

# THE TREATMENT PROCESS OF BIOMASS ASH TO UTILIZED IN CRYSTAL GLASS MATERIAL

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*Received: July 31, 2024; Revised: December 09, 2024; Accepted: December 17, 2024*

## Abstract

This work aimed to synthesize the crystals of glass by using biomass ash as its silica source. Firstly, biomass ash was synthesized by different extraction methods with thermal treatment compared with chemical treatment to remove inorganic impurities, followed by heating at various temperatures. Secondly, silica, which was heated at the first step, was used as the raw material for crystal glass. The crystal glass was prepared by conventional melting at 1400°C. The chemical composition, phase formation, and microstructure of biomass ash were investigated and reported. Moreover, the physical properties and microhardness value of glass preparation were discussed. The highest SiO<sub>2</sub> content of 97.50 was obtained with the chemical treatment by HCl 3M before heating at 1100°C. The XRD pattern of the as-received material showed the presence of amorphous-phase silica. The cristobalite phase was achieved when the biomass ash was heated at 900°C and slightly increased with increasing thermal temperature. Similar results were obtained from samples that were synthesized by chemical extraction followed by a heating process with cristobalite as the main phase. The optimum conditions that showed the highest microhardness value were achieved with the sample of pretreat with HCl 3M and then heated biomass ash at 1100°C.

**Keywords:** Biomass Residual Ash; Glass; Crystal; SiO<sub>2</sub>; Heat Treatment

## Introduction

As an agriculturally dominant nation, Thailand produces immense amounts of post-harvest agricultural waste that can be used as a biomass energy source. As of 2022, 79 biomass power plants in Thailand generated electricity by burning biomass-fuelled agricultural residues, such as rice

husks, maize cobs, and sugarcane bagasse (The Energy Conservation Center of Thailand, 2023). As a consequence of combustion, these power plants produce a substantial amount of biomass ash. Instead of discarding this detritus as waste, scientists have examined its potential as a silica

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source (Rani *et al.*, 2014, Ananthi *et al.*, 2016, Wang *et al.*, 2016, Alves *et al.*, 2017, Jurado-Contreras *et al.*, 2022). Because of its outstanding thermal, mechanical, and optical qualities, the silicon and oxygen compound silica ( $\text{SiO}_2$ ) is essential in the creation of crystal glass.

For the cost-effective purpose and environmentally friendly product, the residual biomass ash, which is rich in silica was used as a precursor in producing crystal glass. The synthesis of silica from residual biomass ash involves multiple stages (Pode, 2016, An *et al.*, 2011, Setiawan and Chiang, 2021, Xu *et al.*, 2023). Ash is initially collected and subjected to pre-treatment procedures, such as washing and dehydration, to eliminate impurities and enhance the integrity of its silica content. The purified ash is then subjected to chemical or thermal extraction procedures to obtain usable silica. Depending on the specific requirements of the synthesis process, these procedures may involve acid dissolution, alkaline extraction, or high-temperature calcination.

This study focuses on a strategy that is consistent with circular economy and sustainability principles because it repurposes biomass residues and reduces dependence on conventional silica sources, such as sand and quartz. The biomass ash (BiA) from a biomass power plant was cleaned with distilled water to remove dust and then sintered at different temperatures. X-ray fluorescence (XRF) was used to conduct a quantitative chemical analysis of the particle, as prepared. The material was utilized to produce the based-glass systems,  $\text{SiO}_2$ - $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{CaO}$ - $\text{NaO}$ , using the conventional melting method. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to examine the phase formation and microstructure of the samples, respectively. Additionally, Vickers hardness was utilized to evaluate the mechanical properties of the samples.

## Experiment Details

Firstly, the biomass ash was cleaned with distilled water to remove dust and adhering solid. The ash was separated into two parts. First, the biomass ash was sintered with various temperatures at As-received, 900°C, 1000°C, and 1100°C. The power was labeled as As-received, 900H, 1000H, and 1100H, respectively. Part 2, biomass ash was dissolved with HCl 37% 3M for 30 min before being sintered with various temperatures at As-received, 900°C, 1000°C and 1100°C. The powder was labeled as 3M, 3M900, 3M1000, and 3M1100, respectively. The ash was washed with distilled water filtered and stored at 90 °C in an Oven for 24

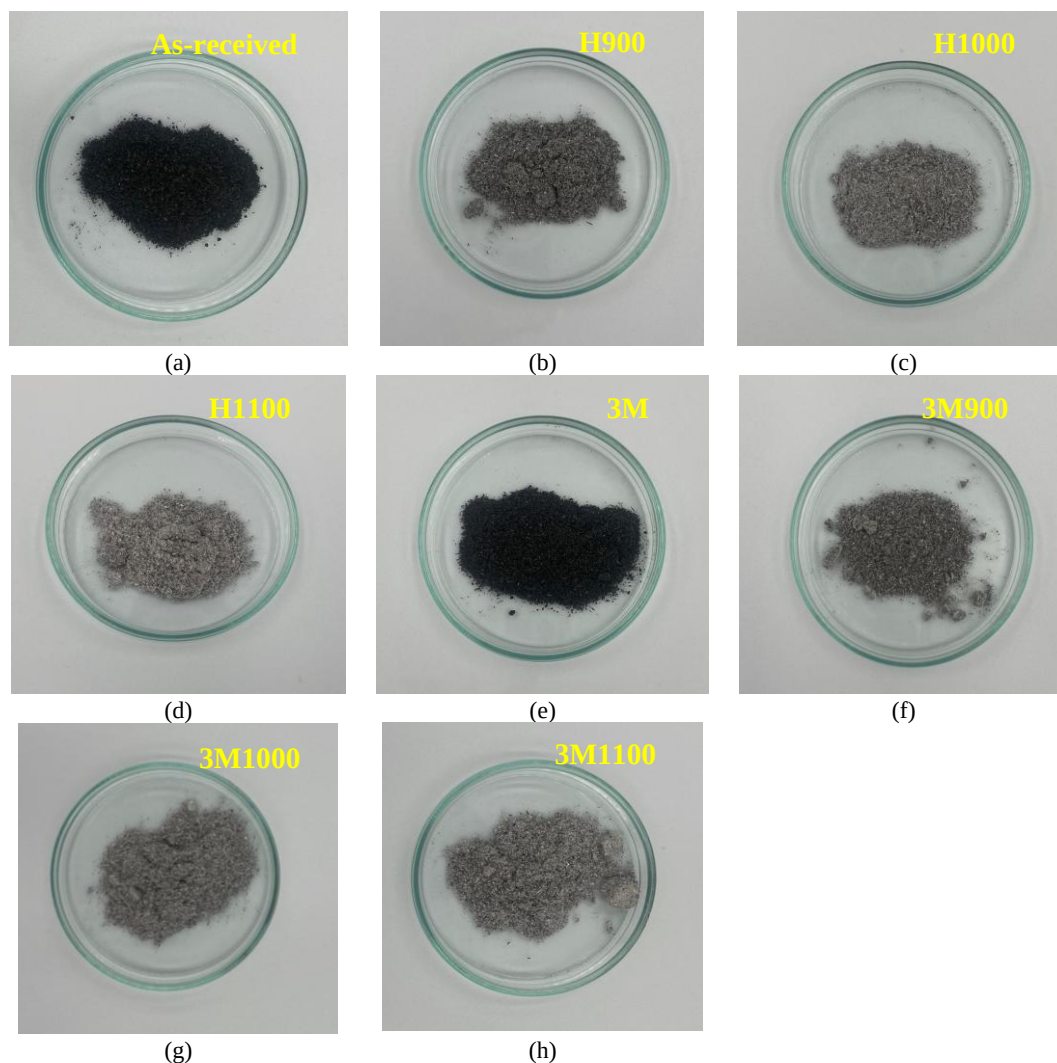
hr. Quantitative chemical analysis of as-prepared powder was accomplished by X-ray fluorescence (XRF). The phase formation of powder was carried out by X-ray diffraction (XRD). The micrograph of the powder extract was analyzed by using a scanning electron microscope (SEM)

Secondly, the glass was produced with composition of  $\text{SiO}_2$  55 wt%,  $\text{Na}_2\text{B}_4\text{O}_7$  15wt%  $\text{CaO}$  15wt%  $\text{Na}_2\text{O}$  15wt% by conventional melting method. The powder was mixed and melted in an alumina crucible for 2 h at 1300°C. The melt was subsequently quenched between stainless steel plates at room temperature to form a glass. The microhardness values were measured by Vickers microhardness measuring, using the load of 200 gf for 15s.

## Results and Discussion

In this study, BiA was heated at various temperatures at non-heat-1100C. The biomass ash powder exhibited different colors based on the calcination temperature as shown in Figure 1. The heat treatment process eliminated organic substances and generated more silica content. The firing process produces silica, whose colouration varies from black to grey after heating at higher temperatures. This colour difference can be observed by the changing of the heat treatment process eliminating organic impurities as well as generating more silica content. The light grey colour has a positive result on the silica content. This result shows similarity with the samples that used chemical route etching followed by heating. After BiA was pretreated with HCl 37% 3M for 1 h, acid pretreatment had the effect of eliminating metal ion impurities and partially hydrolyzed the organic substances of biomass ash. This is consistent with the XRF result (Table 1) where the highest  $\text{SiO}_2$  content yielded was 97.50%, which was achieved by biomass ash synthesis via chemical treatment with HCl followed by heating at 1100°C. When the temperature of heating increases, the content of  $\text{SiO}_2$  increases, as well as the content of other metal ions, such as  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}_2$ , decreases. The BiA had a lower content of  $\text{SiO}_2$  during the heating process, compared to that observed during chemical treatment, followed by heating. This may be attributed to the fact that the organic matter remains in the biomass ash after heating due to difficulty in degrading grains and metal ions, such as  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}_2$ . However, when the biomass ash is acid-leached using HCl before combustion, up to 97% of metallic impurities are extracted. This observation is consistent with those reported by Liou (Liou, 2004), which

indicates that the acid pre-treatment process eliminates metal ion impurities and partially hydrolyses the organic substances of the rice husk raw materials.



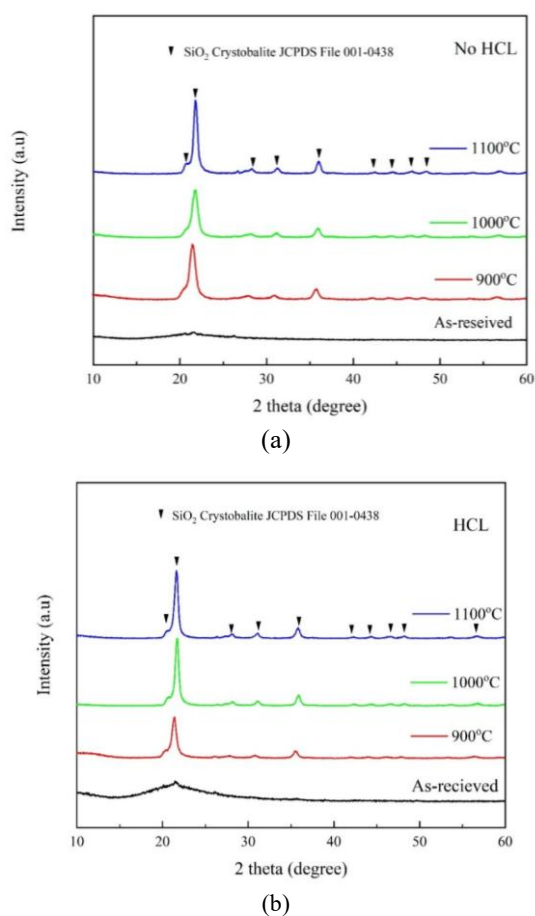
**Figure 1.** Digital photograph of biomass ash heating different temperatures (a) As-received (b) 900°C (c) 1000°C (d) 1100°C and biomass ash using acid pretreated followed by heating different temperatures (e) 3M (f) 3M900°C (g) 3M1000°C (h) 3M1100°C

**Table 1** Chemical compositions of the biomass ash with different route syntheses determined by XRF analysis

| Oxide                          | % Content (wt%) |       |       |       |       |       |        |        |
|--------------------------------|-----------------|-------|-------|-------|-------|-------|--------|--------|
|                                | As-received     | H900  | H1000 | H1100 | 3M    | 3M900 | 3M1000 | 3M1100 |
| SiO <sub>2</sub>               | 93.31           | 94.11 | 94.46 | 94.61 | 97.15 | 97.48 | 97.44  | 97.50  |
| K <sub>2</sub> O               | 2.45            | 2.14  | 2.10  | 2.00  | 1.22  | 1.11  | 1.12   | 1.11   |
| P <sub>2</sub> O <sub>5</sub>  | 1.47            | 1.34  | 1.24  | 1.13  | 0.29  | 0.27  | 0.29   | 0.28   |
| Na <sub>2</sub> O              | 0.06            | 0.06  | 0.05  | 0.03  | 0.03  | 0.00  | 0.00   | 0.00   |
| MgO                            | 0.57            | 0.51  | 0.48  | 0.48  | 0.30  | 0.27  | 0.27   | 0.27   |
| Al <sub>2</sub> O <sub>3</sub> | 0.43            | 0.43  | 0.41  | 0.04  | 0.25  | 0.24  | 0.22   | 0.22   |
| CaO                            | 0.76            | 0.79  | 0.75  | 0.74  | 0.27  | 0.27  | 0.29   | 0.27   |
| TiO <sub>2</sub>               | 0.002           | 0.00  | 0.00  | 0.00  | 0.001 | 0.00  | 0.00   | 0.00   |
| MnO                            | 0.03            | 0.02  | 0.03  | 0.03  | 0.02  | 0.03  | 0.03   | 0.04   |
| Fe <sub>2</sub> O <sub>3</sub> | 0.15            | 0.15  | 0.15  | 0.15  | 0.09  | 0.09  | 0.09   | 0.09   |

\*Cl, SO<sub>3</sub>, ZnO ≤ 0.1%

The XRD patterns of samples heated at different temperature conditions are presented in Figure 2. The data shows a similar trend of phase formation for both biomass ash conditions. The Bia samples without heating appeared to be in the amorphous phase and began to emerge at approximately  $2\theta \approx 22^\circ$ . The phase formation yielded  $\text{SiO}_2$  cristobalite after heating at  $900^\circ\text{C}$  and increased slightly with increasing temperatures in both types of biomass ash extract. The highest phase of  $\text{SiO}_2$  was obtained by heating the biomass ash samples at  $1100^\circ\text{C}$ .



**Figure 2.** XRD pattern of biomass ash of (a) heating different temperatures and (b) acid pretreated followed by heating different temperatures

During heat treatment at higher temperatures, nucleation plays an important role in particle formation (Tsai, 2004). Nucleation occurs mainly due to a small amount of silica phase formation at the beginning of the reaction. The reaction continuously increases, and crystallization begins, slightly increasing the intensity of the crystalline

phase. Then silica will convert a less-ordered structure to a highly-ordered structure (Kalapathy and Proctor, 2000). The literature observed a similar pattern for silica obtained from rice husk combustion (Wu *et al.*, 2008).

Figure 3 displays an SEM micrograph of biomass ash powder with various silica extract methods. SEM images of H0-H1000 powder demonstrated a heterogeneous particle with a 5-15  $\mu\text{m}$  diameter. When the heating temperature increased, the primary particle size increased. In the case of 3M0-3M1100, the primary particle size of the powder resulted in the same shape as the heterogeneous particles. Ash powder particles synthesized by chemical treatment, followed by heating, were smaller in size compared to the ash powder particles synthesized by combustion only. This difference was because acid etching caused a considerable increase in the sample surface area and effectively decreased the grain size of the crystal. However, when increasing the heating temperature to 1000-1100 $^\circ\text{C}$ , the primary particles began to soften and fuse, indicating that acid extraction may induce particle aggregation.

XRF results confirmed the high content of  $\text{SiO}_2$  in biomass ash powder, i.e., 93.31-97.50%. Thus, the high composition of  $\text{SiO}_2$  in ash renders it a possible substitute for other  $\text{SiO}_2$  sources. The crystal glass with 55 wt%  $\text{SiO}_2$ , 15 wt%  $\text{Na}_2\text{B}_4\text{O}_7$ , 15 wt%  $\text{CaO}$ , 15 wt%  $\text{Na}_2\text{O}$ , and silica obtained from biomass ash via various synthesis methods is presented in Figure 4. In the case of glass production by BiA heating only, yellow colour was observed inside the glass sample using BiA with non-heating. However, the other sample that was treated with heat revealed the same result that presented the transparent glass. This is due to the effect of the metal ion, particularly  $\text{Fe}_2\text{O}_3$ , in the biomass ash. Moreover, all glass samples with biomass ash and acid pre-treatment, followed by heating at various temperatures, have transparent glass. From the result, it can be concluded that the high  $\text{SiO}_2$  content is advantageous in producing transparent crystal glass.

The microhardness value of the resulting crystal glass is illustrated in Figure 5. When the sintering temperatures were increased, the microhardness values increased slightly in both  $\text{SiO}_2$  extraction cases. The maximum values of 825 and 867 HV were achieved from H1100 and 3M110, respectively. These values could be due to the fact that the higher  $\text{SiO}_2$  content enhanced the microhardness value of the crystal glass, particularly for the crystal glass produced using ash etching before heating at  $1100^\circ\text{C}$  in the glass structure. Furthermore, the samples with the highest microhardness values, H1100 and 3M110,

exhibited high density ( $>2.50$ ) and refractive index ( $>1.5$ ) as shown in Table 2 (Davison, and Newton,

2003). These characteristics confirm that these samples are crystal glass.

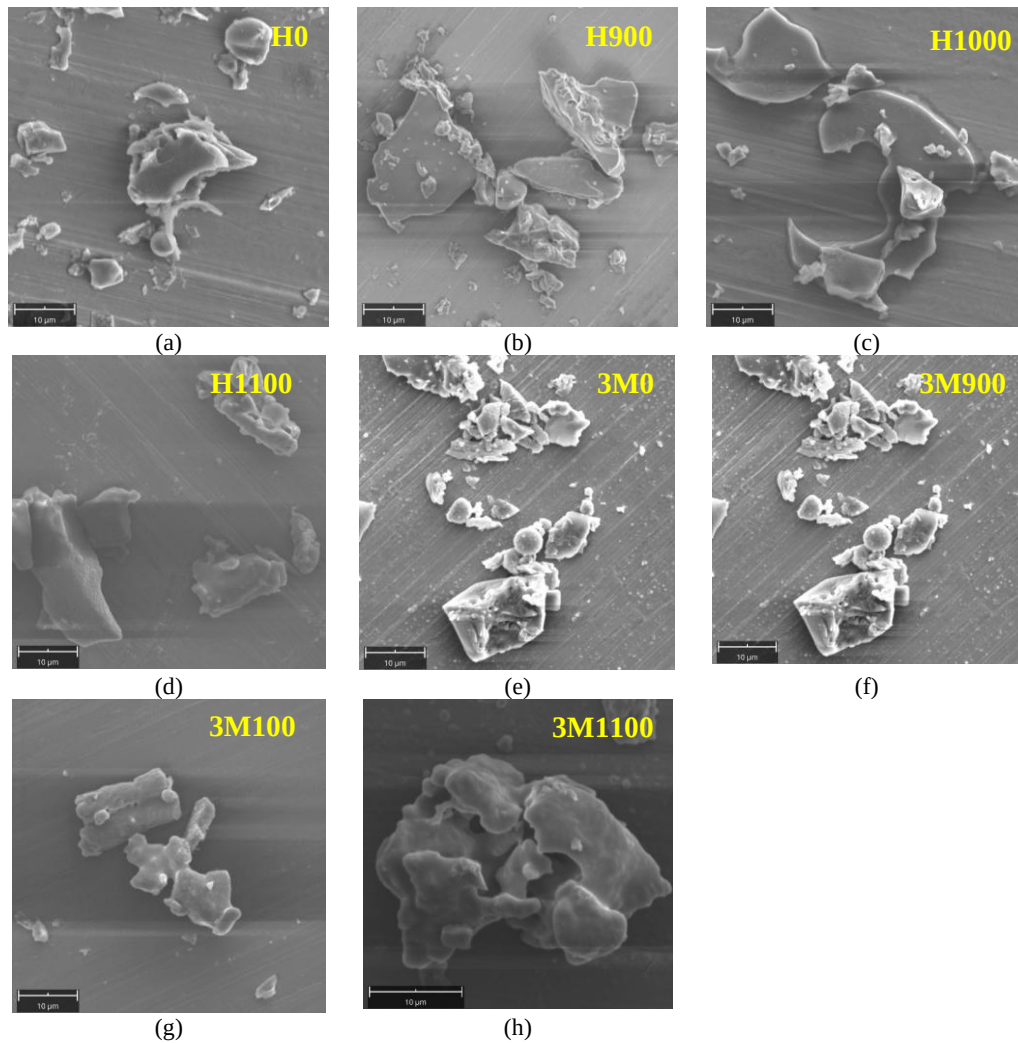


Figure 3. SEM images of biomass ash using different extraction routes

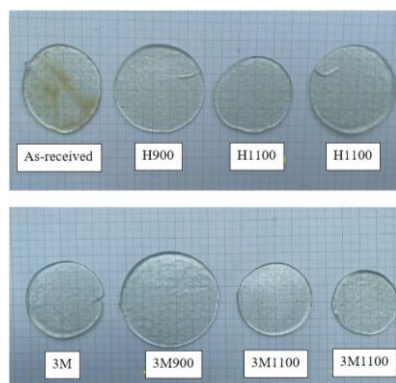


Figure 4. Digital photograph of crystal glass with different  $\text{SiO}_2$  precursor extraction

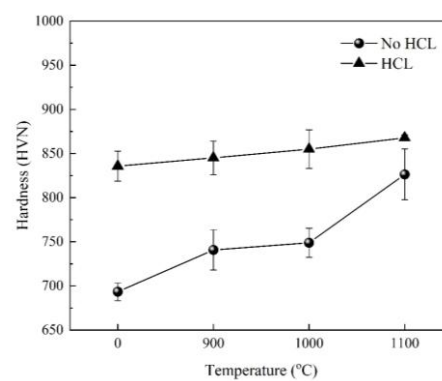
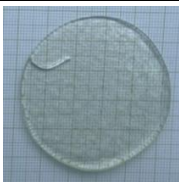
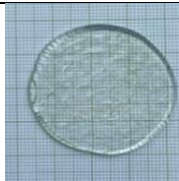


Figure 5. The microhardness values of crystal glass with different  $\text{SiO}_2$  precursor extraction

**Table 2 The results of the density and refractive index of H1100 and 3M1100**

| Samples        | Crystal glass                                                                     | Density (g/cm <sup>3</sup> ) |               | Refractive index (RI) |             |
|----------------|-----------------------------------------------------------------------------------|------------------------------|---------------|-----------------------|-------------|
| <b>H1100</b>   |  | 1                            | 2.857         | 1                     | 1.57        |
|                |                                                                                   | 2                            | 2.753         | 2                     | 1.57        |
|                |                                                                                   | 3                            | 2.824         | 3                     | 1.58        |
|                |                                                                                   | Mean                         | 2.811 ± 0.04  | Mean                  | 1.57± 0.006 |
| <b>F3M1100</b> |  | 1                            | 2.932         | 1                     | 1.57        |
|                |                                                                                   | 2                            | 2.922         | 2                     | 1.57        |
|                |                                                                                   | 3                            | 2.876         | 3                     | 1.57        |
|                |                                                                                   | Mean                         | 2.910 ± 0.024 | Mean                  | 1.57±0.00   |

## Conclusions

Biomass ash is an agricultural waste and a valuable natural precursor for silica sources. In this study, the high SiO<sub>2</sub> content was successfully prepared by using the calcination method only as well as using the acid pretreated following calcination. The phase formation of SiO<sub>2</sub> crystal ballite was achieved a developed in all sample powders. The highest % of SiO<sub>2</sub> content at 97.50 was obtained from the samples with etching HCl 3M followed by heating at 1100°C. The crystal glasses using biomass ash powder were successfully synthesized and showed similar color. The glass samples using ash via acid treatment together with combustion showed the maximum microhardness values.

## Acknowledgment

This work was supported by The Reinventing University Program 2022 from the Ministry of Higher Education, Science, Research and Innovation, Thailand; The National Science, Research and Innovation Fund, Thailand Science Research and Innovation (TSRI) under Grant 4232827; Rajamangala University of Technology Phra Nakhon, Thailand and Faculty of Science and Technology, Thailand for financial support.

## References

- Alves, R.-H., Silva, A., and Costa, M. (2017). Green synthesis and characterization of biosilica produced from sugarcane waste ash. *Journal of Chemistry*, 2017(1). <https://doi.org/10.1155/2017/6129035>
- An, D., Zhang, X., Liu, Y., and Zhang, H. (2011). A study on the consecutive preparation of silica powders and active carbon from rice husk ash. *Biomass and Bioenergy*, 35(3):1,227-1,234. <https://doi.org/10.1016/j.biombioe.2010.12.014>
- Ananthi, A., Ramasamy, P., and Kumar, S. (2016). Preparation and characterization of silica material from rice husk ash-an economically viable method. *Chemical Materials Research*, 8(6):1-7.
- Davison, S. and Newton, R.G. (2003). *Conservation and Restoration of Glass*, 2nd ed. Elsevier, London, p. 392.
- Jurado-Contreras, S., Sánchez-González, J., and Rodríguez, E. (2022). Synthesis and characterization of alkali-activated materials containing biomass fly ash and metakaolin: Effect of the soluble salt content of the residue. *Archives of Civil and Mechanical Engineering*, 46:64-72. <https://doi.org/10.4028/www.scientific.net/JNanoR.46.64>
- Kalapathy, U. and Proctor, A. (2000). A simple method for production of pure silica from rice hull ash. *Bioresource Technology*, 73(3):257-262. [https://doi.org/10.1016/S0960-8524\(99\)00127-3](https://doi.org/10.1016/S0960-8524(99)00127-3)
- Liou, T.-H. (2004). Preparation and characterization of nano-structured silica from rice husk. *Materials Science and Engineering A*, 364(1-2):313-323. <https://doi.org/10.1016/j.msea.2003.08.045>
- Pode, R. (2016). Potential applications of rice husk ash waste from rice husk biomass power plant. *Renewable and Sustainable Energy Reviews*, 53:1,468-1,485. <https://doi.org/10.1016/j.rser.2015.09.051>
- Rani, K.M., Priya, M., and Soni, S. (2014). Synthesis and characterization of amorphous nanosilica from biomass ash. *Materials Today: Proceedings*, 105(2024):21-26. <https://doi.org/10.1016/j.matpr.2023.06.077>
- Setiawan, W.-K., and Chiang, Y. (2021). Crop residues as potential sustainable precursors for developing silica materials: a review. *Waste and Biomass Valorization*, 12:2,207-2,236. <https://doi.org/10.1007/s12649-020-01126-x>

- The Energy Conservation Center of Thailand. (2023). Exploring the procurement of various forms of biomass in 2022. <https://kc.dede.go.th/knowledge-view.aspx?p=375>
- Tsai, M.-S. (2004). The study of formation of colloidal silica via sodium silicate. *Materials Science and Engineering B*, 106(1):52-55. <https://doi.org/10.1016/j.mseb.2003.08.052>
- Wang, Y., Zhao, Y., Li, P., Zhang, Z., and Zhao, X. (2016). Probabilistic modeling of the flows and environmental risks of nano-silica. *Science of The Total Environment*, 545-546:67-74. <https://doi.org/10.1016/j.scitotenv.2015.12.100>
- Wu, J.-J. and Chou, T.-H. (2008). Catalytic ozonation of oxalic acid using carbon-free rice husk ash catalysts. *Industrial and Engineering Chemistry Research*, 47(9):2,919-2,925. <https://doi.org/10.1021/ie071093x>
- Xu, S., Li, Y., Zhang, Q., and Wang, Z. (2023). Synthesis of ordered mesoporous silica from biomass ash and its application in CO<sub>2</sub> adsorption. *Environmental Research*, 231(1):116070. <https://doi.org/10.1016/j.envres.2023.116070>