POZZOLANIC CHARACTERIZATION OF WASTE RICE HUSK ASH (RHA) FROM MUAR, MALAYSIA

J Hadipramana\textsuperscript{1,2,a}, F V Riza\textsuperscript{1,b}, I A Rahman\textsuperscript{1}, L Y Loon\textsuperscript{1}, S H Adnan\textsuperscript{1}, and A M A Zaidi\textsuperscript{3}

\textsuperscript{1}Faculty of Civil and Environmental Engineering Universiti Tun Hussein Onn Malaysia, 86400, Batu Pahat, Johor, Malaysia
\textsuperscript{2}Jamilus Research Centre, Faculty of Civil and Environmental Engineering Universiti Tun Hussein Onn Malaysia, 86400, Batu Pahat, Johor, Malaysia.
\textsuperscript{3}Faculty of Engineering Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi 5700, Kuala Lumpur Malaysia

E-Mail: \textsuperscript{a}josef@uthm.edu.my and \textsuperscript{b}fetravenny@gmail.com

Abstract. Investigation of Rice Husk Ash (RHA) thoroughly under controlled burning is regular issue to obtain result to produce the amorphous silica that has high pozzolanic reactivity characteristic. This paper offered an observation about characteristic of ground and un-ground of un-controlled burning temperature RHA that were taken from rice millings in Muar, Johor Malaysia. Such tests as X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Particle Size Analysis and Specific Area Surface, Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron microscope (SEM) were conducted in this investigation to carry out the characteristic of RHA samples. The results show that the RHA was consist approximately 89.90% of silica and the RHA possessed the amorphous particle were dominant than its crystalline part. This proves that the RHA has a big potential as a pozzolanic material considering the silica content and porous structure. In addition, particle size analysis decides whether the pozzolanic reactivity can be increased by grinding process.

Keywords: rice husk ash, RHA, Muar, pozzolan, amorphous, crystalline

1. Introduction

As demand of sustainable construction material with low cost and regarding to environmental issue, the innovation for new materials have been grown. On the other hand, the agricultural waste especially RHA has raised the environmentalist concern since the ash could generated health problem to the inhabitants nearby. Several rice producing countries produce 2.2 million tons rice in 2006 and projected to increase in the future [1]. For every ton paddy, rice mill will generate 78% rice, 20% rice husk and 2% lost [2]. Rice husk will be used for the fuel in the boiler to generate electricity for the mill and approximately 25% of the husk will be converted to RHA [3]. As a by-product obtained from the rice mill, RHA has very little or no commercial value and commonly will end up as a waste which generates disposal and health problems to the inhabitants.

Producing RHA under controlled burning temperature to obtain expected properties as for obtaining silica is very ideal, nonetheless that will increase production costs. Furthermore, RHA as a by-product from rice milling with uncontrolled burning temperature is an important source of silica. These RHA have the highest silica content from all of the plant residue and have been confirmed to have pozzolanic properties. Having pozzolanic properties means the RHA will create cementitious materials if its finely grind, then combined with calcium hydroxide [Ca (OH)\textsubscript{2}] at ordinary temperature with the presence of...
moisture [3-13]. The RHA is a big potential of renewable alternative source of sustainable cementitious materials as a consequence if the rice will continue to be consumed.

Beginning with Mehta [14] investigation at early 70’s, which stated that highly reactive ash can be obtained from controlled combustion, and the pozzolanicity of the RHA greatly depends on the burning temperature and its specific surface [10, 14-18], then most of the investigation worked on ground and controlled burning RHA. Also majority of researcher showed the trend to incorporate RHA as a supplementary cementitious material in concrete where Ordinary Portland Cement (OPC) as the primary binder [10, 13, 17, 19-31].

However, economical aspect for the bulk production of rice husk ash could not be considered if controlled combustion is used. Therefore, this research tried to investigate the possibility of waste RHA that undergone uncontrolled burning temperature as a pozzolan by using X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), particle size analyzer, Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX). The rest of this paper is organized as follows: section 2 will explain the XRF test while section 3 describe XRD test. Section 4 analyzed uncontrolled RHA by using particle size analyzer where section 5 elaborated the SEM and EDX result. Finally the conclusion of this research will be presented in section 6.

2. Methodology and Experiment

The RHA sample was obtained from the rice milling in Muar Johor Malaysia which was under uncontrolled burning with temperature rate about 700-800ºC (see Figure 1) and is in greyish black color.

![Figure 1. Uncontrolled burning temperature RHA from rice milling Muar, Johor Malaysia](image)

XRF analysis was performed in this research by using Bruker AXS S4 Spectra Plus. XRF was used to determine the composition of RHA chemically. Prior to the test, RHA was ground until 65 μm and then 8 grams of ground rice husk ash were mixed with 2 grams wax before compressed in the mould to prepare the sample into a pellet shape. This pellet then was analyzed in the XRF machine.

XRF analysis was performed in this research by using Bruker AXS S4 Spectra Plus. XRF was used to determine the composition of RHA chemically. Prior to the test, RHA was ground until 65 μm and then 8 grams of ground rice husk ash were mixed with 2 grams wax before compressed in the mould to prepare the sample into a pellet shape. This pellet then was analyzed in the XRF machine.

The phase of amorphous properties of the RHA then were determined by using XRD machine Bruker AXS D8 Advance equipment. Small amount of RHA was placed in the container and the analysis was conducted automatically. This analysis to find out the phase composition of RHA sample.

Both original and grounded RHA which passing 300 μm was analyzed by using Particle Size Analyzer CILAS 582 to determine the particle size distribution and specific surface area.

FTIR identifies chemical bonds in a molecule by producing an infrared absorption spectrum. The RHA spectrums were identified using Perkin Elmer Spectrum 100 FT-IR Spectrometer with range spectrum (wavelength): 4000-600/cm. Scan rate: 16, 32. Universal ATR sampling accessory (not using KBr) was employed to prepare the sample.
3. Result and Discussion

3.1. X-Ray Fluorescence Analysis

XRF is an analytical technique to determined various chemical oxides composition of RHA where the material re-emitted the x-ray in lower energy after itself been bombarded with higher energy X-ray. Table 1 presents the chemical composition of the RHA of Muar.

| Rice Husk Ash | Formula | Concentration |
|---------------|---------|---------------|
| CO₂          | 0.10%   |
| SiO₂         | 89.90%  |
| K₂O          | 4.50%   |
| P₂O₅         | 2.45%   |
| CaO          | 1.01%   |
| MgO          | 0.79%   |
| Fe₂O₃        | 0.47%   |
| Al₂O₃        | 0.46%   |
| MnO          | 0.14%   |
| S            | < LLD   |

According to ASTM C 618, pozzolan is siliceous and aluminous material which in them possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically reacts with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties [14, 15]. Hence the chemical composition of this RHA from SiO₂ + Al₂O₃ + Fe₂O₃ is more than 70%, MgO less than 5%, Na₂O less than 1.5% and SO₃ less than 5%, this RHA can be categorized as pozzolanic material based on the XRF result and classification of ASTM C 618-92a [32].

3.2. X-Ray Diffraction

Previous research mostly worked on amorphous RHA since the ash in amorphous form has higher pozzolanic reactivity. But to obtain RHA in amorphous form, the rice husk need to thermally treated in controlled combustion in temperature ranging from 500ºC to 700º for the best pozzolanic reactivity [16, 18, 33], which consequently will increase the production cost.

In this research we made an attempt to use the original RHA from rice milling that has been through combustion in the boiler as a fuel to generate electricity in the mill without thermally controlled temperature. Figure 2 shows the diffraction graph.

From the diffraction graph in Figure 2, crystalline phase was detected by the sharp peaks that occurred in the 22º and 36º of 2 theta scale, another low peaks also detected at 28.5º, 31.5º, 42.5º, 44.5º, 47 º, 48.5º, 57º of 2 theta scale although amorphous phase also detected in the range 0 to 20º of 2 theta scale indicated by the halo occurred. Mostly found is cristobalite compound which is crystalline silica. By employing Diffract TOPAZ software, it was found out that the degree of RHA crystallinity reach 40%.
Comparing with XRD graph of rice husk ash from rice mill where rice husk was used as the fuel for the parboiling rice [33] and XRD pattern of rice husk ash that burn at temperature 1100ºC [18], apparently the same pattern was shown where it is obvious the peaks of cristobalite and quartz that also verifies the presence of crystalline silica as well as XRD graph from Ramezanianpour et al [16]. From all the graphs, the highest peaks occurred at 22º of 2 theta scale. However, further investigation of the XRD result by X’pert Highscore Plus software showed that the waste RHA possessed amorphous particle higher than its crystalline part, as shown in Figure 3. This means that the rice husks were thermally treated in temperature higher than 800ºC

The waste RHA contain amorphous particle up to 73.3% and crystalline 26.7% however the XRD graphs classified the waste RHA as crystalline. This result support the hypothesis that even waste RHA that is burnt in uncontrolled temperature still possessed amorphousness and hence the pozzolanic reactivity.
3.3. Particle Size and Specific Surface Area

The particle distribution for diameter at 10%, 50%, and 90% of cumulative values was tabulated in the Table 2 as well as its specific surface.

Table 2. Particle size distribution and specific gravity of RHA and OPC.

|                          | Original RHA | Passed 300 µm sieve RHA | Ground RHA | Cement OPC |
|--------------------------|--------------|-------------------------|------------|------------|
| Specific surface (cm²/g) | 1753.8       | 4538.88                 | 14,342.53  | 19,027.98  |
| Diameter at 10% (µm)     | 26.77        | 26.34                   | 2.2        | 1.89       |
| Diameter at 50% (µm)     | 60.54        | 59.52                   | 13.43      | 14.44      |
| Diameter at 90% (µm)     | 102.65       | 97.81                   | 35.65      | 36.68      |

From the table, it is obviously shown that sieving the rice husk ash passing 300 µm could be increased its specific surface almost 3 fold from the original size, and ground it by using jar mill resembled OPC in the view of diameter at 10%, 50% and 90% of cumulative value. RHA color is dark black signified the unburnt carbon content is high, conveying that the physical properties of rice husk ash strongly affected by the burning mechanism in the rice mill. Particle size distribution graphs showed average diameter of original rice husk ash about 60.54 µm, slightly decreased by sieving, but ground process could decreased the diameter tremendously almost equivalent to that of OPC cement around 35.65 µm.

3.4. Fourier Transform Infrared Spectroscopy (FTIR)

Figure 4 shows the result graph of spectrum graph of RHA sample. From this results, RHA Muar can be identified obviously the three distinguishable peaks:

1) The bands 787.76 cm⁻¹ belongs to O-Si-O symmetrical stretching vibrations which conformed with findings of Javed [34] between 806 cm⁻¹ and 797 cm⁻¹, MusićI [35] at 800 cm⁻¹ and Ferraro [27] at 773 cm⁻¹ and all listed in the tables of peak wave number of silica group around 805 cm⁻¹.

2) Bands at 1054.19 cm⁻¹ also showed the presence of O-Si-O vibration attributable to asymmetrical stretching bands vibration. This also conformed with Javed [34] at 1097 cm⁻¹ to 1091 cm⁻¹ and Ferraro [27] at 1080 cm⁻¹. Entire bands still in the range of peak wave number tables at 1200 cm⁻¹ to 1000 cm⁻¹.
3) Free water band observed at 3270.76 cm\(^{-1}\) due to the stretching vibration of H\(_2\)O molecules [35]. This also agree with Javed [34] [27] at 3636 cm\(^{-1}\) to 3427 cm\(^{-1}\) and Ferraro [27] at 3436 cm\(^{-1}\) which in the range of very broad hydroxyl groups between 3500 cm\(^{-1}\) to 2500 cm\(^{-1}\) at the peak wave number tables.

The FTIR result showed that low vibration indicates the crystal formation, what usually detected as crystalline silica as stated by Javed [34].

3.5. Scanning Electron Microscopy (SEM)
To investigate the microstructure of rice husk ash, scanning electron microscope was utilized and the test conducted with analytical SEM JEOL model no JSM – 6380LA. Considering RHA as a powdery material, the sample need to be coated by platinum coating by using JEOL JFC – 1600 Auto Fine Coater so that the powder dust would not contaminate the SEM machine and not resulting blemish and tarnish photo. Energy dispersive X-ray spectroscopy (EDX) test also conducted to make quantitative chemical analysis of RHA at particular spot. Fig.4 shows the comparison of original form (a,b,c) and ground RHA (d,e,f) microstructure with 30X, 250X and 1500X magnification respectively.

![SEM images](image)

**Figure 5.** Comparison of original RHA (a,b,c) and sieved RHA (d) microstructure.

Figure 5(a) indicated the outer epidermis of RHA which has well-arranged cuticles of corrugated and spiky, horn-like structure. Figure 5(d) shows that sieving through 300 µm will reduce RHA size considerably. Figure 5(b) shows the inner and outer epidermis of RHA in higher magnification which has porous structures. While Figure 5(c) indicates the rice husk was melting during combustion.
Park, et. al. [36] has confirmed that the highest concentration of silica in the rice husk is in the outer surface of the husk in the amorphous form. After incineration in the rice mill, the amorphous silica starts to melt and change gradually to crystalline phase.

By assigned EDX program, the chemical composition in particular point can be found out. Figure 6 shows the points (point 1, 2, 3 and 4) which examined with EDX and Figure 6 informed the chemical composition that tabulated in Table 3.

![Figure 6. Location of 4 points observed with EDX.](image)

Points 001 and 004 (see Figure 6) indicate the unburnt carbon of rice husk ash since its exhibit darker color. Point 002 showed the large particle of RHA that apparently most of it carbon was burnt completely indicated by its lighter color as well as point 003 in the smaller particle. Figure 7 showed the compound composition for each respective point.

![Figure 7. Microanalysis of RHA at 4 points: a) point 001 b) point 002 c) point 003 d) point 004](image)
EDX graphs and table confirmed the XRF result that the RHA content high silica oxide. Especially in point 002 where carbon completely burnt, SiO$_2$ content could reach 96%.

### Table 3. Chemical composition of RHA by EDX.

| Compound | Point 001 | Point 002 | Point 003 | Point 004 |
|----------|-----------|-----------|-----------|-----------|
| SiO$_2$  | 89.7      | 96.03     | 89.95     | 87.77     |
| P$_2$O$_5$ | 2.36      | 0.39      | -         | 4.82      |
| K$_2$O   | 6.51      | 3.13      | 4.10      | 4.32      |
| CaO      | 0.18      | -         | 1.92      | -         |
| MnO      | 0.34      | -         | 2.51      | 0.11      |
| MgO      | 0.91      | -         | 1.52      | 2.31      |
| Al$_2$O$_3$ | -        | -         | -         | 0.67      |
| FeO      | -         | 0.45      | -         | -         |

Table 3 shows that the part of RHA which completely burnt (point 002) has highest silica content but lack of another compound such as CaO, MnO, MgO and Al$_2$O$_3$. This could be attributed to the percentage of carbon content burn.

### 3.6. Pozzolanic Reactivity

To investigate the pozzolanic reactivity, Luxan method [37] where conductivity of 200 ml saturated Ca(OH)$_2$ solution at 40°C was recorded and 5 gr of RHA Muar was added and the conductivity was measured again. The difference between initial and last conductivity show the pozzolanic reactivity of RHA Muar.

Also Strength Activity Index (ASTM C 311-04: Standard Test methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland Cement Concrete) were used.

The result shows that strength activity index of waste RHA was 44.1 and its pozzolanic reactivity by Luxan method was 0.42 mS/cm (according to Luxan pozzolanic classification, above 0.4 mS/cm can be classified as pozzolan). These results lower than that of amorphous RHA from other researcher [33] because it was in crystalline phase although still possessed considerable amount of amorphousness.

### 4. Conclusions

Despite general beliefs that the best form of RHA that can be used in concrete or masonry work must be in amorphous form which thermally treated between 500°C to 700°C, this experiment showed the big potential of waste RHA generated by the boiler in the rice mill especially from economic point of view. The waste RHA commonly burnt at high uncontrolled temperature that will change rice husk into crystalline phase.

XRF test confirmed the high silica content of the original rice husk ash where XRD test revealed the phase of the ash has gradually changed from amorphous to crystalline phase almost 40%. FTIR spectrum revealed that RHA Muar was formed from the crystalline silica. Microscopy examination utilizing SEM and EDX confirmed the multiple phase of original RHA from the mill, some part completely burn and another part set aside unburnt carbon content.

Although the result of pozzolanic reactivity lower than that of amorphous silica, with additional sieving or grinding process, diameter of rice husk ash particle could be decreased resembled to that of OPC which in turn will increase the pozzolanic reactivity of the ash.
Acknowledgement
The Author acknowledge to Office for Research, Innovation, Commercialization, and Consultancy Management (ORICC) Universiti Tun Hussein Onn Malaysia (UTHM) that supported and sponsored to project through Short Grant with Vot no 1072.

References
[1] Workman D cited 2016 Top Rice Producing Countries: available from http://www.fao.org/docrep/003/x6905e/x6905e04.htm.
[2] Ash R H cited 2010 Rice Husk Ash: Available from: http://www.ricehuskash.com/.
[3] Cook D J, Pama R P and Paul B K 1977 Building and Environment. 12 281-288.
[4] James J and Rao M S 1986 Cement and Concrete Research. 16 67-73.
[5] Yalçın N and Sevinç V 2001 Ceramics International. 27(2) 219-224.
[6] Hani A S, Ismail A R, Lee Y L and Hamidah M S 2009 MASAUM Journal of Basic and Applied Sciences. 1(3) 493-496.
[7] Hassan M A and Mustapha A H M 2007 Leonardo Electronic Journal of Practises and Technologies. 11 47-58.
[8] Jha J N and Gill K S 2006 Journal of the Institution of Engineers. 87 33-39.
[9] Laksmmono J A 2002 Jakarta: Lembaga Ilmu Pengetahuan Indonesia (LIPI).
[10] Al-Khalaf M N and Yousif H A 1984 International Journal of Cement Composites and Lightweight Concrete. 6(4) 241-248.
[11] Sensale G R D 2006 Cement and Concretes Composites. 28(2) 158-160.
[12] Jauberthie R, Rendell F, Tamba S and Cisse I 2000 Construction and Building Materials 14(8) 419-423.
[13] Ismail M S and Waliuddin AM 1996 Construction and Building Materials. 10(7) 521-526.
[14] Mehta P K 1973 U.S. Patent No. 4,105,459. Washington, DC
[15] Odler I 2000 E & FN Spon, Taylor and Francis Group. London
[16] Ramezanianpour A A, Khani M M and Ahmadiben G 2009 International Journal of Civil Engineering. 7(2) 83-91.
[17] Chareerat T, Pinraksa K, Chindaprasirt P, Maegawa A and Hatanaka S 2008 in Technology and Innovation for Sustainable Development Conference. Thailand.
[18] Nair, D G, Fraaij A Klaassen A A and Kentgens A P 2008 Cement and Concrete Research. 38 861-869.
[19] Bui D D, Hu J, and Stroeven P 2005 Cement and Concrete Composites. 27(3) 357-366.
[20] Chao-Lung H, Anh-Tuan B L and Chun-Tsun C 2011 Construction and Building Materials. 25(9) 3768-3772.
[21] Chatveera B and Lertwattanaruk P 2009 Journal of Environmental Management. 90(3) 1435-1441.
[22] Chatveera B and Lertwattanaruk P 2011 Journal of Environmental Management. 92(1) 59-66.
[23] Chindaprasirt P, Jaturapitakkul C and Rattanasak U 2009 Fuel. 88(1) 158-162.
[24] Cisse I K and Laquerbe M 2000 Cement and Concrete Research. 30(1) 13-18.
[25] Cordeiro G, Toledo F R and de Moraes Rego Fairbairn E 2009 Materials and Structures. 42(7) 983-992.
[26] Ferraro R M 2009 University of Miami: United States - Florida. 142.
[27] Ferraro R M, Nanni A, Vempati R K and Matta F 2010 Journal of Materials in Civil Engineering. 22(10) 1078-1083.
[28] Givi A N, Rashid S A, Aziz F N A and Salleh M A M 2010 Journal of American Science. 6(3) 157-165.
[29] Madandoust R, Ranjbar M M, Moghadam H A and Mousavi S Y 2011 Biosystems Engineering. 110(2) 144-152.
[30] Mehta P K 1992 International Symposium on Advances in Concrete Technology, Athens, Greece.
[31] Qing-ge F, Qing-yu L, Qi-jun Y, San-ying Z, Lu-feng Y and Sugita S 2004 Journal of Wuhan University of Technology - Materials Science Edition. 19(3) 74-77.
[32] Awal A S and Hussin M W 1997 *Fifth International Conference on Structural Failure, Durability and Retrofitting*, Singapore.

[33] Nair D G, Jagadish K S and Fraaij A 2006 *Cement and Concrete Research*. **36** 1062-1071.

[34] Javed S H, Tajwar S, Shafaq M, Zafar M and Kazmi M 2009 *Journal of Pakistan Institute of Chemical Engineers*. **37** 97-101.

[35] Musić I S, Filipović-Vinceković I N and Sekovanić I L 2011 *Brazilian Journal of Chemical Engineering*. **28**(1) 89-94.

[36] Park B D, Wi S G, Lee K H, Singh A P, Yoon T H and Kim Y S 2003 *Biomass and Bioenergy*. **25**(3) 319-327

[37] Luxán M P, Madruga F and Saavedra J 1989 *Cement and Concrete Research*. **19**(1) 63-68.