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Cenospheres characterization from Indonesian coal-fired power plant fly ash and their potential utilization

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ABSTRACT

This study presents the cenospheres formation based on the characteristic of the fly ash and the coal as well as the potential production of cenospheres from fly ash from six coal-fired power plants in Indonesia. For cenospheres characterization, SEM-EDS, petrography analysis, and particle analyzer distribution were applied through all samples. Coal and fly ash chemical composition were analyzed using proximate analysis and ICP-MS. Based on the characterization of cenospheres and fly ash chemical components, we correlate the concentration of SiO_2, Al_2O_3, SiO_2/Al_2O_3, Fe_2O_3, $Fe_2O_3 + TiO_2$, CaO, MgO in the fly ash with cenospheres yield and diameter. The cenospheres yield in six Indonesian coal-fired power plant fly ash is in the range of 0.04–0.16% and inline with the ash content in the initial coal. Moreover, it was found that the cenospheres yield and diameter are in positive correlation with the concentration of SiO_2 and Al_2O_3 in the fly ash, but they are in vice versa correlation with other chemicals. Ternary diagram of the cenospheres was made to their potential application and found that most of the cenospheres are in the ferrocalsialic.

1. Introduction

Coal is considered as the most feasible fuel to generate electricity at the moment. The abundance and easy to process of coal are the main factors affecting its feasibility which leads to the lower price in comparison to other fuel sources. Moreover simple and economical technology applied in the coal-based power plant in comparison to that of gas and oil power plants triggers the escalation of coal-fired power plants worldwide [1,2], including Indonesia, as it can be seen in Fig. 1 [3]. As shown in Fig. 1 (a) and (b), there will be a significant increase in the energy mix in Indonesia based on coal with twice-fold higher within 19 years from 2006-2025. As stated in Indonesian Presidential Regulation No. 5 of 2006, energy demand in the year 2025 will mostly be supplied by coal with a percentage of 33% of total energy consumption [3,4]. This coal dependency in the energy sector is also observed in the Asia Pacific region at which more than 45% of energy demand will be covered using coal [5]. This significant increase of coal usage in power generation, especially in Indonesia produced about 8.31 million tonnes of fly ash in 2019 with 5% per year increase. This abundance of fly ash will indeed possess serious environmental problems, if it is not properly managed [6–9]. Somehow, worldwide, the utilization of fly ash has not been sustainably established with the average percentage of 16% of the total ash [6,10,11]. Most of the utilization is based on the material stuff, soil modification, synthesis of zeolite, and as a filler in composites [12–17]. Another fly ash utilization is based on cenospheres recovery [18–21]. Cenospheres are fly ash-derived particles, which are having hollow spherical appearance, and primarily made from aluminosilicate phases [11]. This materials could be utilized into valuable products, such as lightweight construction products, syntactic foams, functionally gradient materials, metal-matrix composites rubbers, nickel-coated cenospheres for shielding and microwave absorption applications, mullite-coated diesel engine components, metallic alloy, and porous glass crystalline [11,17,22–26].

The amount of cenospheres in fly ash varies between 0.01–4.8%,

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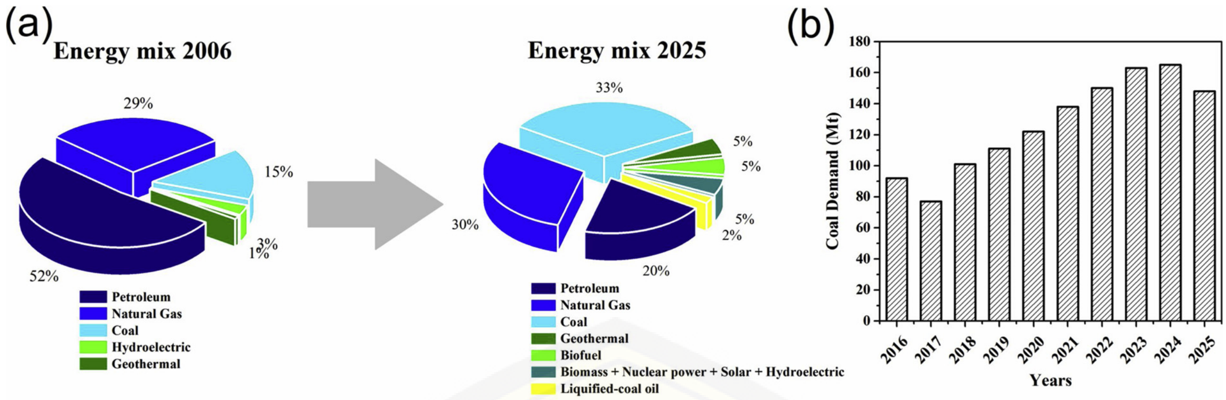

Fig. 1. (a) Indonesian energy consumption profile (energy mix) in the year of 2006 and 2025 and (b) coal demand in the power plan sector released by Ministry of Energy and Mineral Resource.

commonly 0.3–1.5% [22]. The physical structure of cenospheres has been studied by many researchers. The bulk density of cenospheres typically is about 0.2–0.5 g/cm^3; the size of 20–200 µm and shell thickness to diameter ratio of 2.5–10.5 [17,27]. Cenospheres have identifiable favorable characteristics such as low density; great compressive strength; reduced shrinkage; supreme insulation; less water absorption; high purity; good thermal resistance and electrical properties [11,17,23,25]. Many studies have been performed to correlate the particle size and density, resulting in that density lower than 0.857 g/cm^3 has a diameter between 50 and 150 µm (80% w.t.), 150 and 200 µm (15% w.t.), and 200 and 250 µm (5% w.t.) and density lower than 1.282 g/cm^3 consist of diameter between 40 and 50 µm (10% w.t.), 50 and 100 µm (50% w.t.), 100 and 110 µm (20% w.t.) and 110 and 150 µm (20% w.t.) [24–27].

Cenospheres formation throughout the pulverized coal combustion process can be identified by several notable factors, namely coal properties; characteristics of ash droplets; and combustion conditions [17,22,28]. Coal properties regarding chemical composition must have a strong relation with cenospheres formation. Furthermore, the important aspect of the coal properties could be drawn from ash content and its coal properties. Accordingly, the total ash content in the coal affects positively but cenospheres yield [10]. Proximate analysis of fly ash would be a very useful tool to determine the coal properties [28].

Commonly, there are several methods to separate cenospheres from fly ash which are the sink-float method; centrifugal separation; and combination of hydro- and aero-dynamic separation [11]. The frequently used technique is the sink-float method exercised water as the medium for density difference. Another method to separate ash cenospheres in fly ash is the centrifugal separation which employs separation process due to density difference of cenosphere and its media such as water, lithium metatungstate solutions, and combined solvent (mixing carbon tetrachloride, dibromomethane, and di-iodomethane) with density 1.5, 2.0, and 2.2 g/cm^3 respectively [5,11,15]. However, some integrated method with a combination of dry fluid bed gravity separation and carefree cyclone technology also could be employed to detach cenospheres [7,8,11].

The major constituents in cenospheres are an admixture of aluminosilicate with an adequate amount of Ca, Fe, K, Mg; fewer amounts of Na, Ti, S, P, and other trace elements. A ternary phase diagram is developed to allow a preferable overview of fly ash and cenospheres produced, regarding on the 'intersection' of their major oxides which are among the following groups of oxides: $SiO_2 + Al_2O_3 + K_2O + TiO_2 + P_2O_5$; calcic: $CaO + MgO + SO_3 + Na_2O$; and ferric: Fe_2O_3. Therefore, the classification of fly ash and cenospheres based on their major chemical composition could be grouped into Sialic, Ferrocalsialic, Ferrosialic, Calsialic, Ferrocalcic, and Calcic. The chemical compositions can vary each other because inorganic substances of the coal are not homogeneously distributed [7,24,26].

Aside from their benefits and ultimate characteristic for multi-products derivation, cenospheres produced from coal-fired power plants in Indonesia have not been studied. Thus, the objectives of this work are to characterize and to correlate the chemical composition and structure of fly ash with obtained cenospheres from six coal-fired power plants in Indonesia. To have a comprehensive study, detail properties of the cenospheres have observed using several techniques such as scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) and particle size analyzer (PSA). Coal properties and fly ash chemical composition have been identified using proximate analysis and induced coupled plasma-mass spectroscopy (ICP-MS) to identify the correlation with the cenospheres yield.

2. Materials and method

Coal and fly ash samples were obtained from six coal-fired power plants in Indonesia, i.e.: UBJOM Paiton, Indramayu, Tuban, Pacitan, Paiton, and Rembang as shown in Fig. 2. To determine the chemical compositions, those samples were analyzed by ALS Canada Ltd. using ICP-MS and method of ME-ICP06, OA-GRA05 with an analysis certificate of VA17182839.

To determine the number of cenospheres in fly ash quantitatively, float and sink tests were carried out. A mixture of 10 wt% was prepared using 50 g of fly ash and 500 mL of distilled water. Ultrasonication (Elmasonic S300H) was applied for 15 minutes to ensure the stability of individual particles. Afterward, the suspension was gently poured into a 1 L separatory funnel. The separatory funnel was then placed in a holder attached to a vertical bar and was kept steady for 24 h for the segregation process. Thereafter, the solid material which is float and bottom products were collected discharged through a 0.2 µm paper filter, subsequently, dried at 550 °C for 5 h using a laboratory furnace to remove the unburnt carbon, and then weighted after ambient temperature achieved. The top product was mostly consisted of cenospheres, while the bottom product consisted of coal fly ash particles. The procedures were repeated three times for each fly ash and cenospheres yield was calculated from the average value.

Further analyses were conducted on cenospheres using SEM-EDS, petrography analysis, and PSA. The SEM used in this study is JEOL JSM-6510LA equipped with JED-2300 EDS. SEM analysis was operated using an accelerating voltage of 20 kV. The SEM images were used to interpret the morphology of cenospheres particles. To ensure the existence of cenospheres in the fly ash, petrography analysis was conducted through a thin section polished sample of fly ash that was prepared using SpeciFix-20 Kit and Struers Labo System referring to the ASTM D 2798-72. The particle size distributions of the cenospheres were determined using a Horiba SZ-100. Samples were prepared as a 1% suspension of cenospheres and distilled water. To ensure the stability of the individual particles, a liquid dispersant (Tween® 80) was added

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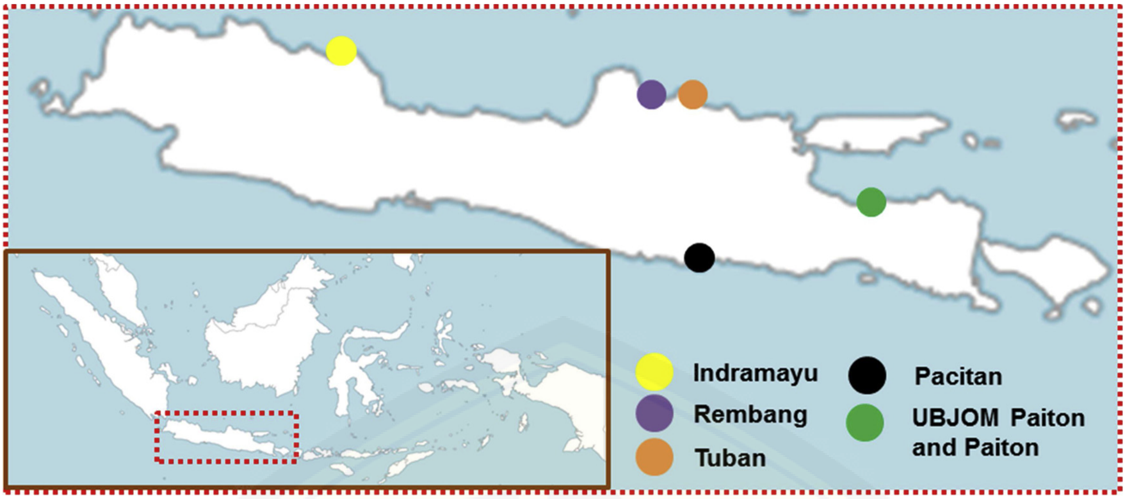

Fig. 2. Indonesian Coal-Fired Power Plant Location of the samples taken in this study.

during the sample preparation process.

3. Results and Discussion

The analysis of chemical constituents of coal, fly ash, and cenospheres are mandatory to be conducted to find the correlation of cenospheres formation with the fly ash and coal composition during the coal-fired process. The proximate analysis of coal and chemical composition analysis of fly ash and cenospheres can be seen in Tables 1–3, and respectively, while Table 4 and Fig. 3 shows the existence of spheres (both cenospheres and plerosphere) in fly ash. Analysis for the size distribution of cenospheres particles is also necessary to draw the correlation of reaction mechanism during combustion which is also being affected by the chemical compositions of fly ash. The correlation of cenospheres' diameter with chemical composition is comprehensively explained in Section 3.2. The chemical compositions analysis of fly ash and cenospheres were compared by some studies from other researchers [17,22,23,29].

From Table 1, the data show that mostly fixed carbon + volatile matter (wt%) values are above 95% with ash content vary from 1.81 to 3.72%. Those data represent the quality of coal used in power plants. The higher the fixed carbon + volatile matter (wt%) value, the better the quality of coal is, while the yield of fly ash and cenospheres was found inline with the percentage of ash content in initial coal. The detailed correlation of ash content and cenospheres yield is discussed in Section 3.1. Tables 2 and 3 show the characteristic of fly ash and cenospheres respectively. The chemical compositions of fly ash and cenospheres have slightly similar values because cenospheres are known as a by-product of fly ash. In Table 4, we can see the composition of cenospheres that is dominating than that of plerosphere observed in the fly ash (see Fig. 3) with a percentage of above 88%.

Table 1
Proximate analysis of coal in this research.

No	Coal sources	Fixed carbon + volatile matter (wt%)	Ash Content (wt%)	Moisture Content (wt%)
1	UBJOM Paiton	97.60	1.81	0.59
2	Indramayu	94.90	3.72	1.38
3	Tuban	96.90	2.68	0.42
4	Pacitan	96.10	3.46	0.44
5	Paiton	95.30	4.01	0.69
6	Rembang	96.20	3.54	0.26

3.1. *Correlation between cenospheres yield and fly ash chemical composition*

Cenospheres chemical composition is generally defined as a mixture of aluminosilicate with a fair amount of other substances [11]. To distinguish fly ash and cenospheres type in this study, a ternary phase diagram was promoted regarded on the major oxides components as follows: ferric (Fe_2O_3); calcic ($CaO + MgO + SO_3 + Na_2O$); and oxides ($SiO_2 + Al_2O_3 + K_2O + TiO_2 + P_2O_5$). The ternary diagram is presented in Fig. 4 with most of the samples, cenospheres, are in ferrocalsialic regime. It means that the cenospheres produced from the power plant are magnetic particles as ferrocalsialic nature. From the fly ash samples of the coal-fired power plant, it was found that the cenospheres are in the region of sialic and ferrocalsialic regimes in accordance with other studies [11–14].

The mechanism of cenospheres reaction has been developed by many researchers [14,30–34]. The first ideal condition to describe the cenospheres formation is by comparing the amount of fly ash formed directly yielding in cenospheres. Meanwhile, the value of float and sink tests results can be seen in Fig. 5a showing the cenospheres yield ranging from 0.045% to 0.16% which is still in the range of cenospheres' concentration in the fly ash [22]. Moreover, it is found that the more fly ash formed in coal combustion, duly, the more cenospheres obtained is; which can be seen from Fig. 5b. Although, the R-square value of Fig. 5b is very small of 0.24. It is due to out-layered data of the Tuban power plant in which the ash content is 2.68%. Also, the chemical composition of the coal used in the Tuban power plant is roughly different from other power plants. From Table 2, the value of Si/Al from fly-ash analysis of the Tuban power plant is under 2 while other power plants possess a ratio value higher than 2. It confirms that the value of SiO_2/Al_2O_3 from fly ash greatly affects the cenospheres yield because the chemical composition of cenospheres is mainly on these oxides [11–14].

A comprehensive comparison between each substance and cenospheres yield was conducted to observe the effect of chemical substances in cenospheres production. As mentioned by some researchers [14,17], the chemical components in fly ash were directly affected by the chemical composition of coal and combustion conditions. As a result, if the correlation of fly ash composition can predict the cenospheres yield, the upscaling process of cenospheres utilization will be easily drawn to calculate the amount of cenospheres production. In this study, the relationship analysis between the major component of silica oxide (SiO_2), Alumina oxide (Al_2O_3), ratio value of silica and alumina (SiO_2/Al_2O_3), iron oxide (Fe_2O_3), iron and titanium oxides (Fe_2O_3 + TiO_2), calcium oxide (CaO), magnesium oxide (MgO) and cenospheres

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Table 2
Oxide compositions of fly ash in this research (ash basis).

No	Components (wt%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Cr_2O_3	TiO_2	MnO	P_2O_5	SrO	BaO	SiO_2/Al_2O_3	LOI
1	UBJOM Paiton	34.10	9.53	22.00	15.40	14.10	0.61	0.99	0.01	0.52	0.37	0.05	0.11	0.25	3.57	0.84
2	Indramayu	42.60	20.40	13.75	9.62	6.61	0.67	0.89	0.01	0.79	0.21	0.23	0.08	0.16	2.08	2.57
3	Tuban	50.90	28.70	9.04	3.31	2.23	0.82	0.85	0.02	1.04	0.07	0.23	0.07	0.06	1.79	1.91
4	Pacitan	41.60	16.86	18.85	10.90	7.32	0.87	0.88	0.01	0.66	0.27	0.14	0.08	0.16	2.50	1.50
5	Paiton	50.60	23.50	10.90	5.13	3.80	0.59	1.59	0.02	1.02	0.09	0.16	0.04	0.10	2.13	1.09
6	Rembang	35.80	16.50	15.95	15.45	10.40	0.69	0.78	0.01	0.62	0.24	0.12	0.10	0.21	2.17	1.28

yield was conducted and presented in Fig. 6a–f (black data points), respectively. It can be seen that the higher concentration of SiO_2 and Al_2O_3, the higher the cenospheres yield will be gained. On the other hand, other chemicals provide a vise versa trend in which the higher SiO_2/Al_2O_3, Fe_2O_3, Fe_2O_3 + TiO_2, CaO, and MgO, the lesser cenospheres yield is obtained. The values of R-square from data fitting for chemical components and cenospheres yield in this study are varied in the range of 0.66–0.93 showing a good correlation in comparison to other studies [17,22,26,34].

It can be seen from the collected data that the coal ash content significantly affects the yield of cenospheres. Meanwhile, the amount of fly ash produced, undeniably, has a chemical composition which also influences the yield of cenospheres with different alteration on every substance. The chemical composition of fly ash is affected by the coal properties; coal type, particle size, mineral characterization, and combustion parameters. The combustion parameters are strongly believed to affect the cenospheres formation because they are related to temperature, pressure, combustion duration, and oxygen fraction in which those parameters determine the atmospheres of the reaction during the combustion process. Three types of substances are widely known in the coal namely organic maters, crystalline and amorphous material. Due to high temperatures during the combustion of coal, crystalline and amorphous material are burnt by a further process such as decomposition, dehydration, further complex reaction, and melted some substances with a lower melting point. At this stage, the remaining product, notably, consists of aluminosilicate substances in the amorphous glass phase (29–90 wt%) and crystalline phases [14,16,31,32]. The major mineralogy constituent of microcrystalline contains several crystalline forms such as ferrite spinel ($FeAl_2O_4$), quartz, feldspars, lime, aluminates, periclase, etc. [31,33,34].

During the combustion process, those associated minerals in coal undergo for the further melting process at a higher temperature (1300–1400 °C in the power plants included in this study), forming various eutectic systems such as $FeO–SiO_2$ (± CaO, Al_2O_3), $FeO–CaO–Al_2O_3–MgO–SiO_2$ and $K_2O–Al_2O_3–SiO_2$ (± FeO, CaO) [11]. Along with other minor oxides (TiO_2, Na_2O, MgO, etc.), these eutectic systems will greatly influence the formation of different spheres (cenosphere, plerosphere, and magnetosphere). As stated in Table 2, fly ash from Tuban possesses the highest SiO_2 content, while the UBJOM Paiton has the lowest content of SiO_2. The opposite trend can be observed for Fe_2O_3. Petrography analysis in Table 4 verifies the effect of initial oxide composition towards the tendency of the formation of different spheres. Fly ash from Tuban with the SiO_2 content contains a relatively higher content of cenosphere (90.8 %), whereas UBJOM

Table 4
Quantitative analysis using petrography analysis on cenospheres and plerosphere

No	Power plant	Cenospheres (%)	Plerosphere (%)
1	UBJOM Paiton	89.1	10.9
2	Indramayu	90.8	9.2
3	Tuban	90.8	9.2
4	Pacitan	92.3	7.7
5	Paiton	89.6	10.4
6	Rembang	89.2	10.8

Paiton's fly ash produces the highest plerosphere content (Fig. 7a). Higher plerosphere content can be obtained due to a higher amount of minor oxides (CaO + MgO + Na_2O) which leads to the formation of complex mineral phases and changes the viscosity of molten materials [11]. The existence of encapsulated complex phases which have different viscosity may cause different cooling rate and solidification process, as well as generation of gases from $CaCO_3$ decomposition and H_2O release from clay minerals. The formation of plerosphere also could be explained by the entrapment of microspheres inside the expanded cenosphere [35]. Based on those facts, the cenosphere formation is highly possible occurred in a higher $SiO_2 + Al_2O_3 + K_2O + TiO_2 + P_2O_5$ content with a certain amount of Fe_2O_3 depends on the chemical compositions of initial coal. Iron oxide is an essential substance for cenosphere formation, and the amount of Fe_2O_3 also determines the appearance and physical properties of the spheres. As the Fe_2O_3 content increase, it is expected there is the incorporation of Fe atoms in Si-Al crystal system, and some of Fe atoms also form ferrospinel phases which lead to an increase of the surface roughness [36], as can be seen in Fig. 7b. The relation oxide compositions towards the tendency of formation of different spheres can be drawn in Fig. 8.

3.2. Correlation between cenospheres diameter and fly ash chemical composition

There is two hypotheses for cenospheres formation process which have been recommended [11]. Firstly, the effective one, condensed gases formed during the decomposition of several substances, i.e. organics compound, carbonates, sulphines, sulfates, etc. and evaporation of water in the pore of molten microsphere escalate the molten up to 500 μm, which takes on spherical and hollow particles formation [17,22,26]. Secondly, the flue gas which initially penetrated the molten

Table 3
Oxide composition of cenospheres determined by EDS analysis.

No	Components (wt%)	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	CuO	SiO_2/Al_2O_3
1	UBJOM Paiton	0.59	11.77	9.01	23.23	1.09	18.39	0.62	34.09	1.20	2.56
2	Indramayu	0.98	6.33	22.93	44.35	0.90	8.71	0.63	13.94	1.22	1.92
3	Tuban	1.39	2.55	31.52	49.90	0.76	3.27	0.86	8.45	1.30	1.59
4	Pacitan	1.54	7.74	20.60	40.01	0.93	11.62	0.78	15.35	1.43	1.92
5	Paiton	0.68	4.70	24.82	49.15	1.48	5.13	1.47	10.81	1.75	1.96
6	Rembang	1.06	8.67	15.94	28.28	0.82	18.28	0.93	24.79	1.22	1.79

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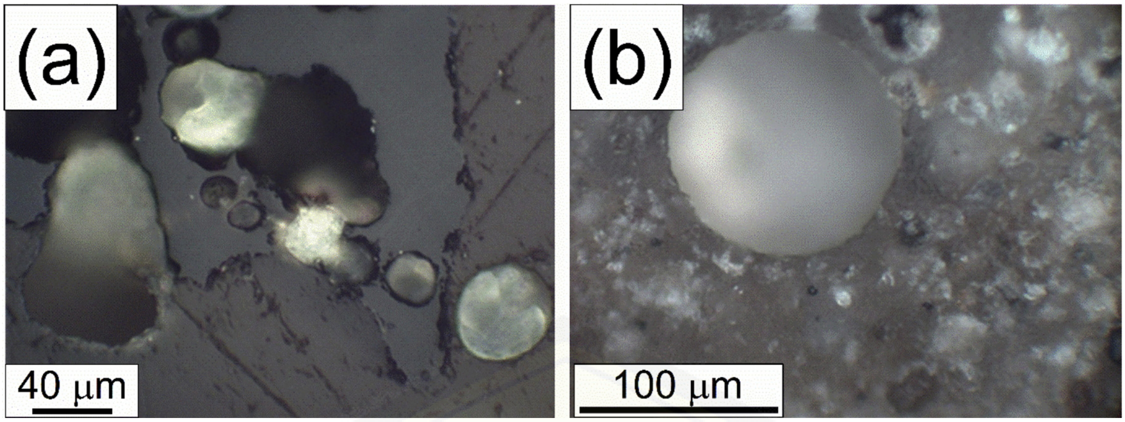

Fig. 3. Petrography analysis of fly ash to detect the existence of: (a) plerosphere and (b) cenospheres.

ash droplet is trapped when the temperature drops [34]. However, after solid material formed, these hollow-spherical materials are called cenospheres. These mechanisms are important to study the reaction process during combustion because broad derived products of cenospheres have been obtained from power plant coal combustion.

The diameter of cenospheres was analyzed using SEM and PSA as shown in Fig. 9 and 10, respectively. From Fig. 9, it can be seen the surface and diameter imaging of cenospheres produced from all power plants. Diameter variations are very noticeable from the figure while the smoothness of the surface for each cenosphere slightly different from UBJOM Paiton and Tuban power plants, as the consequence of higher Fe_2O_3 content among other sources. Based on Fig. 10, we can see that the diameter of cenospheres has formed vary in all of the samples, from the smallest particle size in the range of 1300–5200 nm for Indramayu power plant to the biggest particle size in the range of 1200 – 8500 nm for UBJOM Paiton power plant. Regarding the wide range of cenospheres diameter, we proposed to use the average diameter for each power plant as a parameter to compare with the fly ash chemical composition. From the average diameter calculation, the diameter of cenospheres is formed under specific conditions, confidential operating parameters for each power plant produced various cenospheres diameter which is Particulate Matter$_1$ (PM_1) in which the cenospheres diameter is below 1 μm and Particulate Matter$_{10}$ (PM_{10}) for cenospheres with a diameter in the range of 1–10 μm. From Fig. 10, all cenospheres can be categorized as PM_{10}. The formation mechanism of PM_1 and PM_{10} is strongly believed to follow the mechanism of a previous study [37]. Two pathway categories for PM formation were suggested, namely solid-to-particle processes, resulting in PM_1 and PM_{10} usually through the coalescence of mineral particles included in the same coal/charcoal particles and fragmentation of minerals and / charcoal particles and solid vapors-particle processes, producing good PM_1 and PM_{10} through pathways which may involve homogeneous nucleation, coagulation, and agglomeration [37]. We do agree that the formations of both PM_1 and PM_{10} are through those mechanisms, although, there is unclear data lack of detailed information explaining about the mechanism. We also believe that the formation mechanism of PM_1 and PM_{10} is different due to the huge difference in the cenospheres' diameter resulted. The mechanism of a vaporization-condensation process seems fit for PM_1 and a solid-particle process seems suitable for PM_{10}.

The relationship analysis between the major component of SiO_2, Al_2O_3, SiO_2/Al_2O_3, Fe_2O_3, $Fe_2O_3+TiO_2$, CaO, MgO, and diameter of cenospheres was conducted and presented in Fig. 6a–f (blue data points), respectively. It can be seen that the higher the SiO_2 and Al_2O_3 concentration, the bigger the cenospheres diameter. Meanwhile, other chemical compositions are in vice versa correlation with the cenospheres yield and diameter; the higher Fe_2O_3, Fe_2O_3 + TiO_2, CaO, and MgO concentration, the smaller the cenospheres diameter. The values of *R*-square from data fitting for chemical components and the diameter of cenospheres are varied in the range of 0.53–0.66. Even though the value of *R*-square is less than 0.7, the relationship of each substance to the cenospheres' diameter is confirmed as shown in this study. However, further detailed research should be conducted to explore the effect

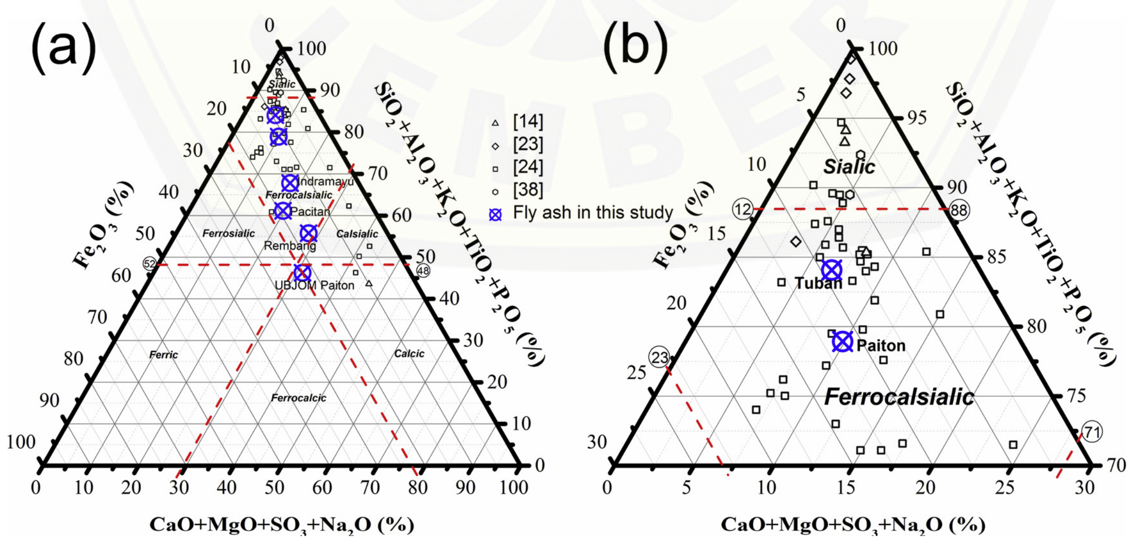

Fig. 4. Classification of fly ash used in this study based on chemical compositions, together with additional data from references [14,23,24,38], (a) full diagram; (b) enlargement of sialic and ferrocalsialic region.

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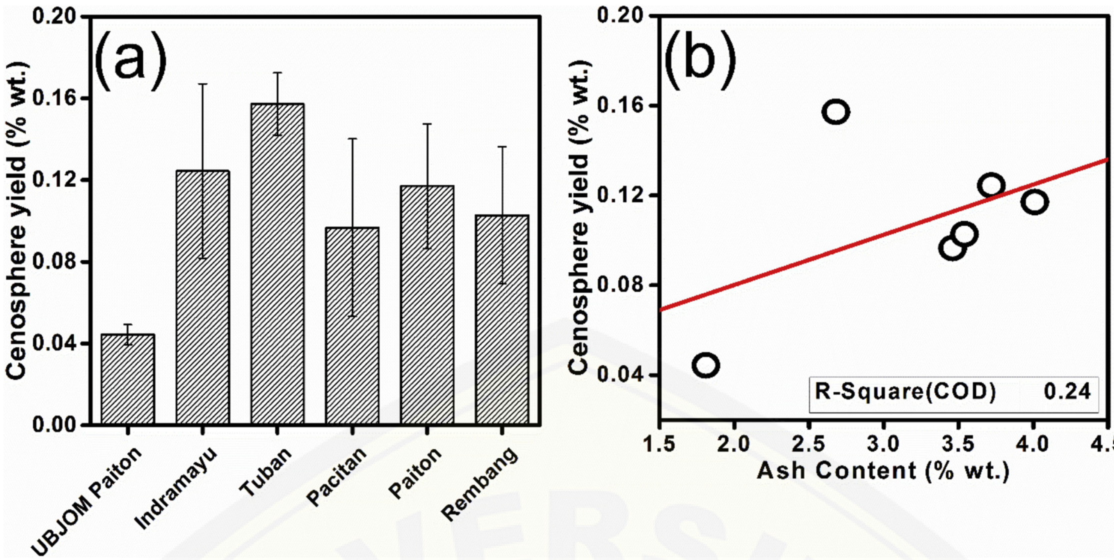

Fig. 5. (a) Cenospheres yield in fly ash from the Indonesian coal-fired power plants and (b) its relation to ash content in the initial coal.

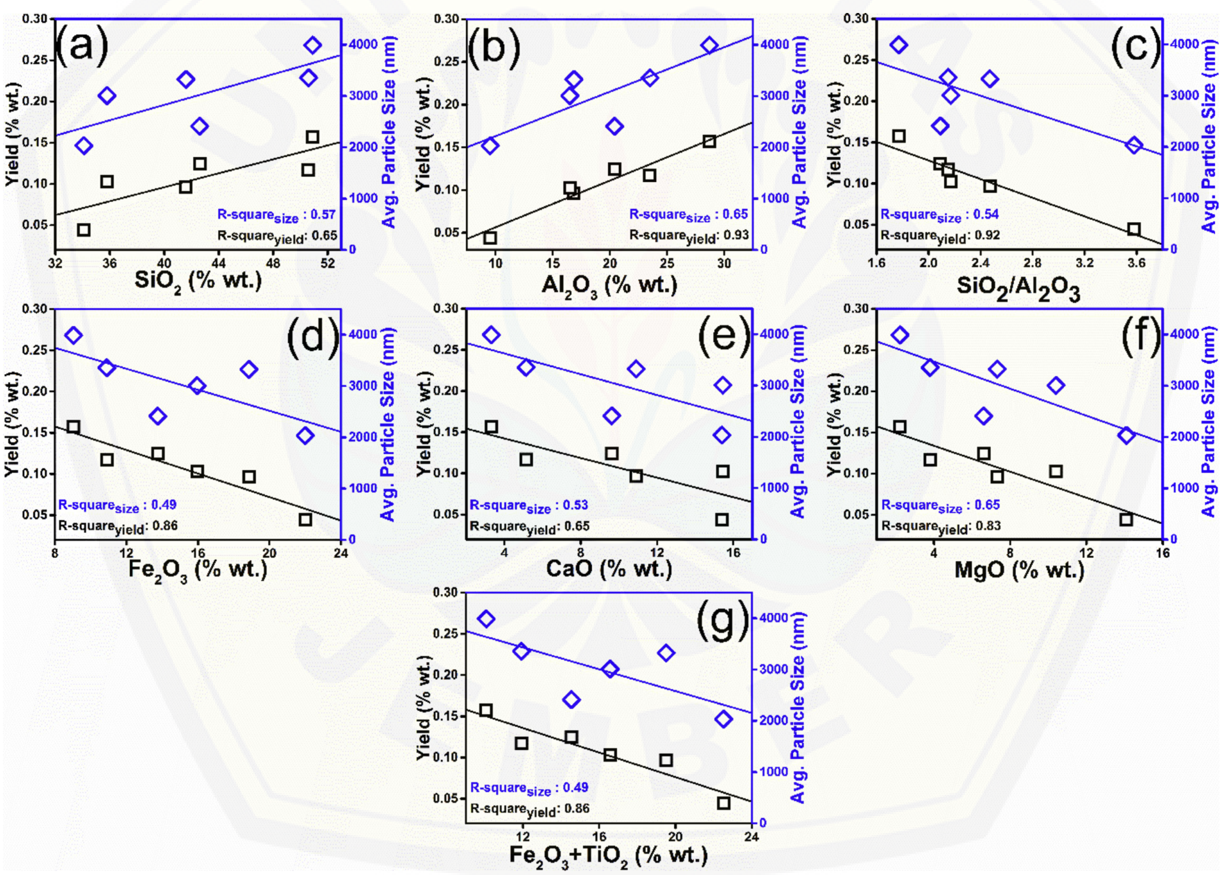

Fig. 6. Correlation of cenospheres yield and average particle diameter as function of: (a) SiO_2, (b) Al_2O_3, (c) SiO_2/Al_2O_3 ratio, (d) Fe_2O_3, (e) CaO, (f) MgO, and (g) $Fe_2O_3 + TiO_2$ content in initial fly ash.

of chemical composition on the cenospheres diameter. The comprehensive comparison with previous studies about the relationship of chemical compositions and the diameter of cenospheres is also presented in Table 5. The data gained in this research gives a more reliable relationship for each chemical composition in comparison to other studies.

3.3. Possible technologies applied to separate cenospheres and the utilization

Due to cenospheres density of about 0.8–0.9 g/cm^3 [18,19,20], there are several separation methods that can be applied. Wet separation with water as a fluid media in a lagoon is the easiest method to recover cenospheres from fly ash with yield of about 90 wt% [18,39], while other wet separation method has been studied using inverted

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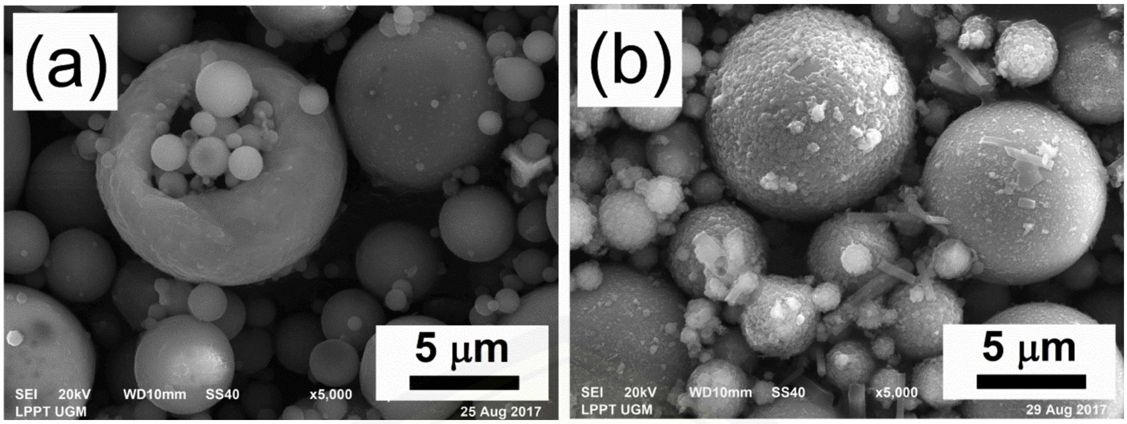

Fig. 7. SEM images showing the existence of: (a) plerosphere in Tuban and (b) magnetosphere in UBJOM Paiton samples with 5000 times magnification.

reflux classifier with similar recovery [21]. However, further drawbacks are observed in wet separation in which cenospheres should be dried containing higher energy consumption in the process and possible metals leaching from the coal fly ash possessing negative environmental impact. Thus, dry separation method using air as a separating media has been applied in cenospheres recovery with lower yield of about 80 wt% [19,20]. In term of cenospheres utilization, some studies have been thoroughly studied and confirmed that many appliances can be fulfilled by cenospheres, from filler in polymer and composites [40,41], automotive brake rotors and enhancing electromagnetic shielding [42,43], refractories, heat exchanger, steel soaking and aluminum reclamation [44,45], to material construction light weight cements [46,47,48].

4. Conclusion

Fly ash and cenospheres from six coal-fired power plants in Indonesia have been successfully characterized. This study briefly explained the relationship of chemical composition-cenospheres' yield and chemical composition-diameter of cenospheres, thus, it would help the understanding of cenospheres formation mechanism during the coal combustion process and estimating the cenospheres production from fly ash produced. Furthermore, the result showed that the higher SiO_2, Al_2O_3, Na_2O_3, and Al_2O_3/SiO_2 value in the fly ash, the higher is the cenospheres yield. Reversely, another chemical component, such as Fe_2O_3, $Fe_2O_3 + TiO_2$, CaO, and MgO, gave lower yield in the increasing of the chemical component value. The data fitting for chemical components and yield had acceptable R-square value in the range of 0.66–0.93. Those chemical existences in fly ash could be initial measuring variables to predict the amount of cenospheres obtained. To study the formation mechanism of the cenosphere, the relationship between diameter formed and chemical composition is often used in many studies. In contrast to other studies, this study used the average diameter for comparison. Every chemical existence in fly ash surprisingly gave the same tendency on the diameter size produced alike the cenosphere yield. Even though, the values of *R*-square value were only at 0.53–0.66 on the relationship between chemical components and cenospheres diameter, these tendencies could provide valuable information in the cenospheres formation mechanism. Hopefully, this work can be useful for the utilization and further application of

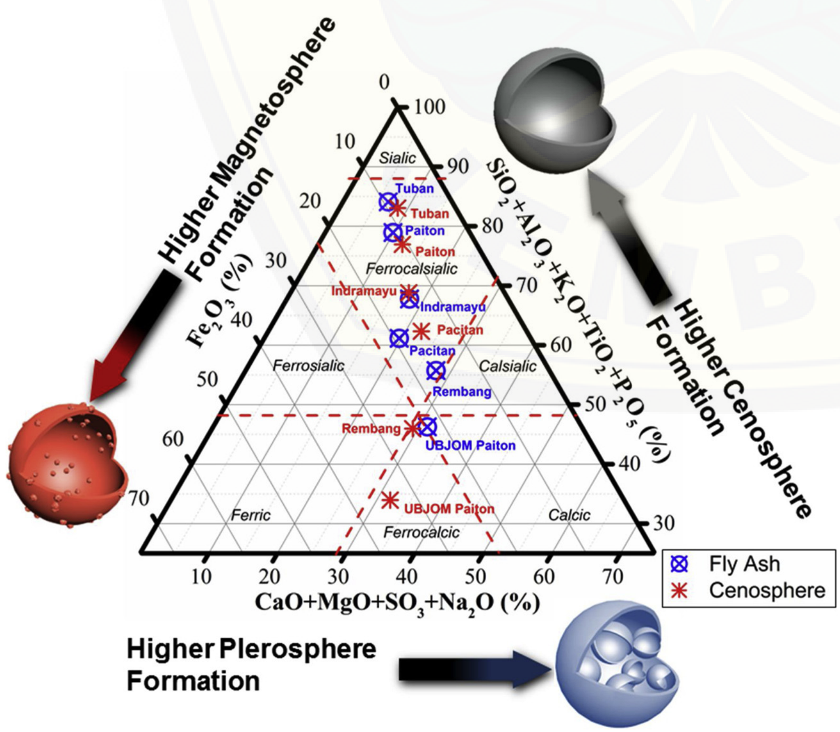

Fig. 8. The dependence of oxide compositions in fly ash (blue crossed-circles) towards the formation tendency of different type of particles (cenosphere, magnetosphere and plerosphere) and corresponding cenosphere's oxide compositions (red stars) determined by EDS. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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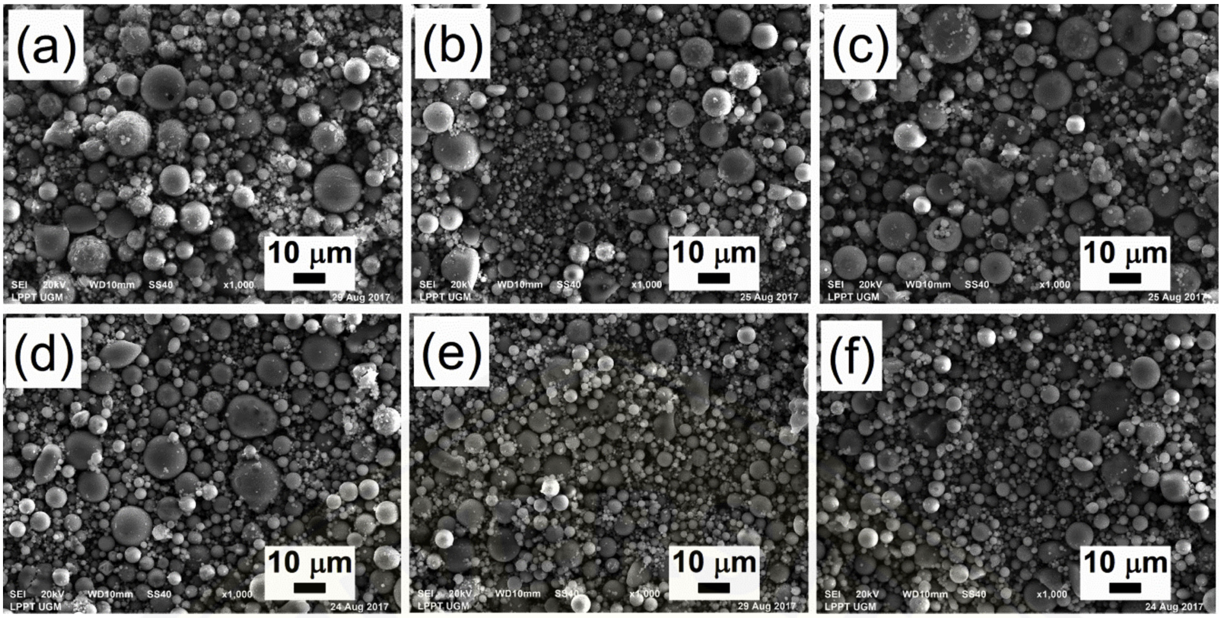

Fig. 9. SEM images of cenospheres from the six Indonesian coal-fired power plants with 1000 times magnification, (a) UBJOM Paiton; (b) Indramayu; (c) Tuban; (d) Pacitan; (e). Paiton; and (f). Rembang.

problematic fly ash management in Indonesia.

CRediT authorship contribution statement

Himawan Tri Bayu Murti Petrus: Conceptualization, Data curation, Funding acquisition, Methodology, Supervision, Validation, Writing - review & editing. **Muhammad Olvianas:** Data curation, Formal analysis, Investigation, Methodology, Software, Visualization, Writing - original draft. **Wisnu Suprapta:** Data curation, Funding acquisition, Investigation, Project administration. **Felix Arie Setiawan:** Formal analysis, Resources, Software, Visualization, Writing - original draft. **Agus Prasetya:** Formal analysis, Funding acquisition, Resources, Writing - review & editing.Data curation, Investigation, Software, Supervision, Validation, Writing - review & editing. **Ferian Anggara:** Conceptualization, Data curation, Methodology, Resources, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

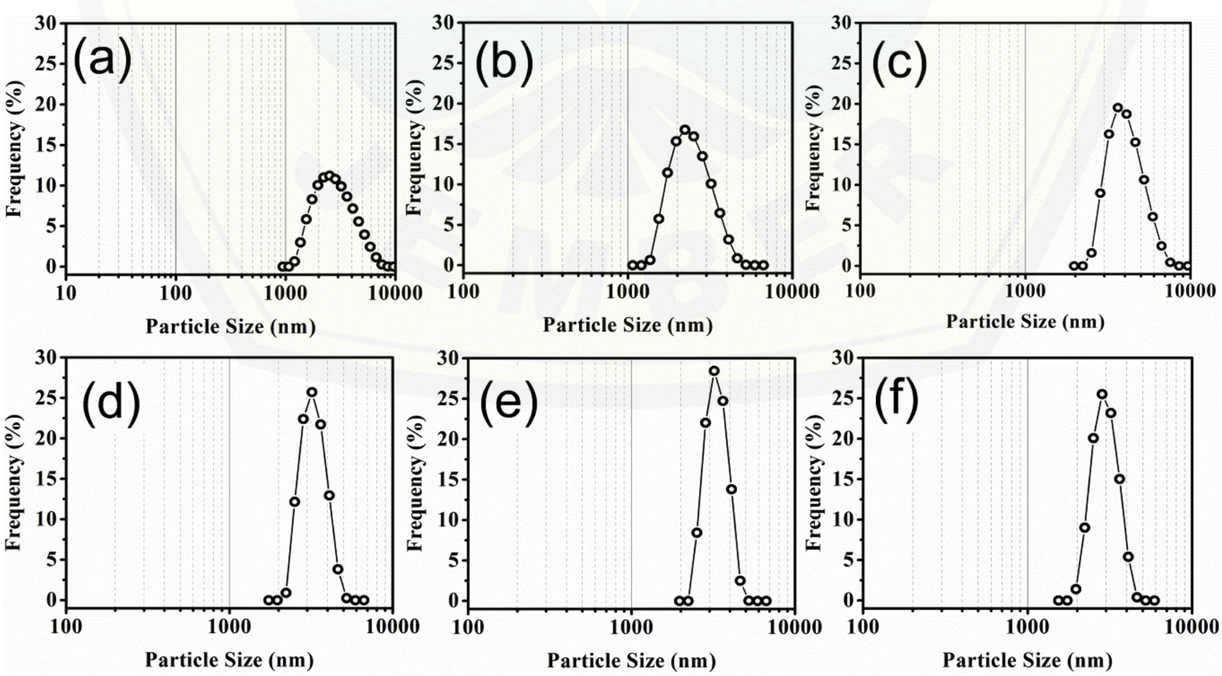

Fig. 10. Particle size distributions of cenospheres from the six Indonesian coal-fired power plants: (a) UBJOM Paiton; (b) Indramayu; (c) Tuban; (d) Pacitan; (e) Paiton; and (f) Rembang.

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Table 5
Particle size relation to chemical composition trend compared to other studies.

Specimens (size ranges)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O	SO_3	Al_2O_3/SiO_2	References
CCC (20–600 μm)	↓	↓	N	↑	↑	N	↓	↑	↑	↑	22
CCV (20–600 μm)	↓	↓	↑	↑	↑	↓	↓	↑	↑	↑	22
HMR (40–250 μm)	↓	↑	↑	N	N	-	↓	N	↓	↑	39
H (40–125 μm)	↑	N	N	↑	N	N	N	N	N	↓	38
M (40–125 μm)	↑	↓	N	N	N	N	N	N	N	↓	38
Li (40–125 μm)	↓	↑	↑	N	N	↑	↑	N	-	↑	17
This study (2 – 4 μm)	↑	↑	↓	↓	↓	↓	↓	↑	N	↑	-

↑ Increase in compound by increasing the particle size, ↓ decrease in compound by increasing the particle size, N no particular trend, – undetected.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jece.2020.104116.

References

[1] S. Mohr, J. Wang, G. Ellem, J. Ward, D.J. Giurco, Projection of world fossil fuels by country, Fuel 141 (2015) https://doi.org/0.1016/j.fuel.2014.10.030.

[2] S. Cornot-Gandolphe, Indonesia's Electricity Demand and the Coal Sector: Export Or Meet Domestic Demand? 2017 Oxford Institute for Energy Studies, 2017.

[3] Keputusan Menteri Energi dan Sumber Daya Mineral Republik Indonesia, No. 5899 K/20/MEM/2016 tentang Pengesahan Rencana Usaha Penyediaan Tenaga Listrik PT Perusahaan Listrik Negara (Persero) tahun 2016 s.d. 2025, (2016).

[4] Peraturan Presiden Republik Indonesia, Nomor 5 Tahun 2006 Tentang Kebijakan Energi Nasional, (2006).

[5] British Petroleum, BP Statistical Review of World Energy 2018 (2018).

[6] R.C. Joshi, R. Lohita, Fly Ash in Concrete: Production, Properties and Uses, CRC Press, Amsterdam, The Netherlands, 1997.

[7] K. Patra, T.R. Rautray, P.J.A.R. Nayak, Isotopes, analysis of grains grown on fly ash treated soils, Appl. Radiat. Isot. 70 (8) (2012) 1797–1802, https://doi.org/10.1016/j.apradiso.2012.03.037.

[8] G. Neupane, R.J.J. Donahoe, Leachability of elements in alkaline and acidic coal fly ash samples during batch and column leaching tests, Fuel 104 (2013) 758–770, https://doi.org/10.1016/j.fuel.2012.06.013.

[9] S.M. Nyale, C.P. Eze, R.O. Akinyeye, W.M. Gitari, S.A. Akinyemi, O.O. Fatoba, L.F.J.J. o, E.S. Petrik, P.A. Health, The leaching behaviour and geochemical fractionation of trace elements in hydraulically disposed weathered coal fly ash, J Env. Sci Heal. A Tox Hazard Subst Env. Eng. 49 (2) (2014) 233–242, https://doi.org/10.1080/10934529.2013.838929.

[10] S. Ghosal, S.A.J. Self, Particle size-density relation and cenosphere content of coal fly ash, Fuel. 74 (4) (1995), https://doi.org/10.1016/0016-2361(95)98354-H.

[11] N. Ranjbar, C.J.F. Kuenzel, Cenospheres: a review, Fuel 207 (2017) 1–12, https://doi.org/10.1016/j.fuel.2017.06.059.

[12] I. Acar, M.J. Atalay, Recovery potentials of cenospheres from bituminous coal fly ashes, Fuel 180 (2016) 97–105, https://doi.org/10.1016/j.fuel.2016.04.013.

[13] H. Cho, D. Oh, K.J.J. o, H. Kim, A study on removal characteristics of heavy metals from aqueous solution by fly ash, Hazard. Mater. 127 (1–3) (2005) 187–195, https://doi.org/10.1016/j.jhazmat.2005.07.019.

[14] V. Drozhzhin, M. Shpirt, L. Danilin, M. Kuvaev, I. Pikulin, G. Potemkin, S.J.S. f. c. Redyushev, Formation processes and main properties of hollow aluminosilicate microspheres in fly ash from thermal power stations, Solid Fuel Chem. 42 (2) (2008) 107–119, https://doi.org/10.3103/S0361521908020110.

[15] E. Fomenko, N. Anshits, L. Solov'ev, O. Mikhailova, A.J.S.F. Anshits, Composition and structure of the shells of fly ash cenospheres from the combustion of coal of the Kuznetsk Basin, Solid Fuel Chem. 48 (2) (2014) 129–139, https://doi.org/10.3103/S0361521914020037.

[16] E.V. Fomenko, N.N. Anshits, N.G. Vasilieva, O.A. Mikhaylova, E.S. Rogovenko, A.M. Zhizhaev, A.G.J.E. Anshits, Fuels, Characterization of fly ash cenospheres produced from the combustion of Ekibastuz coal, Energy Fuels. 29 (8) (2015) 5390–5403, https://doi.org/10.1021/acs.energyfuels.5b01022.

[17] Y. Li, H.J.E. Wu, Fuels, Ash cenosphere from solid fuels combustion. Part 1: an investigation into its formation mechanism using pyrite as a model fuel, Energy Fuels 26 (1) (2011) 130–137, https://doi.org/10.1021/ef201173g.

[18] T. Hirajima, Y. Oosako, M. Nonaka, H. Petrus, K. Sasaki, T.J.J. o. M. Ando, Recovery of hollow and spherical particles from coal fly ash by wet separation process, J. MMIJ. 124 (12) (2008) 878–884, https://doi.org/10.2473/journalofmmij.124.878.

[19] T. Hirajima, H. Petrus, Y. Oosako, M. Nonaka, K. Sasaki, T.J.I.J. o, M.P. Ando, Recovery of cenospheres from coal fly ash using a dry separation process: separation estimation and potential application, Int. J. Miner. Process. 95 (1–4) (2010) 18–24, https://doi.org/10.1016/j.minpro.2010.03.004.

[20] H. Petrus, T. Hirajima, Y. Oosako, M. Nonaka, K. Sasaki, T.J.I.J. o, M.P. Ando, Performance of dry-separation processes in the recovery of cenospheres from fly ash and their implementation in a recovery unit, Int. J. Miner. Process. 98 (1–2) (2011) 15–23, https://doi.org/10.1016/j.minpro.2010.09.002.

[21] J. Li, A. Agarwal, S. Iveson, A. Kiani, J. Dickinson, J. Zhou, K.J.F.P.T. Galvin, Recovery and concentration of buoyant cenospheres using an inverted reflux classifier, Fuel Process. Technol. 123 (2014) 127–139, https://doi.org/10.1016/j.fuproc.2014.01.043.

[22] S.V. Vassilev, R. Menendez, M. Diaz-Somoano, M.R.J.F. Martinez-Tarazona, Phase-mineral and chemical composition of coal fly ashes as a basis for their multicomponent utilization. 2. Characterization of ceramic cenosphere and salt concentrates, Fuel 83 (4–5) (2004) 585–603, https://doi.org/10.1016/j.fuel.2003.10.003.

[23] L. -n. Ngu, H. Wu, D. -k. J.E. Zhang, Fuels, characterization of ash cenospheres in fly ash from Australian power stations, Energy Fuels. 21 (6) (2007) 3437–3445, https://doi.org/10.1021/ef700340k.

[24] S.V. Vassilev, C.G.J.F. Vassileva, A new approach for the classification of coal fly ashes based on their origin, composition, properties, and behaviour, Fuel Process. Technol. 86 (10–11) (2007) 1490–1512, https://doi.org/10.1016/j.fuel.2006.11.020.

[25] P.K. Kolay, S.J.F. Bhusal, Recovery of hollow spherical particles with two different densities from coal fly ash and their characterization, Fuel 117 (2014) 118–124, https://doi.org/10.1016/j.fuel.2013.09.014.

[26] M. Żyrkowski, R.C. Neto, L.F. Santos, K.J.F. Witkowski, Characterization of fly-ash cenospheres from coal-fired power plant unit, Fuel 174 (2016) 49–53, https://doi.org/10.1016/j.fuel.2016.01.061.

[27] N. Anshits, O. Mikhailova, A. Salanov, A.J.F. Anshits, Chemical composition and structure of the shell of fly ash non-perforated cenospheres produced from the combustion of the Kuznetsk coal (Russia), Fuel 89 (8) (2010) 1849–1862, https://doi.org/10.1016/j.fuel.2010.03.049.

[28] L. Yi, J. Feng, Y.-H. Qin, W.-Y.J.F. Li, Prediction of elemental composition of coal using proximate analysis, Fuel 193 (2017) 315–321, https://doi.org/10.1016/j.fuel.2016.12.044.

[29] G. Fisher, D. Chang, M.J.S. Brummer, Fly ash collected from electrostatic precipitators: microcrystalline structures and the mystery of the spheres, Science 192 (4239) (1976) 553–555, https://doi.org/10.1126/science.192.4239.553.

[30] E.V. Fomenko, N.N. Anshits, L.A. Solovyov, O.A. Mikhaylova, A.G.J.E. Anshits, Fuels, composition and morphology of fly ash cenospheres produced from the combustion of kuznetsk coal, Energy Fuels. 27 (9) (2013) 5440–5448, https://doi.org/10.1021/ef400754c.

[31] F.J.F. Goodarzi, Characteristics and composition of fly ash from Canadian coal-fired power plants, Fuel 85 (10–11) (2006) 1418–1427, https://doi.org/10.1016/j.fuel.2005.11.022.

[32] S.V. Vassilev, C.G.J.F. Vassileva, Mineralogy of combustion wastes from coal-fired power stations, Fuel Process. Technol. 47 (3) (1996) 261–280, https://doi.org/10.1016/0378-3820(96)01016-8.

[33] G.J. McCarthy, K.D. Swanson, L.P. Keller, W.C.J.C. Blatter, Mineralogy of western fly ash, Cem. Concr. Res. 14 (4) (1984) 471–478, https://doi.org/10.1016/0008-8846(84)90121-2.

[34] E. Sokol, N. Maksimova, N. Volkova, E. Nigmatulina, A.J.F.P.T. Frenkel, Hollow silicate microspheres from fly ashes of the Chelyabinsk brown coals (South Urals, Russia), Fuel Process. Technol. 67 (1) (2000) 35–52, https://doi.org/10.1016/S0378-3820(00)00084-9.

[35] F. Goodarzi, H. Sanei, Plerosphere and its role in reduction of emitted fine fly ash particles from pulverized coal-fired power plants, Fuel 88 (2009) 382–386, https://doi.org/10.1016/j.fuel.2008.08.015.

[36] B.G. Kutchko, A.G. Kim, Fly ash characterization by SEM – EDS 85 (2006), pp. 2537–2544, https://doi.org/10.1016/j.fuel.2006.05.016.

[37] M. Xu, D. Yu, H. Yao, X. Liu, Y.J.P. o. t, C.I. Qiao, Coal combustion-generated aerosols: Formation and properties, Combust. Inst. 33 (1) (2011) 1681–1697, https://doi.org/10.1016/j.proci.2010.09.014.

[38] J. Yu, X. Li, D. Fleming, Z. Meng, D. Wang, A. Tahmasebi, Analysis on characteristics of fly ash from coal fired power stations, Energy Procedia 17 (2012) 3–9, https://doi.org/10.1016/j.egypro.2012.02.054.

[39] P. Kolay, D.P. Singh, Physical, chemical, mineralogical, and thermal properties of cenospheres from an ash lagoon, Cem. Concr. Res. 31 (2001) 539–542, https://doi.org/10.1016/S0008-8846(01)00457-4.

[40] V.B. Chalivendra, A. Shukla, A. Bose, V. Parameswaran, Processing and mechanical characterization of lightweight polyurethane composites, J. Mater. Sci. 38 (2003) 1631–1643, https://doi.org/10.1023/A:1023203121299.

[41] F. Shutov, Syntactic polymeric foams, Handbook of Polymeric Foams and Foam Technology, Hanser Publishers, New York, 1991.

[42] N. Jha, A. Badkul, D. Mondal, A. Das, M. Singh, Sliding wear behaviour of aluminum syntactic foam: a comparison with Al–10wt% SiC composites, Tribol. Int. 44 (2011) 220–231, https://doi.org/10.1016/j.triboint.2010.10.004.

[43] P.K. Rohatgi, N. Gupta, B.F. Schultz, D.D. Luong, The synthesis, compressive properties, and applications of metal matrix syntactic foams, JOM 63 (2011) 36–42, https://doi.org/10.1007/s11837-011-0026-1.

[44] A. Chávez-Valdez, A. Arizmendi-Morquecho, G. Vargas, J. Almanza, J. AlvarezQuintana, Ultra-low thermal conductivity thermal barrier coatings from recycled fly-ash cenospheres, Acta Mater. 59 (2011) 2556–2562, https://doi.org/10.1016/j.actamat.2011.01.011.

[45] E. Ozcivici, R.P. Singh, Fabrication and characterization of ceramic foams based on silicon carbide matrix and hollow alumino-silicate spheres, J. Am. Ceram. Soc. 88 (2005) 3338–3345, https://doi.org/10.1111/j.1551-2916.2005.00612.x.

[46] V. Lilkov, N. Djabarov, G. Bechev, K. Kolev, Properties and hydration products of lightweight and expansive cements Part I: Physical and mechanical properties, Cem. Concr. Res. 29 (1999) 1635–1640, https://doi.org/10.1016/S0008-8846(99)00150-7.

[47] V. Lilkov, N. Djabarov, G. Bechev, O. Petrov, Properties and hydration products of lightweight and expansive cements Part II: Hydration products, Cem. Concr. Res. 29 (1999) 1641–1646, https://doi.org/10.1016/S0008-8846(99)00149-0.

[48] E.W. Biederman Jr. Lightweight cements for oil wells, Google Patents, 1972.