SonicationTechnique on the Manufacturing of Synthetic Zeolites from Bagasse

Herry Purnama[#], Tri Widayatno[#], Emi Erawati[#], Wasprad Y. Basuntoro[#], Fitriyani A. Putri[#]

[#]*Department of Chemical Engineering, Faculty of Engineering*
Universitas Muhammadiyah Surakarta, Indonesia
[1]hp269@ums.ac.id

***Abstract*—Indonesia has many sugar industries to fulfill the need of sugar consumption on its huge population and all of the sugar industries use sugarcane as raw materials. In the milling process, the side product bagasse will be generated after the sugar solution (molasses) is separated. The amount of bagasse is relatively in huge number,approximately 30% of the sugarcane crushed.The utilization of bagasse unfortunately has not been exploited economically. Since the bagasse has a high silica content, it is enable to be treated to produce synthetic zeolites.There are some methods to produce synthetic zeolites, for example by hydrothermal process, utilizing microwave, or ultrasonication. Sonication technique has been applied to develop the manufacturing of synthetic zeolites. This method utilizing ultrasonication waves with a frequency of about 20 kHz for mixing of aluminate and silicate solutions to form a homogeneous mixture. The sonication technique has a better performance when compared with the hydrothermal technique. The process is simpler and not too much chemical wastes. This technique is also safer compared with microwave technique. The effect of ultrasound has been investigated for various operational conditions, temperature of 60, 70, and 80^{o}C combined with 30, 60, 90 and 120 minutes of sonication.**

At this step, the characteristics of synthetic zeolites from bagasse sugarcanehas been tested for crystalline structure by X-Ray Diffraction (XRD). The next step for characterization will include analyzing of molecular bond using spectroscopic method of Fourier transform infrared (FTIR), and also the characterization of surface area by using BET surface area analyzer. The manufacturing process of synthetic zeolites from bagasse by using sonication technique has been successfully produced. The optimum conditions to synthesize zeolites were shown by diffraction curve of zeolite crystalline at higher temperature and longer time of sonication.

***Key words* – bagasse, sonication, synthetic zeolytes, ultrasound**

I. INTRODUCTION

Sonication technique applies sound energy to agitate particles in a sample. When the ultrasonic frequencies applied, then the process also being known as ultrasonication. Ultrasound is at the high end range of the spectrum and therefore it produces treble tones. Ultrasound devices operate with frequencies from 20 kHz up to several gigahertz.The other frequencies of waves are infrasound, less than 20 Hz, and theaccousticwhich is in the range of 20 Hz to 20 kHz.

Ultrasound is able to be applied in diverse fields. This method can be used for medical imaging, detection of object, measurement of distance and cleaning purposes. At higher power levels, the application of ultrasound which is called ultrasonic, is useful for changing the chemical properties of substances. In many industries, ultrasound is applied for cleaning and for mixing, and also to accelerate chemical processes.

There are many effects of applying ultrasonication, both chemical and physical effects. The chemical effects of ultrasound, or sonochemistry, or sonoluminescence, are concerned with understanding the effect of sonic waves on chemical systems. The chemical effects of ultrasound do not come from a direct interaction with molecular species. There is no direct coupling of the acoustic field with chemical species on a molecular level can account for sonochemistry[1] or sonoluminescence [2]. Instead sonochemistry arises from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid [3].

In water and most liquids, when the amplitude of the sound wave is low, a continuous transition is occured. Since this amplitude increases, the areas of negative pressure in a rarefaction (expansion) area can become so great, creating the liquid splitting at sites of expansion which is known as cavitation phenomenon. Since the wave front passes by, these newly formed bubbles oscillate as the vapor within the bubble evaporates and collapses in order to maintain a constant vapor pressure. Once the bubble becomes too unstable it collapses and releasing shock waves.

It has been reported [4]a physical phenomenon i.e. ultrasonic cavitation is determined by the parameters below: (1).*Frequency*. On the higher sonic frequencies (MHz), the production of cavitation bubbles becomes more difficult rather than lower frequencies (kHz). In this case, cavitation can be achieved by increasing intensity if the sonic frequency increases, to ensure that the cohesive forces of the liquid media are overcome. (2). *Intensity*. The intensity of sonication is proportional to the amplitude of vibration of the ultrasonic source. An increment in the amplitude of vibration will lead to an increase in the intensity of vibration and to an increase in the sonochemical effects. A minimum intensity is required to achieve the cavitation. (3).*Solvents*. The solvent must be chosen carefully to perform sample treatment by sonication. Generally most applications are performed in water although some other less polar liquid i.e. organic solvents can be also used. The cavitation may be inhibited by both solvent viscosity and surface tension. The higher the natural cohesive forces acting within a liquid (e.g., high viscosity and high surface tension) the more difficult it is to

attain cavitation [5]. (4).*Temperature*. Solvent temperature plays two roles in sonication. Firstly, higher temperature helps to disrupt strong solute–matrix interactions, which include Van der Waals forces, hydrogen bonding and dipole attractions between the solute molecules and active sites on the matrix. Furthermore, faster diffusion rates occur at higher temperatures. Secondly, at lower temperature, cavitation is better attained when the ultrasonic power of the generator is constant [6]. As the temperature of the solvent rises, so its vapor pressure increases and so more solvent vapor fills the cavitation bubbles, which then tend to collapse less violently, that means the sonication effects are less intense than expected. Therefore a compromise between temperature and cavitation must be achieved. (5).*External pressure and bubble gas.* If the external pressure is increased, then a greater ultrasonic energy is required to induce cavitation, that is, to break the solvent molecular forces. In addition, there is an increment in the intensity of the cavitational bubble collapse and, consequently, an enhancement in sonochemical effects is obtained. For a specific frequency there is a particular external pressure that will provide an optimum sonochemical reaction [5]. However it must be noted that most ultrasonic applications are performed under atmospheric pressure. (6).*Direct and indirect ultrasonic application*. Direct application is conducted by using ultrasonic probes, immersed into sample, performing sonication directly over the solution without any barrier to be crossed by the ultrasound wave other than the solution itself. This methode has several drawbacks, such as sample contamination with metals detaching from the probe. Meanwhile indirect application is carried out using a sonication bath. The ultrasonic wave needs first to cross the liquid inside the ultrasonic device and then to cross the wall of the sample container. Hence, sonication intensity inside the sample container is lower than expected. Ultrasonic baths are not powerful devices, their applications are much limited by the lack of ultrasonic intensity. In fact, many ultrasonic applications related to baths can be linked to the heating produced in the liquid that the bath contains – heat that is transmitted to the sample – rather than to actual ultrasonic effects, that is, cavitation.

According to[7], the sonication technique enables achievement of reactions under normal conditions, which otherwise would require harsh reaction conditions.

Zeolites can be found naturally as a natural zeolites, and can also be made with a particular technique as a synthetic zeolites. The characteristics of both type of zeolites are totally different. Natural zeolite is performed on the geological and geographical conditions of nature, while the synthetic zeolites are determined by its synthesis, operation conditions and composition of raw materials [8].

Sonication, applying ultrasound energy to agitate particles, can be used for producing nanoparticles. This technique has been also introduced to improve the manufacturing of synthetic zeolites. This method utilizes ultrasonic waves for mixing aluminate and silicate solution to form a homogeneous mixture. Comparing to hydrothermal process for synthesizing zeolites [9], the sonication technique is much better in saving time for preparing and in reducing of chemical wastes. This technique is more secure compared with microwave technique because it uses the wave frequencies below the microwave [10]. The effects of ultrasound have been investigated for different cases, especially the syntheses of various amorphous and crystalline material of zeolites. However, research on the application of ultrasonication is very limited and hence needs to be developed. In this study, the issues to be solved is to determine the optimum conditions of sonication technique in the process of manufacturing synthetic zeolites from bagasse ash.

Bagasse can be found easily in sugarcane milling. Apparently for each 10 tonnes of sugarcane crushed, a sugar factory produces about 3 tonnes of wet bagasse. Since bagasse is a by-product of the cane sugar industry, the quantity of production in each country is in line with the quantity of sugarcane produced.

Rainey [11] reported a typical chemical analysis of bagasse might be (on a washed and dried basis), shown on Table 1.

TABLE I
COMPOSITION OF BAGASSE SUGARCANE

Component	Percentage
Cellulose	45-55%
Hemicellulose	20-25%
Ligmin	18-24%
Ash	1-4%
Waxes	<1%

Many research efforts have explored using bagasse as a renewable power generation source (as fuel) and for the production of bio-based materials such as pulp, paper, board, and veterinary feed.

The high moisture content of bagasse, typically 40 to 50%, is detrimental to its use as a fuel. In general, bagasse is stored prior to further processing. For electricity production, it is stored under moist conditions, and the mild exothermic reaction that results from the degradation of residual sugars dries the bagasse pile slightly. For paper and pulp production, it is normally stored wet in order to assist in removal of the short pith fibres, which impede the papermaking process, as well as to remove any remaining sugar.

Bagasse is an extremely inhomogeneous material comprising around 30-40% of "pith" fibre, which is derived from the core of the plant and is mainly parenchyma material, and "bast", "rind", or "stem" fibre, which comprises the balance and is largely derived from sclerenchyma material. These properties make bagasse particularly problematic for paper manufacture and have been the subject of a large body of literature.

II. METHODOLOGY

Bagassewas collected as a local waste from small scale sugarcane drinking industry in Surakarta, Indonesia. Bagasse ash was then prepared through four stages, 1) drying process

(oven at 190°C for 1 h), 2) charcoal making process (oven at 300°C for 0.5 h), and ash making process (oven at 700°C at 4 h). The chemicals used in the experiment was analytical grade. Hydrochloric acid was applied to separate silica from bagasse ash. A solution of sodium silicate was prepared by mixing bagasse ash, water and sodium hidroxide at room temperature and stirred for an hour. The sodium aluminate solution was prepared by mixing a solution of sodium hydroxide and aluminum oxide under similar treatments. Then a solution of sodium aluminate is added to a solution of sodium silicate gently and stirred for an hour lead to homogeneous. Once homogenous condition achieved, mixed paste was put in sonicator, Elmasonic S10H (capacity 0.8L) within applied frequency of 37 kHz, at various temperatures (60, 70, and 80°C) and sonicating time (30, 60. 90 and 100 minutes). The next stage is the process of washing and screening using demin water until the pH nearly to 7. Then the samples was put in the oven at 110°C for 24 hours and calcined.Then characteristics of synthetic zeolites from bagasse ash then were tested for crystal structure by X-Ray Diffraction (XRD) as in the first stage.

III. Results and Discussion

Initial results on analysing of silica (SiO_2) content of bagasse ash by using X-ray flourescence (XRF) method is shown as follow, i.e. 34.9% (before washed) and 59.4% (after washed). XRF is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis. The investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology often use this technique.

When materials are exposed to short-wavelength X-rays or to gamma rays, ionization of their component atoms may take place. Ionization consists of the ejection of one or more electrons from the atom, and may occur if the atom is exposed to radiation with an energy greater than its ionization potential. X-rays and gamma rays can be energetic enough to expel tightly held electrons from the inner orbitals of the atom. The removal of an electron in this way makes the electronic structure of the atom unstable, and electrons in higher orbitals "fall" into the lower orbital to fill the hole left behind. In falling, energy is released in the form of a photon, the energy of which is equal to the energy difference of the two orbitals involved. Thus, the material emits radiation, which has energy characteristic of the atoms present. The term *fluorescence* is applied to phenomena in which the absorption of radiation of a specific energy results in the re-emission of radiation of a different energy (generally lower).

The wavelength of this fluorescent radiation can be calculated from Planck's Law:

$$\lambda = \frac{hc}{E} \tag{1}$$

The fluorescent radiation can be analysed either by sorting the energies of the photons (energy-dispersive analysis) or by separating the wavelengths of the radiation (wavelength-dispersive analysis). Once sorted, the intensity of each characteristic radiation is directly related to the amount of each element in the material. This is the basis of a powerful technique in analytical chemistry.

The high silica content leads to be explored for producing synthetic zeolites. Silica is absorbed from the soil through the roots of sugarcane. Accumulated silica between the plant'scuticle and cell walls acts as a physical barrier against the penetration of pathogenic fungi and reduceswater loss through transpiration [12].Other small particles detected in the bagasse ash are oxides of P_2O_5, K_2O, CaO, Al_2O_3, SO_3, Cl, MnO, Fe_2O_3, and ZnO.

The X-ray diffraction (XRD) then was applied to investigate a crystal structure in synthetic zeolites. The use of XRD can be more effective to the analysis. Crystals are regular arrays of atoms, and X-rays can be considered waves of electromagnetic radiation. Atoms scatter X-ray waves, primarily through the atoms' electrons. Just as an ocean wave striking a lighthouse produces secondary circular waves emanating from the lighthouse, so an X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as elastic scattering, and the electron (or lighthouse) is known as the *scatterer*. A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg's law:

$$2d \sin\theta = n\lambda \tag{2}$$

Here *d* is the spacing between diffracting planes, $\theta$is the incident angle, *n* is any integer, and λ is the wavelength of the beam. These specific directions appear as spots on the diffraction pattern called *reflections*. Thus, X-ray diffraction results from an electromagnetic wave (the X-ray) impinging on a regular array of scatterers (the repeating arrangement of atoms within the crystal).

Fig. 1 shows the result of XRDdata for zeolites synthesized by sonication technique of bagasseat temperature 70°C. At lower sonication time, i.e. 30 minutes, there is a very small of crystalline of zeolites and mostly the product is amorphous. However by increasing sonication time to 60 minutes, the crystalline of zeolite increased significantly. Increasing time of ultrasonication will increase the degree of crystals which can be evaluated by higher peaks intensity. In this case, high intensity can be achieved at the longest of experiment, i.e. 120 minutes of sonication. The similar pattern of such phenomenon are also found for lower temperature of sonication. At 60°C, shown in Fig. 2, the X-ray diffractogram tends to show the lowest degree of crystallinity. It may be concluded that temperature of ultrasonication affected to the growth of crystal structured. By increasing time of sonication will increase the size and the amount of crystallinity.

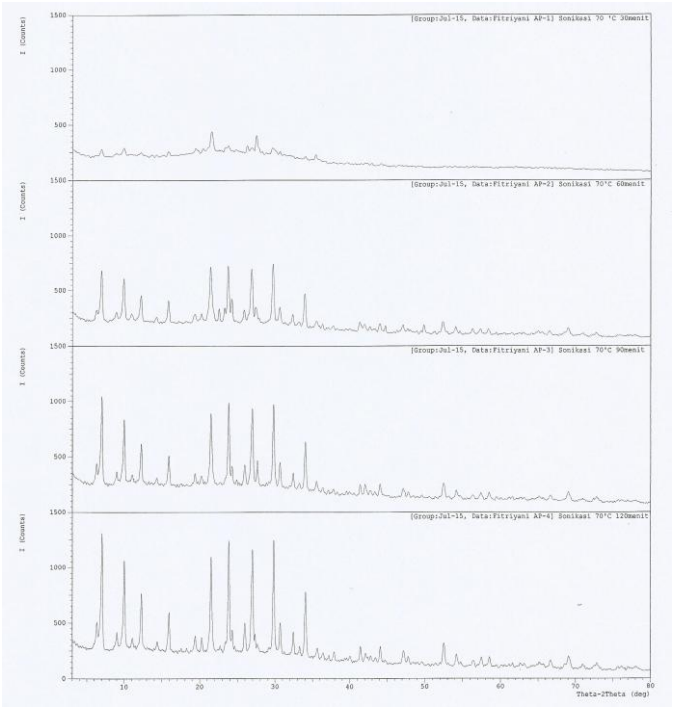

Fig. 1 X-Ray diffractogram of zeolites synthesized in 70°C, and various time of sonication (30, 60, 90 and 120 minutes)

Bagasse shows a very low crystallinity and wideband is observed between 10 and 30 (2-theta), which implies the presence of vitreous matter. This fact isattributed to glass forming constituents since the organic constituents would have been removed duringcombustion. It has been reported that at burning temperatures up to 800°C silica was in amorphous formand silica crystals grew with time and temperature of incineration [13].

Moreover, the XRD patterns suggest the presence of calcite ($CaCO_3$) as themain crystalline compound with quartz (SiO_2) as minor compounds. Theamorphous alumina-silicate nature of bagasse makes its chemical composition difficult to characterize, butalso very versatile, since the glassy phase both react and also goes into solution before the crystallinephase.

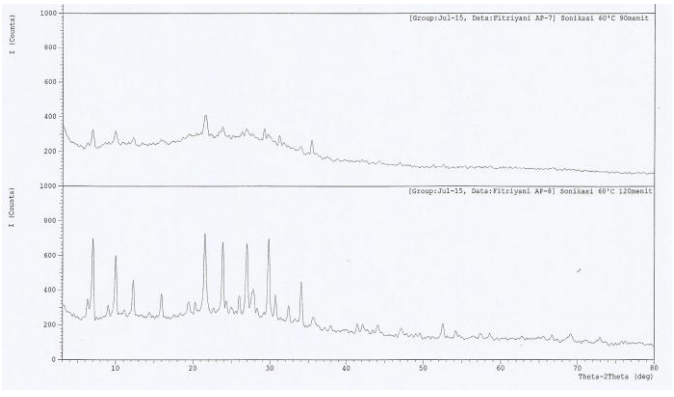

Fig. 2 X-Ray diffractogram of zeolites synthesized in 60°C for 90 and 120 minutes of sonication

The different results has been found in the experiments under the temperature of 80°C, as shown in Fig. 3. By the temperature, the crystalline is already performed and suggested is slightly affected by the time of sonication. However the position of peaks is a bit shifted to the different places.

This result is in accordance with statement of theory that increasing temperature will disrupt solute-matrix interactions and increase diffusion rates. On this diffractogram, it can be seen the clear peaks and the peak intensity of high acuity and sharp on some of them at 2θ positions are: 7-8, 11-17, and 23-35.

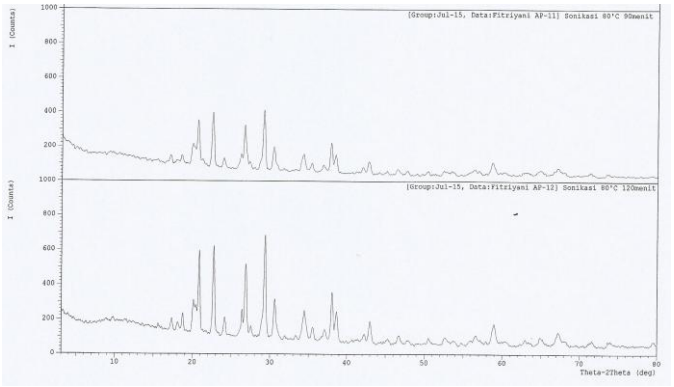

Fig. 3 X-Ray diffractogram of zeolites synthesized in 80°C for 90 and 120 minutes of sonication

IV. Conclusions

The silica content of bagasse ash is relatively high, around 59.4%, suggested a great opportunity to utilize furthermore of bagasse ash into synthetic zeolites. The manufacturing of synthetic zeolites by using ultrasound has been done successfully. The manufacturing process of synthetic zeolites using sonication technique enable to be implemented considering the process is relatively easy, fast, and not too much chemical wastes. Optimum sonicating condition to synthesize zeolites from bagasse ash is carried out at 70°C for 120 minutes. The zeolite resulted from this experiment is suggested similar to Na-Y within silica dominates of its composition.

Acknowledgement

The authors thank to DIKTI Ministry of Research, Education and Culture, Indonesia, through Universitas Muhammadiyah Surakarta for the funding under the research scheme of Penelitian Unggulan Perguruan Tinggi (PUPT) 2015-2016.

References

[1] Suslick, K. S. (1990). "Sonochemistry". Science **247**: 1439–1445.

[2] Suslick, K. S.; Flannigan, D. J. (2008). "Inside a Collapsing Bubble, Sonoluminescence and Conditions during Cavitation". Annual Rev. Phys. Chem. **59**: 659–683.

[3] Suslick, Kenneth S. (February 1989). The Chemical Effects of Ultrasound. Scientific American. pp.62-68 (p.62)

[4] Santos, H. Miguel, Lodeiro, C., Capelo-Martinez, J., 2009, The Power of Ultrasound, in Ultrasound in Chemistry: Analytical Application, Wiley CH, Weinheim

[5] Mason, T.J., 1992, Practical Sonochemistry: User's Guide to Applications in Chemistry and Chemical Engineering, Ellis Horwood Ltd, New York
[6] Mason, T.J., 2000, Sonochemistry, Oxford Chemistry Primers, Oxford, UK
[7] Ashokkumar, M., Lee, J., Kentish, S. and Grieser, F., 2007, Bubbles in acoustic field: An overview, Ultrasonics Sonochemistry, 14: 470-475
[8] Auerbach, S., Carrado, K., and Dutta, P., 2003, "Hand book of zeolite science and technology", Marcel Dekker, Inc., New York
[9] Wu, D., Zhang, B., Yan, L., Kong, H., Wang, X., 2006, Effect of some additives on synthesis of zeolite from coal fly ash, International Journal of Mineral Processing, 80, 266-272
[10] Andac, O., Tatlıer, M., Sirkecioglu, A., Ece, I., Erdem-Senatalar, A., 2005, Effect of ultrasound on zeolite-A synthesis, Microporous andMesoporous Materials, 79(1–3), 225-233
[11] Rainey, Thomas J (2009). A study of the permeability and compressibility properties of bagasse pulp. Brisbane, Australia: Queensland University of Technology.
[12] Fungaro, Denise Alves, Thais Vitória da Silva Reis, 2014, Use of sugarcane straw ash for zeolite synthesis, International Journal ofEnergy and Environment, Volume 5, Issue 5, 2014 pp.559-566.
[13] Le Blond J.S., Horwell C.J., Williamson B.J., Oppenheimer C. Generation of crystalline silica from sugarcane burning. J Environ Monit. 2010, 12, 1459-70.