Int.J.Curr.Microbiol.App.Sci (2017) *6*(10): 1144-1156

EXCELLENT PUBLISHERS

International Journal of Current Microbiology and Applied Sciences
ISSN: 2319-7706 **Volume 6 Number 10 (2017) pp. 1144-1156**
Journal homepage: http://www.ijcmas.com

Review Article https://doi.org/10.20546/ijcmas.2017.610.138

Rice Husk and Its Applications: Review

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Keywords

Rice husk, Rice husk ash, Silica, Refractory industry, Sorbent.

Article Info

Accepted:
10 September 2017
Available Online:
10 October 2017

ABSTRACT

Rice is staple food of more than half world. Therefore, rice processing and associated business are growing vigorously. Rice husk obtain from rice milling process as by product. It is attracting as value added material for domestic and industrial processing such as preparing valuable silicon based materials, cement, as source of pet food fibre and as source of dietary fibre, preparation of activated carbon, refractory industry, polymer, rubber, preparing sorbent for waste water treatments, in bio ethanol production, to control of insect pests in stored food stuffs, ceramic industry and biosynthesis of silica nano-particles. Extensive research has been done to utilize important properties of rice husk and its ash for industrial applications. Summarising all these data could be helpful for smooth future research on rice husk and rice husk ash.

Introduction

Rice husks have been attracted as value added material towards waste utilization and cost reduction in domestic and industrial processing. Rice husk (RH) is widely available in rice producing countries like China and India which contributes 33% and 22% of global rice production respectively, as by-product of the rice milling. RH content ranges from 16-25% of paddy (Della *et al.*, 2002; Giddel *et al.*, 2007; Soltani *et al.*, 2015). Every year approximately 500 million tonne paddy produced by world and 120 million tonnes of paddy produced by India, it gives around 24 million tonnes of RH per year (Shwetha *et al.*, 2014). Rice husk ash (RHA) is the by-product of RH, when it burnt in ambient atmosphere. 20 million tonnes produced per year by world (Koteswara and Pranav, 2011; Soltani *et al.*, 2015). Due to low density and less commercial interest of RH, handling as well as transportation it is problematic, which creates disposal and serious environmental problems (Pode, 2016).

High-value applications such as the use of RHA in synthesis of silica, activated carbon, silica gels, porous carbon, zeolites, silicon carbide, silicon nitride, manufacturing of silicon chip and light weight construction materials insulations, catalysts, cordierite, ingredients for lithium ion batteries, graphene, energy storage/capacitor, carbon capture. Other applications include in the manufacture of soluble silicate, silicones and its alloy, silicon based chemicals, reinforcing filler in natural and synthetic rubber (Karera, 1986; Patel, 1987; Conradt *et al.*, 1992; Krishnarao and Godkhindi, 1992; Wang *et al.*, 1998; Della *et al.,* 2002; Naskar and Chatterjee, 2004; Sun and Tzong-Horng, 2004; Wu *et al.*, 2004; Mohamed *et al.*, 2015; Pode, 2016). Due to lack of awareness of its properties and applications, rice husks are not being utilized effectively. Therefore, application of RH and RHA in domestic and industrial processing not only useful to increase farm income in directly and indirectly way but also it is the alternative solution to disposal problem of RH. In this review we are discussing about composition and applications of RH and RHA in commercial and industrial sectors.

Composition of rice husk

RH contents are hemicelluloses 24.3%, cellulose 34.4%, lignin 19.2%, ash 18.85%, and the other trace elements 3.25%. Hemicelluloses used as recourse of activated carbon, xylose and silicon dioxide. RH contents main elemental components as Carbon 37.05%, Hydrogen 8.80%, Nitrogen 11.06%, Silicon 9.01% and Oxygen 35.03 % (Joseph *et al.,* 1999; Sarang *et al.,* 2009). Husk contains 17-25% silica (Patel *et al.*, 1987; Conradt *et al.*, 1992; Real *et al.*, 1996). Rice husks have bulk density of 96-100 kg/m^3, hardness (Mohr's scale) 5-6, ash 22.29%, Oxygen 31-37%, Nitrogen 0.23-0.32%, Sulphur 0.04-0.08%, Hydrogen 4-5% (Muthadhi *et al.,* 2007). The composition of RH depends on many factors such as rice variety, type of fertilizer used, soil chemistry, and even the geographic localization of the production (Bining and Jenkins, 1992; Muntohar *et al.*, 2002).

Composition of rice husk ash

RH is high in ash content as compared to other biomass fuels ranging 14-25% (Chandrasekhar *et al.*, 2005; Adam *et al.*, 2006). Silica content in RHA varies from 83-98% (Adam *et al.*, 2006; Rozainee *et al.*, 2008 and Pode, 2016). Presence of high amount of silica makes it a valuable material for use in industrial applications. Chemical composition of RHA determined by X-ray fluorescence (XRF) as SiO_2 89%, Al_2O_3 1.20%, C 18.24%, CaO 1%, K_2O 1.22%, Fe_2O_3 1.28% (Mohamed *et al.*, 2015). There are various factors which affects the ash properties such as, incinerating conditions (temperature and duration), rate of heating, burning technique (Govindarao, 1980; Mansaray and Ghaly, 1999).

Application of rice husk

Unique physical and chemical properties of RH, like high ash content, silica content, it can be effectively used in domestic and industrial processing. Many of reports shown that, RH is used as fuel for different purpose, such as in brick kilns, in furnaces, in parboiling process of rice, the raw material for the production of sodium silicate, as an cleaning or polishing agent in metal and machine industry, briquettes molecular sieve (Singh, 2000; Ugheoke *et al.*, 2006; Shwetha *et al.*, 2014).

As source of fuel

The calorific value of RH is 15217.20 KJ/Kg, efficiency of boiler found same as using of coal (68%) so RH is cheaper fuel than coal (Yadav and Singh, 2011; Velupillai *et al.*, 1997). Heat energy is produced by direct combustion and gasification of RH, it can be used for several processing such as generation of steam in parboiling of rice (Shwetha *et al.*, 2014; Prasara and Grant, 2011; Yadav and Sing, 2011). RH is potentially used for electric generation. 1 tonne of RH is required for producing 1 MWH electricity. It is also used as alternative fuel for household energy (Rozainee *et al.*, 2008). Reaction involved in fuel reactor according to composition of RH with 1 mole C, 0.6402 moles hydrogen (H_2), 0.3052 oxygen (O_2) as follows (Monga *et al.*, 2015).

$$C + 0.6402H_2(g) + 0.3052O_2(g) + 2.0298NiO = CO_2(g) + 0.6402H_2O\ (g) + 2.0298Ni$$

As sourse of silica and silicon based materials

Due to high silica content of RH now, it become a source for a number of silicon compounds, silicon nitride, silicon tetrachloride, including silicon carbide, silica, zeolite, and pure silicon. Also for preparing advanced materials like SiC, elemental Si, Mg_2Si, Si_2N_2O, SiN, silanes (Acharya *et al.*, 1980; Karera *et al.*, 1986; Padhi and Patnaik, 1995; Sun and Gong, 2001; Soltani *et al.*, 2014; Patil *et al.*, 2014). The reaction between SiO_2 of rice husk ash and NaOH can be expressed as the following reaction (Della *et al.*, 2002).

$$2xNaOH + ySiO_2 \rightarrow xNa_2O \cdot ySiO_2 + xH_2O$$

Neutralization of the obtained sodium silicate ($xNa_2O \cdot ySiO_2$) gives silica gel as follows (Real *et al.*, 1996)

$$xNa_2O \cdot ySiO_2 + xH_2SO4 \rightarrow ySiO_2 + xNa_2SO_4 + xH_2O$$

Silicon carbide (Si-SiC) also was synthesized from a powder mixture of rice husk ash-C-Mg. The overall chemical reactions can be expressed as (Niyomwas, 2009).

$$2\ SiO_2(s) + C(s) + 4(Mg) = SiC(s) + Si(s) + 4MgO$$

Silicon nitrate is produced by the nitridation of rice husk can be represented by the following reactions (Soltani *et al.*, 2015)

$$SiO_2(s) + C(s) = SiO(g) + CO\ (g)$$

$$SiO_2\ (s) + CO\ (g) = SiO\ (g) + CO_2\ (g)$$

$$SiO\ (g) + 2/3N_2\ (g) = 1/3\ Si_3N_4\ (s) + ½\ O_2\ (g)$$

The amorphous SiO_2 was thus reduced to form silicon according to the following reaction (Bose *et al.*, 1993)

$$SiO_2 + 2Mg = Si + 2MgO + SiO_2\ (unreacted)$$

As organic fertilizer

Today, organic fertilizer plays important role in agriculture. RH is utilized as an organic fertilizer to improve not only productivity but also water use efficiency in field (Govindarao1980; Ebaid, *et al.*, 2007; Badar and Qureshi, 2014). Many researchers reported, RH is used to improve of nitrogen and other macro and micro-elements absorption which enhancing the production and translocation of the dry matter content from source to sink (El-Wehishy and El-Hafez, 1997; Awad, 2001; Ebaid *et al.*, 2005; El-Refaee *et al.*, 2006; Ebaid, *et al.*, 2007). RH is bio transformed of into organic fertilizer through vermicomposting (Lim *et al.*, 2012; Shak *et al.*, 2014). Also it can be used as a source of potassium for growth and yield of cowpea (Priyadharshini and Seran, 2010).

As sourse of pet food fibre and as source of dietary fibre

Traditionally, RH has been used as ingredient in ruminant and poultry (Shqueir *et al.*, 1989; Aderolu *et al.*, 2004; Aderolu *et al.*, 2007). Rice husk has more than 30% dietary fibre, it is also an excellent source of protein and mineral, so it could use in food industry especially developing functional foods.

Enzymatic extraction gives more fiber from rice husk than chemical method (33.97% vs. 67.53%) and the extracted fiber had higher water-binding capacity and exhibited high fat binding capacity (Fadaei *et al.*, 2012).

Used for making bricks (as building material)

More porous and better thermal insulated brick can be made with high percentage of RH. Due to low thermal conductivity of air entrapped in pores, it makes porous fire brick structure suitable for back up insulation (Chesti, 1986; Ugheoke *et al.*, 2006). More adding rice husk less compressive strength and density of specimens, the porosity increases (Mbiminah, 1992; Sutas *et al.*, 2012; Watile, 2015). RH is excellent alternative material to ordinary portland cement for production brick (Chukwudebelu *et al.,* 2015). It is also used for building of roads in environment-friendly way (Lennox and Mackenzie, 2008).

Preparation of activated carbon

The unique properties such as high surface area, large adsorption capacity and fast adsorption kinetics makes activated carbons as valuable material for different industrial applications. Production of activated carbon from rice husk is achieved through activation with chemical or physical means (Della *et al.*, 2002; Rahman *et al.*, 2005; Tongpoothorn *et al.*, 2011; Van and Thi, 2014; Alvarez *et al.*, 2015; Mehta and Ugwekar; 2015). The Nano porous activated carbon with large specific area of 2523.4 m^2 g^{-1} was obtained from RH (Xu *et al.*, 2014).

The effect of alkali carbonate in the activation process can be related to formation of porosity due to SiO2 interaction with the carbonates, CO_2 reacts with the carbon phase with formation of CO, according following reaction (Soltani *et al.*, 2015)

$$M_2CO_3 + SiO_2 = M_2SiO_3 + CO_2$$

$$CO_2 + C = 2CO$$

Used for removal of toxic metals from waste water

The high silica content of RH it makes it insoluble in water, having good chemical stability, structural strength (Lee *et al.*, 1994). So it plays important role in water purification as well as in waste water treatment. Sorbent made by RH effectively used to removal of the six heavy metals such as Fe, Mn, Zn, Cu, Cd and Pb (Munaf, 2010; Daifullah *et al.*, 2003; Yalcın and Sevinc, 2000). RH is also used as adsorbent to remove various pollutants, phenols, dyes, pesticides, inorganic anions, organic compounds and heavy metals (Chauh *et al.*, 2005; Gupata *et al.*, 2006; Lata and Samadder, 2014).

In production of bioethanol

Bioethanol productions from RH are the key of solution to problems such as environmental, economic, and energy which are facing all across the world. Bioethanol is effectively produced by RH (Saha and Cotta, 2007; Srivastava, 2014). The global potential production of bioethanol in order of 20.9 to 24.3 GL per annum from RH, it has potential to satisfy around one fifth of the global ethanol bio fuel demand for 10% gasohol fuel blend (Abbas. 2010. Nyachaka *et al.*, 2013).

Other uses

High surface porous SiO_2/C composites from RH were fabricated by heating pellets composed of RH powders with different sizes (Warati *et al.*, 2006). It is used as adsorption of direct dyes from aqueous solution (Wahab *et al.*, 2005). Also used for production of xylitol, furfural, ethanol, acetic acid. It is more useful in a cleaning and polishing agent in metal and machine industries (Zurina *et al.*, 2004; Khalf and Ward 2010; Attharangsan *et* *al.*, 2012). RH has best binding ability, which reduces the formation of cracks. So it is used in preparing of biodegradable pottery products (Ammara *et al.*, 2012). Sometime it is used for the pillow stuffing (Kumar *et al.*, 2013). RH has been used as an industrial raw material for different purpose such as making panel board, insulating board material, fillers in plastics, filling material, building materials Farooquea *et al.*, 2009).

Application of rice husk ash

RHA plays important role in various industrial applications such as processing of refractory industry, ceramic, cement, fillers of rubber and plastic composites, cement, adsorbent and support of heterogeneous catalysts (Sevdalina *et al.*, 2012). Some of other industrial and domestic applications of RHA are discussing here**.**

Used as silica source

The presence of silica in RH has been known since 1938 (Martin, 1938). Due to its high silicon content RHA has become a source for preparation of silica (Della *et al.*, 2002; Singh *et al.*, 2008; Supakorn *et al.*, 2009; Supitcha *et al.*, 2009; Shelke *et al.*, 2010; Patil *et al.*, 2014). Precipitated silica widely used in many of the industries like electronics, ceramic, paint industry, polymer material, tyre industry, cosmetics, reinforcing agent in rubber, thickening agent in paints, thixotropic agents, thermal insulators, composite fillers, in toothpastes as a cleansing agent and anti-caking agent in food industry (Rama-Rao *et al.*, 1989; Dongmin *et al.*, 2010).

In Cement and Concrete Industries

RHA is used to enhance strength of concrete blocks as the filler in concrete blocks (Cisse, and Laquerbe, 2000). Lime pozzolana mixes with RHA could be a suitable partly replacement for portland cement (Mehta, 1977; Zhang *et al.*, 1996; Nicole *et al.*, 2000; Ganesan *et al.*, 2008; Kartini, 2011; Xu *et al.*, 2014). It is possible to increase compressive and flexural strengths (Zhang *et al.*, 1996; Ismaila, 1996), reduced permeability (Zhang *et al.*, 1996; Ganesan *et al.*, 2007), increased resistance to chemical attack durability and workability (Coutinho, 2002) with use of RHA in concrete.

In polymer industries

RHA have been used as fillers in polyethylene (Cisse and Laquerbe, 2000, Panthapulakkal *et al.*, 2005), polypropylene (Fuad *et al.*, 1995; Premalal *et al.*, 2002; Ismail, 2002), polystyrene (Ismail, 2003). RH and its thermal degraded products are often used as fillers in paper, paint (Chandrasekhar *et al.*, 2003), polymers (Saheb and Jog, 1999; Choi *et al.*, 2006), polymeric composites (Nassar *et al.*, 2007, Premalal *et al.*, 2003).

In vulcanizing rubber

To improve mechanical properties of natural rubber materials, incorporation of RHA with additives/silane coupling agent in rubber or rubber/plastic composites enhanced the mechanical/physical properties, filler dispersion and crosslink density (Ismail *et al.*, 1997; Siriwandena *et al.*, 2001; Ismail *et al.*, 2001; Arayapranee *et al.*, 2005). It is also used as fillers for epoxidized natural rubber compounds (Mehta *et al.*, 1995; Ismail *et al.*, 1997).

Manufacturing refractory bricks

In the manufacturing of refractory brick, RHA can be used profitably (Sutas *et al.*, 2012). The compressive strength of the bricks increased with rice husk ash contents but weight is decreases (Rahman 1988; Amin *et al.*, 2013). As compare to conventional clay bricks, rice husk ash admixture bricks, showed lower compressive strength and higher percentage of water absorption (More *et al.*, 2015; Malik and Arora, 2015).

Control of insect pests in stored food stuffs

RHA is effectively used to control of insects and pests in stored food stuffs. It is used against *Callosobruchus maculatus* (F) and *Sitophilus zeamais* (Mots) (Paneru and Shivakoti, 2000/2001; Adebayo and Ibikunle, 2014; Shazia *et al.*, 2006).

Effective as an oil spill absorbent made with RHA used in waterproofing chemicals, flame retardants, and as a carrier for pesticides and insecticides (Kumar *et al.*, 2012). It has shown that to keep stored potatoes free of the potato tuber moth (*Phthorimaea operculelle*) for up to 5 months of storage, RHA is effectively used (Das and Rahman, 1997).

In the water purification

Arsenic content in drinking water becoming a main problem in these days. 100 million people across the India are suffering such type of health effect. Its removal with the use of RHA has been investigated (Saha *et al.*, 2002; Malhotra *et al.*, 2013; Adams Bhagavanulu, 2015). RHA acts as adsorbent for the adsorption of lead and mercury from aqueous water (Feng *et al.*, 2004). Methylene blue, humic acid, are removed by RHA from wastewater (Imyim *et al.*, 2010; Sharma *et al.*, 2010). Since the main constituent of ash content is silica, the ion- exchange reaction on the silica surface is accomplished through the substitution of protons of the surface silanol groups by the metal ions from solution as (Masoud *et al.*, 2012)

$M^{+n} + x(=SiOH)_x^{(n-x)} + xH^+$

Mn^+= metal ion with n^+ charge.

SiOH = group Silanol on the SiO_2surface.
xH^+= number of protons released

Used in ceramic industries

RHA used in ceramic glazes (Bondioli *et al.*, 2010). It is also used to synthesis of $(Pr,Zr)SiO_4$ ceramic pigment, cordierite ceramics, Si_2N_2O, Si_3N_4 and SiC, mullite $(3Al_2O_3 \cdot 2SiO_2)$, SiO_2 porous ceramic materials (Padhi and Patnaik, 1995; Bondioli *et al.*, 2007; Chen *et al.*, 2014; Serra *et al.*, 2015)

For synthesis of silica nano particles

RHA is efficiently and effectively used in synthesis of silica nanoparticles in eco-friendly way (Thuadaij and Nuntiya, 2008; Premaratne *et al.*, 2013; Sankar *et al.*, 2016).

It is also reported SiO_2 and SiC nanowires, and $SiO_2/CaCO_3$ nanocomposite prepared from RHA (Pukird *et al.*, 2009; Morsy *et al.*, 2014). Nanosilica is synthesised from sodium silicate solution using precipitation method. The reaction is as follows:

$SiO_{2(Ash)} + 2NaOH_{(Caustic\ soda)} \rightarrow Na_2SiO_{3(Sodium\ silicate)} + H_2O_{\ (Water)}$

The silica particles were generated from the solution by adding sulfuric acid as catalyst of silica from sodium silicate by the following reaction (Rafiee *et al.*, 2012).

$Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O.$

Silica nanoparticles (SNPs) are frequently used nano materials in a variety of technological applications such as industrial manufacturing, packaging, composite and ceramics materials, drug delivery, adsorption, bio sensing and catalytic applications (Ghorbani *et al.*, 2015).

Other uses

RHA is effectively used as pigment extender in emulsion paints (Igwebike-Ossi and Dilim, 2014; Ossi and Dilim, 2015). RHA as siliceous materials used as sorbents for the flue gas desulfurization process in small-scale industrial boilers, also it has been subsequently tested for marine diesel spill clean-up (Dahlan *et al.,* 2006; Bazargan *et al.,* 2014). It is used as oil absorbent for absorption of vacuum pump oil also for purifying biodiesel from waste frying oil (Tatum and Winter, 1997; Chou *et al.*, 2001; Manique *et al.,* 2012). A novel application of RHA is for the pre concentration of gold (Nakbanpote *et al.*, 2000; Nakbanpote *et al.*, 2002). Silica extracted from RHA used as corrosion inhibitor for carbon steel (Awizar *et al.,* 2013)**.** RHA has been used as a support for Ni catalyst for various organic reactions (Chang *et al.,* 1998). In developing countries, also it is used to reduce fatty acids from frying oils (Chou *et al.,* 2007). Production of sodium silicate films (Kalapathy *et al*., 2000).

Systematic application of RH and RHA in direct manufacturing and synthesizing new materials could solve the problems of disposal and decrease the cost of waste treatments. More silica content in RH as compare other agriculture waste materials is an important potential for directly and indirectly application in different manner, which makes it good market valuable product. Effective application of RH such as fuel/electricity generation, bio ethanol production could transfer agriculture by product to valuable energy source for industrial sector. RHA also plays important role in various industrial applications such as processing of ceramic, cement, refractory industry. Biosynthesis of silica nanoparticles and its application in different field makes it valuable raw material. Application of RH might help in increasing farm economy and rural development. Systematic approach of this material can give new birth to a new domestic and industrial sectors of Rice husk and Rice Husk Ash in India.

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How to cite this article:

Patil Nita Babaso and Sharanagouda, H. 2017. Rice Husk and Its Applications: Review. *Int.J.Curr.Microbiol.App.Sci.* 6(10): 1144-1156. doi: https://doi.org/10.20546/ijcmas.2017.610.138