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A Direct Comparison of Processing Methods of High Purity Rice Husk Silica

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ABSTRACT
It is an established fact that rice husk is rich in amorphous silica which when extracted in sufficiently pure form, could be used in several industrial applications and in the manufacture of value added products. Many of the processes employed for the purification of rice husk silica involve the use of strong acid and bases, requiring complex unit operations and extended times, apart from their unfriendliness to environment and personnel. The hydro thermobaric process was developed as a viable alternative to these rice husk silica purification processes. This study reported a performance comparison in terms of product purity, yield, structure and processing time between the newly developed hydro thermobaric and other previously used processes. The new process surpasses others in terms of processing time and yield while being at par with them in terms of product quality and structure.

Key words: Rice husk, silica production, hydro thermobaric processing, purification methods, product purity

INTRODUCTION
It has long been established (Tzong-Horng, 2004; Real *et al.*, 1996; Rozainee *et al.*, 2008) that Rice Husk (RH) is a viable source of high quality and quantity opal silica. Rice husk silica has found much use in several applications, examples of which include: as a good pozzolan in cement industry (Zain *et al.*, 2011), aerogels (Tang and Wang, 2006), SiC (Krishnarao *et al.*, 1994), solar grade silicon (Sun and Gong, 2001), zeolites (Panpa and Jinawath, 2009), cordierite (Chandrasekhar *et al.*, 2003), insulating refractories (Goncalves and Bergman, 2007).

The quality and state of rice husk silica determines the application for which it is best suited. Several researches have been targeted at obtaining high purity silica from rice husk. Rozainee *et al.* (2008) applied the fluidized bed combustion method while the sol-gel (or acid-base precipitation) method was used by Kalapathy *et al.* (1999) to produce silica of purity a little over 97%, with lower sodium content from rice husk ash. Tzong-Horng (2004) produced amorphous nano-structured silica powders with average particle size of 60 nm and high specific surface area using a combination of acid leaching, non-isothermal decomposition of rice husk in an air atmosphere at temperatures between 27 and 727°C using different heating rates, followed by basic treatments and water washing. Real *et al.* (1996) and Yalcin and Sevinc (2001), have demonstrated that homogeneous size distribution of nanometric silica particles could be obtained by burning acid pre-treated rice husk at 600-800°C in a pure oxygen atmosphere. Mehdinia *et al.* (2011) worked to purify rice husk silica by reducing the hydrogen sulfide content in it through a physical filtration system.

However, there have been some persistent inherent challenges in these methods. First, is the apparent lack of viability of scaling up these methods to levels of production that could support commercial or industrial applications, at low cost. Secondly, since they involve the use of acids and bases at temperatures not below their boiling points, it is controversial and doubtful if the benefit accruing from the use of these methods can be as advantageous as the dangers they pose to the environment and personnel. In seeking to make the industrial application of rice husk silica attractive, there is need to carry out research into more economically viable ways/methods which are both environmentally and personnel benign to mass produce high purity nanosilica from rice husk, at levels that would support supplies to the industries that use it as raw material. For this reason, a novel method, called the hydro thermobaric process was developed in our earlier paper (Ugheoke And Mamat, 2012), this study postulated that this new method is inexpensive, fast, commercially scalable and viable, environmentally and personnel friendly, when used for the production of high quality nano silica from rice husk.

This study was aimed to do a direct comparison of the developed method with other methods, in terms of processing time, product structure (XRD analysis) as well as product yield and product purity. To achieve this aim, this study has described the theory of the developed method and the procedures employed to evaluate the silica obtained from the method, followed by the comparative analysis of some of the processes that have been used to purify rice husk silica.

MATERIALS AND METHODS

The hydro thermobaric theory: The hydro thermobaric purification refers to a process that utilizes single or heterogeneous phase reactions in aqueous media at high temperature (T>516 K) and pressure (P>3 MPa) to cause leaching or solutionizing of oxide impurities as well as degradation of organic compounds of rice husk. The theory behind the process in which water is the sole aqueous medium, is that water could dissociate at high temperatures and pressure, forming hydronium (or hydrated proton or protonized water) (H_3O^+) ion as well as the hydroxyl (OH^-) ion, thus behaving like an acid-base system, capable of reacting with basic and acidic oxides. This process can leach away or reduces the metal impurities of the rice husk to levels that are compatible with and acceptable in several industries utilizing silica as raw material for manufacture. Also, the organic components (the hemicellulose, cellulose and lignin) of the husk are expected to be converted to sugars and acids or other organic compounds and solvents (to a large degree). This leaves only small portions of these cellulosic components in the post-treatment rice husk, thus reducing the incineration time, smoke generation, cost and rigours required to obtain the silica from the husk.

Materials and procedures for hydro thermobaric treatment: The major material is rice husk obtained from the stockpiled bags of Malaysian rice husk purchased by the Universiti Teknologi PETRONAS. The reactor setup as used in the process is shown in Fig. 1 and the rice husk treatment flow procedures are summarized in Fig. 2, although details of the procedures are reported in our earlier publications (Ugheoke And Mamat, 2012).

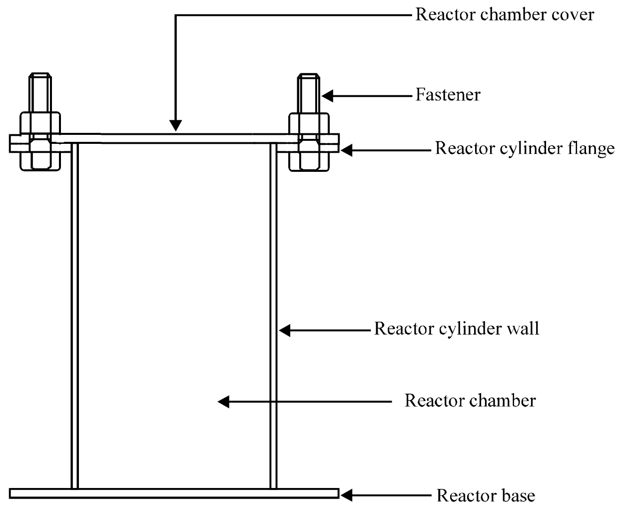

Fig. 1: Setup for the hydro thermobaric process

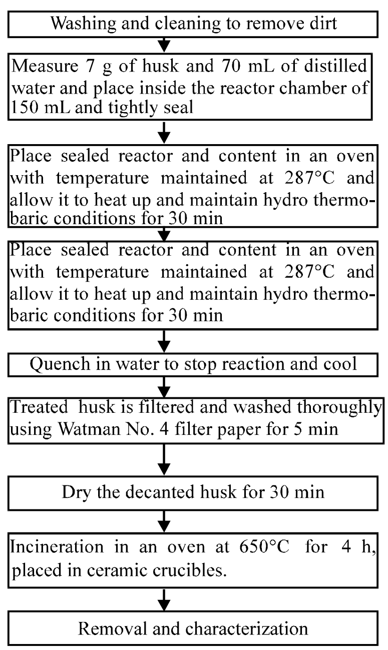

Fig. 2: Process flow for the hydro thermobaric purification of rice husk

Product characterization procedures: The product properties investigations that were undertaken include product yield, product structure and morphology (FESEM and XRD), purity (composition determined by XRF). The procedural details followed in these tests had been reported in our earlier publication . Surface area and pore volume analysis of the silica obtained from this process were carried out using the BET method.

Comparative analysis procedures: In the choice of processing methods to be considered in the present analysis, it was decided that processes which do not focus on product purity and structure improvement would not be included in the analysis. Thus, open field burning and fluidized bed combustion of rice husk processes do not form part of the present study. Basically, the processing methods considered in this research paper are those which employed acid (mineral or organic), alkali or distilled water for treatment of the husk, either before or after (or combined mode- before and after) incineration. Direct comparison of quantitative results is made. Where possible, as in the case of structure and morphology, qualitative statements are considered. Detailed discussion of the information arising from the comparison made follows the results presentation.

RESULTS AND DISCUSSION

Effects of the hydro thermobaric process on purity of product: Table 1 shows the details of chemical composition of both the treated and untreated husk obtained by XRF, indicating the effectiveness of the hydro thermobaric process in removing the impurities in rice husk silica, with the 45 min treatment yielding a product with as high as 98.8% pure silica. Such purity level could support wide ranging industrial products such as zeolite, aerogel and refractory production. The percentage purity of silica obtained from the process in comparison with those obtained from other processes being investigated is shown in Table 2.

Effect of the hydro thermobaric process on the morphology and structure of the product: From Table 3, it is clear that if more time was spent in washing the treated samples prior to the incineration step, more of the oxide of phosphorus would have been leached away (since P_2O_5 is soluble in cold water) giving the hydro thermobaric method percentage purity in excess of those of the other processing methods.

Morphologically speaking, the product is made up of silica with nanometric particle size in the agglomerated form, as revealed by the FESEM image in Fig. 3. Other studies like Tzong-Horng (2004) have reported similar findings. Figure 4 shows the x-ray diffractogram of a representative

Table 1: Composition of the untreated (UTDOO) and treated (HTB45) rice husk silica by XRF analysis

Item (%)	UTDOO	HTB45
SiO_2	91.2500	98.9000
K_2O	3.8290	0.1110
P_2O_5	2.4500	0.5160
CaO	0.8750	0.1800
SO_3	0.6610	0.0000
MgO	0.5730	0.0000
Al_2O_3	0.1800	0.2100
Fe_2O_3	0.0866	0.0829
MnO	0.0726	0.0000
Rb_2O	0.0143	0.0000
ZnO	0.0111	0.0000

Table 2: Percentage pure silica in the obtained product

Parameter	Method	Result (% silica in ash)	References
Purity (That is % silica in the product)	XRF	98.90	Present study
	Weight loss on volatilization	99.66	Yalcin and Sevinc (2001)
	XRF	99.77	Umeda and Kondoh (2008)
	XRF	98.14	Nittaya and Apinon (2008)
	ICP	93.00	Kalapathy *et al.* (2000)

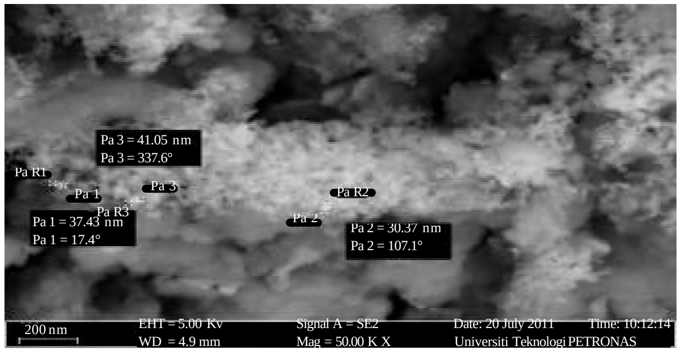

Fig. 3: Representative FESEM image of silica obtained

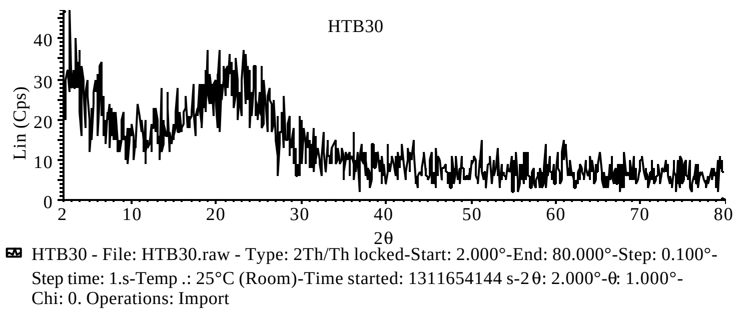

Fig. 4: X-ray Diffraction pattern of representative sample

Table 3: Comparison of silica yield of the process- treated versus untreated samples

Ash yield (g)		
Treated	Untreated	Percentage yield ratio (treated upon untreated samples)
0.9	1.010	89.109
0.95	1.000	95.000
0.925	1.050	88.095
1	1.025	97.561
0.925	1.000	92.500

Table 4: Comparison of effect of processing method on the product structure

Parameter	Method	Result	Remark	References
Structure (either crystalline or amorphous) measured by XRD	XRD	Amorphous		Present study
	XRD	Amorphous		Yalcin and Sevinc (2001)
	-	Not done	It was not part of research aim	Umeda and Kondoh (2008)
	XRD	Amorphous		Nittaya and Apinon (2008)
	XRD	Amorphous		Kalapathy *et al*. (2000)

sample produced after 30 min of hydro thermobaric treatment. It is clear from the crest of the plot that the samples are amorphous in structure. As is evident from Table 4, it implies that, like other process reported by Yalcin and Sevinc (2001) or Nittaya and Apinon (2008), the process does not have negative effect on the structure of the product.

Table 5: Surface area and pore characteristics of the produced rice husk silica

Sample	BET surface area ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Average pore diameter (nm, 4V/A)
UTDOO	21.42	0.0845	17.81
HTB45	133.94	0.2813	6.41

Table 6: Comparison of process yields

Method	Result	References
Hydro thermobaric process	92.3	Present study
Pre and post-chemical treatment	-	Yalcin and Sevinc (2001)
Citric acid leaching	94.6	Umeda and Kondoh (2008)
Precipitation	90.3	Nittaya and Apinon (2008)
Alkaline extraction-acid precipitation	91.0	Kalapathy *et al*. (2000)

Table 7: A comparison of the processing times of different processes

		*Processing time (h)				
Parameter	Method	Pre-treatment	Post-treatment	Others	Total time (h)	References
Processing time	Hydro thermobaric	½			½	Present study
	Boiling in 3% v/v HCl	2	-		2	Yalcin and Sevinc (2001)
	Leaching with citric acid at boiling point	1	-	¼ water rinsing	1 ¼	Umeda and Kondoh (2008)
	Precipitation method by boiling in 5 N NaOH for hours	3	-		3	Nittaya and Apinon (2008)
	Precipitation and back-titration using concentrated acids and bases	-	1	20	21	Kalapathy *et al*. (2000)

*Times shown are those involved in impurity removal from either the raw rice husk or its ash but are non-inclusive of the incineration time required for completely grey ash formation which is assumed to be an average of 4 h

Product surface area and pore size analysis: The surface area and pore size analyses carried out by the BET method yielded acceptable results, as shown in Table 5. These values imply that the product is reactive due to its high surface area.

Process yield: The process yield is an indication of the material wastefulness that results from the use of a given process in purifying rice husk silica. In a nutshell, it is a measure of the process efficiency, when combined in some ways with the processing time. The yield of silica from the process is shown in Table 3 which directly compares the product of the treated and untreated samples. The average of the yield for the five batches was 92.5 for the treated sample. Table 6 compares the yields of the various processes under consideration. As is evident from Table 6, the yield from the hydro thermobaric method surpasses several from other processing methods.

Comparative analysis of different processes

Processing time: In terms of processing time, it is demonstrable from Table 7 that the hydro thermobaric process remains the fastest of all the processes under investigation with a processing time of less than an hour while some other process net as much as 21 h.

Product structure: The HTB process only purifies silica from rice husk by leaching away the oxide and organic impurities in it but like other processes, has no effect on the structure of the product. Thus, like other processes, the silica obtained from the HTB process remains amorphous (Table 4) as long as the temperature used to obtain it is kept at less than 700°C.

Yield of the process: From Table 6, apart from Umeda and Kondoh (2008) who reported a yield of about 94%, the HTB is the next in line in terms of yield and when we consider the time spent in each process (Umeda and Kondoh, 2008) -75 min and the HTB-30 min) together with the safety considerations, the HTB naturally becomes preferable.

Product purity: The product purity of the HTB is at par with the rest processes and when time is factored into the analysis, the HTB gets the upper hand.

CONCLUSION

The study outlines the properties of hydro thermobaric processed rice husk silica and shows that its amorphous structure is unaffected by the process which produces silica of nanometric particle size, with high surface area. The hydro thermobaric method has a processing time of approximately half an hour, with product yield and purity at par with those obtained from the best of all other processing methods. It is therefore, inferable that the newly developed process has an overall better performance index compared to the other existing methods.

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