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Review

A critical assessment and new research directions of rice husk silica processing methods and properties

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Abstract: A review of production and properties of silica produced from rice husk is carried out with assessment of processing and manufacturing methods and suggestion of new research directions with respect to the processing methods. It was revealed that the structural nature of the silica produced from rice husk is independent of the purification methods but largely dependent on the incineration temperature used in the production process. Also, it was established that without pre-treatment, incineration of rice husk results in the production of silica of low purity, surface area and whiteness. The paper concludes by advocating the use of a novel process called hydro thermo-baric process, for producing high-purity reactive nano-silica from rice husk. This novel process, has the advantages of high volume production, versatility of application of its product through varying any of its process parameters and being environmentally benign compared to other processes.

Keywords: rice husk silica, opaline silica, nanosilica, thermo-baric process

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INTRODUCTION

It was estimated that world paddy production in 2010 was over 700 million tons [1]. Around 22% of the paddy mass is husk [2], which consists of opaline silica in combination with a large amount of a phenyl propanoid structural polymer called lignin, hemicellulose and cellulose [3]. Consequently, over 154 million tons of rice husk were generated in 2010. The average composition of rice husk is given in Table 1.

Table 1. Composition of rice husk [4]

Constituent	**%**
Cellulose	35
Hemicellulose	25
Lignin	20
Crude protein (N x 6.25)	3
Ash	17 (silica 94%)

When rice husk is incinerated, it generates between 17-20% ash, made up of about 87-93% opaline silica and other metallic oxide impurities depending on the source of the husk. This kind of high percentage of silica intermingling with plant fibres is quite rare in nature. The close intermingling of silica and lignin has two consequences: the rice hull is not only made resistant to water penetration and fungal decomposition, it is also resistant to the best efforts of man to dispose it. Since the hull represents an average about 22% of the rough harvested weight of rice (paddy), our planet is speedily being filled up with an abundance of this scaly residue. Juliano [5] has also pointed to the fact that of all cereal by-products, the rice hull has the lowest percentage of total digestible nutrients (less than10%). Also reporting a drawback of rice husk usefulness, Olivier [3] stated: “Nowhere could we ever find a cereal by-product so low in protein and available carbohydrates and yet, at the same time, so high in crude fibre, crude ash and silica.” This statement corroborates the fact that rice husk is not even good as a fodder for animals. Though some organic products such as furfural have been produced from rice husk [6], its richness in ash and silica has been of great research interest because many value-added products could be obtained from this agro-waste.

When rice husk is incinerated, two types of products can result, depending on whether the combustion is complete or incomplete. They are white rice husk ash (WRHA) and carbonised rice husk (CRH) respectively. In either forms, rice husk has some applications. Among the uses reported are pozzolan in cement industry [7-13], aerogels [14, 15], SiC [16, 17], porous carbon [18], zeolites [19] and cordierite [20]. In earlier work, we reported an indirect use of rice husk in making insulating refractories [21, 22]. These uses are related to the processing route or method used, which often affect the product characteristics. For example, it has been shown that different methods of preparation of rice husk silica produce different morphology, structure and reactivity [23].

Previous reviews on this subject were in 2001 and 2003 [24, 25] and since then there has not been another review again even though there have been dramatic developments in the technology. This paper is therefore an attempt to review the research depth and directions of the processing methods as well as the characteristics and utilisation of rice husk silica in these intervening years. The paper presents a critical review of the literature by assessing the current production facilities and processes in the field as well as the influence each process has on the product characteristics. It ends by making case for a process currently being developed, which is called the hydro thermo-baric process. It is our hypothesis that this process would be inexpensive and versatile with regard to the effects it would have on the quality of rice husk silica produced by varying the process parameters.

Composition of Rice Husk Ash

There are many reports [26-28] on the varying composition of rice husk ash (Table 2) which is largely dependent on many factors. These include but are not limited to agricultural practices such as the use of fertilisers during rice cultivation, type of fertilisers employed and climatic or geographical factors. Thus, depending on the geographical location, different authors have published different values for the composition of rice husk. The methods used to evaluate the composition quoted are also indicated.

From Table 2, it is clear that though the composition of rice husk may be dependent on several factors, the percentage of silica (SiO_2) in the ash ranges between 87-92%. A trace amount of titania (TiO_2) was also reported [29]. Due to this compositional variation, the suitability of rice husk silica for any given application will therefore be largely dependent on the purity level needed and if it is not met from the beginning for a given application, then a purification process will be carried out to reduce or eliminate unwanted impurities.

Table 2. Composition of rice husk ash by geographical location (Percentage of constituent as per authors in square bracket and method used outside bracket)

Composition	[27]XRF	[28]ICP	[29]*	[**]XRF
SiO_2	91.56	91.5	87.79	91.25
K_2O	4.76	1.23	1.69	3.829
P_2O_5	-	0.30	4.74	2.45
CaO	0.78	0.57	1.24	0.875
SO_3	0.29	-	-	0.661
MgO	-	0.30	1.59	0.573
Al_2O_3	2.36	0.62	0.4	0.18
Fe_2O_3	0.11	0.42	0.37	0.0866
MnO	0.07	0.04	-	0.0726
Rb_2O	-	-	-	0.0143
ZnO	0.01	-	-	0.0111
CuO	0.01	-	-	-
Na_2O	-	0.18	-	-
LOI	N.D.	3.05	2.08	N.D.

* Method not specified; ** From the authors' laboratory; N.D. = Not determined

PROCESSING OF RICE HUSK FOR SILICA

Different processes have been used by different researchers to obtain silica from rice husk. The following discussion reviews these processes, highlighting their advantages and disadvantages.

Direct Incineration without Pre-treatments

Rice husk is directly incinerated to produce silica of varying purity, with or without the use of pre-treatments [30-36]. In an overall process, the temperature of incineration, holding time and pre-treatment techniques employed affect the character, especially the surface area and brightness (whiteness), of the silica produced. The transformation of raw husk to clear white, grey or pale grey ash is critically dependent on the temperature of incineration [31]. For instance, a temperature between 300-450°C only transforms fresh rice husk (Figure 1(a)) to carbonised husk (Figure 1(b)), while that between 500-650°C produces white or grey ash (Figure 1(c)), depending on soaking time, which is the duration for which incineration is allowed to proceed at the stated temperature range.

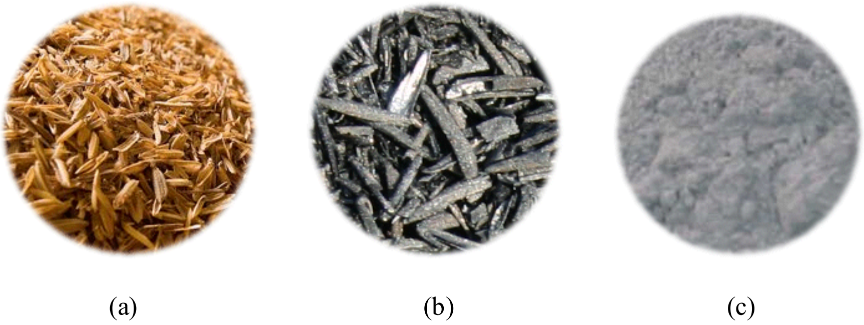

Figure 1. Rice husk (a); carbonised rice husk (b); completely incinerated rice husk (c)

As the incineration temperature increases, there appears to be some accompanying phase changes. The findings of these phase changes will be discussed later. It is noted, however, that rice husk silica produced between 500-650°C with incineration holding (soaking) time of 2.5-6 hr is considered ideal for producing white amorphous silica while crystallinity sets in when incineration temperature increases beyond 700°C. The quantity of the operational phase, whether cristobalite or tridymite, is dependent on the applied temperature range and the impurity level in the rice husk. Also, it was reported [31] that the incineration temperature grossly affects the surface area and hence the reactivity of silica produced from direct incineration process.

Direct incineration of rice husk can be accomplished in open air as reported by Hamdan et al. [23] or in a muffle furnace [37]. Another method used by some researchers [34-36] is the fluidised bed combustion technique to produce rice husk silica, even though the reported purity was not more than 95%. So whether in static or flowing air, complete incineration can be achieved with some varied effects on the properties of the silica produced. A new technology was recently developed in India (Figure 2) for direct incineration of rice husk [38] and it works like a TORBED reactor [39].

Figure 2. A pilot plant for rice husk incineration in India [38]

Pre-treatment Effects on Silica Production from Rice Husk

One of the reasons why it is difficult to obtain silica with purity in excess of 97% from rice husk by the direct incineration process is a consequence of the effects of the metallic impurities the husk contains. For instance, Chandrasekhar et al. [40] reported that oxides, especially K_2O, impart black colour on the particles. Some explanations to support this phenomenon is that there exists a strong interaction between oxides, especially those of potassium and sodium, contained in rice husk and the silica therein, such that it can result in the surface melting of SiO_2 particles and accelerate an early crystallisation of amorphous SiO_2 into cristobalite, as implied by research results [30, 41-43]. This is one of the reasons why Kalapathy et al. [44] could not achieve a purity of up to 98% even after 14 hr of their sol-gel treatment of rice husk ash with bases and acids. The surface melting of these oxides on the silica grossly reduces the surface area, thereby reducing the reactivity of the particles. Thus, it is often necessary to use some pre-treatment methods, which can either be done through acidic or basic medium, to reduce or remove metallic impurities in order to increase the chances of obtaining silica of higher purity and surface area than is achievable in the direct incineration method.

Three main pre-treatment methods have generally been used in the production of high purity silica from rice husk. These are acid leaching, basic pre-treatment and microbiological pre-treatment, usually in combination with some acids. Several kinds of acids, both mineral and organic, have been reported to be used to pre-treat rice husk before other value adding processes such as incineration begin [32, 33, 40, 42, 43, 45]. However, HCl has proved to be most effective in removing metallic impurities from the husk and so it is by far the most widely used. Chakraverty et al. [46, 47] found that leaching of rice husk in 1N HCl is effective in removing most of the metallic impurities. Other researchers [40] used organic acids and compared results with those obtained by using other different mineral acids in pre-treating rice husk and concluded that HCl is better. Their order of efficiency is HCl> H_2SO_4>

HNO_3. However, Umeda and Kondo [48] reported a very high purity (>99.5%) silica from rice husk on pre-leaching it with citric acid.

While acid leaching affects the chemical composition of the husk, it does not affect the structure, whether crystalline or amorphous, of the silica. Thus, the change of phase from amorphous to crystalline is not affected by the pre-treatment method employed. An insight into this dynamics was presented in the research report of Real and coworkers [43]. They found that preliminary leaching of rice husk with a solution of HCl before incineration at 600°C, if properly done, can result in a high-purity silica (approximately 99.5%) with high specific surface area (approximately 260 m^2/g). They indicated that the high-surface-area silica produced was unaffected even after being heated at 800°C. They also performed the HCl leaching on the white ashes obtained from incineration of untreated rice husk at 600°C and obtained an amorphous silica with the same purity, although its specific surface area decreased to as low as 1 m^2/g. They explained the kinetics of this drastic change in surface area, attributing it to the interaction between alkali oxides, specifically K_2O and SiO_2.

Other acids such as H_2SO_4, HNO_3 and their mixture, have also been used in the acid pre-treatment [32, 42, 46, 49-51]. The general leaching effects of H_2SO_4, HNO_3 and HCl are similar, but HCl is superior to H_2SO_4 and HNO_3 in removing the metallic ingredients [46]. Some researchers [42, 44] also attempted chemical post-treatment of incinerated rice husk using HCl but the results were inferior to those of the pre-treatment.

Some alkalis such as NaOH and NH_4OH have been used to pre-treat rice husk [33, 37, 49, 50]. However, the effects of alkali pre-treatment were not as obvious or satisfactory as those of acid pre-treatment. Attempts have been made on the use of microbial fermentation as a pre-treatment of rice husk in order to obtain silica [49, 52]. Although the results were similar to those obtained from acid pre-treatment, the method is disadvantageous in that the time required for the fermentation process to complete is too long, making it unfeasible for practical applications.

Hydrothermal Method

Hydrothermal synthesis has been defined as a process that utilises single- or heterogeneous-phase reactions in aqueous media at elevated temperature (T>25 °C) and pressure (P>100 kPa) to crystallise ceramic materials directly from solution [53]. As stated in the introduction, rice husk contains organic compounds and oxides of metals. Under high temperature, high pressure and acidic or basic medium with strong oxidising activity, the organic compounds are decomposed and the trace metals turned into soluble ions; then, silica is obtained. This processing method can achieve the purification of silica from the husk with only the use of water. However, achieving complete dissolution of the organic matter in the rice husk is a task that is near impossible. So, practically this process still requires an incineration step, though the soaking time may be less compared to incinerating the untreated or pre-treated rice husk. The method does not affect the amorphicity of the silica in rice husk. Some acids with strong oxidising activity such as H_2SO_4 and HNO_3 are used and sometimes H_2O_2 is also used as the oxidative medium. This method had been used by Mochidzuki et al. [26] and Wu [54].

Other Methods

Some researchers [55, 56] reacted carbonised rice husk with Na_2CO_3 solution in a proper ratio for 3 hr, followed by incineration step at 600-650°C for varied soaking time between 3-7 hr to obtain silica. The silica made from this method has good reinforcing properties in rubber. In an earlier review [24], it was reported that this method involved the mixing of rice husk ashes with NaOH to produce sodium silicate which would be reacted with NH_4HCO_3, $(NH_4)_2SO_4$ or H_2SO_4 to produce SiO_2.

Summary of Processing Methods

Apart from the production of rice husk silica done with the TORBED incinerator or the fluidised bed combustion, all other methods were mostly done on a laboratory scale. If they were to be scaled up to commercial level, the cost and personnel risks involved would be quite high, since acids and other corrosive media would be worked with at high temperatures. The quality of the silica obtained from fluidised bed combustion or TORBED incinerator is not more than 95%, which restricts its application to chemically insensitive areas like cement and concrete admixtures where high-purity silica is not essential. For this reason, therefore, it is necessary to evolve a system that can produce high-purity silica at volumes of production capable of supporting industrial needs. This is the current research in our laboratory where we have developed a hydro thermo-baric process for volume production of high purity nanosilica for industrial applications. Some of the work in this research will be briefly explained later.

PROPERTIES OF RICE HUSK SILICA

In this section the properties of rice husk silica are examined, as well as how the production process employed affects such properties.

Structure

Different research reports have presented the structural state of rice husk silica and shown that it is dependent on the processing temperature. Often, the structure of the silica is investigated by X-ray diffraction (XRD) and the state is revealed by the shape of the diffractogram obtained. A study done by Hamdan et al. [23] showed that over various temperature ranges rice husk silica can exist in either crystalline or amorphous state as shown in Figure 3.

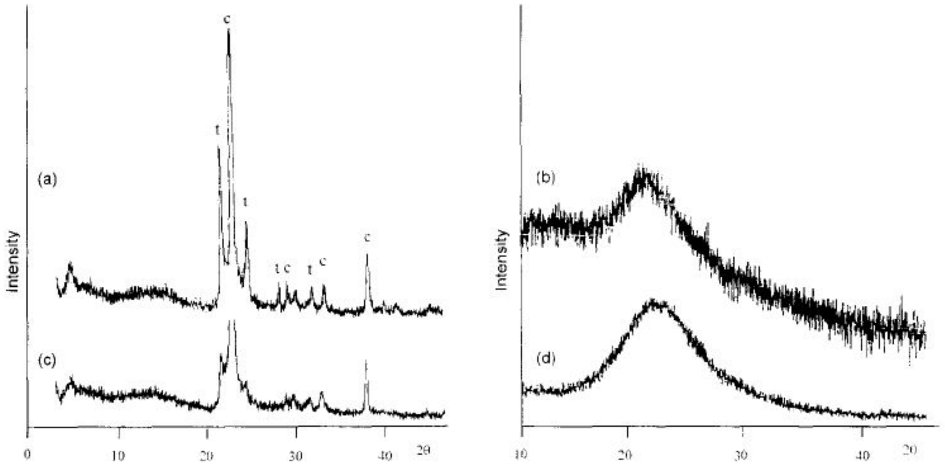

Figure 3. X-ray diffractograms of rice husk silica processed at different temperatures [23]

Figure 3(a) is a diffractogram of rice husk silica processed through open-field burning where temperatures can reach 900°C, while Figure 3(c) represents samples prepared in furnace at 1000°C for 4 hr. Figures 3(b) and 3(d) are from a sample prepared in muffle furnace at 700°C for 4 hr and sample hydrothermally extracted respectively. As is evident from the diffractograms, the samples represented by Figure 3(b) and (d) are amorphous while the other two are crystalline in nature with the formation of crystobalite and traces of tridymite. These findings are in agreement with the work of Kapur [31], who studied the structural behaviour of silica over a temperature range of 400-1500°C and reported that at combustion temperature above 900°C, the silica in rice husk ash consisted of cristobalite and a small amount of tridymite. Other researchers [57] reported similar results. Thus, to obtain amorphous silica from rice husk, the processing temperature should not exceed 700°C, as phase transition to the crystalline structure of crystobalite would soon follow, although no specific temperature has been reported for this transformation.

Surface Area and Pore Volume

The surface area and pore volume of rice husk silica is dependent on the processing temperature, since this affects the surface melting of the silica due to the presence of alkali metal oxides. Different values of surface area and pore volume have been reported [58]. Kapur [31] reported an initial increase in the surface area from 60 m^2/g to 80 m^2/g when the husk was incinerated at 350°C and 600°C respectively. This increase was perhaps due to the burn-off of the residual carbon and the opening of new pores. His work further revealed that between 700-900°C, a sharp drop occurred in the surface area from 40 to only 1 m^2/g as a result of the alkali metal oxides.

Morphology, Particle Size and Chemical Species

It is a generally accepted fact that silica which is formed by incinerating rice husk below 800°C is amorphous [31]. It seems that particles of silica in rice husk ash are agglomerates of small nano-range particles. Thus, it is very common to find aggregates of silica forming fine globules or platelets of varied sizes as can be seen in Figure 4. The first report on the production of nanosilica from rice husk was made by Conradt et al. [49] and later by Liou [58]. Since then other researchers [59] have always stressed the term in reporting their work. From the investigations in our laboratory, we have found that not much work or processing is required to obtain nanosilica since the natural form in which it occurs in the husk is already a wide distribution of sizes in the nano-range, which is less than 100 nm.

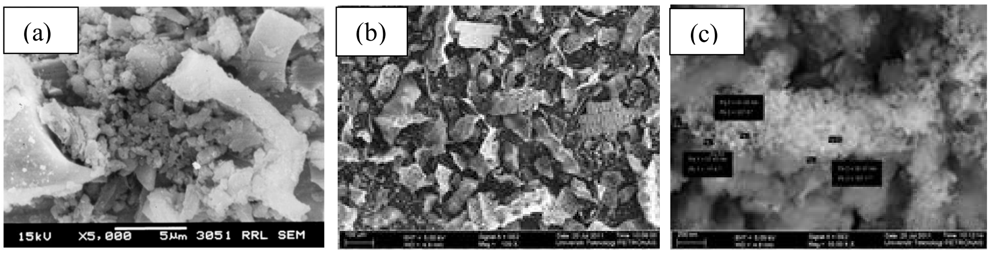

Figure 4. Morphology of rice husk silica (a) SEM micrograph showing mixed platelets and globules [25]; (b) FESEM micrograph of platelets; (c) agglomerated nanoparticles [from our laboratory]

Also studied were the chemical species that exist within the silica produced from rice husk. To demonstrate that the available chemical species in rice husk silica is process dependent, Hamdan et al. [23] and Mochidzuki et al. [26] reported similar data on the species present in rice husk silica using ^{29}Si nuclear magnetic resonance (NMR) when they produced rice husk silica via the hydrothermal process. The ^{29}Si MAS NMR spectra of rice husk silica presented in Figure 5 clearly show the varying chemical species with processing temperature.

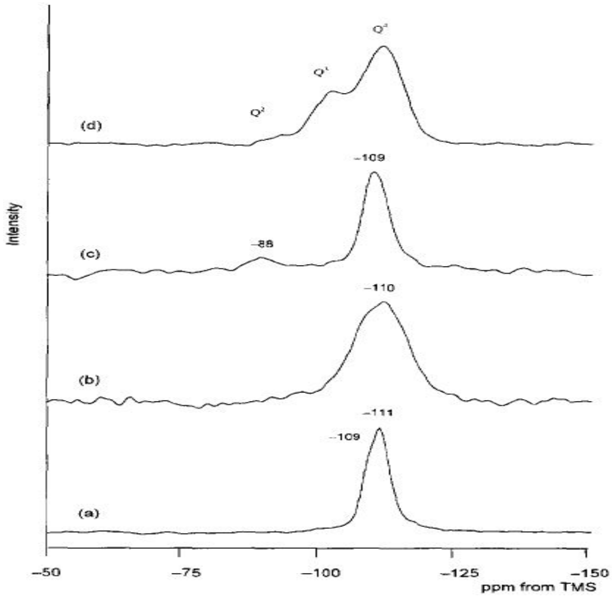

Figure 5. ^{29}Si MAS NMR spectra of rice husk silica samples: (a) open field burning; (b) from muffle furnace at 700°C; (c) from muffle furnace at 1000°C; (d) from hydrothermal processing [23]

A detailed examination of the spectra reveals important features. As explained by Hamdan et al. [23], the spectrum of the sample in Figure 5(a) consists of a single intense and narrow peak at -111 ppm, which corresponds to the presence of Q4 line of siloxane bonds of the crystalline trydimite and a shoulder at -109 ppm corresponding to β-cristobalite. This observation is also true for the sample in Figure 5(c) and is expected since the processing route involved exposure of the rice husk to temperatures in excess of 700°C. The ^{29}Si MAS NMR spectrum of the sample in Figure 5(d) consists of peaks with chemical shifts of around δ 90, 100 and 110 ppm, which correspond to the presence of Q2, Q3 and Q4 units, i.e. silanediol unit [$(OH)_2Si(OSi)_2$], silanol unit [$(OH)Si(OSi)_3$] and silicon-oxygen tetrahedral framework [$Si(OSi)_4$] respectively.

Mochidzuki et al. [27] did a more detailed study of the species change with temperature and remarked that the original rice husk silica consisted of 8.9% Q2, 60.3% Q3 and 30.8% Q4 units and that the percentage of Q4 units existing in the samples tended to increase with increasing treatment temperature, though Q2 and Q3 units remained at non-negligible percentages since the maximum temperature they worked with was 243°C. Hamdan et al. [23] reported that there was a complete absence of Q2 and Q3 units with the Q4 bandwidth increasing when the spectrum for the sample in Figure 5(b) was examined. This suggests that the silicates with Q2 and Q3 structures were converted to Q4 silicates by thermal treatment and since traces of Q2 and Q3 units existed in samples in Figures 5 (a), (c) and (d), the temperature around 700°C is regarded as optimal for the production of high purity silica devoid of silane-diol and silanol units.

Whiteness

One important property worthy of mentioning is the colour of the silica produced at the end of each process. When working with an open-field pile burning of fresh rice husk (Figure 1(a)), there are often spots of incomplete combustion within the pile, resulting in pockets within the pile having particles of carbonised husk as depicted in Figure 1(b). Once this happens, black coloration due to the unburnt carbon remains within the product. Chandrasekhar et al. [20, 40] did extensive studies on the optical properties of rice husk silica processed using different acid pre-treatment methods and concluded that in the processes where there has been substantial leaching of the alkali metal oxides, especially the oxide of potassium, the brightness and whiteness increases. This is due to the fact that when the husk is not substantially treated, the alkali oxides enhance the surface melting of silica, thereby entrapping carbon within the silica; the more residual carbon entrapped, the darker the colour of the husk is.

Guide to Selection of Rice Husk Silica Production Process for Specific Applications

The impurities contained in rice husk silica can have implication in some of the applications. It is therefore important to know what characteristics are needed in an intended application, which will therefore affect the choice of the purification degree that is necessary for such an application. Table 3 gives a summary of applications of rice husk silica. The levels of purity required and the recommended processes are also indicated.

Table 3. Different applications and purity levels required of rice husk silica and recommended processes

Application	Desirable qualities	Authors	Purity level	Recommended process
Filler in polymers	Ability to retard thermo-oxidative and photo degradations. Possession of some silanol group to enhance coupling and good level of residual carbon to inhibit photo degradation	[60-70]	95-98% and possessing Q2 and Q3 groups	Hydrothermal process
Cement and Concrete	High reactivity, high surface area, absence of crystallinity	[7, 9-12, 30, 71-91]	95-98%	Acid pre-treatment before incineration at temperature less than 700°C
Zeolites	High purity and high porosity	[92-105]	> 99.5%	Acid pre-treatment before incineration at temperature less than 700°C in regulated environment
Aerogels	High purity	[14, 15]	> 99.5%	Acid pre-treatment before incineration at temperature less than 700°C in regulated environment
Cordierite	High purity/ reactivity	[20, 106]	> 99.5%	Acid pre-treatment before incineration at temperature less than 700°C
SiC	Complex	[16, 17, 107]	95-98% and possessing Q2 and Q3 groups	Complex

CURRENT RESEARCH AND DEVELOPMENT IN THE PRODUCTION OF RICE HUSK SILICA

The hydro thermo-baric process is currently receiving attention in our laboratory and has a great promise for the production of rice husk silica with varied degree of purity. The process refers to that which utilises single or heterogeneous phase reactions in aqueous media at high temperature (>243°C) and pressure (>3 MPa) to cause leaching or solubilising of oxide impurities as well as degradation of organic compounds in rice husk. The principle behind the process in which water is the sole aqueous medium is that water can dissociate at high temperature and pressure, forming hydronium ions (or hydrated protons or protonised water: H_3O^+) as well as hydroxyl (OH^-) ions, thus behaving like an acid-base system capable of reacting with basic and acidic oxides. This process can leach away or reduce the metal impurities of rice husk to the levels that are acceptable in several industries utilising silica as raw material. Also, the organic components (hemi-cellulose, cellulose and lignin) of the husk are expected to be converted to sugars and acids or other low molecular weight organic compounds to a large degree. This leaves only a small portion of these cellulosic components in the post-treated rice husk, thus reducing the incineration time, smoke generation, cost and rigour required to obtain silica from the husk.

The equipment and set-up used for this process is shown in Figure 6. The reactor vessel was designed and fabricated specially for this purpose from stainless steel grade 304 and consisted of a 150-ml cavity, in which the purification reactions take place. The cavity was bored in a 6-mm-thick, closed-end cylinder, with the closed end having a thickness of 30 mm. The cylinder cover and flange had the same thickness of 15 mm. In this process, a certain amount of the dry rice husk sample is placed in the reactor cavity with one-third of the vessel filled with deionised water. The vessel is sealed tightly and placed in a furnace with a constant temperature of 300°C to heat up and maintain the hydro thermo-baric conditions. The reactor is then soaked at this temperature for a varied period depending on the level of purity desired. At the end of each soaking period, the non-liquid residue in the reactor is dried and heated in a furnace at 650°C for 2-3 hr to get rid of any remnants of cellulosic materials remaining in the residue. After the incineration procedure, the ash obtained is pulverised in a ceramic mortar to afford nanosilica.

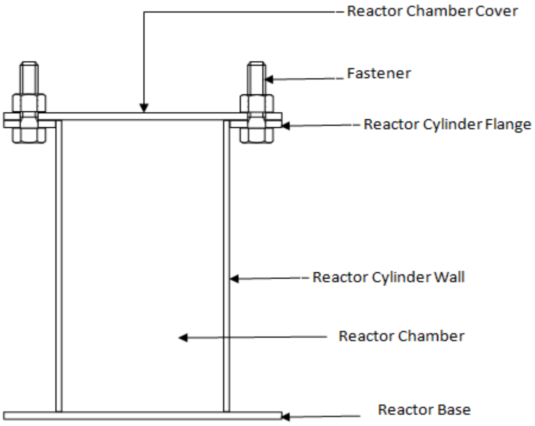

Figure 6. Schematic diagram of a hydro thermo-baric reactor

The advantage of this method is that it can reduce processing time and by controlling process variables, different degrees of purity can be obtained. The process is capable of selective leaching, depending on which process variables are altered. The principal process variables include temperature, soaking time and ratio of husk to water. This process has been optimised in our laboratory and the purity level of silica produced approaches 99.5%. In addition, the silica obtained is porous with high surface area and can be made to retain residual carbon if so desired.

CONCLUSIONS

A review of the processing methods of rice husk and properties of the silica product obtained has been presented. It is clear from the processing methods that, apart from the TORBED system for the production of silica of purity around 95% which has been commercialised, all other processes still have the problem of scalability from laboratory scale to industrial level. This situation is still the same as in a previous review years ago. It is hoped, however, that the research evolving from our laboratory would be able to bridge this gap and take high-purity silica production from rice husk to a level that can support industrial demands at low cost and low environmental and personnel risks.

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