SYNTHESIS OF FAUJASITE WITH HIGH THERMAL STABILITY FROM FLY ASH

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ABSTRACT

Faujasite was hydrothermally synthesized from fly ash at 100^oC in alkaline solution by reflux with various concentration of HCl and fusion with NaOH (weight ratio of NaOH/fly ash = 1.2) pretreatments. Thermal stability of faujasite from fly ash was tested at $400\text{-}900^oC$ and was compared with commercial zeolite Y. The solid products were characterized by X-ray diffraction method, chemical analysis and nitrogen adsorption (BET). Results showed that synthesis of faujasite from fly ash via fusion pretreatment with NaOH has resulted faujasite selectively, however, the faujasite obtained still showed relatively low thermal stability due to its relatively low of Si/Al mol ratio. Reflux pretreatment with HCl was an effective method not only to increase the Si/Al mol ratio but also to decrease the metal impurities in the fly ash sample. Synthesis of faujasite from fly ash via combination of reflux with HCl and fusion with NaOH pretreatment has resulted faujasite selectively with higher Si/Al mol ratio. Faujasite obtained from fly ash via combination of reflux with HCl and fusion with NaOH pretreatment showed thermal stability as high as commercial zeolite NaY.

Keywords: *fly ash, reflux with HCl, fusion with NaOH, faujasite and thermal stability*

INTRODUCTION

Recently, many researchers showed that various types of zeolites could be produced from fly ash by hydrothermal reaction in alkaline solution. Although zeolites have been synthesized from fly ash, most previous studies, showed that the final products were generally a mixture of zeolite materials, such as zeolite P, zeolite A, faujasite, analcime, and hydroxysodalite [1-4]. Since the zeolite materials obtained from fly ash usually contain undesired impurity phases, efforts to achieve the single-phase (selective) zeolites are very important. Attempts to convert fly ash into selective zeolite have been done using many pretreatments before hydrothermal reaction such as fusion with NaOH [5-6] as well as ageing and seeding [7].

By fusion with sodium hydroxide, most of the fly ash particles were converted into sodium salts such as silicate and aluminate, from which hydrothermal reaction without stirring favorably resulted in the formation of faujasite with crystallinity as high as 62% of commercial zeolite X [5]. Although this method can selectively produce faujasite type zeolite (zeolite X), it was clear that the crystallinity of the product was not high enough.

Based on previous study [5], it has been developed a general method for conversion of different fly ashes with a wide range of chemical compositions into zeolites as ion exchangers by separating the supernatant from the sediment of fused fly ash solution [6]. It was found that the supernatant of the dissolved fused fly ash solution could produce higher purity faujasite. The improved result that containing 83.1% of commercial zeolite X was probably related to the fact that unreacted fly ash has been separated from the supernatant. Previously, zeolite were precipitated within the fly ash solutions and mixed with the fly ash therefore, it was difficult to separate the precipitated zeolites from the unreacted fly ash. The formation of zeolites from the supernatant of the fused fly ash solution demonstrated that zeolites could be separated from unreacted fly ash.

Other method to be used for achieving selective zeolite from fly ash was seeding and ageing for synthesizing zeolite Y from fly ash [7]. Seeding and ageing are two important methods in zeolite synthesis in order to obtain a pure crystalline phase. The maximum crystallinity of zeolite Y obtained was 72%. Most of the Si and Al components in fly ash could be effectively transformed into zeolite Y in the presence of seeds but not the mineral phase like mullite.

Although selective faujasite has been synthesized by fusion as well as seeding and ageing pretreatments, however, the results still showed relatively low crystallinity for fusion method and showed an impurity phase like mullite for seeding and ageing method. Therefore, attempts to convert fly ash into faujasite without any impurities

of other zeolite phases and initial phases as well as having higher crystallinity are still clearly challenging. For catalytic application, the faujasite obtained not only have to show a higher thermal stability but also the presence of metal impurities in the faujasite should be controlled. The zeolite with higher Si/Al mol ratio showed a higher thermal stability, therefore the resulted faujasites should have a higher Si/Al mol ratio (silicon rich-faujasite or zeolite Y, Si/Al mol ratio=1.5-3.5).

Without reflux pretreatment of fly ash with HCl, faujasite has been selectively resulted by fusion pretreatment with NaOH followed by hydrothermal reaction. Although the increase of the Si/Al mol ratio in the fly ash sample could be done by direct addition of silicon source such as sodium silicate, it was reported that the addition of sodium silicate solution to increase the Si/Al mol ratio of faujasit was not recommended because it leads to the formation of zeolite P and hydroxysodalite instead of faujasite [8]. In this investigation, synthesis of faujasite-type zeolite from fly ash was conducted by hydrothermal reaction in alkaline solution via combination of reflux with HCl and fusion with NaOH. Reflux with HCl was an effective pretreatment to increase Si/Al mol ratio and to decrease metal impurities in the fly ash [9-10].

EXPERIMENTAL

The fly ash sample was taken from Suralaya Power Plant, Serang-Banten, Indonesia. A mixture of 10 g of fly ash sample and 100 mL HCl (the concentration of HCl was varied) was refluxed at 90°C for 1 hour with magnetically stirring. The solid was repeatedly washed with water and dried at 100°C overnight. The refluxed-fly ash was added with NaOH pellets (the NaOH/fly ash weight ratio was 1.2), milled, and subsequently heated in a nickel crucible at 550°C for 1 hour. The resultant fused-refluxed-fly ash was cooled to room temperature, milled again, and then stirred magnetically in a Teflon beaker with 100 mL water overnight. The slurry was heated in stainless steel autoclave with Teflon beaker inside under autogenous pressure at 100°C for 72 hours without any stirring. After cooling to room temperature, the resulting solid product was recovered by filtration on a Buchner funnel, washed repeatedly with water and dried in an oven at 100°C overnight.

The chemical composition of the fly ash, the fly ash after reflux pretreatment (refluxed-fly ash), and the zeolites obtained were determined by chemical analysis. Silicon and aluminum were measured by UV-Vis spectrometer (Hitachi 150-20 UV-Visible) whereas Fe, Ca, K and Na were measured by atomic absorption spectrometer (Nippon Jarrel Ash AA782). X-ray diffraction (XRD) patterns were obtain by powder method using Ni-filtered CuKα radiation at 40 kV and 30 mA with scanning speed of 4°/minute (Shimadzu XRD-6000). Samples were normally scanned in the 2θ range of 5 to 40°. Nitrogen adsorption measurements were performed on a NOVA 1200 microanalyzer (QUANTACHROME) at liquid nitrogen temperature. The sample was normally outgassed at 200°C for at least 4 hours under vacuum (10^{-4} torr). The sample was then subjected to automatic analysis.

RESULTS AND DISCUSSION

Figure 1 showed the XRD pattern of original fly ash from Suralaya Power Plant, Serang-Banten, Indonesia. It can be seen that the predominant crystalline components of original fly ash were quartz (SiO_2) and mullite ($Al_6Si_2O_{13}$) with traces of hematite (Fe_2O_3) and magnetite (Fe_3O_4).
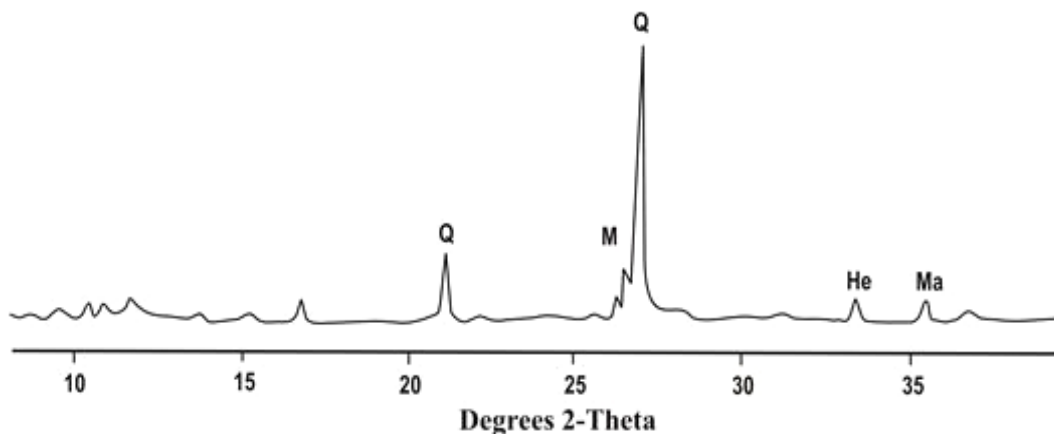

Figure 1 X-ray diffraction pattern of original fly ash from Suralaya Power Plant (Q=quartz, M=mullite, H=hematite, and Ma=magnetite)

Table 1 Chemical composition of original fly ash from Suralaya Power Plant

Oxide	Content (wt %)
SiO_2	55.64
Al_2O_3	31.48
Fe_2O_3	4.94
K_2O	1.49
CaO	1.41
Na_2O	1.02

Table 2 The influence of reflux with various HCl concentrations on the chemical composition of fly ash

HCl concentration (M)	Si/Al mol ratio of fly ash	Decrease of metal oxide content (wt %)[a]			
		Fe_2O_3	K_2O	CaO	Na_2O
0[b]	1.50	-	-	-	-
1	2.18	67.0	8.7	61.0	16.4
3	2.50	73.6	10.7	84.2	25.4
5	2.79	77.3	11.0	85.0	27.1
7	2.79	79.2	11.4	90.2	26.2
9	2.80	82.0	14.1	89.8	19.7

[a]Relative to their content in Table 1; [b]Without reflux pretreatment

Chemical composition of original fly ash from Suralaya Power Plant was shown in Table 1. The predominant components of Suralaya fly ash were silicon and aluminum with Si/Al mol ratio of 1.5 (Table 2). The content of other components was less than 5 percent. Based on the chemical composition, Suralaya fly ash can be classified into Class F fly ash. According to ASTM C204 [11], total calcium in Class F fly ash typically ranges from 1 to 12 %, mostly in the form of calcium hydroxide, calcium sulfate, and glassy components in combination with silica and alumina.

Influence of Reflux with Various HCl Concentrations on the Chemical Composition of Fly Ash

The proposed result of the synthesis was faujasite-type zeolites with Si/Al mol ratio of 1.5-3.5 (zeolite Y) from fly ash with Si/Al mol ratio of 1.5 (see Table 2). It seems that fly ash was lack of silicon source, therefore, attempt to increase the Si/Al mol ratio in the fly ash is needed. In this investigation, the increase of the Si/Al mol ratio was conducted by reflux pretreatment with various HCl concentrations (1-9M).

Table 2 showed that reflux pretreatment with HCl was an effective method not only to increase the Si/Al mol ratio but also to decrease the metal impurities in the fly ash sample. The Si/Al mol ratio of fly ash significantly increased with the increase of HCl concentration (1-5M). Further increase of HCl concentration (5-9M), the Si/Al mol ratio of fly ash remained constant. The relatively constant Si/Al mol ratio of fly ash at higher HCl concentration may be due to the amorphous phase in fly ash has already decomposed. Therefore, the remainder phases were only quartz and mullite with higher stability. The higher stability of quartz and mullite against HCl has also been investigated [7].

The metal impurities in fly ash such Fe^{3+}, Ca^{2+}, K^+ and Na^+ can interfere the synthesis process of zeolites [12]. When Ca^{2+} ions were present in the reaction mixture, their high affinity versus silicate species leads to precipitation and stabilization of silicate. The excess of Na^+ leads to the formation of denser zeolites such as sodalite and K^+ can depolymerize in crystallization. In addition, Fe^{3+} can precipitate OH^- species to form $Fe(OH)_3$, in which their existence in zeolites is unexpected. Reflux with HCl, therefore, can be used to decrease the concentration of metal impurities in fly ash in order to synthesize zeolite selectively.

Synthesis of Faujasite from Fly Ash via Combination of Reflux Pretreatment with HCl and Fusion Pretreatment with NaOH

Without reflux pretreatment of fly ash with HCl, faujasite has been resulted by fusion pretreatment with NaOH followed by hydrothermal reaction [8]. Although faujasite has been selectively resulted with high crystallinity, however, it has quite low both Si/Al mol ratio (see Table 3) and thermal stability (see Figure 2). The faujasite structure drastically destroyed after calcination at 450°C as shown by its crystallinity of 35% compared to the crystallinity before calcination. The relatively low thermal stability of the faujasite obtained was probably caused by its lower Si/Al mol ratio.

X-ray diffraction pattern of the zeolite obtained from refluxed-fly ash with various concentration of HCl showed faujasite without any impurity phases as demonstrated in Figure 3.
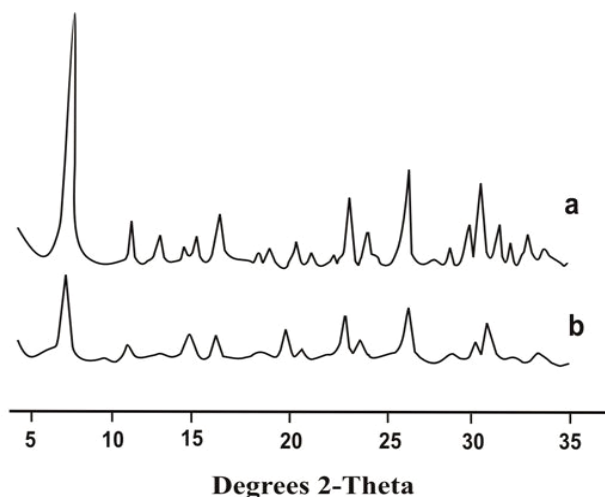

Figure 2 X-ray diffraction pattern of faujasite obtained by fusion with NaOH/fly ash weight ratio of 1.2 for hydrothermal time of 72 hours (a) before and (b) after calcination at 450°C
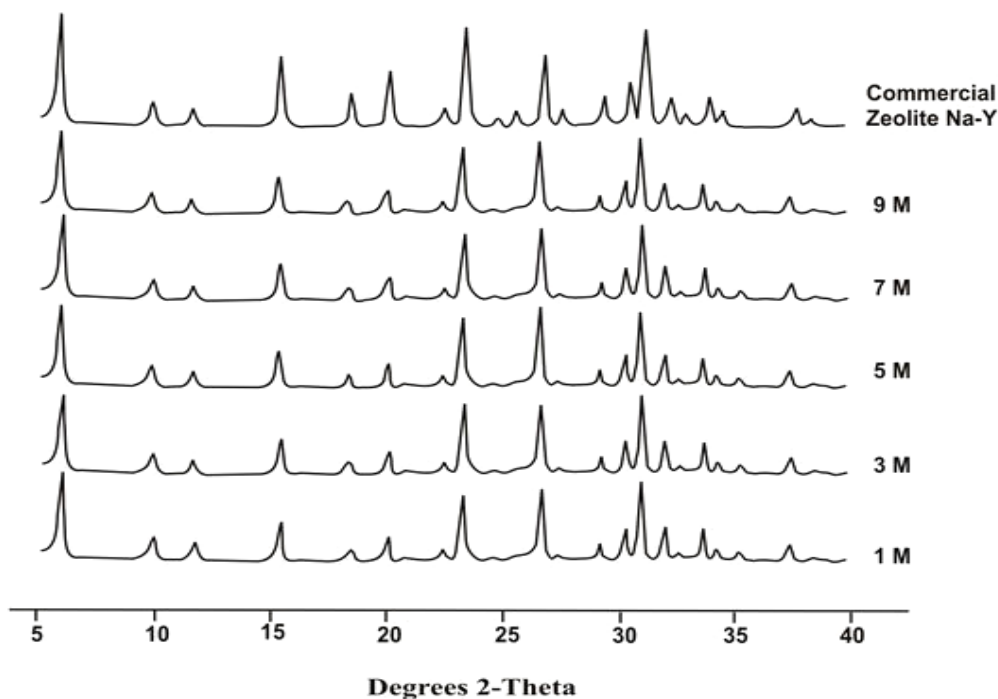

Figure 3 X-ray diffraction pattern of the zeolite obtained for hydrothermal time of 72 hours by combination of reflux pretreatment with various HCl concentration and fusion with NaOH/fly ash weight ratio of 1.2

Table 3 The influence of reflux pretreatment with various HCl concentrations on the crystallinity, Si/Al mol ratio, and specific surface area of the faujasite obtained for hydrothermal time of 72 hours (fusion pretreatment with NaOH/fly ash weight ratio of 1.2)

HCl Concentration (M)	Crystallinity of faujasite (%)	Si/Al mol ratio	Specific surface area (m^2/g)
0[a]	91.88	1.15	420.54
1	64.28	2.66	452.88
3	70.05	2.61	427.23
5	97.06	2.68	452.93
7	68.45	2.56	428.99
9	62.94	2.59	412.69
Commercial zeolite NaY[b]	100.00	3.31	569.76

[a] *Without reflux pretreatment;* [b] *Commercial zeolite NaY was used as reference*

Table 4 Crystallinity of faujasite and commercial zeolite NaY against heat treatment at various temperatures

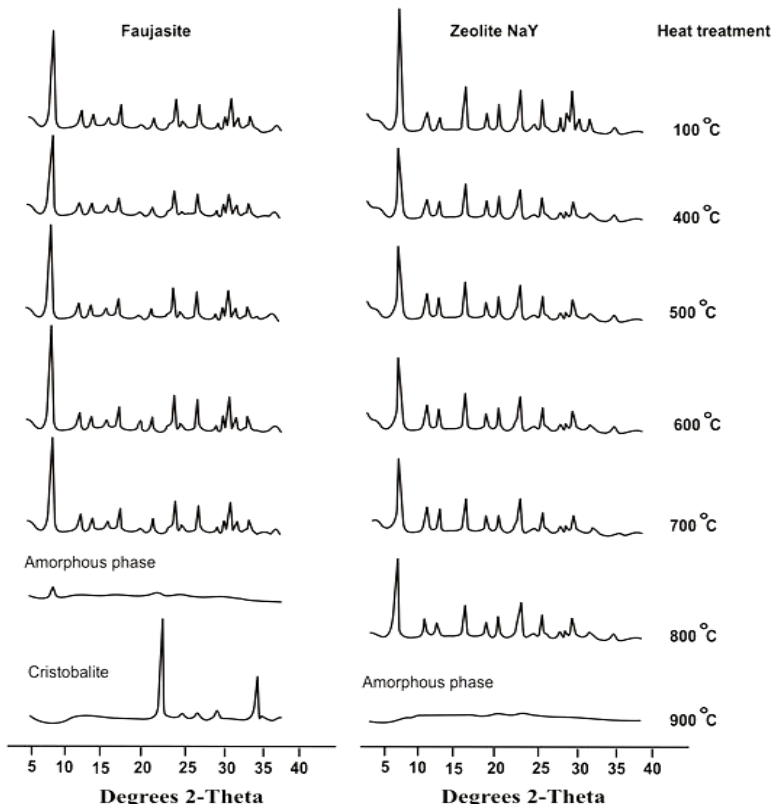| Temperature (^{o}C)	Crystallinity (%)	
	Faujasite[a]	Commercial zeolite NaY
100	97.06	100.00
400	74.75	65.51
500	88.65	70.22
600	94.91	66.67
700	92.90	72.00
800	3.37	76.55
900	0	0

[a] *Commercial zeolite NaY was used as reference*

Figure 4 X-ray diffraction patterns of faujasite (synthesized at 100°C for 72 hours via reflux with 5M HCl and fusion with NaOH/fly ash ratio of 1.2 pretreatment) and commercial zeolite NaY against heat treatment at various temperatures

The influences of reflux pretreatment with various HCl concentration on the crystallinity, Si/Al mol ratio, and specific surface area of the faujasite obtained (fusion pretreatment with NaOH/fly ash weight ratio of 1.2) were shown in Table 3. Figure 3 and Table 3 showed that the increase of HCl concentration (1-5M) resulted the higher crystallinity of faujasite and the highest crystallinity (97.06%) was achieved at the use of 5M HCl. At higher HCl concentration (7-9M), the crystallinity of faujasite gradually decreased.

Table 3 showed that the Si/Al mol ratios of the faujasite obtained by reflux pretreatment with various HCl concentrations were quite similar (2.56-2.68). Faujasite obtained by reflux pretreatment with various HCl concentrations also showed a quite similar specific surface area (412.69-452.93 m^2/g). Both the Si/Al mol ratios and the specific surface areas of the faujasite obtained with reflux pretreatment were generally lower compared to commercial zeolite NaY but were higher compared to faujasite without reflux pretreatment. The higher Si/Al mol ratios of faujasite obtained with reflux pretreatment compared to faujasite without reflux pretreatment may be due to the higher Si/Al mol ratio of refluxed fly ash. The relatively low specific surface area of faujasite from fly ash compared to commercial zeolite NaY may be due to the presence of unreacted fly ash together with faujasite. Based on the results shown in Table 3, it revealed that reflux pretreatment with 5M HCl followed by fusion pretreatment with NaOH/fly ash weight ratio of 1.2 showed the optimum condition for the synthesis of faujasite from fly ash.

Thermal Stability of Faujasite Obtained via Combination of Reflux and Fusion Pretreatment

The stability of faujasite structure against heat treatment (thermal stability) from 100-900°C was monitored by XRD technique. In this investigation, thermal stability was presented as XRD crystallinity in which the higher crystallinity showed the higher thermal stability. The XRD pattern and crystallinity of faujasite (synthesized at 100°C for 72 hours via reflux with 5M HCl and fusion with NaOH/fly ash ratio of 1.2 pretreatment) compared to commercial zeolite NaY against heat treatment were shown in Figure 4 and Table 4, respectively.

XRD pattern presented in Figure 4 proved that structural damage of both faujasite and commercial zeolite NaY occurred at 400°C as indicated by the decrease of peak intensity. The higher decrease of peak intensities (the lower crystallinity as shown in Table 4) indicated the higher structural damage.

Although at initial stage (100°C) faujasite has a lower crystallinity, however, at 400-700°C faujasite showed a higher crystallinity than commercial zeolite NaY.

The relatively higher crystallinity (lower structural damage) of faujasite compared to commercial zeolite NaY against heat treatment at 400-700°C may be due to the presence of amorphous phase (unreacted fly ash) together with faujasite that probably rearranged into aluminosilicate framework during the heat treatment. Complete structural damage of faujasite occurred over 800°C as indicated by transformation of all faujasite into amorphous phase. Furthermore, the appearance of cristobalite at 900°C showed that the available amorphous phase rearranged into more stable phase.

In contrast, commercial zeolite NaY still showed a higher structural stability (76.55% crystallinity) at 800°C than that of faujasite from fly ash. Complete structural damage of commercial zeolite NaY into amorphous phase occurred at 900°C. The relatively higher structural stability of commercial zeolite NaY at 800°C compared to faujasite clearly proved that commercial zeolite NaY had higher Si/Al mol ratio (3.31) than faujasite from fly ash (2.68) as presented in Table 4. This phenomenon was in a good agreement with the previous investigation [13] in which the similar zeolite structure with higher Si/Al mol ratio showed a higher thermal stability.

CONCLUSION

1. Synthesis of faujasite from fly ash via fusion pretreatment with NaOH has resulted faujasite selectively, however, the faujasites obtained still showed relatively low thermal stability due to relatively low Si/Al mol ratio.
2. Reflux pretreatment with HCl was an effective method not only to increase the Si/Al mol ratio but also to decrease the metal impurities in the fly ash sample.
3. Synthesis of faujasite from fly ash via combination of reflux with HCl and fusion with NaOH pretreatment has resulted faujasite selectively with higher Si/Al mol ratio. Faujasite obtained from fly ash via combination of reflux with HCl and fusion with NaOH pretreatment showed thermal stability as high as commercial zeolite NaY.

REFERENCES

1. Lin, C.-F. and Hsi, H.-C., 1995, *Environ. Sci. Technol.*, 29(4), 1109-1117.

2. Singer, A. and Berkgaut, V., 1995, *Environ. Sci. Technol.*, 29(7), 1748-1753.
3. Amrhein, C., Haghnia, G. H., Kim, T. S., Mosher, P. A., Gagajena, R. C., Amanios, T., and Torre, T. D. L., 1996, *Environ. Sci. Technol.,* 30(3), 735-742.
4. Querol, X., Alastuey, A., Soler, A. L., Plana, F., Andres, J. M., Juan, R., Ferrer, P., and Ruiz C. R., 1997, *Environ. Sci. Technol.*, 31(9), 2527-2533.
5. Shigemoto, N. , Hayashi, H. , and Miyaura, K., 1993, *J. Mater. Sci.*, 28, 4781-4786.
6. Chang, H.-L. and Shih, W.-H., 2000, *Ind. Eng. Chem. Res.*, 39(11), 4185-4191.
7. Zhao, X. S., Lu, G. X., and Zhu, H. Y., 1997, *Porous Mater.*, 4(4), 245-252.
8. Sutarno, Arryanto, Y., dan Yulianto, I., 2000, *Pemanfaatan Limbah Abu Layang Batubara sebagai Bahan Dasar Sintesis Faujasit dengan Metoda Peleburan-Reaksi Hidrotermal,* Prosiding Seminar Nasional Kimia VIII, Jurusan Kimia Fakultas MIPA, Universitas Gadjah Mada, Yogyakarta, 265-270.
9. Darwanta, 1997, *Kajian Dekomposisi Abu Layang Batubara dan Sintesis Zeolit 4A dengan Bahan Dasar Fraksi Ringan Abu Layang Batubara Hasil Dekomposisi*, Skripsi FMIPA UGM Yogyakarta.
10. Susilowati, D., Arryanto, Y., dan Sutarno, 2000, *Pemanfaatan Abu Layang Batubara sebagai Bahan Dasar Sintesis Zeolit dengan Metoda Reaksi Hidrotermal Melalui Refluks HCl sebagai Perlakuan Awal, Prosiding Seminar* Nasional Kimia VIII, Jurusan Kimia Fakultas MIPA, Universitas Gadjah Mada, Yogyakarta, 271-278
11. ASTM C204, 1994, *Test Method for Fineness of Portland Cement by Air Permeability Apparatus, American Society for Testing and Materials,* Annual Book of ASTM Standards, Volume 04.02, West Conshohocken, Pennsylvania.
12. Catalfamo, P., Patane, G., Primerano, P., Pasquale, S. D., and Corigliano, F., 1994, *Mater. Eng.*, 5(2), 159-173.
13. Hamdan, H., 1992, *Introduction to Zeolites: Synthesis, Characterization and Modification*, University Teknologi Malaysia.