Investigation of silica crystallization kinetics in rice husk ash for sustainable construction materials

Muhammad Aun Abbas[1], *Kwan Wai* Hoe[1*], and *Muhammad Hasnolhadi* Bin Samsudin[1]

[1]Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman, Kampar 31900, Perak, Malaysia

Abstract. Concrete is one of the most widely used materials in the world, and its utilization is rising drastically with the increasing population. Around 5-8% of global carbon emissions are caused by cement production. On the other hand, approximately 160 million tons of rice husk, considered agro-waste, turn into ash annually. Rice husk ash (RHA) is particularly attractive due to its high silica content and great potential to be used as a cementitious material. However, impurities such as alkali metal oxides and uncontrolled combustion reduce the quality of silica and promote its crystallization. Numerous studies have focused on obtaining active silica through acid leaching to remove impurities, but the study on the reaction kinetics of functionalized rice husk ash is very limited. In this research, 0.1M hydrochloric acid (HCl) was used to leach rice husk at temperatures of 50°C, 60°C, and 70°C for 1.5 hours. The rice husk was then burned at 800°C for 2 hours. Subsequently, the ash was examined using various analytical and computational techniques to develop an in-depth understanding of the burning process, aimed at producing functionalized amorphous silica for sustainable construction. It was observed that 99.39% silica with 95.04% amorphous content was formed by treating rice husk with 0.1M HCl at 70°C for 1.5 hours, followed by combustion at 800°C for 2 hours. Furthermore, reaction kinetics parameters were identified using the Coats-Redfern kinetic model for the two different reaction zones of the burning process.

1 Introduction

Nowadays, several agricultural wastes are in under consideration to be used as cement replacement materials because of their good pozzolanic behavior caused by the amorphous silica content present in it. Among these agricultural wastes, [1] mentioned that the utilization of rice husk ash can enhance the engineering characteristics of mortar, mitigate the adverse ecological impacts, and reduce cost. As stated by [2], the rice husk ash produces more C-S-H gel by reacting with hydration products in cement paste, hence increasing the binding properties. Generally, rice husk is consist of 15%-20% silica, 25%-30% lignin, and around 50% of cellulose. Furthermore, after burning, amorphous silica is yielded however, it can be transform into crystalline form due to uncontrolled burning conditions [3]. Subsequently, the

*Corresponding author: kwanwh@utar.edu.my

silica present in rice husk ash, after losing amorphous state, has low reactivity as a pozzolanic material. Therefore it is essential to burn rice husk in such conditions so that silica do not change their state from amorphous to crystalline form. [4], reported that the silica present in rice husk ash changes from amorphous to crystalline state due to the presence of alkali metals like potassium because they melt on outer surface of rice husk hence promotes the silica crystallization. In the burning process, the metallic impurities starts the eutectic reaction by reacting silica. As a result of this reaction, the crystallization temperature of silica decreases to 700^0C [5]. [6] Highlighted that at higher temperatures, due to impurities, mainly, potassium, the surface of rice husk starts melting and the carbon from organic part of husk dissolves in it. Subsequently, after the solidification, the crystalline silica is formed. Furthermore, the eutectic process during combustion of rice husk hinders the oxidation process due to this number of unburnt carbon increases in rice husk ash [7]. However, to prevent the crystallization of silica, leaching treatment of rice husk before the combustion process plays an important role in the production of rice husk ash containing highly amorphous silica.

Generally, the chemical properties of rice husk depends on geological features while, physical characteristics varies with different burning conditions and chemical treatment. Furthermore, the color of rice husk ash varies between black, grey, and white however, white ash is considered as more active silica. [8] reported that rice husk ash is lightweight, porous and fine material while, its density is around 180-200 Kg/m^3. Moreover, these physical features of rice husk ash can be enhance by enhancing the chemical treatment and combustion process of rice husk. Incorporating rice husk ash in concrete as cement alternative material not only lessens the porosity but provide immune to chemical reaction. [9] Discussed that, addition of rice husk ash in cement matrix initiates the internal curing consequently, more calcium silicate hydrates (C-S-H) compound produces, which increases the strength.

Rice husk ash, due to its high pozzolanic reactivity, can efficiently replace the cement. This would not only reduces the problem of waste disposal of agricultural waste but also promotes the sustainability in construction industry. Furthermore, due to high potential of rice husk ash of being use as a good pozzolanic material, researchers have studied different aspects of improving its productivity by performing acid leaching treatment to remove alkali metals, controlled heating conditions, and grinding conditions. However, the research on the crystallization process of silica during combustion is very limited, this is also second by other researcher as [10] mentioned that the fundamentals of chemical kinetics of rice husk ash should be studied to synthesize highly amorphous silica. The objective of this research is to study the chemical kinetics of functionalized amorphous rice husk ash produced via combustion process. This research will not only improve the process of producing pure amorphous rice husk ash but this will also contribute to fulfill the Sustainable Development Goals (SDGs).

2 Methods

For the experimental part, rice husk was brought from rice producing company located in Perak, Malaysia. The rice husk sample was rinsed thoroughly to remove dirt and dried in an oven at 100°C for 24 hours. After drying, the rice husk was chemically treated with 0.1M HCl solution under different leaching temperature for 1.5 hours as mentioned in Table 1. Moreover, before acid leaching treatment, the morphology and chemical composition of the rice husk was analyzed by energy dispersive x-ray (EDX) and scanning electron microscopy (SEM).

After the chemical treatment of rice husk, all samples were again washed and dried before combustion process. The rice husk was burnt at temperature of 800^0C for 2 hours as mentioned in Figure 1. After producing rice husk ash, the sample was studied using different

 https://doi.org/10.1051/e3sconf/202560304016

characterization techniques, including x-ray fluorescence (XRF), x-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA) to determine oxide compositions, degree of crystallinity, surface morphology, and thermal behavior, respectively. The schematic diagram of the experimental process is depicted in Figure 1.

Table 1. Chemical treatment parameters.

Sample	Leaching Conditions		
	Acid Concentration	**Leaching Temperature**	**Leaching time**
A8	0.1M HCl	50^0C	1.5 hrs
B8		60^0C	
C8		70^0C	

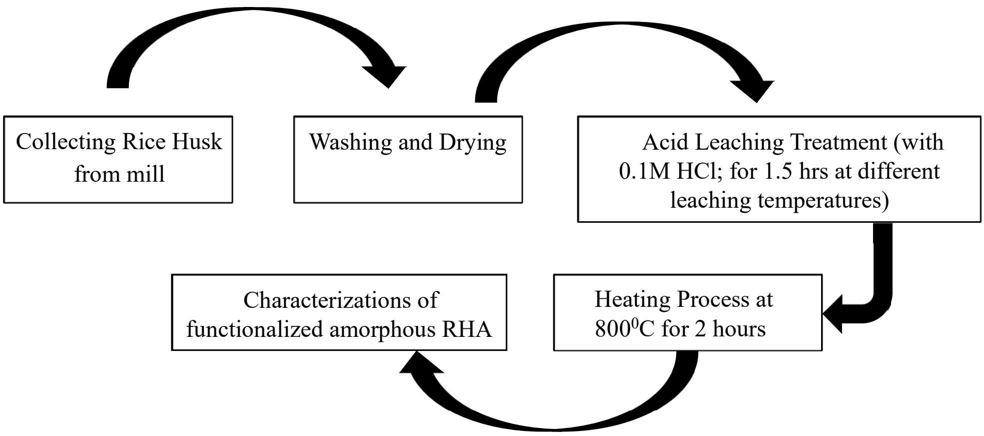

Fig. 1. Schematic diagram for research methodology.

3 Results and discussions

3.1 X-ray Fluorescence

The oxide compositions of the rice husk samples were recorded by using x-ray fluorescence spectrometer as mentioned in Table 2. Overall, it was found that there is no significant difference in the amount of silicon dioxide (SiO_2) by treating rice husk with different leaching temperatures. However, it is evident that metallic impurities can be reduced or even completely removed by increasing leaching temperature. Moreover, sample C8 has 99.39%SiO_2, which is the maximum from the rest of the samples and a slightly better quantity as reported by [11]. Furthermore, C8 does not contain any metallic impurities like other samples.

Table 2. Oxide compositions of rice husk ash samples.

Component	**Mass %**		
	A8	**B8**	**C8**
Al_2O_3	0.13	0.17	0.14
SiO_2	99.08	98.76	99.39
P_2O_5	0.25	0.35	0.21
SO_3	0.07	0.18	0.03
CaO	0.2	0.36	0.1
Fe_2O_3	0.11	0.08	0.11
K_2O	0.13	0.07	-

3.2 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX)

The surface morphology of as received rice husk and rice husk ash were witnessed by scanning electron microscopy (SEM) while, the chemical composition of rice husk was observed by electron dispersive x-ray (EDX). It is evident from the Figure 2 that the surface of rice husk (RH) has several spiked mounds which are arranged in as a parallel line. Furthermore, in the Figure 2 the image of rice husk cross-section represented by X-RH, showed a porous structure of rice husk from inside evident by several openings and because of this rice husk has the low bulk density and lightweight in nature. In addition to this, it was examined in electron dispersive x-ray (EDX) that the most of the silica content were present on the top of the outer surface which is also called epidermis however, the inner part of rice husk have more impurities as shown in Table 3. Furthermore, Figure 3 shows the image of rice husk ash sample C8, it was observed that the rice husk ash become more porous and surface area of rice husk ash is increased due to the leaching treatment. These pores substantially boost the reactivity of ash [8].

Table 3. Elemental composition of RH and X-RH by EDX.

Sample	Elements					
	C	O	Si	K	Mg	Ca
RH	52.34	40.45	7.08	0	0.07	0.05
X-RH	52.77	42.74	4.37	0.09	0	0

3.3 X-ray Diffraction (XRD) analysis

The rice husk ash samples were examined by x-ray diffraction test as depicted in Figure 4. It was monitored that the crystallinity of rice husk ash reduces after leaching treatment and interestingly, leaching treatment with higher leaching temperature has the highest quantity of 95.04% amorphous structure. This reduction in crystallinity is because of the reduction of metallic impurities, like potassium oxide, from the ash [12].

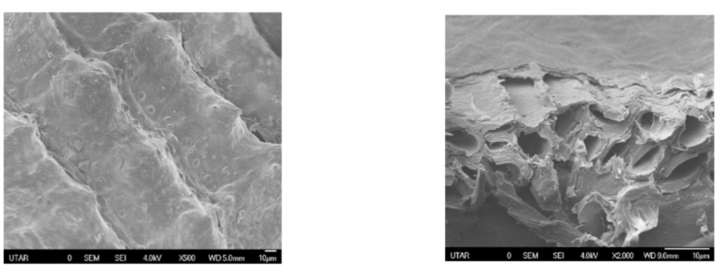

Fig. 2. SEM images of RH (left) and X-RH (right), respectively.

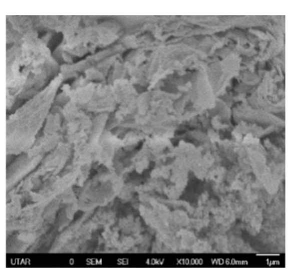

Fig. 3. SEM image of C8.

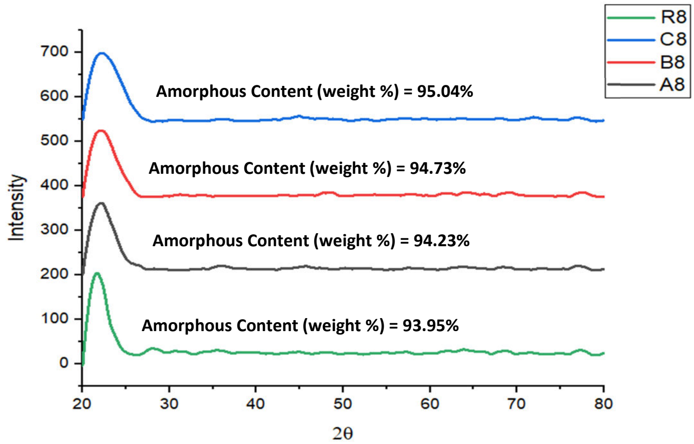

Fig. 4. XRD graphs of rice husk ash samples.

3.4 Thermogravimetric Analysis (TGA)

Figure 5 shows the thermal behavior of the sample C8, observed by thermogravimetric analysis. Two major losses happened while increasing the temperature, showing two major reaction zones of RH burning. Initially, between the temperatures 25.53^{0}C – 218.84^{0}C about 5.8% of the mass was reduced which is attributed to the loss of moisture content from the material. However, a significant mass reduction was observed between the temperatures of 219.37^{0}C – 587.50^{0}C and this loss is due to the burning out of all organic compounds from rice husk. Furthermore, after a certain temperature, the reduction of masses becomes stable which shows that the ash has been formed. In addition to this, the modified form of the Coats and Redfern model was used to identify the reaction kinetics parameters as mentioned in Equation (1). [13]–[14].

$$\ln[-\ln(1-x)] = ln\frac{\mathrm{ART}^2}{\beta E_a} - \frac{E_a}{RT} \quad (1)$$

$$x = \frac{w_i - w_t}{w_i - w_f} \quad (2)$$

Where, in Equation (2), w_i is the initial weight, w_f is the final weight and w_t is the sample's weight at a specific temperature. Furthermore, in Equation (1), β is the heating rate (10^{0}C/min), T is the temperature in kelvin, R is the general gas constant (8.3143 J/mol. K), Ea is the activation energy and A is the pre-exponential factor. Moreover, the plot between ln[-ln(1-x)] and 1000/T is presented in Figure 6 and the activation energy and pre-exponential factor was calculated from the linear equation obtained by the best fitted value of graph. Stage 1 of the reaction has a moderate fit with an R^2 value of 0.6094, indicating that other factors, such as the initial heating rate, should be explored. In contrast, the R^2 value for Stage 2 is 0.9139, indicating a good fit that allows for reliable predictions. The calculated values of Ea and A are mentioned in Table 4.

Table 4. Activation energy and pre-exponential factor values in different stages

Stages	Temperature(K)	E_a (J/mol)	A (M/min)
Stage 1 (Dehydration)	491.84	13785.9	0.256021
Stage 2 (Decomposition)	860.5	37027.7	42.55525

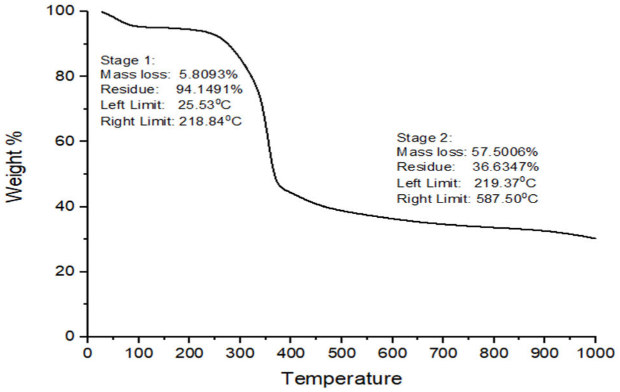

Fig. 5. TGA of rice husk ash sample (C8).

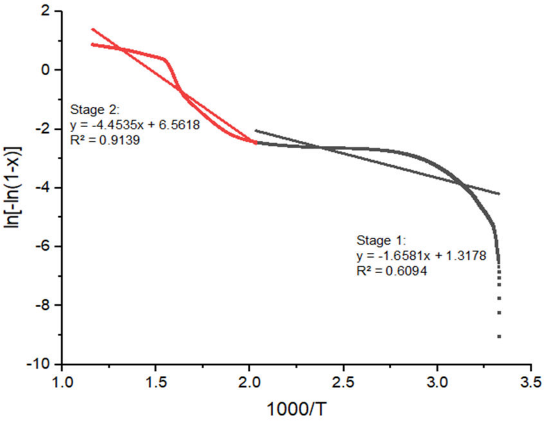

Fig. 6. Plot of ln[-ln(1-x)] vs 1000/T for to stage process of rice husk ash burning.

4 Conclusion

Rice husk ash is a promising material to be used as supplementary cementitious materials in order to promote sustainability in construction industry. This study found that the leaching treatment of rice husk ash with 0.1M HCl for 1.5 hours while having the leaching temperature of 70^{0}C is enough to reduce all the metallic impurities from rice husk ash. Furthermore, the burning of leached rice husk at the temperature of 800^{0}C for 2 hours can have the highest amount of amorphous ash with 99.39% of silica having large surface area. Moreover, this research also provided the fundamental insights on the kinetics of burning process of rice husk which would be beneficial for the large-scale production process.

This research is supported by the Ministry of Higher Education (MoHE) through the Fundamental Research Grant Scheme (FRGS/1/2023/TK01/UTAR/02/2) and by Universiti Tunku Abdul Rahman via research grant (Project No. IPSR/RMC/UTARRF/2021-C2/K05).

References

1. N. Van Tuan, G. Ye, K. Van Breugel, A. L. A. Fraaij, D. D. Bui, "The study of using rice husk ash to produce ultra-high performance concrete," *Constr. Build. Mater.* **25**, 2030–2035 (2011). https://doi.org/10.1016/j.conbuildmat.2010.11.046

2. E. Mohseni, M. Khotbehsara, F. Naseri, M. Monazami, P. Sarker, “Polypropylene fiber reinforced cement mortars containing rice husk ash and nano-alumina,” *Constr. Build. Mater.* **111**, 429–439 (2016). https://doi.org/10.1016/j.conbuildmat.2016.02.124
3. S. Asavapisit, N. Ruengrit, “The role of RHA-blended cement in stabilizing metal-containing wastes,” *Cem. Concr. Compos.* **27**, 7–8, 782–787 (2005). https://doi.org/10.1016/j.cemconcomp.2005.03.003
4. G. C. Cordeiro, R. D. Toledo Filho, E. de Moraes Rego Fairbairn, “Use of ultrafine rice husk ash with high-carbon content as pozzolan in high-performance concrete,” *Mater. Struct.* **42**, 983–992 (2009). https://doi.org/10.1617/s11527-008-9437-z
5. S. S. Darewalja, G. Sharma, S. Thakur, K. Singh, “Agricultural wastes as a resource of raw materials for developing low-dielectric glass-ceramics,” *Sci. Rep.* **6**, 24617 (2016). https://doi.org/10.1038/srep24617
6. R. V. Krishnarao, and T. K. J. Subrahmanyam, “Studies on the formation of black particles in rice husk silica ash,” *J. Eur. Ceram. Soc.* **20**, 7–8, 1229–1235 (2000). https://doi.org/10.1016/s0955-2219(00)00170-2
7. P. Chen, H. Bie, R. Bie, “Leaching characteristics and kinetics of the metal impurities present in rice husk during pretreatment for the production of rice husk particles,” *Korean J. Chem. Eng.* **35**, 191–198 (2018). https://doi.org/10.1007/s11814-018-0103-2
8. Y. Zou, T. Yang, “Rice Husk, Rice Husk Ash and Their Applications,” Elsevier Inc. (2019). https://doi.org/10.1016/B978-0-12-812238-2.00009-9
9. N. Bheel et al., “Experimental study on recycled concrete aggregates with rice husk ash as partial replacement,” *Civ. Eng. J.* **4**, 2035–2314 (2018). https://doi.org/10.28991/cej-03091160
10. B. A. Tayeh, R. Alyousef, H. Alabduljabbar, A. Alaskar, “Recycling of rice husk waste for a sustainable concrete: A critical review,” *J. Clean. Prod.* **312**, 127734 (2021). https://doi.org/10.1016/j.jclepro.2021.127734
11. Y. S. Wong, W. H. Kwan, M. Lim, “Enhancing pozzolanic properties of rice husk ash using acid leaching treatment,” *AIP Conf. Proc.* **1865**, 020026 (2017). https://doi.org/10.1063/1.5012652
12. Q. Feng, H. Yamamichi, M. Shoya, S. Sugita, “Study on the pozzolanic properties of rice husk ash by hydrochloric acid pretreatment,” *Cem. Concr. Res.* **34**, 521–526 (2004). https://doi.org/10.1016/j.cemconres.2003.09.005
13. M. Ajirad, A. Hassan, M. N. M. Hafiz, Z. Zakaria, “Effect of 3-methacryloxypropyl trimethoxysilane, hydroxypropyl cellulose nanowhiskers on properties of montmorillonite/poly(lactic acid) nanocomposites,” *Int. J. Biol. Macromol.* **98**, 998–1010 (2016). https://doi.org/10.1016/j.ijbiomac.2015.11.028
14. S. Ramukutty, E. Ramachandran, "Reaction rate models for the thermal decomposition of ibuprofen crystals," J. Cryst. Process Technol. 2014, 71–78 (2014). http://www.scirp.org/journal/PaperInformation.aspx?PaperID=44499