Reuse of Coconut Shell, Rice Husk, and Coal Ash Blends in Geopolymer Synthesis

Tjokorde Walmiki Samadhi1, *, Winny Wulandari1, Muhammad Iqbal Prasetyo1, Muhammad Rizki Fernando1

1Chemical Engineering Program, Faculty of Industrial Technology, Institut Teknologi Bandung, Labtek X Bldg., Jalan Ganesha 10 Bandung 40132 Indonesia

Abstract. Mixtures of biomass and coal ashes are likely to be produced in increasing volume as biomass-based energy production is gaining importance in Indonesia. This work highlights the reuse of coconut shell ash (CSA), rice husk ash (RHA), and coal fly ash (FA) for geopolymer synthesis by an activator solution containing concentrated KOH and Na2SiO3. Ash blend compositions are varied according to a simplex-centroid mixture experimental design. Activator to ash mass ratios are varied from 0.8 to 2.0, the higher value being applied for ash compositions with higher Si/Al ratio. The impact of ash blend composition on early strength is adequately modeled by an incomplete quadratic mixture model. Overall, the ashes can produce geopolymer mortars with an early strength exceeding the Indonesian SNI 15-2049-2004 standard minimum value of 2.0 MPa. Good workability of the geopolymer is indicated by their initial setting times which are longer than the minimum value of 45 mins. Geopolymers composed predominantly of RHA composition exhibit poor strength and excessive setting time. FTIR spectroscopy confirms the geopolymerization of the ashes by the shift of the Si-O-Si/Al asymmetric stretching vibrational mode. Overall, these results point to the feasibility of geopolymerization as a reuse pathway for biomass combustion waste.

1. Introduction
As Indonesia heads for an increased contribution of biomass-based energy to reach its planned national energy mix by 2025, the increased production of biomass ash as a waste of biomass thermal conversion is expected as well. Alternative reuse pathways for the ashes should help to ensure the economic sustainability of biomass-based energy.

Geopolymer is a generic term for a class of alkali-aluminosilicate solid materials produced via complex reactions between aluminosilicate solid materials and an activating solution. The activating solution is a concentrated alkali aqueous solution – typically NaOH or KOH – with or without the addition of soluble sodium silicate (Na2SiO3). Key feature in the geopolymeric structure is the presence of a solidified, crosslinked gel phase consisting of a random network of silica and alumina tetrahedra. The gel phase acts a continuous binder phase bridging unreacted aluminosilicate particles and aggregates into a coherent cementitious mass. Geopolymer may be applied as Portland cement substitute; when applied to concrete preparation, geopolymers exhibit early compressive strengths that are comparable to, and elastic moduli that are somewhat lower than ordinary Portland cement (OPC) concrete [1].

Geopolymer offers several environmental advantages. Unlike Portland cement which require massive amount of energy to sinter the raw minerals into clinker at temperatures in excess of 1400 °C, the aluminosilicate – alkali activator reaction may be conducted at ambient or very mildly elevated temperatures. Concrete made by using geopolymer has been argued to reduce the global warming
potential relative to OPC concrete by approximately 45% [2]. Another advantage of geopolymer stems from the fact that various aluminosilicate waste materials have been proved to be good candidates for geopolymer synthesis. These include coal fly ash, metallurgical slag, building demolition waste, and several biomass ashes such as rice husk ash, palm oil fuel ash (POFA), and others [3-5].

This paper is a part of an ongoing study on the synthesis of geopolymers from biomass ashes that are abundant in Indonesia, with an emphasis on rice husk ash (RHA) and coconut (Cocos nucifera) shell ash (CSA). Coal fly ash (FA) is included, as it is expected that biomass combustion needs to incorporate the blending of coal with the biomass fuel to increase the ash fusion temperatures of the fuel, hence reducing its tendency to form slag in the combustion chamber [6]. The primary objective of this work is to determine the impact of biomass ash blend on key engineering properties of geopolymer, and the compliance of these properties to industrial standards.

Successful development of geopolymer from biomass ash is therefore of significant impact for Indonesia. Not only does it provide a pathway for better waste management of the biomass-based energy industry, it also reduces the national industrial CO₂ emission through partial substitution of the energy-intensive Portland cement.

2. Methodology

2.1. Materials

Starting materials for the biomass ashes are rice husk and coconut shell charcoal. The rice husk was obtained from a local farmers’ cooperative in the greater Bandung area. The coconut shell charcoal was purchased from a local market in Bandung. The coal fly ash is an ASTM Class F fly ash produced by the Suralaya powerplant in Banten province. Based on thermogravimetric analyses of the biomass materials, they are combusted at 550 °C for 3 hours in an electric furnace for ashing. The activator solution is an aqueous solution of 10.0 M KOH with the addition of technical-grade Na₂SiO₃ at a sodium silicate to KOH solution mass ratio of 2.0. Ash characterizations include phase analyses using X-ray diffractometry (XRD) and oxide composition determination using X-ray fluorescence (XRF).

2.2. Experimental Design

Key engineering properties examined in this work are early strength as measured by compressive strength after 7-day setting of geopolymer-sand mortars, and initial setting time of geopolymer paste. To prepare the geopolymer paste, dry ash blends are mixed with the activator solution in a low-speed planetary mixer until a smooth paste is obtained (approximately 2 minutes). The activator solution to ash mass ratios are varied from 0.2 to 2.0, with higher values assigned to higher ash Si/Al ratios. Ternary ash blend compositions consisting of RHA, CSA, and FA are varied according to a conventional simplex centroid mixture experimental design. Statistical analysis of the measured data is undertaken by the ANOVA method using the Minitab software package.

For initial setting time measurement, the pastes are directly hand-shaped after mixing into balls for testing using a Vicat apparatus. For the compressive strength measurement, the paste is further blended with a graded sand at a sand to geopolymer mass ratio of 2.75. The mortar is then cast into a 5x5x5 cm steel mold, tapped by hand, and transferred to an electric oven for a quick curing at 60 °C for 24 hours. The filled molds are then taken out of the oven, the mortars removed from the mold, and left to stand at ambient conditions for 6 additional days. The 7-day compressive strength is then measured using a universal uniaxial load tester.

3. Results and Discussion

The oxide compositions of the RHA, CSA, and FA used to formulate the ash blends for geopolymer synthesis are presented in table 1. Figure 1 compiles the X-ray diffractograms of the three ashes. RHA is characterized by a very high SiO₂ content of 89.6 %-mass and Si/Al molar ratio of 544, and a largely amorphous structure. A diffuse hump in the diffractogram in the vicinity of 2θ = 21° is a fingerprint of a random network structure consisting predominantly of SiO₄ tetrahedra. The CSA is characterized by a high alkali content (particularly K₂O), relatively low Al₂O₃ and SiO₂ contents, and Si/Al molar ratio of 0.49. Crystalline phases observed in CSA include quartz, sylvite (KCl), and
calcite (CaCO$_3$). Oxide composition of the Suralaya powerplant FA indicates that it belongs to the ASTM Class F category. The Si/Al molar ratio is 2.04, and the observed crystalline phases are quartz and hematite. The presence of these crystalline phases in biomass ashes has been reported in the literature [7].

Table 1. Oxide compositions of RHA, CSA, and FA.

| Ash  | Al$_2$O$_3$ | SiO$_2$ | CaO | Fe$_2$O$_3$ | MgO | Na$_2$O | K$_2$O | P$_2$O$_5$ | SO$_3$ |
|------|-------------|---------|-----|-------------|-----|---------|--------|----------|--------|
| RHA  | 0.14        | 89.6    | 1.14| 0.18        | 0.37| 0.14    | 5.26   | 1.57     | 1.29   |
| CSA  | 5.71        | 3.28    | 13.6| 13.6        | 15.4| 5.89    | 30.4   | 6.93     | 3.83   |
| FA   | 21.1        | 50.7    | 15.8| 3.71        | 2.29| 1.24    | 2.09   | 0.52     | 1.91   |

Figure 1. X-ray diffractograms of rice husk ash (RHA), coconut shell ash (CSA), and coal fly ash (FA) (Q = quartz, H = hematite, Sy = sylvite, Ca = calcite).

Table 2 compiles the early strength measurement results of the geopolymer mortars after a quick curing at 60 °C for 24 hours followed by setting at ambient conditions for 6 days. The mean strengths vary from 1.40 to 15.7 MPa, with the lowest strength exhibited by the RHA-only ash composition, and the highest by the FA-only composition. Compared to the SNI 15-2049-2004 Indonesian national standard Portland cement mortar minimum early strength value of 2.0 MPa, RHA-only geopolymer formulation is unfavorable, while the CSA-only composition produces an acceptable 3.15 MPa early strength. Most (5 out of 7) ash blend compositions in this work produces satisfactory early strength with respect to the SNI industrial standard. As a comparison, the early strength of the Portland cement mortar specimens lie approximately in the middle of the geopolymer mortar strength range.

The decrease of geopolymer strength with increasing Si/Al molar ratio at Si/Al above 1.90 has been reported in the literature. The RHA has Si/Al ratio that is two orders of magnitude higher than CSA and FA. It has been argued that at high Si/Al ratios, the geopolymer mechanical strength decreases with increasing Si/Al due to the higher content of unreacted aluminosilicate raw materials [8].

To quantify the effect of ash blend composition on the geopolymer mortar early strength, the data in table 2 are analyzed using the Minitab statistical software package. Table 3 summarizes the ANOVA data treatment results using a special cubic mixture model. At a confidence level of 95%, the table indicates that the RHA*CSA quadratic blending and the RHA*CSA*FA cubic blending terms are not statistically significant. By dropping these terms, the geopolymer mortar early strength is adequately represented by an incomplete quadratic mixture model as described in equation 1.
Table 2. Early strength (7-day compressive strength) measurement results of the geopolymer mortar specimens.

| Run no. | Ash blend composition (mass fractions) | Compressive strength (Mpa) | Initial setting time (mins) |
|---------|---------------------------------------|-----------------------------|-----------------------------|
|         | RHA  | CSA  | FA  | Rep. I | Rep. II | Mean |                      |
| 1       | 1.0  | 0    | 0   | 1.4    | 1.4     | 1.40 | > 300                   |
| 2       | 0    | 1.0  | 0   | 3.0    | 3.3     | 3.15 | 90.0                    |
| 3       | 0    | 0    | 1.0 | 16.5   | 14.8    | 15.7 | 51.8                    |
| 4       | 0.5  | 0.5  | 0   | 2.1    | 1.6     | 1.85 | > 300                   |
| 5       | 0.5  | 0    | 0.5 | 3.5    | 3.4     | 3.45 | > 300                   |
| 6       | 0    | 0.5  | 0.5 | 6.7    | 8.3     | 7.50 | 57.5                    |
| 7       | 0.33 | 0.33 | 0.33| 2.6    | 2.3     | 2.45 | 271.7                   |
| 8       | -    | -    | -   | -      | -       | -    | -                       |

Table 3. ANOVA treatment results of the geopolymer mortar early strength data.

| Source               | Deg. of freedom | Sum of squares | Mean squares | F     | P-value |
|----------------------|-----------------|----------------|--------------|-------|---------|
| Linear               | 2               | 241.58         | 120.79       | 287.11| 0.000   |
| Quadratic            |                 |                |              |       |         |
| RHA*CSA              | 1               | 0.241          | 0.241        | 0.57  | 0.474   |
| RHA*FA               | 1               | 34.34          | 34.34        | 81.63 | 0.000   |
| CSA*FA               | 1               | 4.81           | 4.81         | 11.44 | 0.012   |
| Special cubic        |                 |                |              |       |         |
| RHA*CSA*FA           | 1               | 1.21           | 1.21         | 2.88  | 0.133   |

Table 2 also compiles the initial setting times of the geopolymer paste specimens measured by the standard Vicat apparatus method. The SNI 15-2049-2004 Indonesian national standard calls for a minimum initial setting time for Type I Portland cement of 45 minutes. The initial setting time is a measure of the workability of the cement paste, in which longer setting time translates to better workability. Data in table 2 suggest that the geopolymers in general exhibit good workability. However, RHA-containing formulations exhibit excessively long setting time, in accordance with their low early strengths. Of the three ashes, FA produces the shortest setting time. The presence of excessively long setting times of RHA-containing formulations prevent the ANOVA treatment of the data.
Figure 2. FTIR spectra of the RHA-CSA-FA ternary ash blend geopolymer paste.

To verify the reactivity of the biomass ashes to geopolymerization, chemical bonds in the geopolymer paste specimens are identified by FTIR spectroscopy. Figure 2 presents the FTIR spectra of the ternary ash blend (RHA-CSA-FA) geopolymer. The silanol group asymmetric stretching vibrations at 1018 cm⁻¹ is shifted with respect to its position in the spectra of unreacted aluminosilicate geopolymer precursor materials such as fly ash and metakaolin, which typically lie in the 1070 – 1080 cm⁻¹ range. This shift is an indication of the formation of the geopolymer gel phase [9, 10], thereby confirming the reactivity of the RHA and CSA biomass ashes to geopolymerization.

4. Conclusions
The technical feasibility of the reuse of rice husk ash (RHA) and coconut shell ash (CSA) for geopolymer synthesis has been demonstrated, with and without the addition of ASTM Class F coal fly ash (FA). A shift in the ash blend composition towards RHA reduces the geopolymer compressive strength, while a shift towards FA increases the strength. RHA-only geopolymer does not comply with the Indonesian industrial standard for early strength, and produces excessively long initial setting time, while CSA-only geopolymer produces acceptable said properties. Low strength and excessive setting time at high ash Si/Al molar ratio is likely to be due to higher content of unreacted aluminosilicate raw materials. The presence of FA in the ash blend can ensure that the strength and setting time are satisfactory. Biomass ash blends reactivity towards geopolymerization has been proved by the shift in the silanol group stretching vibrational mode, which is an IR-absorption fingerprint of the geopolymeric gel phase.

5. References
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