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Methodology To Produce Hard Coherent Water Adsorbent Using Modified Fusion Method

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ABSTRACT

Efforts were given to find suitable method to produce hard and coherent water adsorbent for ethanol water mixture. Three methods were studied. In the first method, calcined clay was mixed with alumina and KOH or NaOH. Water was added to get 40 - 50% solution and thoroughly mixed. The mixture was aged for 48 hours in closed container at 38°C followed by crystallization. In the second method, calcined clay or pure silica and alumina sources were mixed with NaOH or KOH and fused in furnace at 550°C for 12 hours. The fused mixture was mixed with water to get 40-55% solution of KOH or NaOH. Aging was carried out at 38°C for 48 hours before crystallization took place. In the third method, fused mixture from method 2 was mixed with NaOH or KOH and 5 part of water. The mixture was vigorously stirred for 3 hours and left for aging/crystallization at 60°C for 24 hours in oven. All the products from the three methodologies were washed and dried before being tested for water adsorbance. Results showed that method 2 was able to produce water adsorbent. The experimental results also revealed that the repetition of reflux may improve the water adsorbance performance of the adsorbent. However XRD analysis showed that the product was not the type of zeolite A.

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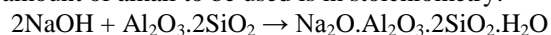
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INTRODUCTION

Ethanol or bioethanol is recognized as alternatives to fossil fuel. This biofuel offer potential environmental benefits such as reduced toxic gas and lower greenhouse emissions (Walls *et al.*, 2011). It can be produced from renewable sources and can be used without engine modification when blended with gasoline (Padala *et al.*, 2012). In order to be blended with gasoline to produce gasohol, the ethanol must be anhydrous (Pereira *et al.*, 2012). Conventional distillation process is able to purify ethanol-water mixture up to 89.4 % mol ethanol due to the formation of minimum boiling point azeotrope composition of 89.4 % mol ethanol and 10.6 % mol water at 78.2 °C and atmospheric pressure. Various ways have been used to produce anhydrous ethanol such as azeotropic distillation, extractive distillation, vaccum distillation, adsorption processes, membrane processes etc (Kumar *et al.*, 2010).

One of the attractive methods was adsorption using water adsorbent. It was claimed that adsorption was one of the technique that used less energy (Simo *et al.*, 2007; Huang and Chang, 2009). There were varieties of methodology to produce water adsorbent especially zeolite A from various silica and alumina sources.

Haden *et al.* (1961), described the method for making hard and coherent zeolite A from from kaolin, $Al_2O_3 \cdot 2SiO_2 \cdot (2-4)H_2O$. To produce zeolite A, the ratio of silica to alumina should be 1.177 (± 0.030) by weight. This ratio can be adjusted by additional source of alumina or silica in clay-alkali mixture. The clay must be dehydrated by calcination at a temperature of about 427 -871°C, preferably at 649 – 816°C. Calcination below 427°C is not sufficient and mullite is formed when the temperature exceeding 871°C. According to this patent, the amount of alkali to be used is in stoichiometry:



Sodium hydroxide or potassium hydroxide or mixture of both can be used as the alkali source. The range of alkali aqueous concentration should be around 30 – 50%, preferably at 40 – 50%. Low concentration yield fine powder or soft aggregate. Excess of alkali should be washed before crystallization takes place. It was reported that no zeolite A is formed when 50% weigh excess of NaOH was used. The alkali-clay mixture can be mechanically shaped by extrusion, milling, molding etc. Later, the reaction between clay and alkali is carried out at low temperature, 21°C – 46°C, preferably at 38°C to avoid the formation of sodalite at 52°C.

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The reaction time for completion is between 6 – 24 hours, but to ensure completion of reaction, the reaction time can be prolonged to 48 – 96 hours in closed reaction vessel to retain water. A suitable method to crystallize is refluxing the amorphous mass in 5 part 5% NaOH for 48 hours. The polycrystalline aggregate then is washed and dried preferably at 204°C – 370°C.

Klamrassame *et al.* (2010), synthesized sodium aluminosilicate from coal fly ash. In their experiment, the coal fly ash was mixed with NaOH with the ratio of 2.25 by weight and fused in furnace at several different temperatures in air. Later the fused product was crushed and mixed with 10 ml distilled water/g coal fly ash and shake for 12 hour at room temperature. Crystallization was performed under static condition at 90°C for 4 hours. Rios *et al.* (2009), fused kaolin with NaOH with the ratio of kaolin/NaOH 1: 1.2 at the temperature of 600°C for 1 hour. The fused product was grounded and dissolved in water (ratio 1: 4.9) under stirring condition. The hydrogel was aged under static condition for 24 hours and crystallization took place in PTFE bottles at 100°C for 24, 48 and 96 hours. XRD diffraction pattern showed that the products were zeolite A.

Tanaka and Fujii (2009), synthesized zeolite A from coal fly ash. They concluded that single phase pure zeolite A was obtained when the ratio of SiO₂/Al₂O₃ was 1.0. At the ratio of SiO₂/Al₂O₃ = 0.5, zeolite A was still present with trace amount of hydroxysodalite. Na-X zeolite started to emerge at the SiO₂/Al₂O₃ ≥ 2 and single phase Na-X was formed at SiO₂/Al₂O₃ = 4.5. Kosanovic *et al.* (2011), used SiO₂/Al₂O₃ ranged from 1.0 to 2.2 to synthesize zeolite from sodium aluminate and sodium silicate using the method of hydrothermal treatment of the hydrogel. The zeolite produced was the type of zeolite A with different morphological forms. Purnomo *et al.* (2012), studied the synthesis of zeolite from bagasse fly ash using silicate extraction method followed by hydrothermal treatment. They found that pure zeolite X can be produced at the Si/Al ratio of 1.8. At the ratio higher than 1.8, Na-X and Na-P was formed. At lower ratio less than 1.8, zeolite Na-A plus Na-X was formed and pure Na-A can be produced using Si/Al ≤ 1.

In this paper, three methodologies were compared to produce water adsorbent for ethanol water mixture. Those methodologies were selected based on the availability of equipment, raw material and financial constraint. KOH and NaOH were used as the promoter or activator with alumina and silica sources from clay, spent bleaching earth, pure alumina and pure silica.

MATERIALS AND METHODS

Method 1 was based on the Haden *et al.* (1961), method 2 was modified fusion method of method 1 followed by hydrothermal treatment and method 3 was generally fusion method followed by hydrothermal treatment.

1. Method 1:

Clay (Kaolin Malaysia Sdn. Bhd.) was calcined at 700°C for 17 hours in furnace (Carbolite ELF 11/6B). Alumina (Sigma Aldrich) was added to clay to get ratio of silica to alumina about 1.1. The calcined clay was mixed with 40%-55% NaOH (Merck) or KOH (Merck) solution in distilled water. The mixture was reacted for 48 hours in closed container at 38°C in oven (Thermo Scientific). Crystallization was carried out in reflux apparatus for 48 hours in 5% NaOH or KOH in water. The product was washed and dried in oven (PEL-EKO) overnight.

2. Method 2:

Clay or pure silica alumina source was mixed with NaOH or KOH. The mixture was fused in furnace at 550 – 600°C in furnace for 12 hours. The fused mixture was mixed with water to get 40% -55% solution of NaOH or KOH. The mixture was reacted for 48 hours in closed container at 38°C. Crystallization was carried out in reflux apparatus for 48 hours in 5% NaOH or KOH in water. Washing and drying was carried out at 85 – 220°C in oven.

3. Method 3:

Fused mixture from method 2 was mixed with NaOH or KOH to get weight percent 120%. The mixture was added to 5 part of distilled water and vigorously stirred for 1 – 3 hours. The mixture then left in oven at 60°C for 24 hours. After that washing was carried out. The mixture was dried in oven at 85 – 220°C for 24 hours.

Water analysis for water adsorbance test from ethanol water mixture was carried out using Karl Fisher Titrator (Metrohm, 870 KF Titrino Plus). SEM-EDX analysis was carried out to determine the content of silica and alumina in kaolin. X-Ray diffractometry measurements (Rigaku, Miniflex II) were conducted to identify types of water adsorbent present in some selected synthesized samples at ambient temperature with CuK α at 30 kV and 15 mA in the range of 2 θ from 3 – 80° with sampling step of 0.02°.

RESULTS AND DISCUSSION

Table 1 shows the results of synthesized water adsorbent using the three different methods. Run 1 and 2 were of method 1, based on Haden *et al.* (1961). Run 3 and 4 were of method 2, the modified fusion method and lastly run 5 and 6 were of method 3, fusion followed by hydrothermal treatment. Run 8 and 9 were products from run 1 & 2 which were crystallized for second time in 5% NaOH or KOH in reflux apparatus for 48 hours. Run 10 was the product of run 4 which was crystallized for the second time.

Results from run 1 to run 6 showed that, the products of method 1, 2 and 3 were not able to adsorb water from ethanol water mixture. These can be seen from the initial and final water content of the ethanol water mixture. However the product of run 10 showed that it was able to adsorb water from 10.2% to 6.2%. This water adsorbent was produced by re crystallization of product from run 4. Run 4 used method 2, modified fusion method, with KOH as the activator and using pure alumina and pure silica for the alumina silica source. Second refluxing or crystallization of run 1 and 2 (method 1) were not able to produce water adsorbent. These were shown by the results of run 8 and 9.

Table 1: Synthesized products using method 1, 2 and 3

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10*
Method	1	1	2	2	3	3	3	1	1	2
Material (gram)								Re Reflux Product Run 1	Re Reflux Product Run 2	Re Reflux Product Run 4
Kaolin	91.800					3.570	3.736			
Alumina	27.540	10.017	10.520	10.280	3.000	1.070	1.122			
Silica		11.011	12.360	12.230	3.700					
NaOH	42.900	7.574	8.160				5.827			
KOH				11.240	8.760	5.580				
Water	65.000	7.574	8.160	11.240	77.300	38.180	53.390			
Water % initial	4.300	4.830	4.490	4.250	4.486	4.640	4.640	10.040	10.040	10.778
Water % final	4.600	4.770	4.761	4.151	4.714	5.295	4.539	10.152	10.650	6.226

Run 1 (method 1), according to Haden *et al.* (1961), should produced water adsorbent the type of zeolite A. However this experiment showed negative result. Run 7 was based on Rios *et al.* (2009). Using this fusion method followed by hydrothermal treatment, water adsorbent the type of zeolite A should be produced. Again, the result showed by the experiment was negative. Therefore, method 2 was selected and believed was able to produce water adsorbent for ethanol water mixture.

To check for consistency of method 2 in producing water adsorbent, kaolin and spent bleaching earth (SBE) were used as the source of silica. Alumina was added to achieve ratio of silica/alumina 1.1. Tanaka and Fuji (2009), reported that pure zeolite was produced from coal fly ash when the silica/alumina ratio was 1.0. Purnomo *et al.* (2012) claimed that pure zeolite A can be produced from bagasse fly ash when the silica/alumina ratio ≤ 1 . SEM-EDX analysis was carried out on kaolin and SBE to determine the composition of alumina and silica. The results of the analysis were shown in table 2 and table 3.

Table 2: SEM-EDX analysis of silica and alumina in kaolin

	Sample 1	Sample 2	Sample 3	Sample 4	Ave
O	52.65	55.77	57.82	55.86	55.53
Al	13.70	6.68	1.93	14.08	9.10
Si	21.00	31.84	32.96	19.50	26.33
	Ave Alumina (wt %)				17.18
	Ave Silica (wt %)				56.41

The results of SEM-EDX for 4 samples of kaolin were as in table 2. The deviation of aluminum and silica content were quite large. The average alumina weight % was 17.18% and average silica content was 56.41% in kaolin. The supplier specification for alumina was in the range of 7 – 12% whereas the specification for silica content was in the range of 80 – 90%. Based on the average alumina and silica content from the SEM-EDX analysis, to get the ratio of silica/alumina 1.1, 30 gram of alumina need to be added for every 100 gram of kaolin (30 g alumina/ 100 g kaolin).

Table 3 showed the results of SEM-EDX for 4 samples of regenerated SBE. Again, the deviation of alumina and silica was quite high from the average. The average alumina weight % was 6.16% and average silica content was 74.53% in SBE. Based on the average alumina and silica content from the SEM-EDX analysis, to get the ratio of silica/alumina 1.1, 60 gram of alumina need to be added for every 100 gram of SBE (60 g alumina/ 100 g SBE).

Table 3: SEM-EDX analysis of silica and alumina in regenerated SBE

	Sample 1	Sample 2	Sample 3	Sample 4	Ave
O	53.56	53.30	52.74	52.03	52.91
Al	1.56	1.18	8.86	1.44	3.26
Si	36.90	40.88	23.69	37.66	34.78
Ave Alumina					6.16
Ave Silica					74.53

Several promoters or activators can be used to synthesize type A zeolite. According to Haden *et al.* (1961), molecular sieves are available in several types such as 3A, 4A and 5A. Type 3A is potassium dehydrated zeolite, type 4A is sodium dehydrated zeolite and type 5A is calcium dehydrated zeolite. Al-Asheh *et al.* (2007), studied the separation of ethanol-water mixtures using commercial molecular sieves of type 3A, 4A and 5A. The breakthrough curves of water sorption at different content showed that type 3A gave the best separation. The type 3A molecular sieves were determined to have the largest surface area and the highest value of water uptake. Therefore, KOH was selected to be the promoter for the rest of the experiment.

Method 2 was repeated for silica source from kaolin and spent bleaching earth (SBE). Table 4 showed the water adsorbed by the adsorbent synthesized from kaolin and SBE in unit of gram water adsorbed per gram adsorbent. For kaolin, 50 g alumina added/ per 100 g kaolin was also tested. The water adsorbed for 50 g alumina/100 g material was better (0.0303 g H₂O/g adsorbent) compared to 30 g alumina added/100 g kaolin (0.0145 g H₂O/g adsorbent). This may be attributed to distribution of contents in kaolin which were not uniform as shown in table 2. Results in table 4, also showed that the method 3 was able to produce water adsorbent from SBE (0.0245 and 0.0156 g H₂O/ g adsorbent). For comparison, commercial zeolite 3A was able to adsorb 0.0373 g H₂O/g adsorbent from ethanol water mixture. The results revealed that the water adsorbed by adsorbent synthesized from kaolin was better than SBE. This may be due to higher impurities in SBE such as ferum and calcium (2008). The ferum content in SBE was 1.63% and in kaolin was 0.68% based on the SEM-EDX results.

Table 4: Water adsorbed by water adsorbent synthesized from kaolin and SBE using method 2

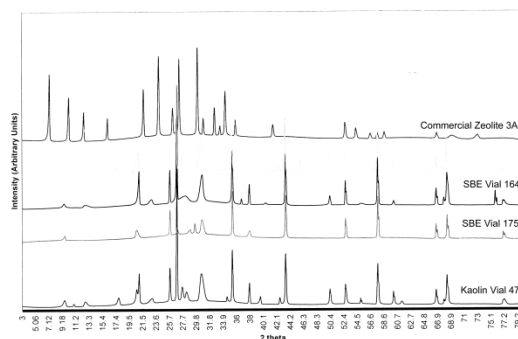
Material	g alumina/ 100 g material	g H ₂ O/g adsorbent
Kaolin	30	0.0145
Kaolin	50	0.0303
SBE	60	0.0245
SBE	60	0.0156
Commercial		0.0373

Re-crystallization or re reflux was found to increase the adsorbance of water for the water adsorbent. This test has been carried out for kaolin and SBE. Table 5 shows amount of water adsorbed for kaolin (50 g alumina/100 g kaolin) and SBE (60 g SBE/ 100 g kaolin). For kaolin, after 6 repetition of recrystallization, the water adsorbance increase from 0.0156 (for 1st reflux) to 0.3930 g H₂O/g adsorbent (for 6th refflux) which was comparable to commercial zeolite 3A performance. The water adsorbance for water adsorbent synthesized from SBE also increase from 0.0910 (1st reflux) to 0.0231 g H₂O/g adsorbent after the third recrystallization. In other words, repetition of crystallization was able to boost the water adsorbance for the synthesized material. This may due to the rearrangement (redissolution and recrystallization) of the crystal during repetition of reflux. Secondly, drying before recrystallization create passages or channels for the reflux solution to contact with adsorbent material

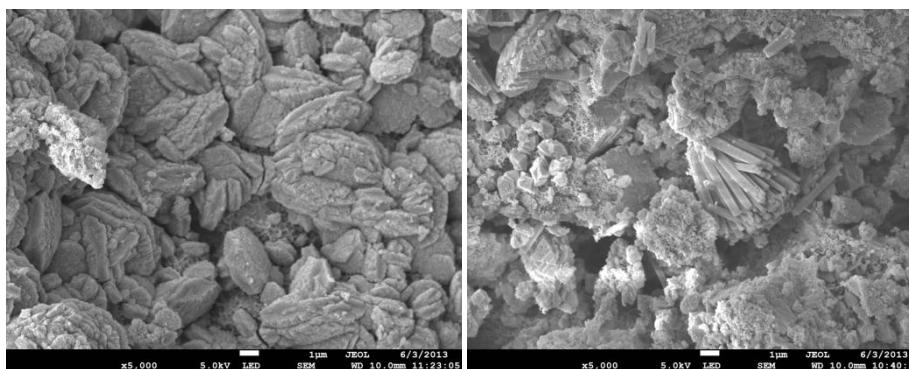
Some selective samples were analyzed using XRD machined for identification. The diffractograms of the samples and commercial zeolite A was presented in figure 1. The autosearch function of the XRD machines revealed that none of the samples were of the zeolite type A, although they were able to adsorbed water from ethanol water mixture. From the diffractogram, the phases for all three products synthesized from kaolin and SBE were similar. It was believed that, the product was a mixture of zeolite A and other phases. This can be seen by some emerging peaks at the angle similar to commercial zeolite 3A, such as at the angle 21.6 °, 25.7° and 27.0°.

Table 5: Effect of crystallization repetition to the water adsorbed by the water adsorbent.

Reflux Repetition	Water Adsorbed (g H ₂ O/ g adsorbent)	
	Kaolin (50 g/ 100 g)	SBE (60 g /100 g)
1	0.0156	0.0019
2	0.0188	0.0156
3	0.0202	0.0231
4	0.0230	
5	0.0268	
6	0.0393	
7	0.0312	
8	0.0352	

**Fig. 1:** Diffractogram of water adsorbent synthesized using method 2

The FESEM image of SBE vial 175 (0.0222 g H₂O/ g adsorbent) and SBE vial 164 (0.0096) were as in figure 2. From the images, for SBE vial 164 with the water adsorbance of 0.0222 g H₂O/ g adsorbent, the cuboid crystal was believed to crystal of zeolite A. The image also showed that there were a lot other phases present in the adsorbent due to impurities and the technique used to synthesize the adsorbent.

**Fig. 2:** FESEM image of sample SBE vial 164 (left) and SBE vial 175 (right)

Conclusion:

Hard and coherent water adsorbent for ethanol water mixture can be synthesized from pure alumina silica source, kaolin or SBE using method 2, modified fusion method. By repetition of reflux, the performance of the water adsorbent can be increased. However, XRD analysis showed that the products were not the type of zeolite A. However based on the SEM images, it was believed that some zeolite A was formed during crystallization.

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