Can We Make Money From Rice Husk

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Rice is the world's second most important cereal crop following only to corn. The Food and Agriculture Organization's (FAO) statistics says world milled-rice production in recent years is about 750 million metric tons. According to the Department of Census and Statistics in Sri Lanka the contribution to the world's rice production from Sri Lanka in recent years is about 1.8 million metric tons per annum. Milling is a vital step in post harvest production of rice. The major objective of rice milling system is to remove the husk and the bran layers, and produce white rice kernel that is well milled and free of impurities. Scholars found that $1/5^{th}$ of the paddy represent the shell which in turn tells us that approximately 0.45 million metric tons of rice husks are produced per annum.

Disposal of rice husk is one of the major challenges faced by many rice-millers all over the world because hundreds of millions of tons entering the waste stream each year. In some countries the husks are burnt in electricity producing incinerators. However that process creates millions of tons of ash. When rice husk burns $1/4^{th}$ of the content is ash, which is still a great environmental threat but on a positive note, the rice husk ash (RHA) contains 60% to 80% amorphous silica, which has application in various industries such as rubber reinforcement as in tyre industry, plastic reinforcement industry, food, healthcare, cosmetics, catalyst, coatings, pulp and paper processing. Thus the ash generated can be stored for silica extraction.

For a moment if we assume all the rice husks produced in Sri Lanka can be collected and if the ash contains 70% of silica then we should be able to extract 78750 metric tons of Silica. In practical conditions, it is impossible to collect all the rice husks produce all over the country. However, if we have a proper mechanism we can easily collect 50% of the rice husks. That means we should be able to produce 39375 metric tons of silica per annum. The conventional silica that is exported for tire industry in Sri Lanka costs around 800 USD. If we can replace conventional-exported-silica from RHA-silica we can save around 31.5 million USD per year. If the production cost is 500 USD per metric ton still we will have net profit of 11.8 million USD per year. This saving is purely form-extracted silica. Along with silica, there are other by-products like carbon and sodium carbonate that are useful in various industries and can generate additional dollars for the country.

The extracted silica from RHA has several advantages over the conventional silica. First and foremost, it is from a bio source and is non-toxic. Secondly, this silica is extracted from waste hence nullifying the raw material cost. Further, any industry that uses rice husk as fuel for cogeneration can benefit from this technology.

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If we can't sell the silica for local industries one might think who is going to purchase this renewable silica. The good news is many industries including US based tire manufacturer, Goodyear, is producing fuel-efficient tires though the use of rice husk waste. According to the Goodyear's web page (*last access on20/10/2019*) they plan to use ash leftovers from the burning of rice husks to produce electricity as an "environmentally friendly source of silica" for use in their tires. Silica is a compound that mixed with rubber used in tire treads to increase the rubber's strength and help reduce the tire's rolling resistance. Lower rolling resistance helps improve a vehicle's fuel economy. Some of the Chinese companies have already worked with Goodyear to make more environmentally friendly tires. Further, Goodyear is negotiating with potential suppliers to purchase rice husk ash silica because sustainable supply is the challenge. According to the statistics of the Goodyear Tire and rubber company the current suppliers of this silica can satisfy only a very small percentage of Goodyear's needs. Thus, we have a potential to enter to this emerging market.

In conventional silica productions sodium silicate is manufactures by fusing pure silica sand with Soda ash in Rotary furnace at 1300 °C, using various SiO_2/ Na_2O ratios. This technique is highly energy intensive, as it requires the reactants to be heated to high temperatures. Then this sodium silicate is subjected to acid precipitation to produce precipitated silica. Sodium sulphate is a waste that is generated and this liquid effluent requires elaborate treatment to meet emission standards. In contrast preparation of conventional silica, RHA silica can be extracted in few steps. First, RHA is digested with sodium hydroxide to make sodium silicate solution.

$$NaOH + RHA \rightarrow Na_2SiO_3 + H_2O$$

Once sodium silicate solution is prepared to pH of the medium should be lowered to precipitate SiO_2. pH adjustment can be basically done using any acid. We have used hydrochloric acid, sulfuric acid and even CO_2 gas. As reported in many scholarly works use of mineral acids introduces many issues such as costly effluent treatments. Our research group has successfully used CO_2 for sol-gel process as well as in-situ powder formations by spray drying method. The formation of SiO_2 with CO_2 is shown in the following equation.

$$2Na_2SiO_3 + 2CO_2 \rightarrow 2Na_2CO_3 + 2SiO_2$$

The details of the CO_2 process can't be disclosed at this moment. In this process the chemicals used can be regenerated as shown in the following reaction thus eliminating expensive effluent treatment plant.

$$Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3$$

Then CO_2 can be prepared by thermally treating the $CaCO_3$ and resulting carbon dioxide can be used for the precipitation step.

$$CaCO_3 \rightarrow CaO + CO_2$$

One drawback of regeneration step is the use of high temperature of about 850^oC to decompose the $CaCO_3$. In an industrial process the energy requirement can be achieved by incinerating the rice husk. Calcium oxide can be reacted with water to give calcium hydroxide, which is sent to the regenerator so that sodium hydroxide and calcium carbonate is produced when sodium carbonate reacts with it.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Theoretically this process is zero cost in terms of chemicals needed for the process. The materials obtained through this method exhibit high levels of purity and homogeneity.

Our research group is extensively work on this specific project to produce silica with tunable characteristics and check the compatibility with rubber matrices to improve the mechanical properties. The microstructure, elemental compositions, functionality and porosity extracted SiO_2 powder was evaluated by using SEM-EDX technique, X-ray diffraction spectroscopy (XRD), FT-IR technique, Brunauer-Emmett-Teller (BET) surface area analysis.

The Figure 1 a shows the gel of silica formed in presence of different acids while Figure 1 b shows the purified silica.

Figure 1. Photograph of (a) silica gel and (b) Purified silica

The microstructure and elemental composition of the purified silica was evaluated by SEM-EDX technique. The Figure 2 shows the SEM images of the silica while Table 1 shows the elemental composition of the samples obtained by EDX technique. It is interesting to note that silica was found to be present in solid aggregates.

Further zoomed-in images confirm the presence of fine particles of size less than 1µm. This confirms the solid chunks are the accumulated smaller particles.

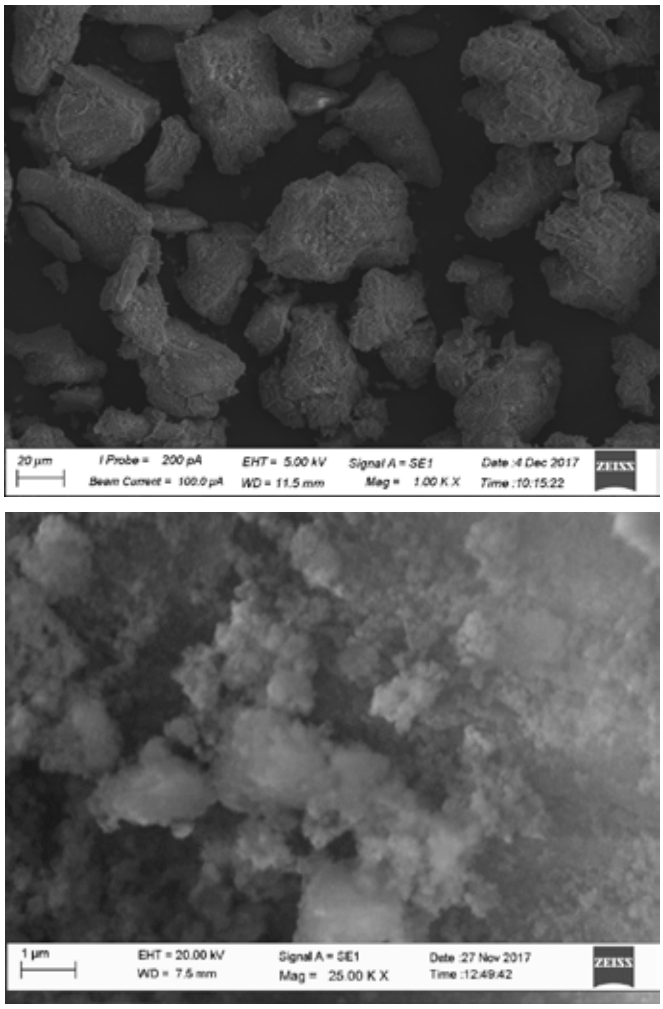


Figure 2. Scanning Electron Micrograph of purified silica extracted from RHA

An elemental composition analysis of the purified and unpurified RHA silica was carried out by energy dispersive X-ray spectroscopy (EDX). The data is given in the Table 1. The EDX spectra of both samples showed the characteristic peaks for the two elements at 0.5 keV and 1.73 keV, which correspond to the spectral lines of O and Si. In addition, several other peaks were observed for unpurified silica, which were absent in the purified silica. This is further confirmed by the XRD analysis of unpurified silica as shown in the Figure 3 a. It confirms the purification process that we followed were sufficient enough to remove the impurities present in the silica. Moreover, the EDX analysis confirmed that the synthesized materials formed in a good stoichiometric ratio.

Table 1. Elemental composition of unpurified and purified silica determined by Energy dispersive X-ray diffraction technique

Element	Weight Percentage (%)	
	Unpurified Silica	Purified silica
C	14.11	-
O	58.08	70.42
Na	3.01	-
Si	23.12	29.58
K	0.27	-
Fe	0.07	-
S	1.33	-

The XRD pattern of the extracted SiO_2 powders from RHA is shown in Figure. 3. The presence of sharp peaks with broad halo in Figure 3 a confirmed the presence of crystalline impurities in amorphous silica. After acid wash the peaks disappears. Absence of sharp peaks in the XRD pattern indicated the absence of crystalline materials while the broad halo confirms the presence of amorphous nature of the material. The Figure 3 c shows the XRD pattern of commercially used silica in tyre tread industries which is identical to the pattern of extracted silica. Therefore, the RHA silica powder confirms the characteristics of the commercially available silica.

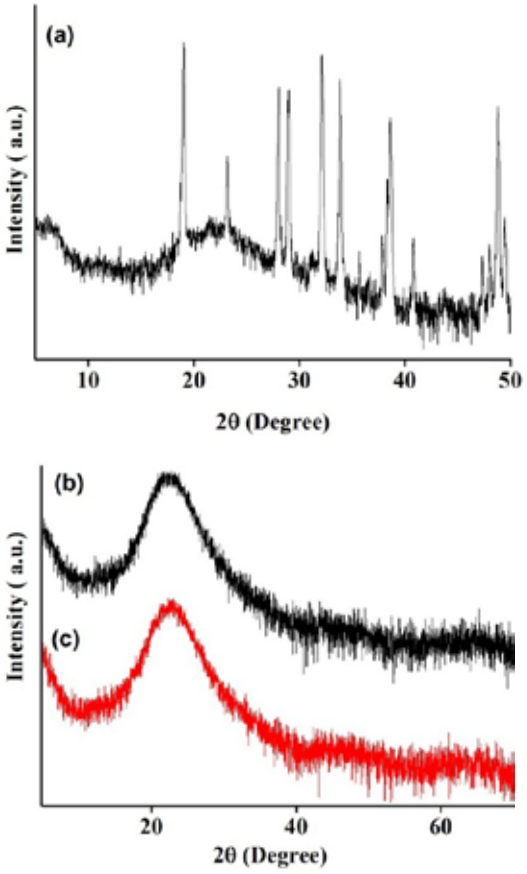


Figure 3. X-ray diffraction pattern of (a) unpurified silica (b) purified silica using acid digestion and (c) commercially used silica in local tyre tread industry

To evaluate the chemical bonding of the purified SiO_2 powder, Fourier transform infrared (FTIR) transmittance spectra were taken. The FTIR spectrum of the silica powder is shown in Figure 4. The corresponding bond vibration modes for different peaks are labeled on the spectrum.

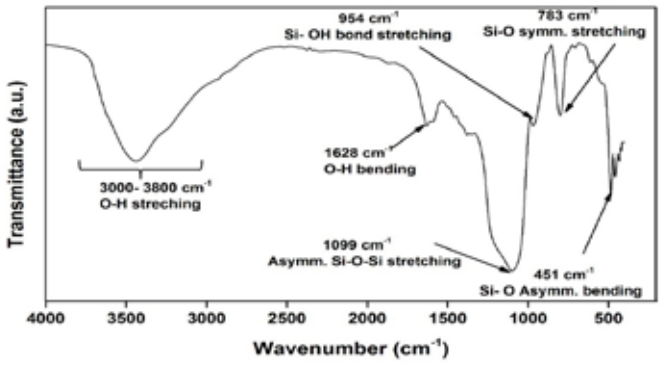
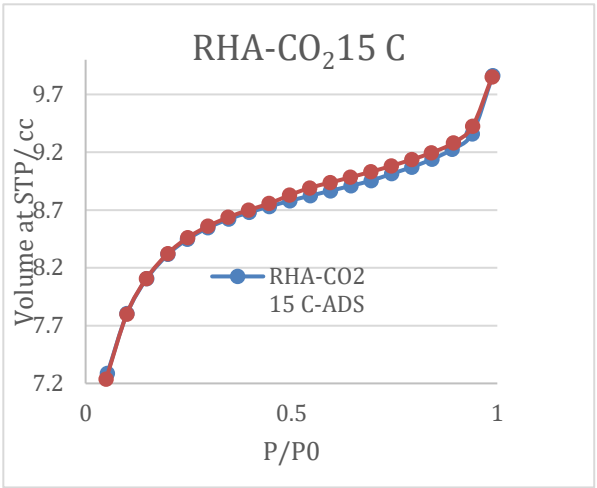


Figure 4. FTIR spectrum of purified silica extracted from rice husk ash

One of the major goals of project was to develop silica particles with tuneable surface characteristics so that the extracted silica can be applied to many different applications. The surface area and the pore characteristics of the silica particles were determined using the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods. Representative adsorption-desorption isotherms of the porous silica are shown in Figure 5. It is clearly seen that the surface adsopption-desorption behavior is different in the same silica extracted from different methods. The surface characteristics are summarized in Table 2. The results confirms that we have synthesized silica particles with spectrum of surface characteristics compared to the commercial silica used in local tyre tread industry.



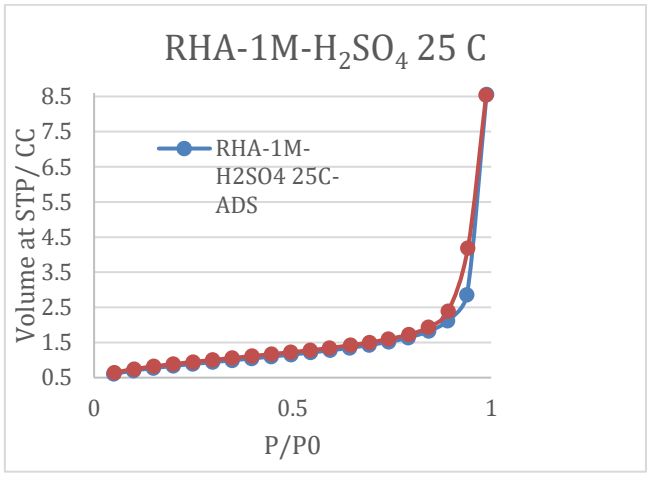


Figure 5. The nitrogen adsorption-desorption isotherm of the extracted silica

Table 2. Surface characteristics of extracted silica powders.

Sample name	Specific surface area/ m^2g^{-1}	Total pore volume/ ccg^{-1}	Average pore radius/ nm
RHA-CO2 15 °C	626.545	0.3676	1.17331
RHA-CO2 50 °C	460.788	0.3966	1.7216
RHA-CO2 80 °C	290.835	0.3205	2.20367
RHA-1M-H_2SO_4 25 °C	116.807	0.5233	8.96079
RHA-1M-HCl 25 °C	43.054	0.1726	8.01578
RHA-5M-HCl 25 °C	25.881	0.05985	4.16135
Commercial silica	150.957	0.439	0.58161

In rubber industry, silica is widely used as a non-black reinforcing filler to improve the mechanical properties particularly tensile strength, tear resistance, abrasion resistance and hardness of NR and synthetic rubber composites. However, a major problem with silica-reinforced rubber is the incompatibility between the hydrophilic silica and hydrophobic rubber molecules. A well-known method for improving the reinforcement effect is to treat the silica surface with Silane coupling agents to promote interaction between silica and polymer chains. In our work we have tried to reinforce the NR and synthetic rubber lattices with *in situ* coupling of silica with silane coupling agents. As a representative data the Figure 6 and Figure 7 shows the abrasion volume loss and percentage of equilibrium swelling in presence of toluene in NR/NBR/silica composites. We have developed this material as O-rings and oil/solvent sealers for Rotary-evaporators.

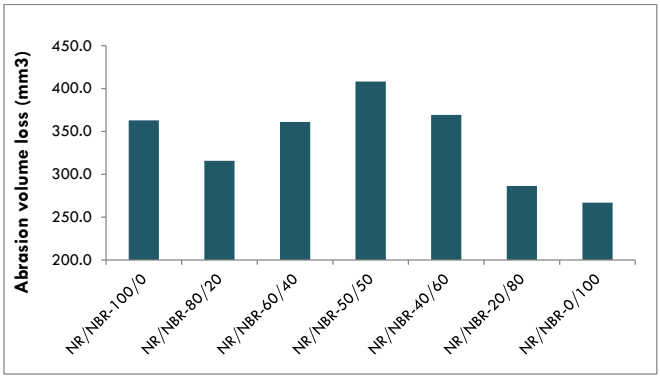


Figure 6. Abrasion volume loss of NR/NBR/silica composites with different NBR and silica loadings

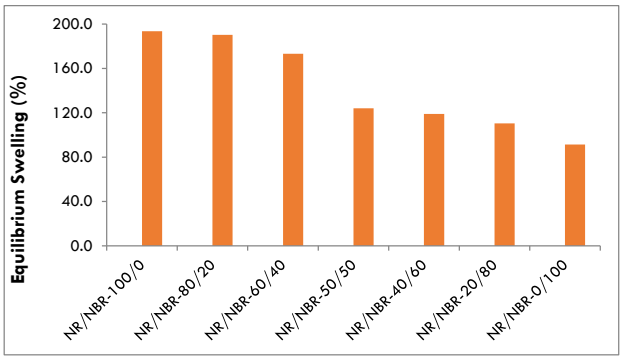


Figure 7. Equilibrium percentage of swelling of NR/NBR/silica composites with different NBR and silica loadings

We have used these oil/solvent sealers in the rotary evaporators used in our laboratory. So far these sealers are being used for approximately six months and no failures have been reported. The Figure 8 shows the sealer that we made and the instruments that the sealer was fixed. Our research group is producing many rubber-based products using this extracted silica and evaluation of their performances are undergoing.

Figure 8. Photograph or sealers made by the NR/NBR/silica composites and its uses

Last but not least, I belive our scientists must tap on the technology to extract this valuable resource from basically almost zero-cost waste at the moment in Sri Lanka. If our entrepreneurs enter to this emerging industry one day we might be able to see many rubber-based products made using RHA-silica. On top of that we can be very proud considering the impact on the environment in the sense of waste management.

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