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Kepada: Agus Hermawan <karimagushermawan@gmail.com>

Agus Hermawan:

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- Giving information
- Respresenting a confirmation
- Nothing some new

2. Priority to be published in Journal of Tropical Soils

- High
- Middle
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5. Manuscript's repairment:

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PHYSICAL PROPERTIES OF FLY ASH-AZOLLA-UREA COMPOSITE

AS A FERTILIZING MATERIAL

Fertilizer

ABSTRACT

Fly ash has a vast potential for use as a soil ameliorant that may improve soils physical, chemical and biological properties. The addition of biomass of azolla as an organic manure and granulation of fly ash is necessary to make the ash applicable to fertilization and to improve its handling and storage characteristics. The objective of the current research was to determine the physical properties of fly ash-Azolla biomass-urea composite as a fertilizing material. The research were arranged

fertilizer

(Latin name/greek name?) green manure

Cation exchange properties

or make

fertilizer

according to Factorial Completely Randomized Design with three replicates. The composite treatments tested were made from fly ash-Azolla biomass FAZ (w/w of 40:60, 50:50, 60:40; 21 days incubation) and urea (46% N) at the rates of 90:10, 80:20, and 70:30 (w/w basis). Results of the research showed that the coal fly ash and Azolla biomass potentially to be use as a fertilizing material. The formulation of FAZ-U (60:40)70:20 and (60:40)70:30 tend to have the compressive strength, bulk density, porosity and water holding capacity better than the other formulation and indicated can release nutrient from urea slowly.

The result

fertilizer

FAZ

soil strength

particle specific density (soil moisture)

Optimum data respectively (mentioned)

Keywords: Azolla biomass, Coal fly ash, composite, fertilizing material

alphabetically
max: 5 word
(Single)

fertilizer

INTRODUCTION

Coal fly ash, a by-product of coal combustion, is an amorphous aluminosilicate material and composed of particulate matter collected from flue gas stream. The use of coal produces about 5% ash (fly ash and bottom ash), and about 10-20% is bottom ash and 80-90% is fly ash (Kishor et al., 2010). The increasing use of coal for electric power generation will generate large quantities of ash. The fly ash, which is a resource material, if not managed well, may pose environmental challenges. Therefore, efforts are being made to recycle these materials to prevent further environmental problems.

(soil?)

chimney

PLTU

HAVE

Concept 1 paragraph to fly ash description.

26 Fly ash is a heterogeneous mixture of an amorphous aluminosilicate material (Carlson and
27 Adriano, 1993; Kishor *et al.*, 2010). Chemically, fly ash contains oxides, hydroxides, carbonates,
28 silicates, and sulfates of calcium, iron, aluminum, and other metals in trace amount i.e. almost all
29 the nutrients present in the soil. Fly ash was also found to have high pH value, and high cation
30 exchange capacity (Carlson and Adriano, 1993; Kishor *et al.*, 2010). Physically, fly ash is a material
31 containing granules which are fine in size (0,01 – 100 μm). It comprised of about 69 percent silt and
32 clay size fractions (Singh *et al.*, 2011). Fly ash materials are pozzolanic, exhibiting cementitious
33 properties when exposed to water and an activator (Adriano *et al.*, 1980; Singh *et al.*, 2011).
34 Because of its physico-chemical characteristics, fly ash has a vast potential for use as a soil
35 ameliorant that may improve soils physical, chemical and biological properties.

36 The chemical constituents of coal ash are commonly found in soil, rock and other parts of
37 the earth's crust. Therefore, coal fly ash is relatively safe to use as an ameliorant on agricultural land and is
38 known to increase crop production (Mitra *et al.*, 2003; Aggarwal *et al.*, 2009; Kishor *et al.*, 2010;
39 Pandey and Singh, 2010). It was also realized that fly ash addition could also decrease the bulk
40 density of soils, which, in turn, improved soil porosity and workability and enhanced water
41 retention capacity (Kishor *et al.*, 2010). Pandey and Singh (2010) found that incorporating of fly ash
42 into the soil modifies the physico-chemical, biological and nutritional quality of the soil. Sajwan *et*
43 *al.* (2006) described that the use of fly ash as a soil ameliorant can be enhanced by blending it with
44 organic matter. The benefits may include better nutrient balance, reduction in toxins or
45 contaminants, improved moisture content, and improved soil conditioning effects (Hanani *et al.*,
46 2010).

47 That kind of fly ash is very dusty and contains no N, and the amounts of C are minor.
48 Therefore, addition of biomass of azolla as an organic manure and granulation of fly ash is
49 necessary to make the ash applicable to fertilization and to improve its handling and storage
50 characteristics (Trenkel, 2010; Teixeira *et al.*, 2016). The aim of this study was to determine the

please, add biomass of various types of Azolla sp. like its chemical composition and benefits to improve soil properties and growth of plants. I enclosed 1 paragraph

51 possibilities to improve the handling and fertilization characteristics of fly ash through addition of
52 organic manure as an composite. *(Urea)?* *The aim of this study not compatible with title of article.* *(related)*

54 MATERIALS AND METHODS

55 Coal fly ash obtained from a coal-fired thermal power station in Muara Enim District, *PTU*
56 South Sumatra. Biomass of azolla taken from the azolla cultured pond Soil Science Department
57 Sriwijaya University. Coal fly ash and biomass of azolla was air dried and sieved with 0,05 mm *diameter*
58 2.0 mm size, respectively. The coal fly ash-azolla mixture (FAZ) with composition of 40:60, 50:50,
59 60:40 (w/w basis) *dry weight* were mixed thoroughly, weighed to 5 kg on dry-weight basis, potted, and
60 incubated for 21 days. During the incubation period, the water content of the mixture was maintained
61 at field capacity by adding deionized water based on water losses. After incubation, FAZ was air
62 dried and sieved with 2.0 mm *diameter* size.

63 The research were arranged according to Factorial Completely Randomized Design with three
64 replicates. The composite treatments tested were made from fly ash-Azolla biomass FAZ (w/w of
65 40:60, 50:50, 60:40; 21 days incubation) and urea (46% N) at the rates of 90:10, 80:20, and
66 70:30 (w/w basis). *dry weight* The FAZ-Urea mixture (FAZU) for each composition were mixed thoroughly
67 with 5% starch as a binder. *Deionized water 1000 ml* Ionic free water were added to the mixture to form a paste and then fed
68 into the mold and compacted. The composite mold is made using a *PVC* paralon pipe with diameter 1,90
69 cm and cut along 4 cm. The produced composite were dried at a temperature of $\pm 50^{\circ}\text{C}$ for 24 hours.

70 The produced of the FAZU composite were analysed of the physical characteristics include:
71 *1)* porosity, *2)* bulk density, *3)* water holding capacity, *4)* compressive strength, and *5)* dissolution rate. Statistical
72 analysis for all observed parameters was conducted by using Analysis of Variance (ANOVA) followed
73 by Least Significance Difference (LSD) test at level of $P < 0.05$.

75 RESULTS AND DISCUSSION

76 Characteristics of Coal Fly Ash and Azolla Biomass

PTU
how to mixe? coal-azolla please to mix with feed capacity
how many gram with FAZU?
any figure?
add methods of the analysis and references
please: add any more parameters e.g. organic stability etc

Table 1 showed that Please give explanation based on Ref. (concerning)

77 Coal fly ash used in this study is classified as base. The total P and K content of this material
78 is low. The levels of C-organic and N-total are also very low (Table 1). Low content of organic C
79 and total-N is caused by the burning processes of coal at high temperatures (Singh *et al.*, 2011;
80 Mupambwa *et al.*, 2015). In addition, the used of coal fly ash is dominated by silt and clay-sized
81 particles (713.20 gkg^{-1}) (Table 1), suggesting that they easily react with the organic manures. Coal
82 fly ash is a complex material dominated by fero-aluminosilicate minerals, has pozzolan properties
83 (like cement) and contains Ca as dominant cations (Adriano *et al.*, 1980; Kishor *et al.*, 2010; Singh *et*
84 *al.*, 2011). The characteristics of this material indicate its potential as a fertilizer coating material
85 (Qiu *et al.*, 2011).

86 The results of the analysis of some of the chemical characteristics of azolla biomass used in
87 this study (Table 1) show that this organic fertilizer has a slightly acidic pH, with a high total N, P
88 and K content. Meanwhile, the total P-content of this material is relatively low. The C / N biomass
89 of azolla is very low which indicates that this biomass can decompose to form organic compounds,
90 such as humic acid. Organic acids can play a role in binding nutrients, so it is not easily soluble and
91 washed (Nainggolan *et al.*, 2009). Organic matter is known to play a role in the retention of nutrients
92 such as ammonium into the structure of organic compounds either directly or indirectly through
93 microbiological activity (Tan, 2003; Havlin *et al.*, 2005).

95 Characteristics of Coal Fly Ash-Azolla Biomass and Urea Composite

96 ✓ a. Compressive strength

97 The results of analysis of variance (Table 2) showed that the proportion of coal fly ash,
98 azolla biomass and both interaction have a very significantly effect on the compressive strength of
99 the composite produced. Table 3 shows that the level of compressive strength of the composite with
100 the composition of coal fly ash:azolla biomass:urea ((60:40)70:30) not significantly different when
101 compared to composition of (60:40)80:20, (60:40)90:10, (50:50)90:10, and (50:50)80:20, but
102 significantly higher than other compositions.

use treat. code please give explanation

103 Table 3 also shows that the increased proportion of coal fly ash will increase compressive
104 strength of the composite significantly. Meanwhile, the increased percentage of added urea will
105 decrease the level of compressive strength of the composite. Figure 1 also shows that the level of
106 compressive strength of the composite tend to decrease by increasing the proportion of urea
107 addition.

108 The compressive strength of the composite in the various compositions of coal fly ash and
109 azolla biomass varied between 1.13 and 1.87 kg / cm² (Table 3). The level of compressive strength
110 is influenced by water content, organic matter content, and mineral content (Kurnia *et al.*,
111 2006). Water content (Table 5) and higher organic content tends to decrease the level of
112 compressive strength, and increased mineral content tends to increase the compressive strength of
113 the composite. In this case, the composites with higher compressive strength are considered better, as
114 they are less easily destroyed and the ease of transport of composite fertilizer produced.

115 116 ✓ **b. Bulk Density**

117 ~~The results of the analysis of variance~~ (Table 2) showed that the proportion of coal fly ash
118 and azolla biomass have a very significantly effect and their interaction has significantly effect on
119 the bulk density of the composite produced. Table 4 shows that bulk density of the composite with
120 the composition of coal fly ash: azolla biomass: urea ((60:40):70:30) is not significantly different
121 when compared to (60:40):90:10, and (60:40):80:20, but significantly higher than other
122 compositions. Table 4 and Figure 2 also show that the increased proportion of coal fly ash
123 significantly increases the bulk density of the composites or the increased proportion of azolla
124 biomass significantly decreases the bulk density of the composite produced. Meanwhile, changes in
125 urea percentages addition were relatively variable and there was a tendency to increase the
126 composite bulk density by increasing the percentage of urea added.

127 Bulk density describes the weight of the composite per total composite volume, so that the
128 high value of bulk density characterizes the solids contained in the composite will be higher, the

Fig 1
not
mentioned

Please
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explanation

Use
best
core

129 lower the pore space and the higher of the compressive strength. Table 4 and Figure 2 show that the
130 composite compressive strength level is getting higher with the increase in the proportion of coal fly
131 ash on the composite. This condition also reflects the porosity of composites, where low bulk
132 density will tend to have higher porosity than composites with higher bulk density values (Table 6).

133 The bulk density of the composites produced in this study varied between 0.66 - 1.09 gram /
134 cm³. Kurnia *et al.* (2006) suggests that mineral soil bulk density varies between 0.80 to 1.40 g/cm³
135 and peat soils vary between 0.60 to 0.80 g/cm³. Bulk density composites with a higher proportion of
136 organic matter (biomass azolla) were significantly lower than in composites with a lower proportion
137 of organic matter. It appears that increased composite bulk density is also followed by increased the
138 compressive strength of the composite (Table 3).

139
140 **c. Water Content** *no differences in the materials and methods.
 - in different methods measure water holding capacity?*

141 ~~The water content of the composite was measured after the composite was dried in an oven~~
142 ~~with a temperature of 50⁰C for 24 hours. The results of the analysis of variance (Table 2) showed~~
143 that the proportion of coal fly ash, azolla biomass and their interaction has a very significantly effect
144 on the water content of the composite produced. Table 5 shows that the water content of the
145 composite in the coal fly ash composition - azolla biomass in the ratio of 40:60 and 50:50 is
146 significantly higher than that of composites in compositions with a higher proportion of coal fly
147 ash.

*Please
give
explan
tion /
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understand
ration*

148 In addition, the composites in treatment with higher fly ash compositions (50:60) had
149 significantly lower water content than other compositions (Table 5). Figure 2 also shows that the
150 organic matter content of the composite appears to have a significantly effect on the water content
151 of the composite produced (Table 5). Organic matter is known to have high water holding capacity
152 (Stevenson, 1994), so that water content will increase as the proportion of azolla biomass in the
153 composite increases.

154

155 **d. Water Holding Capacity** ✓

156 The treatment of coal fly ash and azolla biomass composition significantly affected the
157 water holding capacity of the composite (Table 2). The least significance difference (LSD) test result
158 (Table 6) shows that the WHC of the composite with the composition of coal fly ash: azolla biomass:
159 urea ((40-60)90:10) is not significantly different when compared to (40-60) 70:30, but significantly
160 higher than other compositions. idm

161 Table 6 also shows that the increased proportion of azolla biomass will increase WHC
162 significantly or an increase in the proportion of coal fly ash on composites will significantly
163 lowering WHC of the composite. Meanwhile, the increasing percentage of urea fertilizer added
164 tends to vary. Organic materials with a high water holding capacity cause WHC of the composite
165 will increase. Water holding capacity is related to the content of organic materials and mineral
166 materials in a material. Organic matter is known to have a high water retention (Stevenson, 1994),
167 and coal fly ash which is a mineral material known to have lower water retention (Carlson and
168 Adriano, 1993). idm

170 **e. Porosity** ✓

171 Porosity or total pore space is the volume of all pores in a volume of a material expressed in
172 percent. Porosity reflects the degree of the passage of water mass flow (permability) or the velocity
173 of water flow to pass through the mass of a material. Porosity determines the value of the bulk
174 density. The greater the number of pores, the lower the density of the mass or the higher porosity
175 and the lower the number of pores, the higher the density of the mass or the porosity is lower
176 (Hardjowigeno, 1993). idm

177 Table 7 showed that the composite with the composition of coal fly ash: azolla biomass: urea
178 (60-40)70:30 is not significantly different than other compositions. However, there is a tendency to
179 increase the composite porosity by increasing the proportion of azolla biomass. Higher organic
180 content (biomass azolla) can cause the amount of pores in the composite to increase, so that the

181 composite porosity tends to increase. Soil porosity is influenced by organic matter content, soil
182 structure, and soil texture. Soil porosity is high when organic matter is high (Hardjowigeno, 1993).

183 Meanwhile, Figure 2 shows that an increase in the percentage of urea added to the coal fly
184 ash-azolla biomass composition (40:60) tends to increase the composite porosity. but on the lower
185 azolla biomass composition ((50:50) and 60:40)), the composite porosity tends to decrease with
186 increasing percentage of added urea fertilizer. This is thought to be due to the increased proportion
187 of coal fly ash will decrease the amount of pores in the composite and cause the porosity to
188 decrease. The size of coal fly ash particles dominated by silt and clay particles ($<50\mu\text{m}$) (Hermawan
189 *et al.*, 2014) causes the composite become denser. The reduced of pore amount causes the bulk
190 density of the composite to be higher (Table 4) and is associated with increased the compressive
191 strength (Table 3).

192

193 CONCLUSION AND SUGGESTION

194 The coal fly ash and Azolla biomass potentially to be use as a fertilizing material. The
195 formulation of FAZ-U (60:40)70:20 and (60:40)70:30 tend to have the compressive strength, bulk
196 density, porosity and water holding capacity better than the other formulation and indicated can
197 release nutrient from urea slowly.

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198

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205

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250

251 Tables and Figures:

252

253

254

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256

257

Table 1. Characteristics of Coal Fly Ash and Azolla Biomass

Parameters	Unit	Results	
		Coal Fly Ash	Azolla Biomass
pH H ₂ O	-	8,74	5,75
Organic-C	g kg ⁻¹	1,10	33,80
Total-N	g kg ⁻¹	0,10	18,50
Total-P	g kg ⁻¹	0,60	0,60
Total-K	g kg ⁻¹	0,60	18,70
Fraction:			
Sand	g kg ⁻¹	285,90	
Silt	g kg ⁻¹	552,50	
Clay	g kg ⁻¹	160,70	

heavy metals?

Method of analysis?

258

259

Table 2. Summary of analysis of variance (ANOVA) the effect of coal fly ash-azolla and urea fertilizer formulation on some physical characteristics of the composite

Parameters	Effect of Treatment		
	FAZ	Urea	Interaction
✓ Compressive Strength ✓	**	**	**
✓ Bulk Density ✓	**	**	*
✓ Water Content	**	**	**
✓ Water Holding Capacity ✓	**	**	ns
✓ Porosity ✓	ns	ns	**

Remarks: ns/ */ ** = not significantly/ significant/ very significant

261

262

263

Table 3. The effect of coal fly ash-azolla and urea fertilizer formulation on compressive strength (kg/cm²) of the composite

FAZ Composition	Urea			Effect of FAZ
	10	20	30	
(40:60)90,80,70	1,30ab	1,23a	1,13a	1,22a
(50:50)90,80,70	1,77cd	1,80cd	1,57bc	1,71b
(60:40)90,80,70	1,87d	1,83cd	1,63cd	1,78c
Effect of Urea (U)	1,64b	1,62 b	1,44a	

BNT_{(0,05)Comb} = 0,28 ; BNT_{(0,05)FAZ and Urea} = 0,20

Remarks : Numbers followed by the same letter are not significantly different (P<0.05)

265

266

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268

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Table 4. The effect of coal fly ash-azolla and urea fertilizer formulation on bulk density (gram/cm³) of the composite

FAZ Composition	Urea (%)			Effect of FAZ
	10	20	30	
(40:60)90,80,70	0,66a	0,83b	0,84b	0,78 a
(50:50)90,80,70	0,83b	0,93c	0,82b	0,86b
(60:40)90,80,70	0,96c	1,09d	0,95c	1,00c
Effect of Urea (U)	0,82a	0,95b	0,87a	

BNT_{(0,05)Comb} = 0,08 ; BNT_{(0,05)FAZ and Urea} = 0,06

Remarks : Numbers followed by the same letter are not significantly different (P<0.05)

270

271

FAZ 40:60 (90)
= FAZ-1
FAZ 40:60 (86)
= FAZ-2
etc
Urea (U)
U₁₀ = U₁
U₂₀ = U₂
U₃₀ = U₃
FAZ Urea

272

273 Table5. The effect of coal fly ash-azolla and urea fertilizer formulation on water content (%) of the
274 composite

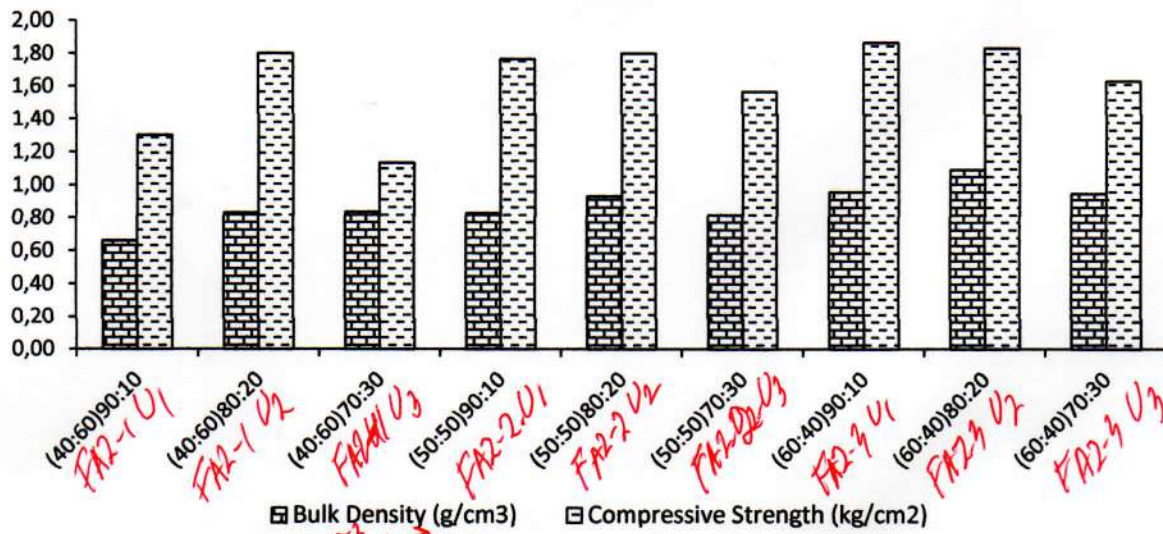
FAZ Composition	Urea (%)			Effect of FAZ
	10	20	30	
(40:60)90,80,70	46,07f	30,03cd	33,78cd	36,63b
(50:50)90,80,70	34,29d	33,96d	41,36e	36,54b
(60:40)90,80,70	22,53a	29,23bc	30,91cd	27,56a
Effect of Urea (U)	34,30ab	31,08a	35,35b	

BNT_{(0,05)Comb} = 4,56 ; BNT_{(0,05)FAZ and Urea} = 3,23

275 Remarks : Numbers followed by the same letter are not significantly different (P<0.05)

276

*little
much*



277

278 Figure 1. Compressive strength and bulk density of the composite with various formulation of
279 coal fly ash, azolla biomass and urea

280

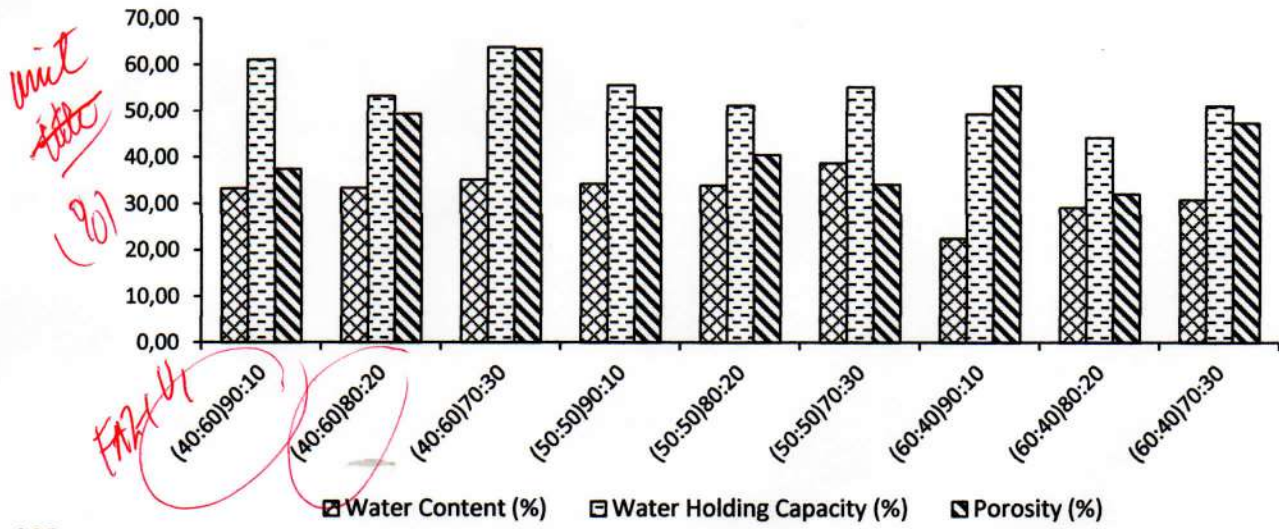
281 Table6. The effect of coal fly ash-azolla and urea fertilizer formulation on water holding
282 capacity (%) of the composite

FAZ Composition	Urea (%)			Effect of FAZ
	10	20	30	
(40:60)90,80,70	61,12d	53,25bc	63,82d	59,40 c
(50:50)90,80,70	55,60c	51,27b	55,28c	54,05 b
(60:40)90,80,70	49,32b	44,25a	51,16b	48,24a
Effect of Urea (U)	55,35c	49,59a	56,75c	

BNT_{(0,05)Comb} = 4,29 ; BNT_{(0,05)FAZ and Urea} = 3,03

283 Remarks : Numbers followed by the same letter are not significantly different (P<0.05)

284



285
286 Figure 2. Water content (%), water holding capacity and porosity of the composite with various
287 formulation of coal fly ash, azolla biomass and urea
288

289 Table7. The effect of coal fly ash-azolla and urea fertilizer formulation on porosity (%) of the
290 composite

FAZ Composition	Urea (%)			Effect of FAZ
	10	20	30	
(40:60)90,80,70	37,47ab	49,29bcd	63,39d	50,05a
(50:50)90,80,70	50,78bcd	40,49abc	34,17ab	41,81a
(60:40)90,80,70	55,49cd	32,15a	47,36abcd	44,00a
Effect of Urea (U)	47,92a	40,64a	48,31a	

BNT_{(0,05)Comb} = 17,06 ; BNT_{(0,05)FAZ and Urea} = 12,06

Remarks : Numbers followed by the same letter are not significantly different (P<0.05)

291
292

Please should be write

Treatments code

1. FAZ-1 U₁

2. FAZ-1 U₂

3. FAZ-1 U₃

4. FAZ-2 U₁

5. FAZ-2 U₂

6. FAZ-2 U₃

7. FAZ-3 U₁

8. FAZ-3 U₂

9. FAZ-3 U₃

Parameters

Table 3. The effect of coal fly ash-azolla and urea fertilizer formulation on compressive strength (kg/cm²) of the composite

FAZ Composition	Effect of FAZ		
	10	20	30
(40:60)90:80:70	1.30ab	1.23a	1.22a
(50:50)90:80:70	1.77cd	1.80cd	1.71b
(60:40)90:80:70	1.87d	1.83cd	1.78c
Effect of Urea (U)	1.64b	1.62b	1.44a

BNT_{0.05}Comp = 0.28 ; BNT_{0.05}FAZ and Urea = 0.20
 Remarks : Numbers followed by the same letter are not significantly different (P < 0.05)

Table 4. The effect of coal fly ash-azolla and urea fertilizer formulation on bulk density (gram/cm³) of the composite

FAZ Composition	Effect of FAZ		
	10	20	30
(40:60)90:80:70	0.66a	0.82b	0.78 a
(50:50)90:80:70	0.83b	0.92c	0.86b
(60:40)90:80:70	0.96c	1.09d	1.00c
Effect of Urea (U)	0.82a	0.92b	0.87a

BNT_{0.05}Comp = 0.08 ; BNT_{0.05}FAZ and Urea = 0.06
 Remarks : Numbers followed by the same letter are not significantly different (P < 0.05)

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Inderalaya, 1 November 2018 (place and date)

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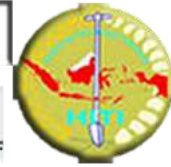
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Physical Properties of Briquette Fertilizers Made from Urea and Fly Ash-Azolla

By Agus Hermawan

Physical Properties of Briquette Fertilizers Made from Urea and Fly Ash-Azolla

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ABSTRACT

Coal fly ash and Azolla biomass are potential materials to be used as raw materials for the manufacture of briquette fertilizers. In this study, the coal fly ash, azolla and urea in various compositions were mixture to make briquette fertilizers. The study was conducted to evaluate the physical properties of briquette fertilizers, *i.e* bulk density, compressive strength, porosity, and water holding capacity on various compositions of fly ash-azolla and urea. The research was arranged in a Completely Randomized Design with three replicates. The formulation of briquette fertilizers as treatments was made with the composition (w/w, dry-weight basis) of (fly ash : azolla) + urea as follows: (40:60)90+10; (40:60)80+20; (40:60)70+30; (50:50)90+10; (50:50)80+20; (50:50)70+30; (60:40)90+10; (60:40)80+20 and (60:40)70+30. The results showed that the variation in composition of coal fly ash-azolla and urea significantly affected the compressive strength, bulk density, water holding capacity and porosity of briquette fertilizers produced. The increase in the proportion of fly ash or the decrease of azolla biomass proportion tends to increase compressive strength and bulk density, and tends to decrease the water holding capacity and porosity of briquette fertilizers produced.

Keywords: Azolla, briquette fertilizer, fly ash, urea

ABSTRAK

Abu terbang batubara dan biomassa Azolla merupakan bahan yang potensial untuk digunakan sebagai bahan baku pembuatan pupuk briket. Pada penelitian ini dilakukan pencampuran abu terbang batubara, azolla dan urea dengan berbagai komposisi untuk membuat pupuk dalam bentuk briket. Penelitian ini dilakukan untuk mengevaluasi beberapa karakteristik fisika pupuk briket pada berbagai komposisi abu terbang batubara-azolla dan urea, yang meliputi kerapatan isi, kuat tekan, porositas, dan kapasitas menahan air. Penelitian ini dilakukan dengan menggunakan Rancangan Acak Lengkap dengan tiga ulangan. Perlakuan yang diterapkan adalah formulasi pupuk briket yang dibuat dari campuran (abu terbang batubara:Azolla) + Urea dengan komposisi (b/b, berat kering) sebagai berikut: (40:60)90+10; (40:60)80+20; (40:60)70+30; (50:50)90+10; (50:50)80+20; (50:50)70+30; (60:40)90+10; (60:40)80+20 and (60:40)70+30. Hasil penelitian menunjukkan bahwa variasi komposisi abu terbang batubara-azolla dan urea berpengaruh nyata terhadap kuat tekan, kerapatan isi, kapasitas menahan air dan porositas pupuk briket yang dihasilkan. Peningkatan proporsi abu terbang batubara atau penurunan proporsi biomassa Azolla cenderung meningkatkan kuat tekan dan kerapatan isi, dan cenderung menurunkan kapasitas menahan air dan porositas pupuk briket yang dihasilkan.

Kata kunci: Abu terbang batubara, Azolla, pupuk briket, urea

INTRODUCTION

Fertilization efficiency is known to be very low, in which around 40-70% N, 80-90% P, and 50-70% K applied in the form of fertilizers are lost to the environment and can not be taken up by plants

(Trenkel 2010; Lubkowski 2014). One way to improve fertilizer use efficiency is by coating artificial fertilizers using a material that can slow down the release of nutrients from fertilizers, which is called as slow release fertilizer (Trenkel 2010; Lubkowski 2014).

The release of nutrients from coated fertilizers basically occurs through a diffusion process that passes through permeable or semi-permeable coatings (Shaviv 2005; Trenkel 2010). In general,

thin and porous layers have a high release rate, while smooth, uniform and thicker layers indicate more control over nutrient release and can substantially withstand nutrient release rates. Physical characteristics of coating materials such as size, shape and surface also affect nutrient release patterns (Trenkel 2010; Ali and Danafar 2015). Therefore, the rate of release of nutrients can be controlled through characteristic manipulation of coating materials, such as thickness or physical-chemical composition.

A good fertilizer coating material must have at least 4 characteristics, namely low prices, biodegradable, non-toxic, and abundant availability (Trenkel 2010; Ali and Danafar 2015). Some inorganic minerals and organic materials have been reported to be used in the manufacture of slow release fertilizers, including silicate compounds, sulfur, gypsum, lime, cement, zeolite, fly ash, lignin, organic acids, chitosan and humic (Nainggolan *et al.* 2009; Sulakhudin *et al.* 2011; Qiu *et al.* 2011; Hou *et al.* 2014; Lubkowski 2014; Behin and Sadeghi 2016; Teixeira *et al.* 2016). Nevertheless, the process of making slow release fertilizers is still relatively complicated and relatively more expensive than conventional fertilizers, making it difficult to be accepted at the farm level (Qiu *et al.* 2011; Dong *et al.* 2016).

Coal fly ash and Azolla biomass are potential materials to be used as raw materials for the manufacture of slow release fertilizers. Coal fly ash, a by-product of coal combustion, is an amorphous aluminosilicate material and composed of particulate matter collected from flue gas stream (Singh *et al.* 2011). Coal fly ash is dominated by fine-sized particles (0.01-100 μm) and has podzolic properties (like cement), so it can act as an adhesive and fertilizer coating. Coal fly ash contains Ca cations as the dominant cation followed by Mg, Na and K (Kishor *et al.* 2010; Singh *et al.* 2011; Yao *et al.* 2015), which can play a role in cation exchange. In addition, this material also contains other plant nutrients, such as P, S, B, Fe, Cu, Zn, Mn and Mo, so it will enrich the nutrient content of fertilizer (Kishor *et al.* 2010; Singh *et al.* 2011; Srinavas *et al.* 2017).

Organic materials also have characteristics that are very potential to be used as a fertilizer coating material. Decomposition of organic matter will produce organic acids such as humic and fulvic acids, which are dominated by negative charges (Sposito 2008). Therefore, organic acids can bind nutrients from fertilizers through chemical reactions directly or indirectly through microbiological activity and decomposition of microbial biomass (Havlin *et al.* 2005; Sulakhudin *et al.* 2011; Teixeira *et al.* 2016).

One potential source of organic material is azolla (*Azolla sp.*). Azolla is a water fern. Symbiosis of Azolla with cyanobacteria *Anabaena azollae* is able to fix nitrogen from the atmosphere around 30-60 kg N ha^{-1} (Kollah *et al.* 2015; Roy *et al.* 2016). The low C/N ratio of Azolla biomass (between 9-10) indicates that the biomass will rapidly decompose and produce available nutrients and organic acids as decomposition products (Bhuvaneshwari and Kumar 2013; Roy *et al.* 2016). The use of coal fly ash and organic matter mixtures is known to increase the efficiency of using N, P, and K fertilizers by 45.8%, 33.5% and 69.6%, respectively compared to the use of chemical fertilizers or a combination of chemical fertilizers and organic matter (Mitra *et al.* 2003; Kishor *et al.* 2010). Hermawan *et al.* (2014) also reported that the use of a mixture of coal fly ash and organic fertilizer in bulk form could increase the efficiency of fertilizer use by 42.4%.

The coal fly ash that has podzolic properties (like cement) with a high content of alkaline oxide, and azolla biomass that is rich in N and will produce organic acids show its potential as an alternative to urea fertilizer coatings. In this study, mixing of coal fly ash, azolla biomass and urea fertilizer in various compositions was carried out to make briquette fertilizers which are expected to be able to release nutrients slowly into the soil. Physical characteristics of briquette fertilizers are known to affect the rate of release of nutrients from fertilizers into the soil (Trenkel 2010; Ali and Danafar 2015). Therefore, a study was conducted to evaluate the physical characteristics of briquettes, such as bulk density, compressive strength, porosity, and water holding capacity of briquettes on various compositions of coal fly ash, azolla and urea.

MATERIALS AND METHODS

Preparation of Briquette Fertilizer

Coal fly ash was obtained from a coal-fired thermal power station in Muara Enim District, South Sumatra. Biomass of azolla was taken from the azolla cultured pond at Department of Soil Science, Sriwijaya University. The coal fly ash is dominated by silt and clay-sized particles (713.20 g kg^{-1}), water content (21 g kg^{-1}), pH (8.74), organic-C (0.11 g kg^{-1}), total-N (0.01 g kg^{-1}), total-P (0.6 g kg^{-1}) and total-K (0.6 g kg^{-1}). The chemical characteristics of azolla biomass used in this study are as follow: pH (5.75), organic-C (33.80 g kg^{-1}), total-N (18.5 g kg^{-1}), P (1.60 g kg^{-1}), and K (18.70 g kg^{-1}). Coal fly ash and biomass of azolla were air dried and

sieved with 0.05 mm and 2.0 mm diameter size, respectively.

The experiment was conducted in the Laboratory of Chemistry, Biology and Soil Fertility, Department of Soil Science, Faculty of Agriculture, Sriwijaya University in September 2017 to January 2018. The research was arranged in a Completely Randomized Design with three replicates. The formulation of briquette fertilizers as treatments was made with the composition (w/w, dry-weight basis) of (fly ash (F) : biomassa of azolla (AZ)) + urea (U) as follows: (40:60)90+10 (FAZ₁-U₁); (40:60)80+20 (FAZ₁-U₂); (40:60)70+30 (FAZ₁-U₃); (50:50)90+10 (FAZ₂-U₁); (50:50)80+20 (FAZ₂-U₂); (50:50)70+30 (FAZ₂-U₃); (60:40)90+10 (FAZ₃-U₁); (60:40)80+20 (FAZ₃-U₂) and (60:40)70+30 (FAZ₃-U₃). The coal fly ash-azolla mixture (FAZ) and urea of each composition were mixed thoroughly with 5% starch as a binder. Ionic free water was added to adjust the moisture content of about 25% and then the mixture was put into the mold and compacted. The briquette mold was made using a PVC pipe with a diameter of 1.90 cm and cut along 4 cm. The produced briquettes were dried at a temperature of ± 50°C for 24 hours.

Data Collection and Analysis

The briquette fertilizers were analysed for their physical properties including water retention capacity, porosity, bulk density, and the compressive strength. Water retention capacity of briquette fertilizer is the difference between initial weight and final weight of the briquette. Briquette fertilizer

samples that have been known for their water content were weighed as initial weight. Then it was saturated with ion free water using a beaker glass for 1 hour. The samples of briquette fertilizer that were saturated with water were then weighed, as the final weight. Porosity was calculated by dividing the volume of water absorbed by the volume of briquette fertilizer. Bulk density of briquette fertilizer was calculated by dividing the dry weight of briquette fertilizer with the total volume of briquette fertilizer. The compressive strength test was carried out using the Hand Penetrometer to determine the strength of briquettes in holding the load with a certain pressure. The sample pressure was followed by the addition of the load until the sample had an initial crack. The initial crack is considered a failure, because the sample is considered to be unable to withstand the heavy load more than the load that causes the initial crack. Statistical analysis for all observed parameters was conducted by using Analysis of Variance (ANOVA) followed by Least Significance Difference (LSD) test at level of $p < 0.05$.

RESULTS AND DISCUSSION

Compressive Strength

The results of analysis of variance showed that the briquette fertilizers with the proportion of coal fly ash-azolla biomass and urea have a significant effect on the compressive strength of the briquette fertilizers produced. Table 1 shows that the level of compressive strength of the briquette

Table 1. The effect of coal fly ash-azolla and urea proportion on some physical properties of briquette fertilizers.

Treatments Code (Fly Ash:Azolla)+Urea	Parameters			
	Compressive Strength (kg m ⁻²)	Bulk Density (g cm ⁻³)	Water Retention Capacity (%)	Porosity (%)
FAZ ₁ -U ₁ (40:60)90+10	1.50 ab	0.66 a	61.12 d	37.47 ab
FAZ ₁ -U ₂ (40:60)80+20	1.43 a	0.83 b	53.25 bc	49.29 bcd
FAZ ₁ -U ₃ (40:60)70+30	1.17 a	0.84 b	63.82 d	63.39 d
FAZ ₂ -U ₁ (50:50)90+10	1.25 a	0.83 b	55.60 c	50.78 bcd
FAZ ₂ -U ₂ (50:50)80+20	1.88 bc	0.93 c	51.27 b	40.49 abc
FAZ ₂ -U ₃ (50:50)70+30	1.42 a	0.82 b	55.28 c	34.17 ab
FAZ ₃ -U ₁ (60:40)90+10	1.90 bc	0.96 c	49.32 b	55.49 cd
FAZ ₃ -U ₂ (60:40)80+20	2.08 c	1.09 d	44.25 a	32.15 a
FAZ ₃ -U ₃ (60:40)70+30	1.53 ab	0.95 c	51.16 b	47.36 abcd
LSD _{0,05}	0.40	0.08	4.29	17.06

Note: The numbers followed by the same letters in the same column are not significantly different ($p < 0.05$).

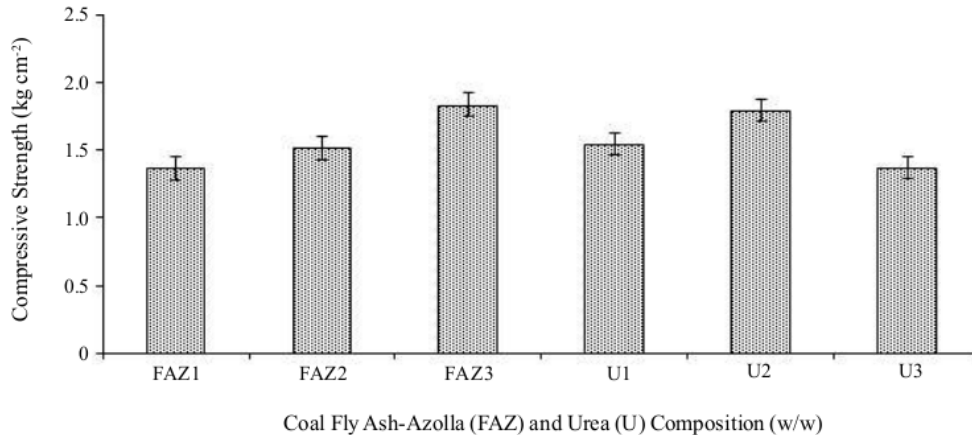


Figure 1. Compressive strength of the briquette fertilizers with various proportion of coal fly ash-azolla (FAZ) and urea (U).

fertilizers with the composition of (coal fly ash:azolla biomass) + urea (60:40)80+20 (FAZ₃-U₂) is not significantly different from FAZ₃-U₁ and FAZ₂-U₂, but significantly higher than other compositions. Table 1 also shows that the increased proportion of coal fly ash-azolla will increase the compressive strength of the briquette fertilizers. Meanwhile, the increased percentage of added urea will decrease the level of compressive strength of the briquette fertilizers.

Figure 1 shows that the composition of coal fly ash and azolla tends to affect the compressive strength of the briquette fertilizers produced. The increasing proportion of coal fly ash tends to cause the briquette fertilizers produced to be harder, and vice versa an increase in the proportion of azolla tends to reduce the compressive strength of the briquette fertilizers produced. Coal fly ash is generally podzolic (such as cement) (Yao *et al.* 2015; Ma *et al.* 2017), so the increase in proportion will cause the compressive strength of briquette fertilizers to be increased. Meanwhile, an increase in the proportion of urea in briquette fertilizers tends to reduce the compressive strength of briquette fertilizers produced.

The compressive strength of the briquette fertilizers in the various compositions of coal fly ash and azolla biomass varies between 1.17 and 2.08 kg cm⁻² (Table 1). Figure 1 also showed that the higher azolla biomass proportion (FAZ-1) tends to decrease the level of compressive strength, while the increased of mineral content (fly ash proportion) tends to increase the compressive strength of the briquette fertilizers. The level of compressive strength is influenced by water content, organic

matter content, and mineral content (Kurnia *et al.* 2006). In this case, the composites with higher compressive strength are considered better, as they are less easily destroyed and the easily to transport of the briquette fertilizers produced.

Bulk Density

The results of the analysis of variance showed that the proportion of coal fly ash-azolla biomass and urea have a very significant effect on the bulk density of the briquette fertilizers produced. Table 1 shows that bulk density of the briquette with the composition of (coal fly ash:azolla biomass) + urea (60:40)80+20 (FAZ₃U₂) is significantly higher than other compositions of the briquette fertilizers produced. Figure 2 shows that the increased proportion of coal fly ash tends to increase the bulk density of the briquette fertilizers or the increased proportion of azolla biomass tends to decrease the bulk density of the briquette fertilizers produced. Meanwhile, changes in urea percentage addition are relatively variable and there is a tendency to increase the briquette bulk density by increasing the proportion of urea added.

Bulk density describes as the weight of the briquette fertilizers per total of the briquette volume, so that the high value of bulk density characterizes the solids contained in the briquette will be higher, the lower of the pore space and the higher of the compressive strength. The bulk density of the briquette fertilizers produced in this study varies between 0.66 - 1.09 g cm⁻³ (Table 1). The bulk density of briquette fertilizers produced is still relatively low when compared to the general bulk density of soil. Kurnia *et al.* (2006) suggest that mineral soil bulk density

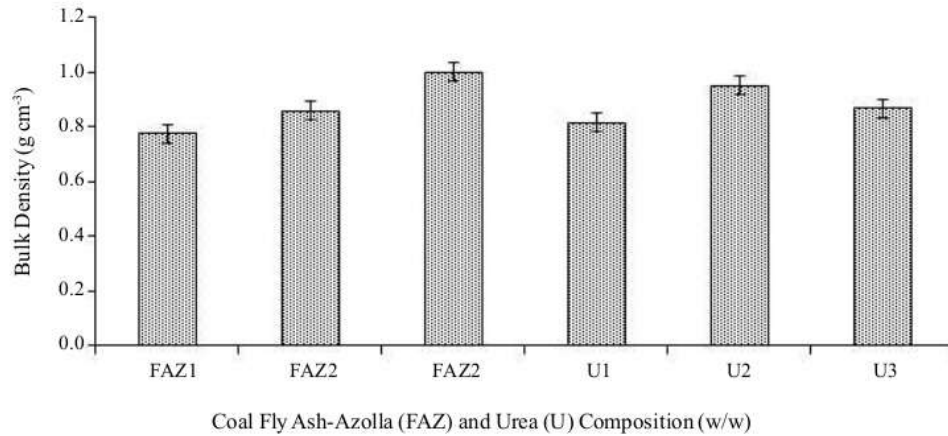


Figure 2. Bulk density of the briquette fertilizers with various proportion of coal fly ash-azolla (FAZ) and urea (U).

varies between 0.80 to 1.40 g cm⁻³, and peat soil bulk density vary between 0.60 to 0.80 g cm⁻³.

Figure 1 and 2 showed that the compressive strength and the bulk density level are getting higher with the increase in the proportion of coal fly ash on the briquette fertilizers produced. This condition also reflects on the porosity of briquette fertilizers, in which low bulk density will tend to have higher porosity than composites with higher bulk density (Table 1). Coal fly ash is dominated by silt and clay sized particles and has podzolic properties (like cement) because it is dominated by aluminosilicate and calcium compounds (Singh *et al.* 2011; Yao *et al.* 2015). Therefore, an increase in the proportion

of coal fly ash will result in more dense briquette fertilizer which is characterized by higher bulk density and compressive strength.

Water Retention Capacity (WRC)

The results of the analysis of variance showed that the treatment of coal fly ash-azolla biomass and urea composition significantly affected the water retention capacity of the briquette fertilizers produced. The results of the Least Significance Difference (LSD) test (Table 1) show that the WRC of the briquette fertilizers with the composition of (coal fly ash: azolla biomass) + urea (60:40)80+20 (FAZ₃U₂) is significantly lower compared to the

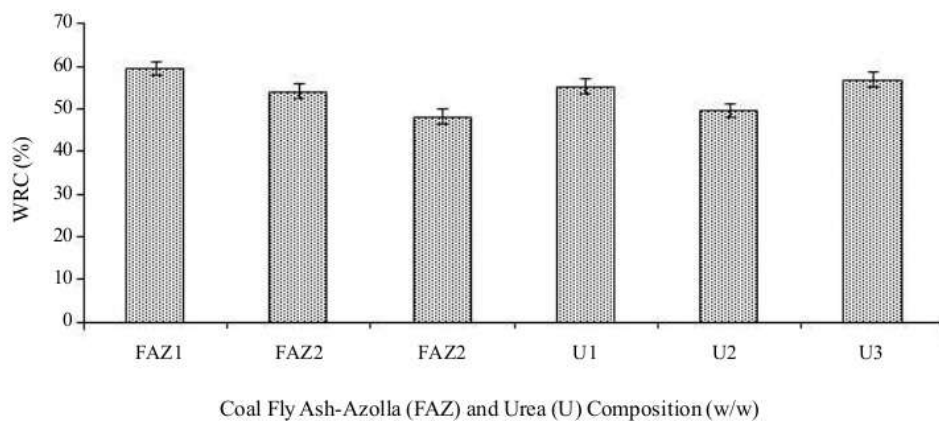


Figure 3. Water retention capacity of the briquette fertilizers with various proportion of coal fly ash-azolla (FAZ) and urea (U).

other compositions of the briquette fertilizers produced.

Figure 3 also shows that the increased proportion of azolla biomass will significantly increase WRC or an increase in the proportion of coal fly ash on briquette fertilizers will significantly lower WRC of the briquette fertilizers. Meanwhile, the increasing percentage of urea fertilizer added tends to vary. Organic materials with high water holding capacity cause WRC of the composites to increase. Water holding capacity is related to the content of organic materials and mineral materials in a material. Organic matter is known to have high water retention (Havlin *et al.* 2005; Obour *et al.* 2018), and coal fly ash which is a mineral is known to have lower water retention capacity (Carlson and Adriano 1993; Singh *et al.* 2011).

Water holding capacity is related to the ability to bind and then release water to the soil solution (Obour *et al.* 2018). Therefore, the greater the ability of the briquette to retain water, the ability to release water along with the element of fertilizer into the soil solution will also increase. Nevertheless, the briquette fertilizer with high water holding capacity tends to have a lower level of the compressive strength (Table 1), so it will be more easily destroyed and will be difficult when transporting and applying the fertilizer in the field.

Porosity

Porosity or total pore space is the volume of all pores in a volume of a material expressed in percent. Porosity reflects the degree of the passage of water mass flow (permeability) or the velocity of water

flow to pass through the mass of a material. Porosity determines the value of the bulk density. The greater the number of pores, the lower the density of the mass or the higher porosity; and the lower the number of pores, the higher the density of the mass or the porosity is lower (Nimmo *et al.* 2004; Obour *et al.* 2018)

Table 1 showed that the porosity of the briquette fertilizer with the composition of (coal fly ash : azolla biomass) + urea (60:40)70+30 (FAZ₃U₃) is not significantly different from the porosity of other compositions. However, there is a tendency to increase the composite porosity by increasing the proportion of azolla biomass. Higher organic content (azolla biomass) can cause the amount of pores in the composite to increase. Soil porosity is influenced by organic matter content, soil structure, and soil texture. Soil porosity is high when organic matter is high (Nimmo *et al.* 2004; Havlin *et al.* 2005).

Figure 4 shows that the increase in the proportion of coal fly ash tends to cause the porosity of briquette fertilizers to decrease, or conversely an increase in the proportion of azolla tends to cause porosity of briquette fertilizers to increase. Meanwhile, changes in the proportion of urea tend to fluctuate the porosity of briquette fertilizer. This is probably due to the increased proportion of coal fly ash will decrease the amount of pores in the composite and cause the porosity to decrease. The size of coal fly ash particles dominated by silt and clay particles (<50 μm) causes the composite becomes denser (Singh *et al.* 2011; Yao *et al.* 2015). The reduced number of pore causes the bulk density of the composite to be higher and is associated with

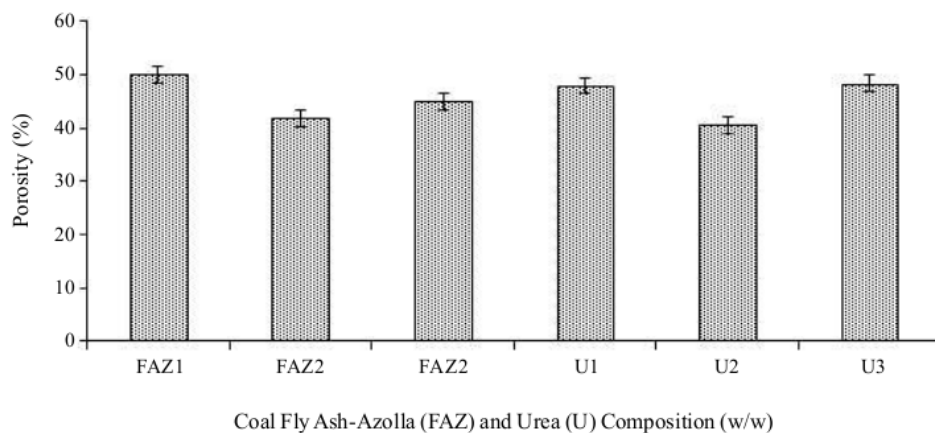


Figure 4. Porosity of the briquette fertilizers with various proportion of coal fly ash-azolla (FAZ) and urea (U).

the increased compressive strength (Table 1). As explained previously, the porosity of briquette fertilizer illustrates the speed of release of water from fertilizer ingredients to the surrounding soil. The greater the porosity, the water will be absorbed more quickly and released back to the soil solution. In relation to the release of nutrients from fertilizers, the lower porosity of briquette fertilizer can be expected to release water with nutrients from fertilizer to be slower.

CONCLUSIONS

1 Variation in composition of coal fly ash-azolla and urea significantly affected the compressive strength, bulk density, water holding capacity and porosity of briquette fertilizers produced. The increase in the proportion of fly ash or the decrease of azolla biomass proportion tends to increase compressive strength and bulk density, and tends to decrease the water holding capacity and porosity of the produced briquette fertilizers.

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