

THE OPTIMIZATION OF PRODUCTION ZEOLITE Y CATALYST FROM RHA BY RESPONSE SURFACE METHODOLOGY

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Abstract

Rice husk is the milling byproduct of rice and is a major waste product of the agriculture industry. Amorphous silica, commonly referred to as rice husk ash, was extracted from rice husk by acid leaching, pyrolysis, and carbon-removing processes. These properties make the ash a valuable raw material for many industries. This paper is study of synthesized of zeolite Y from rice husk ash. Zeolite Y synthesis is used for petroleum industry as expensive catalyst. Rice husk was calcined at temperature 700°C for two hours using furnace to produce pure silica. The composition of synthesized of zeolite Y from rice husk was 2.24 Na₂O:Al₂O₃:8SiO₂:112 H₂O. The gel solution was mixed at room temperature for 24 hours using autoclave. Then, the gel solution was heated with variable temperature and time crystallization. The product zeolite synthesis Y was filtered and washed with distilled water until pH lower than ten, than dried at oven. This product was analyzed with X-Ray Diffraction (XRD). From XRD analyze result indicated that from rice husk ash can produced zeolite synthesis Y which high crystallization degree. The optimum conditions for synthesis of zeolite Y from rice husk ash are temperature at 100°C for 48 hours, silicate at 20%, and aluminate at 10%.

Key words: response surface methodology, rice husk ash, synthesized, zeolite Y

Abstrak

Sekam padi merupakan hasil samping penggilingan beras dan limbah utama pada industri pertanian. Silika amorf, biasa disebut abu sekam padi, diekstraksi dari sekam padi dengan proses leaching asam, pirolisa, dan penghilangan karbon. Kandungan silika dalam abu sekam padi menjadikannya bahan baku yang bermanfaat untuk banyak industri. Makalah ini mempelajari pembuatan zeolit Y dari abu sekam padi. Zeolit Y sintetis digunakan untuk industri petroleum sebagai katalis yang harganya mahal. Sekam padi dikalsinasi pada suhu 700°C selama dua jam menggunakan furnace untuk menghasilkan silika murni. Komposisi zeolit Y sintetis adalah 2,24 Na₂O : Al₂O₃ : 8 SiO₂ : 112 H₂O. Larutan gel dicampur pada suhu kamar selama 24 jam menggunakan autoklaf. Kemudian, larutan gel dipanaskan dengan variabel suhu dan waktu kristalisasi. Produk zeolit sintetis Y disaring dan dicuci dengan air suling hingga pH kurang dari sepuluh, kemudian dikeringkan dengan oven. Produk tersebut dianalisis dengan X-Ray Diffraction (XRD). Dari hasil analisa X-Ray Diffraction (XRD) menunjukkan bahwa dari abu sekam padi dapat dibuat zeolit sintetis Y dengan derajat kristalisasi yang tinggi. Kondisi optimum sintesis zeolit Y dari abu sekam padi adalah pada suhu 100°C selama 48 jam, silikat 20%, dan aluminat 20%.

Kata kunci: response surface methodology, abu sekam padi, sintetis, zeolite Y

INTRODUCTION

The present world rice production of about 400 million tons per year will probably increase in the future, owing to the great increase in population, particularly in Asian countries. When rice grains are husked, the husks make up about 14 to 35%, depending on the variety of rice; since the husks have a low bulk weight of about 100 kg/m³, they take up 560

to 1400 million m³. In Indonesia, rice husk ash is produced in abundance after rice harvesting reason (Report of Indonesian Statistic Centre, 2002).

Chemical analysis of rice husks shows the following typical composition : 9% of water, 3.5% of Protein, 0.5% of Fats, 30-42% of Cellulose, 14-18% of Pentosan, and 14-30% of Mineral ash (Tutsek *et al*, 1977). Silica is the major constituent of rice husk ash

(RHA). The composition of the mineral ash is normally within the following limits: 92-97% of SiO_2 , 0.75-3.0% of Al_2O_3 , 0.17-2.0% of Fe_2O_3 , 0.36-3.0% of CaO , and 0.32-1.5% of MgO (Tutsek *et al*, 1977).

In addition, up to 30% carbon is found, depending on the degree and nature of combustion of the organic constituents before analysis. Because of its non-biodegradable property, the presence of the silica ash causes a number of problems to the environment. In order to solve this problem, useful applications of the waste product are desirable, including the large-scale synthesis of zeolite. Preliminary efforts were made in the synthesis of zeolite using this source. Thus, Bajpai *et al* (1981) obtained mordenite, Wang *et al* (1998) obtained ZSM-48 type zeolite, Ramli (1995); Ramli and Bahruji, (2003) obtained X and ZSM-5, and Prasetyoko *et al* (2006) obtained zeolite beta using RHA as a silica source. They were found that zeolite Beta started to form after 12 hours and the complete crystallization of zeolite Beta phase was achieved after 2 days.

Zeolite Y synthesis is used for petroleum industry as expensive catalyst (Scherzer J., 1990). Type Y zeolite is prepared using a minimum excess of reactants by a method wherein required sodium hydroxide, silica, alumina and water reactants are combined in multi-stage procedure to obtain a uniform fluid reaction slurry. The procedure permits the efficient commercial production of high quality type Y zeolite and minimizes the formation of excess silicate containing by-product effluent (Vaughan *et al*, 1979). Sand can be used as a source of silica in the production of zeolite Y by activating the sand with from 50 to 2000 ppm alumina (Kostinko *et al*, 1981). Rice husk was calcined at temperature 700°C for two hours using furnace to produce pure silica. This paper is optimization study of synthesized of zeolite Y from rice husk ash by response surface methodology.

Response surface methodology (RSM) is a method to determine the optimum condition of a process. RSM has similarity with regression analysis. In regression analysis, empirical mathematical model are derived from the experiment data. RSM is a set of techniques designed to find the optimum value of the response and the influencing factors. RSM technique has been successfully applied in the field of quality experimental work (Amin and Anggoro, 2004; Kasankala *et al*, 2007; Mundra *et al*, 2007; Pio and Macedo, 2007; K \ddot{u} orbahti *et al*, 2007; Macedo and Pio, 2007; Ushakumari *et al*, 2007; Psomas *et al*, 2007; Anggoro and Istadi, 2008).

This article estimates the optimization of temperature, % of silicate and % of aluminate on crystallinity of Y zeolite from RHA using response surface methodology (RSM). The temperature, % silicate and % aluminate concentration used were 70°C , 90°C , 110°C ; 10%, 20%, 30% and 5%, 10%, 15%, respectively, resulting in a two-level experimental design, with 16 experiments. Empirical parameters were estimated with standard least-square

procedure, using the Design Expert Statsoft software "Statistica" version 6.0.

EXPERIMENTAL METHOD

The raw material rice husk was obtained from a rice mill. Their major constituents are cellulose, lignin and ash. Amorphous silica, commonly referred to as rice husk ash (RHA), was extracted and purified from rice husk by acid leaching, pyrolysis, and carbon-removing processes. In this experiment, the raw rice husk was washed with distilled water to remove adhering soil and was then dried at 100°C in an air oven. The dried rice husk was refluxed with 3N HCl solution in a glass round-bottomed flask at 100°C within a thermostat for 1 h. After leaching, the husk was thoroughly washed with distilled water and dried.

The composition of synthesized of zeolite Y from rice husk was $2.24 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 8 \text{ SiO}_2 : 112 \text{ H}_2\text{O}$. The gel solution was mixed at room temperature for 24 hours using autoclave, as shown Figure 1. Then, the gel solution was heated with variable temperature and time crystallization. The product zeolite synthesis Y was filtered and washed with distilled water until pH lower than ten, than dried at oven. This product was analyzed with *X-Ray Diffraction* (XRD). All of the products were characterized by powder X-ray diffraction (XRD) for the crystallinity and purity of the solid materials, using a Siemens 5000 diffractometer with the Cu Ka radiation as the diffracted monochromatic beam. The pattern was acquired in the 2θ $0-60^\circ$ range.



Figure 1. Stainless steel Autoclave with stirred

The actual design experiment is shown in Table 1. It was found that a total of 16 runs were necessary in order to optimize processing parameters for enhanced crystallinity of zeolite. The design experiment was carried out using the Design Expert Statsoft software "Statistica" version 6.0 2001.

Table 1. The experiment design with difference temperature, silicate, and aluminate

Run No	Temperature	Si	Al
1	70	10	5
2	70	10	15
3	70	30	5
4	70	30	15
5	110	10	5
6	110	10	15
7	110	30	5
8	110	30	15
9	90	20	10
10	54	20	10
11	125	20	10
12	90	2.3	10
13	90	37.6	10
14	90	20	1.2
15	90	20	18.8
16	90	20	10

RESULTS AND DISCUSSION

Effect of Time and Temperature of Crystallization

X-ray diffractogram of commercial zeolite Y (CY) and synthesis zeolite Y (Y1, Y2, and Y3) is shown in Figure 2.

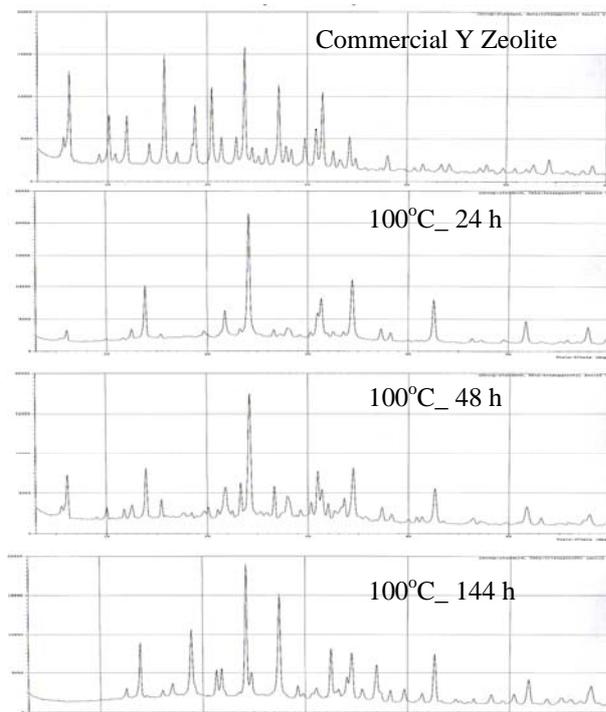


Figure 2. X-Ray Diffractogram of Four Samples

It indicates that all samples have zeolite Y crystal, but have different crystallinity percent. Percent of crystallinity and unit cell are calculated by following equation (Glusker and Trueblood, 1972):

$$\text{Crystallinity (\%)} = \frac{\text{Intensity of peak (sample)}}{\text{Intensity of peak (s tandard)}} \times 100\%$$

$$\text{Unit cell} = n \lambda / 2 \sin \theta$$

Where : $(\lambda \text{ CuK}\alpha = 1.54060 \text{ \AA})$
 $\theta (hkl) = (n00), (0n0), (00n)$

The unit cell and solid crystallinity of commercial Y zeolite and synthesis Y zeolite (Y₁, Y₂, and Y₃) with difference of crystallization time are tabulated in Table 2. The unit cells of all samples are nearly similar, while the solid crystallinity of all synthesis Y zeolite (Y₁, Y₂ and Y₃) is lower than commercial Y zeolite.

Table 2. Unit Cell and Percent of Four Samples

Sample	Unit Cell (Å)	% Crystallinity
Commercial Y Zeolite	24.6	100.0
Y1 (100°C_ 24 h)	25.6	37
Y2 (100°C_ 48 h)	24.4	74.0
Y3 (100°C_ 144 h)	24.4	39.0

Time of crystallization can be optimized in the synthesis of zeolite. In system that produce only one zeolitic phase, optimizing maximum crystallization over a short span of time is important from a practical standpoint, and is accomplished by applying knowledge of the contribution of the many component in the synthesis mixture to minimize the crystallization time. Crystallization parameters must be adjusted to minimize the production of the other phases while also minimizing the time needed to obtain the desired crystalline phase (Szostak, 1989).

X-ray diffractograms of commercial Y zeolite and synthesis Y zeolite (Y₂ and Y₄) with difference of crystallization temperature are shown in Figure 3. It indicates that all samples have Y zeolite crystal, but have different the solid crystallinity percent. Crystallization of all synthesis Y zeolite is lower than commercial zeolite Y, as tabulated in Table 3.

Temperature influences several factors in zeolite synthesis. It can alter the zeolite phase obtained as well as change the induction period before the start of crystallization. This induction period decreases with increasing temperature. For any mixture as the temperature increases, the rate of crystallization increases. As the temperature increases, the solubility of the aluminate and silicate species increase, causing a shift in the concentration of the liquid phases (Szostak, 1989).

Optimization

The solid crystallization of all samples with difference concentration of silicate and aluminate is lower than commercial Y zeolite. The different behavior shown between the silica RHA and the commercial silica is attributed again to the form of silicate anions in the initial mixture. The crystallization of zeolite starts from the liquid phase that leads to the crystallization of zeolite Y depends on the silica source.

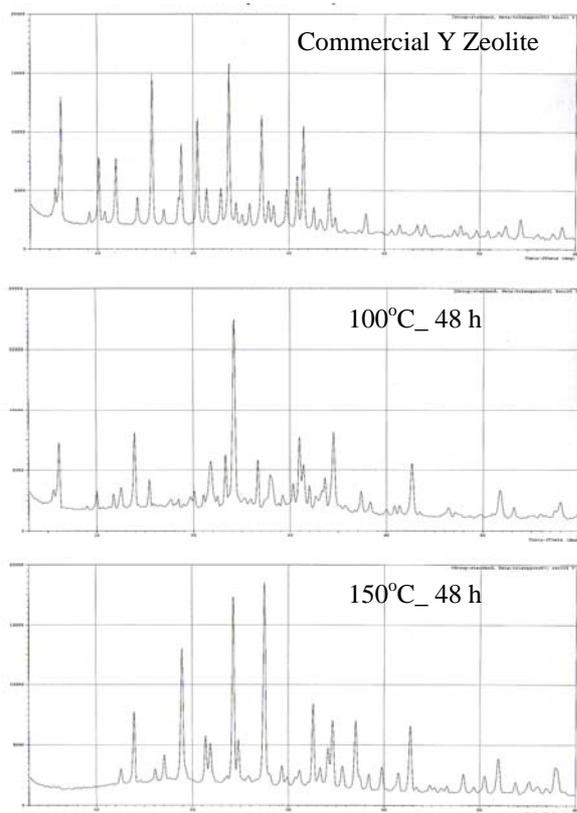


Figure 3. X-Ray Diffractogram of Four Samples

Table 3. Unit Cell and Percent of Four Samples

Sample	Unit Cell (Å)	% Kristalinitas
Commercial Y Zeolite	24.6	100.0
Y2 (100°C_48 jam)	24.4	74.0
Y4 (150°C_48 jam)	24.3	48.0

In both cases, the different solubilities of the silicate anions and the resulting interaction with the aluminate anions presence in the solution contribute to the different behaviors of both types of silica (Szostak, 1989).

The optimum condition (100°C and 24 hours), which obtained in early experiments, is used to study the effect of silicate and aluminate. For this purpose, the experiment design and results is tabulated in Table 4. From Table 4, the effect temperature and silicate on zeolite Y synthesis can be obtained by pareto chart analysis, as shown Figure 4. Figure 4 indicated that the temperature has more effect than silicate.

The optimum condition between temperature and silicate for zeolite Y synthesis can be obtained by 3D analysis using statistica 6.0 software, as shown Figure 5. Figure 5 indicated that the optimum condition for synthesis zeolite Y is the temperature at 100°C and silicate at 20%.

Table 4. The solid crystallinity of zeolite with difference temperature, silicate, and aluminate

Run No	Temperature	Si	Al	The solid crystallinity
1	70	10	5	70
2	70	10	15	75
3	70	30	5	78
4	70	30	15	80
5	110	10	5	82
6	110	10	15	85
7	110	30	5	88
8	110	30	15	78
9	90	20	10	95
10	54	20	10	72
11	125	20	10	76
12	90	2.3	10	80
13	90	37.6	10	75
14	90	20	1.2	80
15	90	20	18.8	78
16	90	20	10	94

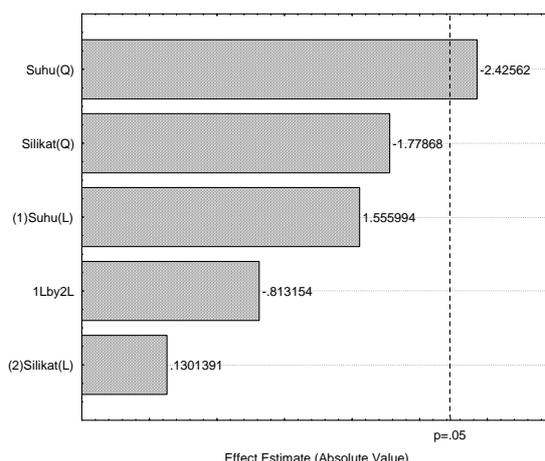


Figure 4. Pareto chart analysis for temperature versus silicate

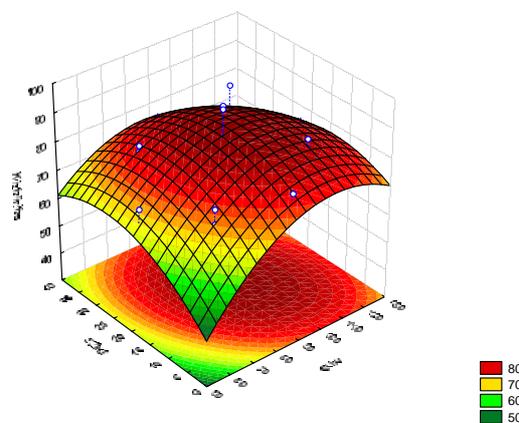


Figure 5. The 3 D analysis for temperature versus silicate

From Table 4, the effect temperature and aluminate on zeolite Y synthesis can be obtained by pareto chart analysis, as shown Figure 6. Figure 6 indicated that the temperature has more effect than aluminate. The optimum condition between temperature and aluminate for zeolite Y synthesis can be obtained by 3D analysis using statistica 6.0 software, as shown Figure 7. Figure 7 indicated that the optimum condition for synthesis zeolite Y is the temperature at 100°C and aluminate at 10%.

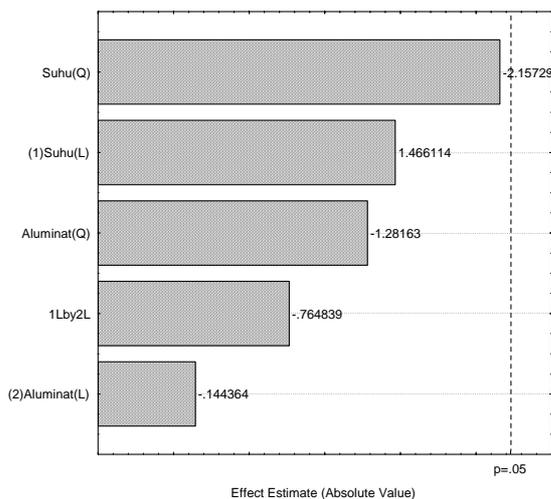


Figure 6. Pareto chart analysis for temperature versus aluminate

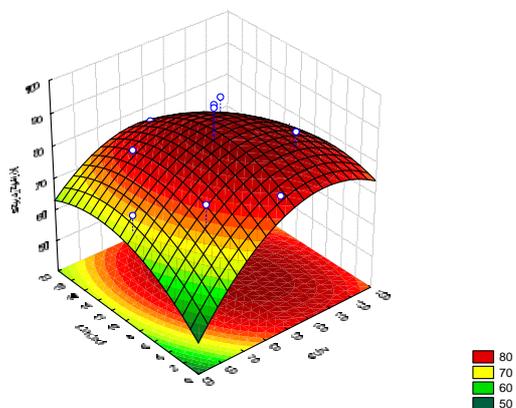


Figure 7. The 3 D analysis for temperature versus aluminate

From Table 4, the effect silicate and aluminate on zeolite Y synthesis can be obtained by pareto chart analysis, as shown Figure 8. Figure 8 indicated that the crystallinity of zeolite Y synthesis not depend on both silicate and aluminate. The optimum condition between silicate and aluminate for zeolite Y synthesis can be obtained by 3D analysis using statistica 2002 software, as shown Figure 9. Figure 9 indicated that the optimum condition for synthesis zeolite Y is the silicate at 20% and aluminate at 10%.

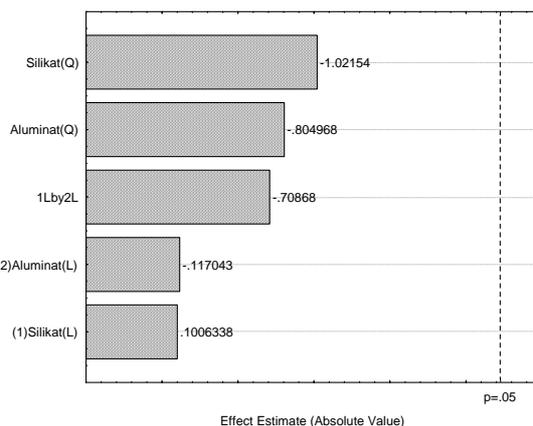


Figure 8. Pareto chart analysis for silicate versus aluminate

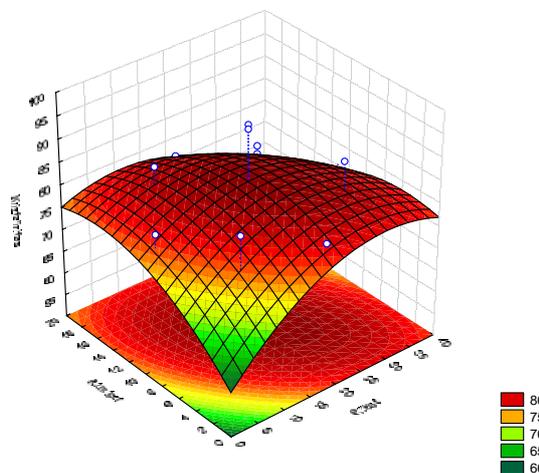


Figure 9. The 3 D analysis for silicate versus aluminate

CONCLUSIONS

From the experimental result for synthesis zeolite Y using rice husk ash, characterization analysis using X-Ray Diffraction (XRD), and optimization analysis using statistica 6.0 software can conclude that rice Husk Ash is potential silica sources for produce synthesis zeolit Y. Temperature and time of synthesis are not affected of unit cells length, but affected of percent of the solid crystallinity. Temperature at 100°C and time at 48 hours are the best operation condition of synthesis zeolite Y. The optimum conditions for synthesis of zeolite Y from rice husk ash are temperature at 100°C, silicate at 20%, and aluminate at 10%.

ACKNOWLEDGMENTS

The authors express their gratitude to the Indonesian's Ministry of National Education, Directorate General of Higher Education for financial support of this work by *Hibah Kompetensi Program 2008*.

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