Rev. Adv. Mater. Sci. 34 (2013) 37-43

REVIEW ON THE VARIOUS ASH FROM PALM OIL WASTE AS GEOPOLYMER MATERIAL

Y. Zarina[1], A. M. Mustafa Al Bakri[1], H. Kamarudin[1], I. Khairul Nizar[2] and A. R. Rafiza[1]

[1]Center of Excellence Geopolymer and Green Technology, School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), 01007, P.O. Box 77, D/A Pejabat Pos Besar, Kangar, Perlis, Malaysia
[2]School of Environmental Engineering, Universiti Malaysia Perlis (UniMAP), P.O. Box 77, D/A Pejabat Pos Besar, 01007, Kangar, Perlis, Malaysia

Received: September 09, 2012

Abstract. The solid waste from palm oil mill industry has been increasing annually where it has been reported that the palm oil waste was produced 4 million tons/years in Malaysia only. Hence, the solution to overcome the problems is to reuse the waste and produced new composites that are benefit. There are two types of palm ash waste which are palm oil fuel ash (POFA) and boiler ash. POFA is by product from power electricity generation plants that used palm oil shells and palm oil bunches as burn materials. Meanwhile boiler ash is the biomass known as mesocarp fiber and shell that consists of clinkers and ash that has been burnt in the boiler. Both of these ashes contain silica (Si) which has potential to develop as geopolymer composites. However, only POFA has been successfully produced ash geopolymer materials but it required other raw material that rich in alumina (Al) to produce geopolymer with suitable strength. In order to produce geopolymer, the POFA has been activated by alkaline activator consists of mixture of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH). On the other hand, the use of boiler ash as geopolymer materials was never been investigated.

1. INTRODUCTION

In recent years, various researchers were concentrated on producing environmental friendly products such as geopolymers. The production of geopolymers required alumina-silicate based materials which are rich in silicon (Si) and aluminum (Al), where it was activated by alkaline solutions [1]. The most alumina-silicate based materials that has been explored in the production of geopolymers were fly ash [2-4], metakaolin [5] and kaolin [6-8], palm oil fuel ash (POFA) [9], combination of ground granulated blast furnace slag (ggbs) and metakaolin [5], combination of fly ash and metakaolin [10-11], combination of POFA and metakaolin [12], combination of POFA and fly ash [9]. As result from the previous researches it was prove that geopolymers have excellent mechanical properties, high resistance to chemical attack and also abilities to encapsulate hazardous waste [13-15]. Moreover, there are potential applications of geopolymer as fire resistance panel [16] or as fire resistant coatings on metal [17].

The large production of palm oil in Malaysia has made it become the second largest oil palm producer in the world on 2010; where 18.6 million metric tons production has been made [18]. However, waste from the palm oil industry also abundantly produced which caused criticism and complaint. The waste such as palm fibers, nut shells, palm kernel and empty fruit bunches are the solid waste the obtained from palm oil processing for oil extraction. Furthermore, these wastes were incinerated in boilers and from

Corresponding author: Yahya Zarina, e-mail: zarinayahya@unimap.edu.my

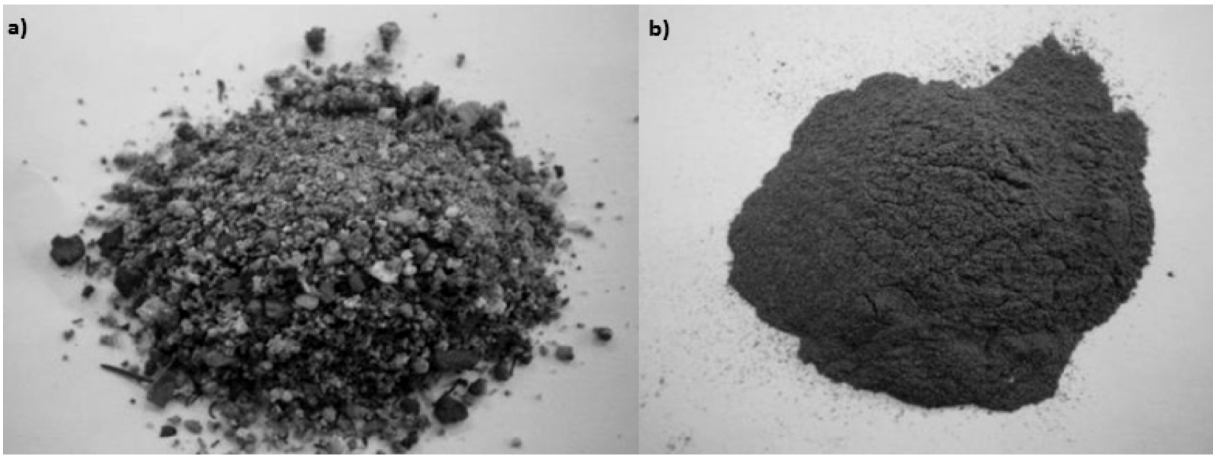

Fig. 1. (a) Original boiler ash, (b) Ultrafine boiler ash.

this process two types of palm ashes were produced which is boiler ash and palm oil fuel ash (POFA). Boiler ash was obtained from burning the palm fiber and kernel shells in the boiler where it consists of clinkers and ash [19]. Meanwhile POFA is by product from power plant that generate electricity which used palm fiber, shell and empty fruit bunches as fuel and burnt at 800-1000 °C [20]. The production of these two ashes was estimated more than 4 million tons/year in Malaysia only [21]. In order to reduce the problems, the palm ash has been utilized in many applications such as raw material for geopolymer composite [9,12], cement replacement in production of concrete [22,23], wastewater treatment and air purifier in cleaning atmospheric contaminants [24]. This paper reviews about the application of palm ashes (boiler ash and POFA) as geopolymer materials.

2. SAMPLE PREPARATION

Fig. 1a showed the original boiler ash, meanwhile Fig. 1b was ultrafine boiler ash and Fig. 2 display the POFA. The original boiler ash that has been collected directly from the boiler has large particles compared to POFA. Hence in order to be used as material in the production of geopolymer, the original boiler ash has been ground and sieved passing through 100 μm sieve which known as ultrafine boiler ash (UBA).

However, for POFA preparation there are a few different steps that have been used by previous researchers. Chandara *et al.* [25] remove the incomplete combusted fibers and nutshells from the POFA by sieved it using 300 μm sieve. Then, the POFA was ground using ball mill for 45 minutes to obtain more fine particles. After that, the ground POFA (GPOFA) was heated in furnace for 1 hour at temperature 500 °C to remove unburned carbon and increasing the pozzolanic properties.

Conversely, Megat Johari *et al.* [23] try a slightly different approach to prepare the POFA. Firstly, to remove the coarse particles such as fiber and kernel which are incomplete burned, the POFA was dried in oven at temperature 105 ± 5 °C for 24 hour and then sieved passing through 300 ìm sieve. The following step was ground the POFA to achieve more fine particles and then heated again in furnace at temperature 500 ± 5 °C for 90 minutes to remove unburned carbon.

The same method was practice by Nurdeen *et al.* [26] where there are only differ in heat treatment temperature of POFA. The steps where the POFA was dried and sieved passing through sieve were the same as above [23]. Then the untreated POFA was ball milling for approximately 6 hours at 45 rpm to increase the reactivity and in order to prevent formation of glassy phase crystallization and also agglomeration, the untreated POFA was heated again at temperature 450 °C for 1.5 hours. The colour

Fig. 2. Original POFA.

Table 1. Mix design details for geopolymer concrete, see [9].

Mix designratio	(PFA:POFA) 70:30	(PFA:POFA) 50:50	(PFA:POFA) 30:70	(PFA:POFA) 0:100	(PFA:POFA) 70:30
liquid: solid	0.4	0.4	0.4	0.4	0.4
Na_2SiO_3: NaOH	2.5:1	2.5:1	2.5:1	2.5:1	1:1
Molarity of NaOH	8 M & 14 M	8 M & 14 M	8 M & 14 M	8 M & 14 M	8 M & 14 M
Curing temperature	60 & 90 °C	60 & 90 °C	60 & 90 °C	60 & 90 °C	60 & 90 °C
Curing period	24 hours	24 hours	24 hours	24 hours	24 hours

Table 2. Chemical composition of POFA [23, 26-29].

Chemical Components	Palm Ash Composition (wt. %)				
	Malaysia[23]	Thailand[26]	Thailand[27]	Thailand[28]	Malaysia[29]
SiO_2	51.18	65.3	63.6	57.7	43.6
Al_2O_3	4.61	2.5	1.6	4.5	11.4
Fe_2O_3	3.42	1.9	1.4	3.3	8.4
CaO	6.93	6.4	7.6	6.5	4.8
MgO	4.02	3.0	3.9	4.2	0.4
SO_3	0.36	0.4	0.2	0.2	2.8
K_2O	5.52	5.7	6.9	8.2	3.5
Na_2O	0.06	0.3	0.1	0.5	4.7
LOI	21.6	10.0	9.6	10.5	18.0

Table 3. Chemical composition of treated POFA, see [23].

Chemical Composition	Ground POFA (wt. %)	Ultrafine POFA (wt. %)
SiO_2	51.18	65.01
Al_2O_3	4.61	5.72
Fe_2O_3	3.42	4.41
CaO	6.93	8.19
MgO	4.02	4.58
SO_3	0.36	0.33
K_2O	5.52	6.48
Na_2O	0.06	0.07
C	19.05	0.09
LOI	21.6	2.53

of treated POFA was turned from light brown to grayish red after the unburned residue was removed.

Besides that, other researchers who have used POFA in their study usually sieved the POFA to remove unburned fiber and kernel before ground the POFA to obtain more fine particles [27,28].

For the production of geopolymer by using POFA and pulverized fly ah (PFA), alkaline activator consists of mixture of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) was used. Mohd Azreen *et al.* [9] use NaOH with concentration of 8 M and 14 M, and also ratio of sodium silicate to NaOH were 2.5 and 1, whereas ratio of alkaline activator (liquid) to POFA (solid) was fixed at 0.4 for all samples. Table 1 showed the summary of mix design details.

3. CHARACTERIZATION OF POFA AND BOILER ASH

The chemical composition of POFA as analyzed by X-Ray Fluorescence (XRF) was shown in Table 2 below. From the table it was obviously showed that POFA was rich in silicon dioxide (SiO_2), where more than 40% was found [23, 27-30]. From the table also showed that each country produced different chemical composition of POFA. Besides that, a study by Megat Johari *et al.* [23] showed that the chemical composition between ground POFA and ultrafine POFA also vary, where the content of SiO_2 was increasing when the POFA fineness increased as in Table 3. The ground POFA was produced by ball milling, where ultrafine POFA was formed by heat treatment and second stage grinding using ball mill. When the ultrafine POFA was heated, the content of carbon (C) and also loss of ignition (LOI) was decreased compared to ground POFA. In addition, the other content that important in geopolymer production such as silicon oxide (SiO_2), aluminum oxide (Al_2O_3) and ferum oxide (Fe_2O_3) increased in ultrafine POFA. Hence, heat treatment plays an important role in order to increase the reactivity of the POFA. Meanwhile the chemical composition of boiler ash detected the existence of minerals and metal such as Al, Mg, Cr and Fe [19].

The X-Ray Diffraction (XRD) pattern demonstrate the major phase of palm ash was α-quartz (SiO_2)

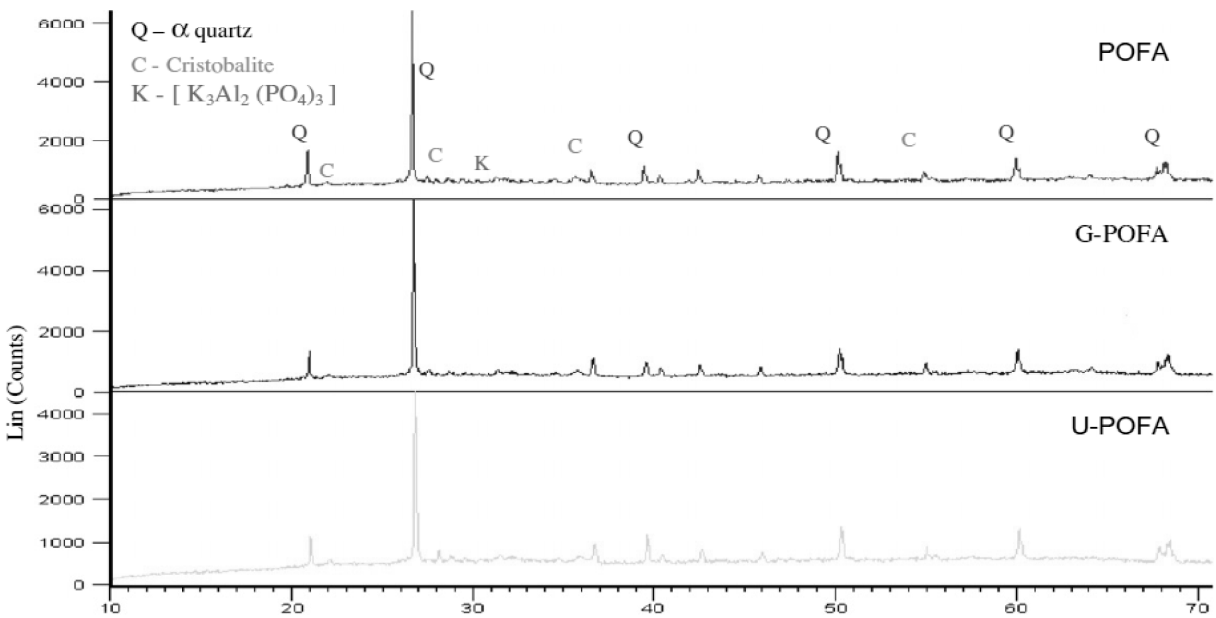

Fig. 3. XRD diffractogram of original POFA, ground POFA (G-POFA) and ultrafine POFA (U-POFA) [23], reprinted with permission from M.A. Megat Johari, A.M. Zayed, N. Muhamad Bunnori and K. S. Ariffin // *Constr. Build. Mater.* **30** (2012) 284, (c) 2012 Elsevier.

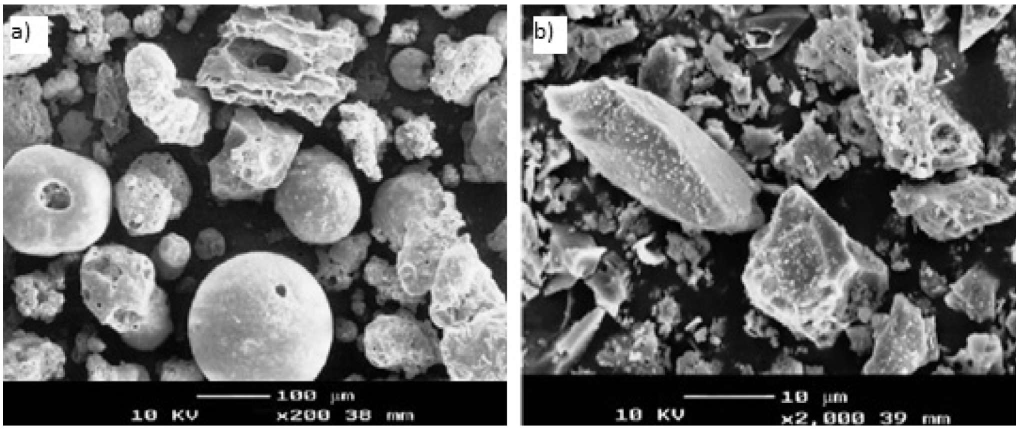

Fig. 4. (a) Microstructure of original POFA (b) Microstructure of ground POFA [31], reprinted with permission from C. Jaturapitakkul, K. Kiattikimol, W. Tangchirapat and T. Saeting // *Constr. Build.Mater.* **21** (2007) 1400, (c) 2007 Elsevier.

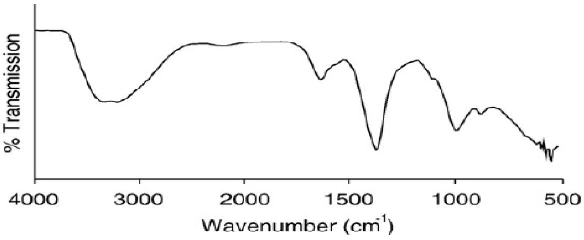

Fig. 5. FTIR spectrum of original POFA [32], reprinted with permission from C.Y. Yin, S.A.K. Sharifah Aishah, Y.P. Lim, S-A. Sharifah Nawirah and Z. Zurinawati // *Fuel Processing Tech*. **89** (2008) 696, (c) 2008 Elsevier.

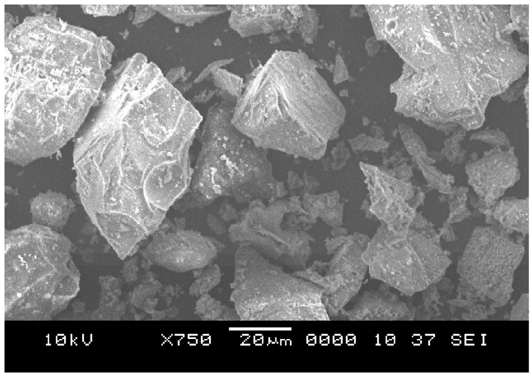

Fig. 6. Microstructure of boiler ash.

as major phase, cristobalite (SiO_2) and potassium aluminum phosphate as minor phase [22-23]. Fig. 3 showed the XRD diffractograms of original POFA, ground POFA, and ultrafine POFA that has been done by Megat Johari *et al.* [23]. The figure shows that all three types of POFA display almost similar pattern of peak cristobalite, quartz and also potassium aluminum phosphate [$K_3Al_2(PO_4)_3$]. From this study it proved that by change the fineness of POFA did not alter the crystalline phase which is amorphous content [23].

The morphology of POFA has been observed under Scanning Electron Microscope (SEM) and presented in Figs. 4a – 4b, respectively. POFA particles are porous and spongy texture with irregular and angular shapes [28,29,31]. In addition, the original POFA also consists of median particle sizes of 183.0 μm, meanwhile for ground POFA consists of median particle sizes of 15.9 μm [31]. The textures of ground POFA are more irregular and crushed shape compared to original POFA [31].

Fig. 5 contains FTIR analysis of original POFA [32]. By referring to the figure the broad band appeared about 3500 cm^{-1} was due to stretching vibration of –OH and HOH [33]. Meanwhile, around the area of 1050 cm^{-1} is assigned to stretching of Si-O and Al-O bonds [34]. The band was about 800 cm^{-1} was caused by Al-O or Si-O-Al [35].

4. UTILIZATION OF POFA AS GEOPOLYMER MATERIAL

For the recent years, the utilization of waste material in construction industry has been growth rapidly. Normally POFA was used as supplementary cementitious material in the production of concrete. From the previous researches it was found that the consumption of POFA in concrete improved the resistance against sulfate and chloride penetration [29,36]. Moreover the use of POFA also enhances the other properties of concrete such as compressive strength, tensile strength, modulus of elasticity and expansion [23,27,29,31,36,37]. In the same time, the water permeability, drying shrinkage and water-to-binder ratio (w/b) has been reduced [26,36, 38,39].

Tangchirapat *et al.* [27] studied on the use of POFA in the production of high strength concrete, where it was found that at 90 days the compressive strength of concrete containing 20% of ground palm ash was 70 MPa with drying shrinkage and water permeability lower than high strength concrete containing Type I Portland cement. Meanwhile, Megat Johari *et al.* [23], studied about the influence of POFA fineness in the production of high strength concrete. From the research it was concluded the compressive strength of concrete with ultrafine POFA was more than 95 MPa at 28 days. Moreover, the other mechanical properties such as porosity, water permeability, initial surface absorption, gas permeability and rapid chloride permeability were enhancing with the inclusion of ultrafine POFA.

Recently, research about incorporating POFA in concrete containing recycle aggregates also has been done. As a result the combination of ground POFA and recycled aggregate in concrete showed good result in water permeability depending on the level of cement replacement [39].

Besides that, the utilization of POFA in the production of geopolymer composite has been quite limited, where only research about geopolymer mortar and concrete has been done [9,12]. Mohd Azreen *et al.* [9] studied about geopolymer concrete utilizing blended ash of pulverized fly ash (PFA) and POFA. From the result it demonstrated that the compressive strength of concrete sample with only POFA was lower than sample with the mixture of POFA and PFA. Moreover when the ratio of PFA: POFA increased, the compressive strength and workability of also increased. The same situation also occurred with the increasing of molarity of NaOH and ratio of alkaline activator to solid. Besides that, the maximum compressive strength of 25 MPa was contributed by PFA: POFA ratio of 70:30.

In different investigation carried by Chubuppakarn *et al.* [12], the mechanical properties of geopolymer made from metakaolin and palm ash was investigated. Since palm ash was rich in silica but lack of alumina which is the two important components to produce geopolymer with good strength, the addition of metakaolin was sufficient due its property which is rich in alumina. The result from this study showed that the higher volume of metakaolin added to the geopolymer mixture produced higher compressive strength.

5. POTENTIAL OF BOILER ASH AS GEOPOLYMER MATERIAL

The other ash that produced from palm oil mill is boiler ash. Nowadays, the boiler ash only used as application on roads and ground in the plantations and mills [40]. The compositions of boiler ash were consisting of potassium, silicon, phosphorous which is suitable to use as fertilizer and also additive in concrete and cement [40]. However, so far no study has been done about utilization of boiler ash in production of geopolymer. As such, future work will be study about the utilization of boiler ash as geopolymer material. From the SEM analysis of boiler ash, it is shown that the microstructure of boiler ash was almost similar with POFA. Fig 6 showed the microstructure of boiler ash where it can be seen that it has angular and irregular shape. Thus, there is possibility to use boiler ash as geopolymer material.

6. CONCLUSION

As conclusion, boiler ash and palm ash have the potential to use ash geopolymer materials. Nevertheless, only POFA has been use ash as raw material for geopolymer but not for boiler ash. Since boiler ash also consist silicon, further study was required in order to investigate the probability to use boiler ash as raw material for geopolymer.

REFERENCES

[1] A.M. Mustafa Al Bakri, H. Kamarudin, M. Bnhussain, I. Khairul Nizar, A.R. Rafiza and Y. Zarina // *Rev. Adv. Mater. Sci.* **30** (2012) 90.

[2] D. Hardjito, S.E. Wallah, D.M.J. Sumajouw and B.V. Rangan // *ACI Mater. J.* **101** (2004) 468.

[3] M.M.A. Abdullah, H. Kamarudin, H. Mohammed, I. Khairul Nizar, A.R. Rafiza and Y. Zarina // *Adv. Mater. Res.* **328-330** (2011) 1476.

[4] A. Fernandez-Jimenez and A. Palomo // *Cem. Concr. Res*. **35** (2005) 1985.

[5] T.W. Cheng and J.P. Chiu // *Minerals Eng.* **16** (2003) 206.

[6] V.F.F. Barbosa, K.J.D. MacKenzie and C. Thaumaturgo // *J. Inorg. Mater.* **2(4)** (2000) 311.

[7] D.L.Y. Kong, J.G. Sanjayan and K. Sagoe-Crentsil // *Cem. Concr. Res*. **37** (2007) 1584.

[8] Y.M. Liew, H. Kamarudin, A.M. Mustafa Al Bakri, M. Luqman, I. Khairul Nizar, C.M. Ruzaidi and C.Y. Heah // *J. Constr. Build. Mater*. **30** (2012) 795.

[9] M.A. Mohd Azreen, H. Mohd Warid and B.M. Aamer Rafique // *Adv. Mater. Res.* **339** (2011) 453.

[10] J.C. Swanepoel and C.A. Strydom // *App. Geochem*. **17** (2002) 1144.

[11] J.G.S. van Jaarsveld, J.S.J. van Deventer and G.C. Lukey // *Chem. Eng. J.* **89(1-3)** (2002) 64.

[12] T. Chub-uppakarn, N. Thaenlek and R. Thaisiam, In: *Palm Ash – Based Geopolymer Mortar Incorporating Metakaolin* (Pure and Applied Chemistry International Conference, 2011), p. 347.

[13] J. Davidovits // *J. Mater. Edu.* **16** (1994) 100.

[14] P. Duxson, A. Fernandez-Jimenez, J.L. Provis, G.C. Lukey, A. Palomo and J.S.J. van Deventer // *J. Mater. Sci.* **42** (2007) 2918.

[15] K. Komnitsas, D. Zaharaki // *Mineral Eng*. **20** (2007) 1262.

[16] T.W. Cheng and J.P. Chiu // *Mineral Eng*. **16** (2003) 208.

[17] P.V. Krivenko, Ye.K. Pushkareva, M.V. Sukhanevich and S.G. Guziy // *Ceramic Engineering and Science Proceedings* **29(10)** (2008) 135.

[18] *Foreign Agricultural Service, Production, Supply and Distribution Online, United States Department of Agricultural (USDA)*. Available at: <http://www.fas.usda.gov/psdonline/psdHome.aspx>.

[19] V. Subramaniam, M.A. Ngan, C. Yuen May and N.M. Nik Sulaiman // *American J. Environ. Sci.* **4(4)** (2008) 314.

[20] W. Kroehong, T. Sinsiri and C. Jaturapitakkul // *Procedia Eng.* **14** (2011) 361.

[21] A.R. Mohamed, K.T. Lee, N.M. Noor and N.F. Zainudi // *Chem. Eng. Tech*. **28(8)** (2005) 939.

[22] W. Kroehong, T. Sinsiri, C. Jaturapitakkul and P. Chindaprasirt // *Constr. Build. Mater*. **25** (2011) 4096.

[23] M.A. Megat Johari, A.M. Zayed, N. Muhamad Bunnori and K. S. Ariffin // *Constr. Build. Mater.* **30** (2012) 284.

[24] I. Dahlan, A.R. Mohamed, A.H. Kamaruddin and K.T. Lee // *Chem. Eng. Tech.* **30(5)** (2007) 665.

[25] C. Chandara, M.A. Khairun Azizi, A. Zainal Arifin and S.H. Syed Fuad // *Constr. Build. Mater.* **27** (2012) 79.

[26] M.A. Nurdeen, M.J. Megat Azmi and S.H. Syed Fuad // *Int. J. Civil Environ. Eng.* **11(5)** (2011) 101.

[27] W. Tangchirapat, C. Jaturapitakkul and P. Chindaprasirt // *Constr. Build. Mater.* **23(7)** (2009) 2642.

[28] W. Tangchirapat, T. Saeting, C. Jaturapitakkul, K. Kiattikomol and A. Siripanichgorn // *Waste Management* **27** (2007) 82.

[29] P. Chindaprasirt, S. Rukzon and V. Sirivivatnanon // *Constr. Build. Mater.* **22** (2008) 934.

[30] A.S.M. Abdul Awal and M.W. Hussin // *Cem. Conc. Comp.* **19** (1997) 368.

[31] C. Jaturapitakkul, K. Kiattikimol, W. Tangchirapat and T. Saeting // *Constr. Build. Mater.* **21** (2007) 1400.

[32] C.Y. Yin, S.A.K. Sharifah Aishah, Y.P. Lim, S-A. Sharifah Nawirah and Z. Zurinawati // *Fuel Processing Tech*. **89** (2008) 696.

[33] D. Panias, I.P. Giannopoulou and T. Perraki // *Colloids and Surfaces A: Physicochem. Eng. Aspects* **301** (2007) 249.

[34] S. Andini, R. Cioffi, F. Colangelo, T. Grieco, F. Montagnaro and L. Santoro // *Waste Management* **28** (2008) 418.

[35] J. Bai, W. Li and B. Li // *Fuel* **87** (2008) 587.

[36] P. Chindaprasirt, S. Homwuttiwong and C. Jaturapitakkul // *Constr. Build. Mater.* **21** (2007) 1493.

[37] A.S.M. Abdul Awal and M. Warid Hussin // *Cem. Conc. Comp.* **19** (2007) 370.

[38] V. Sata, J. Tangpagasit, C. Jaturapitakkul and P. Chindaprasirt // *Cem. Conc. Comp.* **34** (2012) 99.

[39] W. Tangchirapat, S. Khamklai and C. Jaturapitakkul // *Mater. and Design* **41** (2012) 150.

[40] V. Subramaniam, M.A. Ngan, C.Y. May and N.S. Nik Meriam // *American J. Environ. Sci.* **4(4)** (2008) 315.