Optimization of process condition of nanosilica production by hydrothermal method

N Qisti1a, N S Indrasti2b*, and Suprihatin2c

1 Student of Agroindustrial Technology, Bogor Agricultural Institute, 16680 Dramaga, Bogor, Indonesia
2 Supervisor of Agroindustrial Technology, Bogor Agricultural Institute, 16680 Dramaga, Bogor, Indonesia

E-mail: a nuqyss@gmail.com, b nastiti.indrasti@gmail.com, c suprihatin167@gmail.com

Abstract. Bagasse ashes have high silica content thus it can be used in nanosilicaproduction to increase its benefit value. This study aimed to get the best time for synthesis and to determine the optimum synthesis time and temperature. This study used the hydrothermal method, a simple method with relatively low reaction temperature and provide a good chemical homogeneity. Time varieties in synthesizing silica were 8, 10 and 12 hours, at the temperature of 150 °C. But the results were not as expected. Moreover, optimization of synthesis temperature and time used 4 hours at the temperature of 150 °C based on previous studies. Optimization was conducted using the Response Surface Methodology (RSM). Later, a test using PSA (Particle Size Analyzer) was performed to obtain particle sizes and PDI values (Polydispersity Index). The results showed that the prediction model of temperature synthesis was 152.67 °C, synthesis time of 6 hours, particle size of 276.288 nm and PDI value of 0.189642. The tests showed that the size of particle obtained was 330.39 nm and PDI value at 0.3580. Actual results and predicted results were not significant different.

1. Introduction
Bagasse ashes is the solid waste of burned bagasses. Its improved presence in the industrial area caused environmental pollution, especially air pollution caused by dust. Indonesia's sugar industry is still operating in various capacities which generates residue of bagasse combustion on boilers as bagasse ash in huge amount. Total production of bagasse ash is about 0.3% of the bagasse weight, so that sugar industry with production capacity of 5 000 tons a day results in bagasse ash for about 15 tons a day [1]. Bagasse ashes utilization is currently only limited as the manufacture of organic fertilizers and burial material [2], the rest is disposed as a solid waste. The most dominant inorganic mineral elements of bagasse ash is silica (SiO₂) with maximum concentration up to 70.97% [3]. Thus, idea to utilize bagasse ash by making nanosilica as alternative product is generated. Nanosilica is a modified silica by using some treatments to produce nano-size particle.

Nanosilica used in science and industrial applications, such as catalysts, pigments, pharmaceuticals, [4], medicines, cosmetics, and food [5]. One material to be a deep concern of researchers is nanoparticles of silica (SiO₂) due to its good stability, chemically inert, biocompatible character that able to work in harmony with the body's work systems, and ability to form a single spherical [6]. It is also revealed that the silica nanoparticles can be used as support material that is ideal for magnetic nanoparticleas it is able to experience functionalization with ease, prevent anisotropic dipolar magnetic attraction when get an external magnetic field, and increase resistance to corrosion of magnetic nanoparticles. Silica particles have different roles for each resulted products as well as the quality of the product is determined by the size and particle distribution of silica itself within the system [7].

Sizing silica to the nanoscale requires special treatment by several methods such as sol-gel process, gas phase process, coprecipitation method, emulsion techniques, and plasma spraying and
foging process (polymerization of dissolved silica into organo silica) [8]. In this study, the method used was the hydrothermal method in synthesizing SiO$_2$ to produce nanosilica that was uniform and homogeneous.

Hydrothermal method has many advantages such as simple in preparation, the reaction temperature is relatively low, uniform dispersion of the doping metal ions, as well as stoichiometry control and provide a good chemical homogeneity [9-10] stated that the hydrothermal method can improve the crystallinity, thermal stability, surface area and photocatalytic activity. In addition, the hydrothermal method used in this study because this method can be used in large-scale industry due to the equipment used is quite simple.

Based on statement [11], it is suggested to use higher temperature variations or longer variation of hydrothermal time in expecting to get crystalline silica without calcination. This study was reviewed by results of previous studies [12] which had already obtained best temperature in the synthesis process of nanosilica. Thus, this study only performed synthesis time modification by extending the synthesis time to get the best time for nanosilica synthesis so that it can proceed to the next stage, the optimization stage. Synthesis temperature and time optimization of hydrothermal methods in this research used the Response Surface Methodology (RSM) to obtain information about the relationship between the response and several influenced factors [13]. In this study, responses to be included are nanosilica particle size and yield linked with the process factors of temperature and time. Expected results to be obtained are the relationship between the response and factors of nanosilica production process using the hydrothermal method as well as the optimum condition of temperature and time that will proceed to the next stage that is the scale up stage.

2. Methodology

This study was divided into two steps: Nanosilica Synthesis and Optimization of Synthesis temperature and time.

2.1 First Step: Nanosilica Synthesis

This step was conducted to get the best treatment of synthesis time.

2.1.1 Preparation of materials

Bagasse ashes were washed with distilled water then dried on oven at 105 °C for 5 hours. Dry ashes were heated at 700 °C for 6 hours to remove minerals and other impurities compounds. Results of incineration produced ash powder. Incinerated bagasse ashes then were stored in a desiccator to maintain the water contain[14].

2.1.2 Production of nanosilica

About 10 grams of boiler ashes were extracted in 80 ml of NaOH for 3.5 hours. The solution was filtered and washed using 20 ml of hot water. filtrate then was cooled down to the room temperature and was added with 5 N H$_2$SO$_4$ to get pH 2 and was added with NH$_4$OH until pH 7. Sol subsequently formed through the aging process for 3.5 hours at room temperature and then was dried at 105 °C for 12 hours [15].

Pure silica which was obtained then was put in a hydrothermal reactor to be processed. Temperature used product was flushed with sulphate was 150 °C while the time applied were 8, 10 and 12 hours. After that, the product of hydrothermal was titrated with 5 N H$_2$SO$_4$ to get pH 8.5. Furthermore, it was rinsed for 7 times using warm distilled water to remove impurities contained in the product. Products which had been free of impurities then was aginned for 3 hours at temperature of 60 °C and was dried on oven with temperature of 105 °C for 12 hours. Product of drying results then was mortared to get nanosilica with fine powder. The weighing then was done to obtain the yield.
2.1.3 Characterization of nanosilica
The particle size distribution was observed with Vasco Particle Size Analyzer. A total of 0.1 grams of nanosilica powder was dispersed in distilled water, was rotated with a magnetic stirrer for 10 minutes and was sonicated for 1 to 2 minutes. Scanning of nanosilica particles was carried by PSA for 2 to 5 minutes [16].

2.2 Second Step: Optimization of synthesis temperature and time
This step was conducted to obtain the optimum temperature and time of synthesis.

2.2.1 Experimental design
The experimental design used to determine the optimization of synthesis temperature and time was Respone Surface Methodology (RSM) with ANOVA (α = 5%). This method was expected to obtain the optimum time and temperature of nanosilica synthesis by observing the relationship between responses (particle size, PDI and yield) and factors (temperature and time) of nanosilica production. Before establishing the experimental design, a trial was performed to determine the optimum conditions based on variable factors used. After that, median (center point) was determined in accordance with the optimum conditions obtained. The experimental design was the Central Composite Design (CCD) with two variable factors: X1 (temperature) and X2 (time).

Data of study results further were processed by regression analysis using software Design Expert 7.0.0 to generate a polynomial equation and contours of relationship between variables (factors) and responses. Validation of the Final Optimum Conditions in this study was the validation of optimal conditions in response to the particle size, PDI and yield recommended by the program. The validation phase was aimed to prove the response value of solution of factor combination recommended. After the trial phase, actual response result obtained was compared with the value of response prediction which was generated by the program.

The results of the optimum time and temperature of nanosilica synthesis then analyzed with the analysis of characterization as described below.

The particle size distribution was observed by Vasco Particle Size Analyzer. A total of 0.1 grams of nanosilica powder was dispersed in distilled water, was rotated with a magnetic stirrer for 10 minutes and sonicated for 1 to 2 minutes. Scanning nanosilica particles was carried by PSA for 2 to 5 minutes [16].

3 Results and Discussion
3.1 Nanosilica Synthesis
3.1.1 Results of particle size test and particle size distribution
The best treatment of particle size test by [12] became the basic reference in this study which functioned to determine the treatment of first step which is able to be seen in Figure 1.

Results in Figure 1 showed that there was decline of particle size at temperatures of 150 °C which was the best temperature in the previous study [12] in sixth hours. Based on statements of [11], it was suggested to use higher temperature variations or longer variation of hydrothermal time with expectation to get crystalline silica without calcination. This suggestion led to hypothesis that longer extraction time will reduce the particle size, thus treatment time of nanosilica for 8, 10 and 12 hours were conducted in step one.

Particle size measurement in this step showed that there was increase in the particle size for each increase time of synthesis reaction when reaction time was added from 8 hours to 10 hours or from 10 hours to 12 hours. This was due to the agglomeration process between particles which formed larger particles along with the increasing time of synthesis. It was also associated with Ostwald's Law in which particles with a big size will be formed by dissolving the particles with a smaller size [17].
After comparing the two results, it was obtained that the best time that was 4 hours. Furthermore, the best treatment obtained was 150 °C for 4 hours which will used to determine the optimum temperature and time of this treatment.

This step can be seen PDI value as homogeneous indicator for nanosilica product. Polydispersity Index (PDI) can be seen on figure 2.

Figure 2 showed that results of PDI value were high enough. It showed in synthesis time on 8, 10 and 12 hours. It indicated that homogeneous level of nanosilica was bad when synthesis time increased.

3.2 Optimization of synthesis temperature and time
3.2.1 Analysis of factor combination and response optimization of particle size
Result of particel size test resulted in the particle size of 193.7 nm - 879.7 nm with average of 397.67 nm. Appropriate models to optimize the process conditions with particle size response was quadratic polinominal model.

The graph of contour and 3D surface of particle size value are presented in Figure 3.
Based on Figure 3(a), it is seen that there are circular contour lines with a red point places between the third and the fourth inner circle. Five red points on the contour are the central points of the design made. In particle size response, the value to be determined is nanosilica with minimum particle size. Circular contour line which points out direction and has blue area showed the best response value as it resulted in smaller size of particle. Five central points on the contour are not exactly at the center point of the circle. These conditions shows that the best response will be obtained by conditioning factors not at the center, but by shifting them to the top and the bottom right toward the blue area. Response of particle size will be optimum in an increased concentration of synthesis temperature and synthesis time in certain time range.

Figure 3 (b) is a 3D surface response of nanosilica particle size that shows that synthesis time and temperature was significantly affected the particle size of produced nanosilica. It is also seen that the relationship between temperature and time was very influential. When the synthesis temperature was increased and the synthesis time was lowered, particle size of nanosilica produced decreased. This result occurred since the rising temperature (to some extent) impacted on an increase of solubility level of nanosilica produced. The increase of solubility level generated a high level of ionic mobility, low viscosity and higher ion concentration that resulted in agglomerates to be separated and formed smaller size of particle [18].

Meanwhile, factor of particle size also became smaller when time was decreased (to some extent). This is due to the reason that agglomeration between particles did not occur in relatively short time. Therefore, longer reaction time of agglomeration process between particles impacted on larger particle formed when time was increased (up to certain extent). It is also associated with Ostwald's Law in which big size particles will be formed by dissolving smaller size particles [17]. However, within range of 5 - 6 hours, particle size decreased as a result of other dissolving process of large size particle. In addition, the separation between the particles also occurred thus the particle size tended to decrease [19].

3.2.2 Analysis of factor combination and response optimization of PDI (Polydispersity Index)
Result of PDI test showed PDI value of 0.0001 – 0.56 with average value of 0.32. The average value of PDI indicated that particle distribution was quite good because the value was less than 0.7. Based on statement [20], polydispersity index (PDI) is a parameter defines particle size distribution. PDI value between 0.01 to 0.5 - 0.7 is classified as monodispers (homogeneous) particle. Appropriate model to optimize the process conditions with PDI response is the quadratic polinominal model.

Contour graph and 3D surface of particle size value are presented in Figure 4.
Based on Figure 4 (a), circular contour lines with a red point placed between the fourth and the fifth outer circle is seen. Five red points on the contour are central points of the design made. In response of particle size, the value to be determined is nanosilica with minimum value of PDI. Circular contour line which points out direction and has blue area shows the best response value where the PDI value generated was getting smaller. Five central points on the contour are not exactly located at the center point of the circle. This condition showed that the best response will be obtained not by conditioning factors at the center, but by shifting them upward towards the blue area. Response of particle size will be optimum in an increased concentration of synthesis temperature and a certain range of synthesis time.

Figure 4 (b) is the 3D of nanosilica PDI value surface response which indicates that temperature and time of synthesis significantly affected the PDI value produced by nanosilica. It is also seen that the relationship between temperature and time was very influential. When synthesis temperature and synthesis time were increased, PDI value of nanosilica produced decreased. The decline of PDI value indicated that uniformity of particle size which resulted in stronger bond between particles. According to [21], when synthesis temperature and time were raised, value of PDI will decrease. Thus, the longer the reaction time, the more controlled the process of formation and growth of particles. Similarly, increase on synthesis temperature up to certain point will result in lower PDI value. This is because the higher the synthesis temperature, the faster the formation rate and the growth of such particles [22]. In addition, it can also be influenced by the tendency of particles joining one another which forms particles with larger size and high stability.

3.2.3 Analysis of factor combination and yield response optimization

Based on the result of particle size test, particle size value of 15.7% - 32.8% with average yield of 26.86% was obtained. Appropriate model to optimize the process conditions with yield response was the 2FI polynomial model.
The contour graph and 3D surface of yield value are presented in Figure 5.

![Figure 5](image)

**Figure 5** Effect of synthesis temperature and time of nanosilica production on responses of nanosilica yield: graph (a) contour and (b) three-dimensional response

Figure 5 (a) and 5 (b) above were results which were not accepted by the model as synthesis temperature and time did not affect the yield response. Large or small influence on yield generated affects the washing process of materials used to remove the sodium compounds, thus pure silica and nanosilica can be obtained.

### 3.2.4 Optimization and validation of optimum condition

Particle size and PDI value are extremely important variables in nanosilica production as they significantly affect the characteristics of nanosilica produced and are also used as quality standards of good nanosilica. After all variables and responses were given the importance weight, the solution of optimization results was further obtained to be 152.67 °C for 6 hours synthesis process. In this case, the model will be considered as good model if the value of response prediction is close to the actual verification value [23].

After the optimization solution was obtained, validation on the prediction of given response variable was conducted. Result of Design Expert 7.0.0 program showed that there was value of response prediction, followed by 95% of prediction interval which was the confidence value of individual observations. Prediction Interval (PI) was divided into two, namely 95% PI low and 95% PI high. As the 95% PI low was the lowest value of the predicted interval, 95% PI high was the highest value of the predicted interval. Comparison between response prediction value of optimization solutions and the actual value can be seen in Table 1.

| Response | Actual | Prediction | 95% PI |
|----------|--------|------------|--------|
|          |        |            | Low    | High   |
| Particle size | 330.39 | 276,288    | 346.79 | 639.03 |
| PDI      | 0.3580 | 0.189642   | 0.137  | 0.42   |
Based on the result of validation test of response variable, it was revealed that nanosilica obtained from the synthesis temperature treatment of 152.67 °C and synthesis time of 6 hours produced particle with size of 330.39 nm and PDI value of 0.3580. Compared with the value of response prediction given by the program, response value of validation result was not significantly different.

4 Conclusions
Result of preliminary study showed that the particle size increased when the synthesis time was increased. Thus, the best result used was from the previous study that was synthesis at temperature of 150 °C for 4 hours.

Data processing of RSM resulted in prediction model showing synthesis temperature of 152.67°C, synthesis time of 6 hours, particle size of 276.288 nm and PDI value of 0.189642.

Validation results were in the form of particle size of 330.39 nm and PDI value of 0.3580. Overall, actual result and predictive model results were not significantly different.

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