloride that soluble. Chloride also react with sodium, aluminium, magnesium and ferrous [1,2].Increasing of ammonium chloride concentration can enhance the activity of dealumination reaction, thereby increasing the amount of cations change with ammonium ion.

$$Y = 17.0895 + 12.1826X_1 + 28.2924X_2 + 0.6305X_1^2 + 28.2775X_2^2 + 16.5935X_1X_2 \quad (6)$$

Furthermore coefficients in equation 6 evaluated with t test and variance that used an α= 0.05. The results of analysis presented in Tables 2 and 3. Table 2 show that the all coefficients have a value of t (3) is greater than value of p, except for quadratic X_1 variable and blocking variable. The t(3) values in Table 2 is positive. It is indicate that the all variable (single, quadratic and interaction variable) have a direct relationship with Y. So it can be concluded all variable have a significant influence on Y.

Table 2. Results of regression coefficient and t test

Parameter	Regressn	Std.Err.	t(3)	p	-95.%	+95.%
Mean /Interc.	17.0895	20.1874	0.8465	0.4594	-47.1560	81.33497
Block	-4.0723	9.0281	-0.4511	0.6825	-32.8037	24.65915
X_1 (L)	12.1826	10.0937	1.2069	0.3139	-19.9402	44.30530
X_1 (Q)	0.6305	13.3527	0.0472	0.9653	-41.8639	43.12488
X_2 (L)	28.2924	10.0937	2.8029	0.0676	-3.8304	60.41512
X_2 (Q)	28.2775	13.3527	2.1177	0.1244	-14.2169	70.77188
1L by 2L	16.5935	14.2746	1.1624	0.3291	-28.8349	62.02191

F test is used to determine whether the independent variables simultaneously significant effect on the dependent variable. The degree of confidence that is used is 0.05[13-14]. TheF value has more than p for all parameter except X_1 quadratic variable and blocking.

F value = 0.0022 and p=0.9653 for X_1 quadratic variable.

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Table 3. Result of analysis of variance

Parameter	SS	df	MS	F	p
Blocks	165.84	1	165.836	0.2035	0.6825
X_1 (L)	1187.32	1	1187.320	1.4567	0.3139
X_1 (Q)	1.82	1	1.817	0.0022	0.9653
X_2 (L)	6403.67	1	6403.671	7.8566	0.0677
X_2 (Q)	3655.39	1	3655.392	4.4848	0.1244
1L by 2L	1101.38	1	1101.377	1.3513	0.3291
Error	2445.20	3	815.066		
Total SS	15697.91	9			

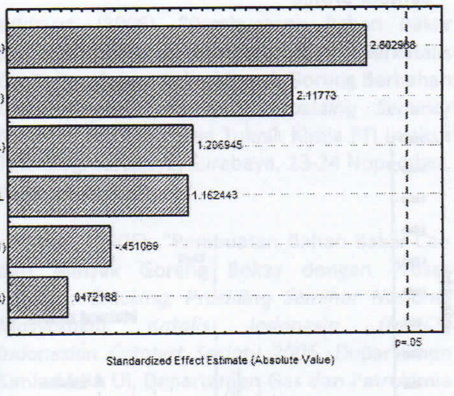


Figure 2. Pareto chart

Pareto diagram is histogram of the data that sorted based on categories of greatest to smallest. Thus, pareto diagrams can assist in efforts on the most important on process [13-14]. Pareto diagram of data processing results in this study are presented in Figure 2. Figure 2 show that a quadratic variable of X_1 has smaller value. So this variable can be neglected or not effect in this process. The all variable have histogram don't cross the line p = 0.05. Pareto chart show linier variable of X_2 has a histogram near with line p = 0.05. This is show a linier variable X_2 most effect in preparation catalyst and indicate that ammonium chloride concentration and initial diameter of natural zeolite is not optimum. This condition can be increase for obtain optimum condition.

Mathematical model in 6 equations was validated with experiments data. The result of this analysis presented in Figure 3. Mathematical model is less valid because the experimental data coincide with the results of the calculation very little. The coefficient determination obtain R^2=0.8442. This value is more than 0.7, that mathematical model can be used in experiment analysis or optimization process can be follow to obtain optimum condition.

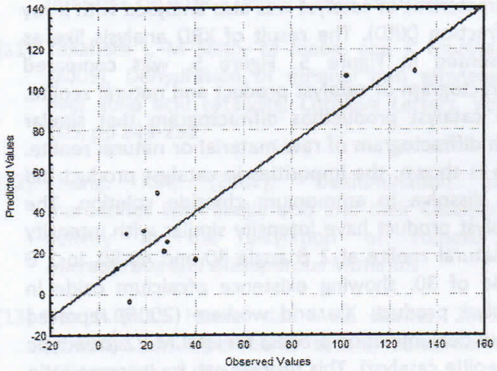


Figure 3. Graph of validation model mathematics

Optimization Results

The optimum conditions can be seen in Figure 4. Figure 4 is 3-dimensional graph (Figure 4. a)and surface contours graph (Figure 4. b). Figure 4. a /surface responsegraph consists of axis x, y, and z.x and y axis variables was independent variable (X_1 and X_2) and the z-axis was dependent variable and this research was the increasing of surface area (Y).Surface contour graph consists of axis x and y. in surface contours figuring in colour areas, so it can be seen from this graph the points of interaction of two variables is clear, where most interactions are optimal in the red region of the oldest. Figure 4 has the form a saddle point. This is shown the type of optimization process is already minimized. The critical value for each variable is shown in the following table:

Table 3. Critical value each variables

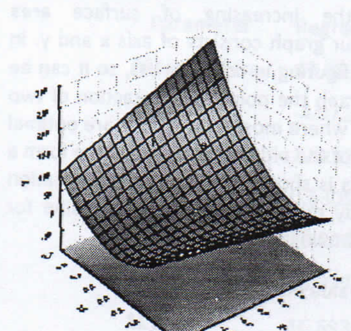
Solution: saddle point Predicted value at solution: 16.1730

variable	Observed	Critical	Observed
X_1	-1.4142	1.0759	1.4142
X_2	-1.4142	-0.8159	1.4142

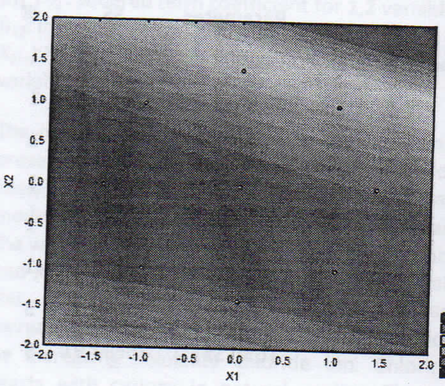
In table 3, the critical value of dimensionless numbers for each variable. Critical dimensionless value obtained for X_1 (ammonium chloride concentration) is 1.0759 and X_2 (initial diameter of natural zeolite) -0.8159. These values were input in 6 equations and obtained increasing of surface area is 16.1730%. These values were obtained in condition are ammonium chlorideconcentration 4.0750 M and initial diameter of natural zeolite 0.2822 mm.

X-ray Diffraction Analysis

The catalyst product commonly have grey colour. After calcination process, the colour of catalyst change to become yellow, white or grey. The catalyst products have a yellow and brown colour because the catalyst contain Fe, ZnPb and Cu component[15]. The characteristic of catalyst was also analysed with X-ray Diffraction (XRD). The result of XRD analysis like as presented in Figure 5. Figure 5. was compared diffractogram of catalyst product and natural zeolite. The catalyst producthas diffractogram that similar with diffractogram of raw material or natural zeolite. This is shown, the impurities in catalyst product did not dissolve in ammonium chloride solution. The catalyst product have intensity similar with intensity in natural zeolite at 2 θ angle 30 and 40-50. in 2 θ angle of 30, showing existence ofcalcium oxide in catalyst product. Xia and workers (2006) reported about dealumination process for HMCM-22 (new type of zeolite catalyst). This process can be increase ratio of SiO_2/Al_2O_3. The dealumination process by using acid (citric and oxalic acid) and steaming[16]. Boveri and workers (2006) also research about dealumination process on zeolite type mordenite. It has been found that catalysts obtained by combined steam dealumination and acid washing show a dramatic increase in the intrinsic activity and a significantly lower tendency to suffer deactivation when compared to the parent zeolite and samples obtained by acid treatments[17].



a. surface response



b. contour profile

Figure 4. Y_1 versus X_1 and X_2

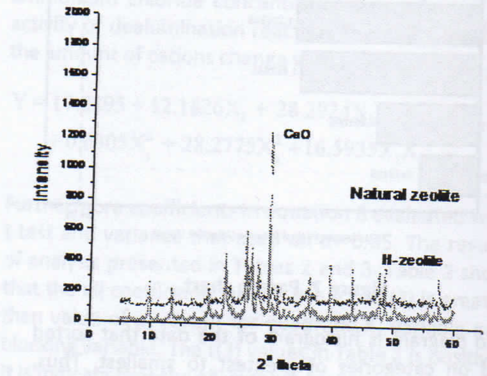


Figure 5. X-ray Diffractogram of catalyst product (green) and natural zeolite (red)

Conclusions

The Surface Response Method (SRM) employed for optimization and analysis of preparation of H-zeolite from natural zeolite. The experiments conducted in reactor and batch system. The minimum of increasing surface was obtained at 16.1730% that found at ammonium chloride concentration 4.0750 M and initial diameter natural zeolite 0.2822. The coefficient determination for mathematical model is 0.8442.

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