Fly Ash and Bottom Ash Utilization as Geopolymer: Correlation on Compressive Strength and Degree of Polymerization Observed using FTIR

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Abstract. Concerning on the dependancy of coal on electric generation worldwide, study on fly ash, the solid waste of fired coal electricity generation, has been comprehensively conducting, i.e. geopolymer, cenosphere, soil remediation, and adsorbent. However, only few studies dealing with the utilization of bottom ash. Having of about 53% of coal in the 2050 energy mix, Indonesia will be dealing with more than 200 million tonnes of fly ash and bottom ash (FABA). In this study, FABA was mixed in certain proportion of 50:50, 75:25, dan 100:0. The formation of geopolymer was conducted with sodium hydroxide and sodium silicate in certain concentration. Once the mixture had been homogenized, it was casted and cured in varied temperature of 30, 60, dan 90 °C with curing time of 1, 3, 5, 14, 21, dan 28 days. In each curing time, sample was then analyzed using compressive strength apparatus and FTIR in order to observed the geopolimerization of the FABA mixture. It was found that compressive strength representing the macro characteristic of the geopolymer is in line with the CORR analysis of the FTIR results showing that the formation of aluminosilicate is responsible for the mechanical strength of the geopolymer. The higher the bottom ash ratio in the mixture with decrease the strength of the geopolymer in the order of one per second. Higher temperature results higher compressive strength to the value of 42 Mpa (FABA ratio is 75:25 at temperature of 90 °C) above the Indonesian standard for concrete. From this study, kinetics of FABA geopolymerization can be generated in accordance to diffusion model with R² of 0.9135. Thus the utilization of FABA for geopolymer is going to be a potential solution to overcome the increasing amount of FABA resulted from fired coal electrical generation in Indonesia.

1. Introduction
Energy is the most crucial need for mankind worldwide. The need of energy is driven by the increase
of population requiring high productivity in which energy is highly required. Based on the data collected by Energy Information Administration, there will be increase by 56% on energy demands in the year of 2040 as depicted in Figure 1.

![Figure 1](image_url)

**Figure 1.** The prediction of world’s energy demand for all energy resources.

From Figure 1, it can be seen that the dependency on fossil fuel to fulfill the energy demand is still high. Among those fossil fuel sources is coal possessing the lowest production cost in electricity generation. Likewise, Indonesia has similar tendency in coal usage as energy source.

Based on the energy mix to the year of 2025, about 50% of the energy supply in Indonesia will be generated from the coal burning power generation in order to fulfill the 35 GW of electricity (Keputusan Menteri Energi dan Sumber Daya Mineral Republik Indonesia, 2016). Increasing needs of coal to fulfill energy sector will implicate to the increasing amount of coal ashes resulted. In general, the ash burning coal will be of about 10% of the total amount of coal used in the coal fired power plant. Amounting of about 10 million tonnes in 2019, this problematic coal fly ash will accumulate to its peak in the year of 2050.

In order to eliminate and or mitigate the potential danger of fly ash, some scientists have been developing utilization of coal fly ash. Not only mitigating the potential danger of fly ash, the studies are also dealing with the potential economic benefits resulted from coal fly ash, i.e., cenospheres recovery (Hirajima et al., 2008; Hirajima et al., 2010; Petrus et al., 2011), fly ash for heavy metals adsorbent (Dasmapatra et al., 2001; Alinnor, 2007), and for building materials including pozzolanic matter (Singh and Garg, 1999), and geopolymer as for called green concrete (Wilson et al., 1994; Davidovits, 1999, Adelizar et al, 2018, Petrus et al, 2019). The newest trend of coal fly ash utilization is for rare earth element resources (Ferian et al, 2016, Ferian et al., 2018, Ferian et al., 2018, Seredin, 2010, Seredin et al., 2012). Aside from many studies conducted on coal fly ash utilization, it is the coal bottom ash that has not been well utilized due to its characteristic with higher unburned carbon content. Thus, in this study, geopolymer based on fly ash and bottom ash mixture has been developed. Different from other studies on geopolymer, the characterization will include micro phenomenon in the form of Si-O-Al functional growth observation using FTIR (Olvanias et al, 2017, Petrus et al, 2019). The result will then compared with the compresive strength of geopolymer resulted. Thus it can be described the effect of bottom ash in the geopolymerization of coal fly ash.

2. Research methodology

Equipment used for the synthesis process in this research include ball mill, Avery-Denison universal testing machine, mold cube with the size of 5x5x5 cm$^3$, Memmert UN oven, sieve 300 mesh, mortar,
stirrer, and digital analytical balance, while for the equipment used for the characterization of the results are the Fourier Transform Infra Red (FTIR) 8201PC Shimadzu, X-Ray Diffraction (XRD), and X-Ray Fluorescence (XRF) spectrophotometers.

The materials used in this research include fly ash and bottom ash obtained from PLTU Tanjung Jati Jepara, NaOH pellet and sodium silicate (waterglass) solution purchased from PT. Brataco Chemical with technical grade chemicals.

2.1. Preparation of raw materials
Fly Ash and bottom ash are dried first with an oven to reduce moisture content, then ground with a ball mill and sifted with a 300 mesh sieve. Particles of raw materials that have not yet reached 300 mesh are re-milled with ball mills and sifted continuously.

2.2. Chemical and Mineralogical Analysis of Raw Materials
The raw materials to be used in this study are fly ash and bottom ash need to be analyzed in order to identify the character and composition of the material. The instruments used includes the Fourier Transform Infra Red (FTIR), the X-Ray Diffraction (XRD), and the X-Ray Fluorescence (XRF).

FTIR of raw materials are carried out in order to compare the spectrum before and after the geopolymerization process so that it can be modelled kinetics by calculating the value of the peak absorbance of corr at certain wavelengths indicating the function group of aluminosilicate. XRD analysis is conducted to know the mineral content of raw materials to know the reactivity of ingredients. XRF analysis is conducted to determine the content of oxide compounds in raw materials especially the content of SiO2 and Al2O3, so that each variation of fly ash and bottom ash composition is used always in the ratio of SiO2/Al2O3 which ranges from 3.0 to 3.8.

2.3. Polymerization experiments
Experiments were conducted by varying the composition of fly ash and bottom ash composition (100:0, 75:25, 50:50). The concentration of NaOH used in the mixture is 12 M. Geopolymer paste is stirred until homogeneous and printed on the cube mold in the size of 5x5x5 cm³. The Geopolymer paste mold is left 2 days, then dried with a variation of curing temperature 30 (room temperature), 60, and 90°C. Samples of dried geopolymer paste, taken for analysis of pressure strength and FTIR tests at any time (1, 3, 5, 14, 21, 28 days). Each experiment with each variation of the fly ash and bottom ash composition is performed in 2 times repetition to validate the test data.

2.4. Compressive Strength Analysis
The geopolymer being resulted is tested by robust test press with the Universal Testing Machine Avery-Denison performed against the entire sample according to the long duration of drying of each sample.

2.5. Geopolymer Bond Formation Analysis
Geopolymer materials that have passed the drying process (curing) is further analyzed Geopolimernya bonds using FTIR instruments. This analysis will result in the spectrogram data of geopolymer bonds. Through the analysis of the FTIR will be obtained peaks on the number of waves that indicate a specific group of functions or bonds, so that this analysis can be used as a standard for viewing the fingerprint of a compound. Geopolymer samples shall be compared with zeolite to view fingerprint suitability and see the formation of aluminosilicate bonds. The number of waves that can indicate the formation of Si-O-T (T: Si or Al) bonds is 900-1300 cm⁻¹. Based on the peak on the number of such waves, the correlation value (CORR) is calculated with the equation of 2.1 and 2.2 against the zeolite which is then modeled by the isoconversional method. These results are then compared with the value of kinetics based on compressive strength. Geopolymer concrete produced from each variation is tested for concrete compressive strength and Fourier Transform Infrared (FTIR). Geopolymerization reaction is approached using iso-conversion method, where this method is used to facilitate kinetic modeling
for reactions that take place in a solid-state. The model of FTIR characterization is obtained based on the absorbance peak at each wave number that shows the characteristics of alumino-silicate.

Table 1. FTIR Interpretation for aluminosilicate content characterization (Krol, dkk., 2016)

| Wave Number | Interpretation                        |
|-------------|---------------------------------------|
| 900-1300 cm\(^{-1}\) | Si-O-T (T: Si, Al Tetrahedral) asymmetric stretching |
| 1650 cm\(^{-1}\) | H-OH bending                             |
| 3400-3650 cm\(^{-1}\) | -OH symmetric and asymmetric stretching |

The results of FTIR characterization were processed using a correlation equation (corr) to compare geopolymer samples with standard zeolites (Varmuza, dkk., 2002).

\[
\begin{align*}
    r &= \frac{(a_i - \bar{a})(b_i - \bar{b})}{\sqrt{(a_i - \bar{a})^2(b_i - \bar{b})^2}} \\
    Corr &= \frac{999(r+1)}{2}
\end{align*}
\]

(1) (2)

3. Results and Discussion

Raw material characterization is an important stage that has to be accomplished in order to predict the potential utilization of the fly ash-bottom ash as geopolymer raw material. Furthermore, FTIR analysis shows both fly ash and bottom ash has relatively low Si-O-Al component in comparison to the standard zeolite used in the experiment, as seen in figure 2.a.

Figure 2. FTIR characterization of fly ash and geopolymer samples (curing temperature of 30\(^{\circ}\) and 90\(^{\circ}\)C) in comparison with zeolites

In addition, silica and alumina are found abundantly in the fly ash and bottom ash with the chemical composition as shown in table 2.

Table 2. Chemical composition of fly ash and bottom ash

| Chemical composition | SiO\(_2\) | Al\(_2\)O\(_3\) | P\(_2\)O\(_5\) | SO\(_3\) | K\(_2\)O | CaO | Fe\(_2\)O\(_3\) | LOI | Others |
|----------------------|---------|-------------|-------------|---------|---------|-----|---------------|-----|--------|
| Fly ash (%)          | 37.5    | 12.5        | 1.89        | 2.07    | 1.97    | 19.7| 19.9          | 1.87| 2.5    |
| Bottom ash (%)       | 46.7    | 14.7        | 1.97        | 0.45    | 2.64    | 2.37| 15.8          | 12.9| 2.42   |

As shown in table 2, it can be counted that the SiO\(_2\)/Al\(_2\)O\(_3\) in fly ash is 3.01 while it is found of about 3.31 in bottom ash. According to De Silva et al (2007), in order to have a good geopolymerization phenomenon, the SiO\(_2\)/Al\(_2\)O\(_3\) of the raw material should be in the range of 3.0-3.8. Thus, the fly ash
and bottom ash from PLTU Tanjung Jati Jepara possess sufficient amount of SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio to form high performance geopolymer. In term of percentage of loss on ignition (LOI) at which it was found that the LOI in bottom ash is higher than that of fly ash in the ratio of twelve time fold showing the abundance existence of unburned carbon in bottom ash. The existence of unburned carbon in the raw material of geopolymer will decrease its compressive strength due to low affinity with silica aluminate structure as the backbobe of geopolymer structure (Ha et al., 2005). As for the geopolymer product, longer time sequence creates greater absorbance which indicate larger geopolymerization of aluminosilicate. The compressive strength of geopolymer sample represents the degree of aluminosilicate formation. As it can be seen from Figure 3 that the compressive strength increases as the temperature increase for all fly ash and bottom ash composition. However it can be seen that the higher the bottom ash addition into the geopolymer product, the lower the compressive strength as shown in figure 3.c. Similar tendency was also observed in the CORR FTIR product.

![Figure 3](image-url)

Figure 3. The comparison between compressive strength and Corr FTIR on fly ash to bottom ash ratio of (a) 75:25, (b) 50:50, and (c) Compressive Strength and CORR FTIR comparison at room temperature of curing.

Conversion factor (α) inserted into each of kinetic model for every composition to determine the
fittest kinetic model for fly ash – bottom ash geopolymerization model, which is diffusion model with the highest $R^2$ value of 0.9888. This statement supported by previous research that the diffusion model mostly used for pozzolanic reaction (De Silva et al., 2007; Khawam and Flanagan, 2006).

### Table 3. Arrhenius equation value for each FA:BA composition

| FA:BA Composition | ln A   | A (day$^{-1}$) | -E/R     | E (J/mol) |
|-------------------|--------|---------------|----------|-----------|
| 50:50             | -0.6651| 0.514222      | -2750.7  | 22869.32  |
| 75:25             | 1.9725 | 7.188626      | -3061.5  | 25453.31  |
| 100:0             | 5.1664 | 175.2827      | -3777.2  | 31403.64  |

Based on Table 3, the increase of bottom ash weight ratio causes lower Arrhenius reaction rate constant. The unburned carbon in bottom ash causes low formation of aluminosilicate, thus decreasing the compressive strength.

4. Conclusions

Geopolymer successfully formed using fly ash from PLTU Tanjung Jati B Jepara with the highest compressive strength of 58 MPa resulted by 100:0 fly ash – bottom ash ratio with curing temperature of 90°C for 28 days. The increase of compressive strength as a function of temperature and series of time sequence is in accordance with the semi quantitative FTIR analysis represented by corr value. The addition of bottom ash in the geopolymer formation decreases the compressive strength due to its unburned carbon content. The kinetics of fly ash geopolymerization has fitted with the diffusion model, in which diffusion control in the process including dissolution, gel formation, and solidification. The diffusion model fits the phenomenon with highest $R^2$ value of 0.9888. Greater bottom ash concentration causes lower compressive strength of geopolymer sample with the same curing temperature and time sequence.

Acknowledgement

Highly appreciate to the Minister of Higher Education of Indonesia for the financial support to conduct this project under PTUPT scheme with contract number 2702/UN1/DITLIT/DIT-LIT/LT/2019.

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