The application and effectiveness of fly ash granule using tapioca flour and sugarcane molasses as granule agents for soil ameliorant and fertilizer

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Abstract. The most popular fly ash application as coal combustion energy waste is as a mixing agent for cemented infrastructure and building construction. However, due to its appropriate various mineral content from vegetation fossil, the usage for fertilizer and soil amelioration agent was tested in small pots on the field. The experiment's purpose was to confirm the effectiveness of fly ash granule application using tapioca flour and sugar cane molasses as granule agents for soil ameliorant and fertilizer. Specifically, for the sorghum growth, development, and potential bioethanol yield harvested in the vegetative stage. The granule binding agents' source is from an agricultural product, byproduct, or agricultural waste. Hence, environmental management and the fly ash granules' production system exhibit the advantage of a sustainable production system. The concentration of 10% of the granule binding agents concentration for the application at a rate of 8 tons ha⁻¹ was effective enough to improve the soil properties, plant growth, and the doubling of potential bioethanol yield.

1. Introduction
As a byproduct and waste of coal combustion plants, fly ash is less considered a useful resource. Even in Indonesia, according to Indonesian Government Regulation No. 101/2014, it is classified as hazardous and poisonous waste. Consequently, there is no other sustainable management solution except the permitted application for cement or concrete mixing agents in a limited volume. The rest is for the landfill as the final disposal management purpose. Its contents on various mineral nutrition should be beneficial as a mineral resource for agricultural purposes to provide essential minerals for plant growth. Its proportion for the agricultural application is less than 0.05% [1]. However, in the 30-OECD country members, fly ash waste is subjected to green control procedures and not classified as hazardous materials [2].

Granule or pellet formulation for applying fly ash for fertilizer and soil ameliorant is a reasonable method to make the agent fabrication more feasible, spread into the soil more affordable, and enable safer distribution systems. Direct application of fly ash into the soil is not recommended due to fine and possibly nanoparticle dimensions [3], which considers the human respiration health system. In the granulation procedure, various granule agents such as synthetic polymers, molasses, and tapioca were
applied for the binding and stabilization agents [4,5]. The addition of clay to the fly ash has no influence on the soil's physical characteristics after application [6]. Sorghum plant has appropriate adaptability to marginal soil such as acidic soils, dry land, saline soil, and basic soil. Multiple culturing purposes for human consumption, feed, and bioenergy resource are advantages of the sorghum production system for sorghum planting development. The purpose of this experiment was to evaluate the application of fly ash granule using tapioca flour and sugarcane molasses as granule binding agents for soil fertilizer and ameliorant on sorghum plant on acid soils. The objective of the experiment was to ensure the effectiveness of the new granule products for agriculture.

2. Methodology
Molasses and tapioca flour in 10% concentration were applied as binding agents in a pan granulator to produce fly ash granule in the method described procedure [5]. The applied fly ash was sourced from the fertilizer industry in East Borneo. The fly ash and the granules were priorly analyzed for total mineral contents (HNO₃ 65% + HClO₄ 60%, SNI, and AOAC Methods) and TCLP (Toxicity Characteristic Leaching Procedure, CH₃COOH & CH₃COOH + NaOH, US-EPA Method No. 1311 in 1992).

A small pot experiment was applied for the testing of effectiveness in acidic soil in the first experiment. 20 kg of soil with pH value 5.1 ±0.2 were installed outdoors at the Leuwipuro Research Station of Institut Pertanian Bogor from April–August 2016. Fly ash granulated with tapioca as a binding agent (FAGT–fly ash granulated with tapioca) and molasses (FAGM–fly ash granulated with molasses) were applied at the planting time in the dosage of 80 g per pot or equivalent to 8 ton FAGT and FAGM application per ha. The sorghum cultivar planted was Super-2. This experiment was six times replicated in a randomized block design. The altitude of the location site is about 204 m above sea level. Data on the government climate station of Cikarawang situated about 2 km from the site location during the experimentation time showed that the monthly precipitation ranged 161.6-304.3 mm, daily temperature 22.0 º-32.8º, and sunlight intensity 143-405 cal/cm²/day.

The granules' capacity to improve soil properties, especially soil pH, was arranged in weeks 1-2-3-4-5-6-8-10-12-14. Harvesting of the sorghum plant was conducted at the end of the vegetative stage. Biomass and the content of sugar at the plant crown was measured with digital Brix-Refractometer Milwaukee MA871. Bioethanol yield potency was calculated averagely by 49% [7–10]. The fermentation of biomass could produce bioethanol in the amount of 0.354 g per g biomass [11].

3. Results and discussion

3.1. Fly ash, granule, and soil characteristics
The fly ash used in this experiment contained not only 3.25% Mg and 8.71% Ca as macro essential nutrients but also 82315 ppm Fe and 2262 ppm Mn as micro essential nutrients. However, total heavy metals concentrations were also found in the fly ash as the following: 0.195 ppm Hg, 40.62 ppm Pb, 2.51 ppm Cd dan 11.80 ppm As. The addition of binding agent molasses and tapioca did not significantly affect the granule's heavy metals concentration. Due to pH improvement on acidic soil, the immobilization of heavy metal would increase, so that the mobile and available heavy metals for the plant should be reduced. The concentration of macroelements, microelements, and heavy metals in the soil, in the fly ash, and the granulated fly ash, is presented in table 1. The incorporation of fly ash granules at the rate of 80 g into 20 kg of acidic soil would be equivalent to the application of 8 tons of fly ash granules per ha. This application would enrich heavy metal into the soil in the amount of 0.32 g total Hg per ha or approaching soil Hg concentration in the proportion of 0.16 x 10⁻³. The enrichment of Cd due to the granule application would amount to an averagely 3.2 kg total Cd per ha or total soil Cd concentration in the proportion of 1.6 x 10⁻³. There was no substantial difference concentration on Pb and As in fly ash, in the soil, and the granules, so the possible enrichment on both heavy metals in the soil after applying the granules was not considered.

The resulting test showed that TCLP concentration on the granules was considerable, not higher than in the soil. Since the granules' application rate into the soil was only 4 tons per ha, the potency of dilution
or mobility of the heavy metals in the soil was not affected expressively by the application of the granules. The TCLP of the heavy metals in the soil was not affected expressively by the application of the granules. The TCLP of the soil, the fly ash, and the applied granules were presented in Table 2.

### Table 1. Total mineral content the soil, fly ash and fly ash granules.

| Source | Ca (%) | Mg (%) | Mn (ppm) | Fe (ppm) | Hg (ppm) | Pb (ppm) | Cd (ppm) | As (ppm) | pH (H₂O 1:5) |
|--------|--------|--------|----------|----------|----------|----------|----------|----------|-------------|
| Soil   | 0.19   | 0.20   | 587      | 37913    | <0.010   | 42.44    | 0.00     | 7.70     | 5.1         |
| Fly ash| 8.71   | 3.25   | 2262     | 82315    | 0.1954   | 40.62    | 2.51     | 11.80    | 11.1        |
| FAGT   | 8.25   | 2.83   | 1854     | 66892    | 0.1934   | 32.13    | 1.78     | 7.24     | 10.2        |
| FAGM   | 8.56   | 3.08   | 2495     | 78696    | 0.1914   | 42.40    | 2.32     | 9.47     | 9.8         |

Note: Extraction method: HNO₃ 65% + HClO₄ 60%; Measurement: AAS

### Table 2. Toxicity characteristic leaching procedure of soil, fly ash and fly ash granules.

| Source    | Hg (ppm) | Pb (ppm) | Cd (ppm) | As (ppm) |
|-----------|----------|----------|----------|----------|
| Acidic soil | 0.004    | <0.07    | <0.002   | 0.83     |
| Fly ash   | 0.004    | <0.07    | <0.002   | 0.92     |
| FAGT      | 0.004    | <0.07    | <0.002   | 0.60     |
| FAGM      | 0.004    | <0.07    | <0.002   | 0.72     |

Note: Incubation and Extraction method: CH₃COOH& CH₃COOH+NaOH (US EPA 1311/1992); Measurement: AAS

3.2. Soil pH improvement

Due to its alkaline pH value, fly ash might have the capability to improve soil pH, especially in acidic soils, which predominate Indonesian soil properties. However, the slight acidic characteristic of the binding agents with pH value 4.8 of the tapioca binding emulsion and pH value 5.5 of molasses binding solution reduced the pH value of fly ash granule formula slightly from 11.1 to 9.8-10.2. Both of the granule types had the sufficient capability to improve the acidic soil properties after four weeks of application time and remained effective until the harvest time in the vegetative stage, i.e., in 14 weeks after application or after the planting time (Table 3).

### Table 3. The capability of fly ash granules to improve acidic soil pH during the experiment time.

| Source   | pH Value in the Week after the Application Time |
|----------|-----------------------------------------------|
|          | 1  | 2  | 3  | 4  | 5  | 6  | 8  | 10 | 12 | 14 |
| Acidic Soil | 5.20 | 4.47 | 3.77 | 3.60 | 3.30^a | 4.27^a | 4.27^a | 4.60^a | 4.40^a |
| FAGT     | 5.00 | 4.67 | 3.87 | 3.93 | 3.57^b | 5.17^b | 4.97^b | 5.13^b | 4.97^b |
| FAGM     | 5.03 | 4.40 | 3.36 | 4.07 | 3.67^b | 4.92^b | 4.97^b | 5.27^b | 4.93^b |

Note: an unequal indexed letter at the same column represents DMRT significant difference at the 5% level

3.3. Biomass production and theoretical yield of bioethanol

Fly ash granules with tapioca and molasses applications significantly increased the production of Brix-sugar by more than 90%, crown biomass yield by 197-226%, and bioethanol yield potential 185-213% compared to control treatment without fly ash granule application. The result of biomass yield and bioethanol yield potential is presented in Table 4.

### Table 4. Improvement of Brix-sugar production, crown biomass, and bioethanol yield potential due to fly ash granules application

| Granule Type | Brix-sugar (kg/ha) | Crown Biomass (kg/ha) | Bioethanol Yield Potential (l/ha) |
|--------------|--------------------|-----------------------|-----------------------------------|
|              |                    |                       | Brix-sugar | Biomass | Total  |
| Control      | 230.0^a            | 2723^a                | 112.7      | 963.9   | 1077   |
| FAGT         | 441.7^a            | 8083^a                | 216.4      | 2861.4  | 3078   |
### 4. Conclusion

Fly ash granule formulation with tapioca and molasses as binding agents are technically appropriate for using the granule as fertilizer for macronutrients, fertilizer for micronutrients, and soil ameliorant, significantly to improve acidic soil properties. The granule binding agents source is from agricultural product or byproduct or agricultural waste so that environmental management and the production system of the fly ash granules exhibit the advantage for a sustainable production system. Sorghum plants exposed positive responses to produce more biomass and bioethanol yield potential on acid soils. Both approximately in a double productivity value from 2723 kg/ha biomass or 1077 l/ha bioethanol yield potential to averagely 8486 kg/ha biomass or 3207 l/ha bioethanol yield potential after the application of fly ash granules agglomerated with tapioca or molasses binding agent.

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