Optimization of High Temperature Silica Extraction from Palm Oil Mill Fly Ash in Pressurized Extractor

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ABSTRACT

Silica extraction from Palm Oil Mill Fly Ash (POMFA) using sodium hydroxide solvent was done at temperature above its boiling point in pressurized stainless steel extractor. The main composition of the POMFA was 39.99% silica and 40.83% unburned carbon. The response surface method (RSM) was applied to optimize the temperature and the stirring speed. The extract silica was analyzed using Inductively Plasma Optical Emission Spectroscopy (ICP-OES) to measure the silica content. At the optimum temperature and stirring speed the effect of the mass ratio NaOH to POMFA was studied. The optimum conditions were temperature of 156 ^{o}C, stirring speed of 461 RPM and mass ratio of NaOH to POMFA 0.02. The silica conversion at the optimum conditions was 76.44 ± 0.44 %.

Key Words: *Palm Oil Mill Fly Ash, Silica, Optimization, Pressurized Extractor*

1. Introduction

Market of Synthetic Amorphous Silica (SAS) including silica gel, precipitated silica and fume silica in the world grows rapidly. The largest market is in Asia Pacific region around 882,000 metric ton in 2009 and predicted grows 8.9% per year (Rubber World, 2011). The conventional process for producing silica is using silica sand as the raw material. Silica sand needs to be fused with soda ash to form sodium silicate in temperature higher than 1300^{o}C. This process is required a tremendous amount of energy and need high cost investment. In the recent years, silica industry faced challenging conditions, primarily due to a sharp increase in prices of raw material and energy cost. It is needed to search new material and developing cost effective process to produce specialty silica.

The agro-waste especially ash containing silica as the source for silica production are promising because inexpensive and available in abundant amount (Benke, et. al 2006). The other advantages is the process involves fewer steps since each plant species has a constant chemical composition, and the final product contains only a narrow range of metal oxide impurities (Zemnukhova et al, 2006). However, until now the researches focused on the rice hull ash (de

Lima et. al, 2009; de Sousa et al, 2009, Benke, et. al., 2006 and Rozainee et al, 2008) and sugar cane bagasse ash (Affandi et al, 2009) as the silica source.

In the other side, palm oil plantations grow rapidly especially in South East Asia. In 2006 Indonesia, Malaysia and Thailand produced 89% of world palm oil production (USDA, 2006). Shell and fiber are used as fuel in boiler to produce steam and electricity. The unburned material, ash, is sent to land fill rather than being to put in use. However, only few researchers utilized this ash to produce the SAS. The leaching process using citric acid was applied to produce silica from palm oil mill ash (Faizul et al, 2013).The weakness of the leaching process is cannot separate the amorphous silica and the crystalline silica which are found in the ash. The optimization silica extraction from Palm Oil Mill Fly Ash has been studied, the concentration of NaOH and the mass of POMFA to volume of NaOH ratio gave significant effect to the process. The atmospheric pressure and boiling point temperature was used, the extraction efficiency resulting is quite low only around 60 % (Utama et. al., 2012). In this work, the sodium extraction process in high pressure and temperature was studied to increase the extraction efficiency.

2. Methods

2.1. Materials

The POMFA was obtained from the palm oil mill at Petapahan, Kampar, Riau (PT. Perkebunan V). The POMFA was dried at 110 ^{o}C before used as the raw material. The POMFA was analyzed using XRF an XRD to determine the chemical composition and the form of silica in the POMFA.

2.2. Experimental Design

Silica was extracted from POMFA as sodium silicate using sodium hydroxide solvent. The operating condition were time 60 minutes, mass ratio of POMFA to liquid volume 1:5 (g/cm^3). To optimize the temperature and stirring speed the Response Surface Method – Central Composite Design (RSM-CCD) was applied. The full factorial design with 4 cube points, 4 axial points and 5 center points in cube was used. The proposed model for the response (η) was:

$$\eta = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^{\,2} + \beta_{22} x_2^{\,2} + \beta_{12} x_1 x_2 + \varepsilon \qquad (1)$$

The η was the predicted response for silica conversion (%), β_0 (constant term), β_1, β_2 (linear effects), β_{11}, β_{22} (quadratic effects), β_{12} (interaction effects) and ε (random error). The independent variable x_1 was the temperature (^{o}C) and x_2 was the stirring speed (RPM). The process variables being studied and optimized were temperature (low 120 ^{o}C; high 150 ^{o}C) and stirring speed (low 200 rpm; high 400 rpm). In the optimization process the mass ratio of NaOH to POMFA was set fixed of 0.2. The extraction process was done in 1500 cm^3 pressurized stainless steel extractor equipped with stirrer and temperature controller. The silica content

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of extract silica was analyzed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) to calculate the silica conversion that can be extracted from POMFA. The Regression analysis, ANOVA and the optimization were done using the Minitab 16.1.1 software. The ANOVA was used to test the compatibility of the model with the experimental data by showing the Lack of Fit (LoF) which can be used to investigate the adequacy of the model. The optimum condition was verified by conducting experiments at that condition. Responses were monitored and results were compared with model predictions (Ramos-de-la-Pena et al, 2012). To study the effect of mass ratio of NaOH to POMFA at the optimum stirring speed and temperature, the mass ratio of NaOH to POMFA of 0.02 to 0.3 were used. The silica conversion at the mass ratio of NaOH to POMFA 0.2 was used to verify the model.

3. Results and Discussions

The chemical composition of the POMFA sample which was obtained from XRF can be seen in Table 1.

Table 1. Chemical composition of the POMFA

No	Oxide	% (weight)
1	SiO_2	34.988
2	Al_2O_3	1.011
3	Fe_2O_3	0.587
4	CaO	7.495
5	MgO	3.589
6	K_2O	5.028
7	P_2O_5	4.723
8	Rb_2O	0.029
9	SrO	0.034
10	ZrO_2	0.012
11	TiO_2	0.073
12	SO_3	1.321
13	LOI	40.830

The Lost in Ignition (LOI) was 40.83 % and can be assumed it was the carbon content in the ash. It can be said that the main composition of the POMFA was silica and unburned carbon.

The morphology of POMFA was shown in Figure 1 with magnification 500 times and 4000 times. The mineral, because of heat, will be fused or partially melted. The glassy particles tend to form spherical particles. In the high temperature combustion process, the minerals will become liquid and react with

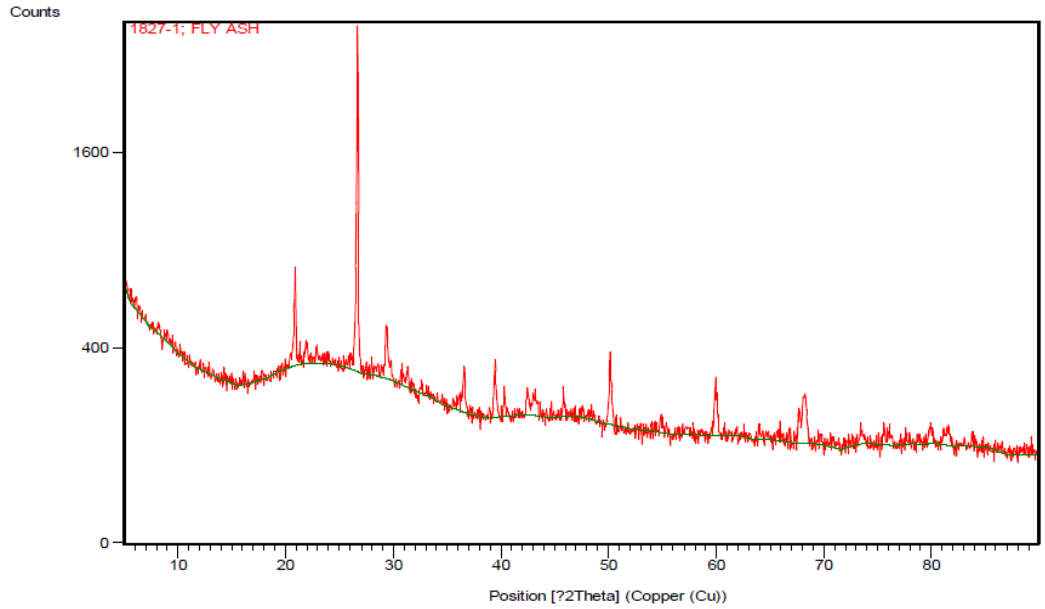

Figure 2. The XRD pattern of the POMFA

The variables and the result of the experiment are shown in Table 1.

Table 2. Extraction variables and experimental data.

No.[a]	Variables			SiO_2 Concentration in Extract (mg/L)	Conversion (%) (η)
	PtType	Temperature (°C) x_1	Stirring Speed (RPM) x_2		
1	-1	120	400	31477.00	44.98
2	0	156	300	52499.00	75.02
3	1	150	200	51246.35	73.23
4	0	135	300	43023.70	61.48
5	0	135	300	42750.78	61.09
6	-1	135	441	43471.58	62.12
7	-1	135	159	41344.18	59.08
8	-1	114	300	30175.38	43.12
9	1	135	300	43422.59	62.05
10	1	135	300	41974.00	59.98
11	0	150	400	50490.57	72.15
12	1	135	300	43135.67	61.64
13	0	120	200	34437.16	49.21

R-Sq = 98.43% R-Sq(pred) = 90.00% R-Sq(adj) = 97.31%

[a] Treatments are run in random order

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The response surface model proposed was fitted to the experimental data using RSM procedure. The coefficients of the proposed model, the significance of variables and adequacy of the model are shown in Table 3.

Table 3. Significance of regression coefficient for silica conversion (%) and ANOVA

Source	Variable constant	Regression Coefficient	p values
Regression			0.000[a]
Linear			0.000[a]
	β_0	-115.283	0.000[a]
x_1	β_1	1.934	0.000[a]
x_2	β_2	-0.0535	0.833
Square			0.278
x_1^2	β_{11}	-4.776E-03	0.632
x_2^2	β_{22}	-3.0963E-05	0.010[a]
Interaction			0.367
$x_1 x_2$	β_{12}	5.250E-04	0.367
Residual error			
Lack of Fit			0.032[a]

[a] significance at α = 0.05

From Table 3, it can be seen that the regression model for silica conversion is significant. The temperature gives significant effect to the process, but the stirring speed at the range which is used in this study does not give significant effect. Furthermore, to investigate the adequacy of the model, the residual analysis was done qualitatively by plotting the residual test curve; the graph was depicted in figure 4.

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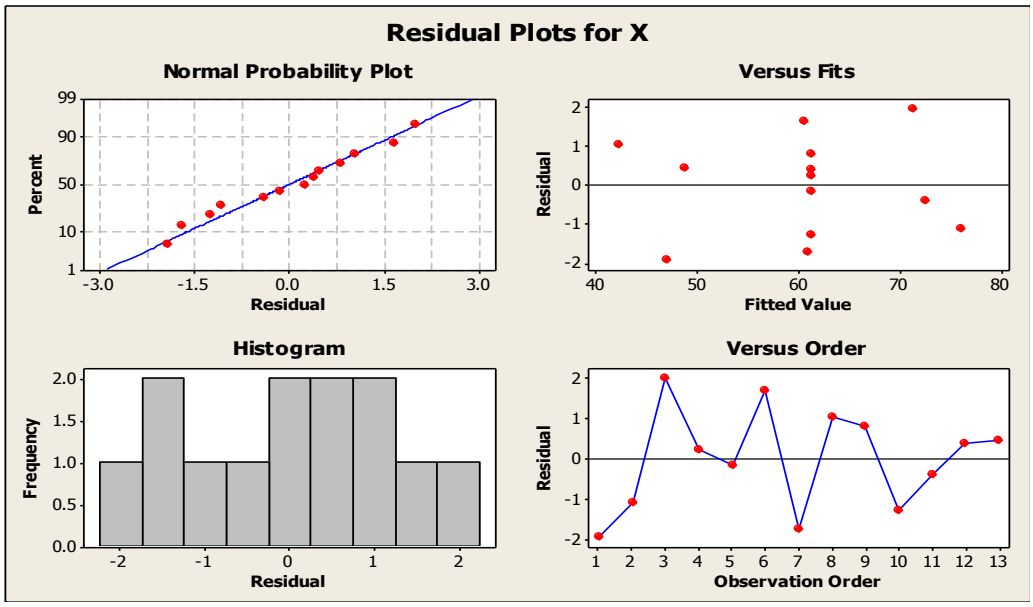

Figure 4. The residual test curve

The normal probability plot shows that the residuals follow straight line indicates the data are normally distributed, no other variables are influencing the response and no outliers exist in the data. From the residuals versus fitted values curve shows the residuals appear to be randomly scattered about zero. There no evidence of non constant variance, missing terms, outliers, or influential points exists. The histogram shows there are no long tail and no bar that far away from the other bar indicates there is no evidence that skewness and outliers exist. The residuals versus order of the data curve show the residuals randomly scattered around zero point, indicates there are no systematic effects in the data due to time or data collection. The statistical analysis above indicates that the proposed model is adequate.

The optimization process was done using Minitab 16.1.1. The goal is to maximize the silica conversion. The optimum operating conditions are the temperature of 156 ^{o}C and the stirring speed of 441 RPM. The predictive result of the silica conversion at the optimum condition is 76.9 %.

The NaOH to POMFA mass ratio effect on silica conversion at the optimum condition above was depict in Figure 5.

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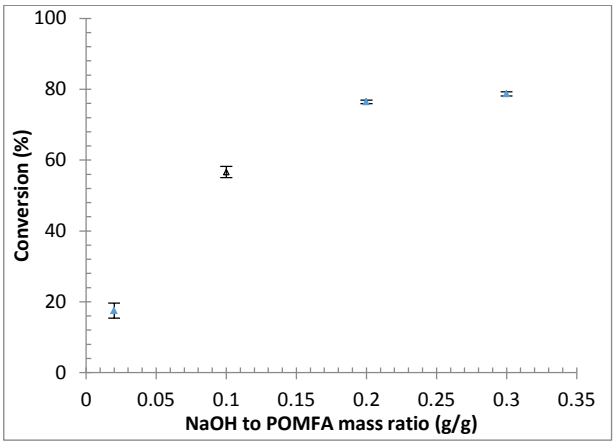

Figure 5. The plot of the NaOH to POMFA mass ratio versus silica conversion

It can be seen that at the range of 0.02 to 0.2 the NaOH to POMFA mass ratio effect was significant, but the effect was small at the NaOH to POMFA mass ratio higher than 0.2. It might be at the higher value, the viscosity of sodium hydroxide and the sodium silicate formed inhibit the rate of sodium hydroxide diffusion into porous structure (Benke et. al., 2006). It can be concluded that the optimum NaOH to POMFA mass ratio is around 0.2.

The silica conversion at the optimum conditions above was 76.44 ± 0.44 %, this result is higher than the silica conversion of the value 69.4 ± 1.0 % reported by de Sousa et. al. (2009) and the value 60 ± 4.65 % reported by Utama et. al. (2012).

4. Conclusion

The extraction efficiency of silica extraction from the POMFA can be increased by using temperature above the mixture boiling point in a pressurized extractor. The proposed model adequately represented the experimental data and can be used to optimize the temperature and the stirring speed variables. The optimum conditions for silica extraction from POMFA were temperature of 156 ^{o}C, stirring speed of 461 RPM and mass ratio of NaOH to POMFA 0.02. The silica conversion at the optimum conditions was 76.44 ± 0.44 %.

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