ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 5, pp. 999–1005.

Rice Hull as a Renewable Raw Material and Its Processing Routes

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Received November 1, 2010

Abstract—It was shown that rice hull has a unique composition and can be used as a renewable raw material. A method for rice hull conversion into polyfunctional materials was proposed, which gives a solid product, a liquid organic product, and a mixture of noncondensable gases. The solid product is suitable as a filler for elastomers, fodder supplement for farm poultry, and sorbent for noble and rare metal recovery. The liquid product acts as a highly selective collector of lead minerals in beneficiation of complex rebellious ores, plant growth stimulant, and antiseptic agent. The mixture of noncondensable gases can be used for carbon black production or as a high-calorific fuel.

DOI: 10.1134/S1070363212050349

Rice hull, a unique large-tonnage waste material from cultivation and processing of crops, is dissimilar in the composition and properties to some other plant wastes. Specifically, rice hull contains lignin, carbohydrates, nitrogenous substances, vitamins, organic acids, and mineral components, whose content depends on the rice variety and is affected by the geographical location and agronomic method of rice cultivation. The carbohydrate components of rice hull include cellulose (the main component) and hemicelluloses (contained in a slightly lesser amount) dominated by pentosans. Depending on the technique applied, crude or purified lignin can be recovered from rice hull. Crude lignin contains cellulose and ash; nitrogenous substances are represented primarily by proteins, with a small amount of nitrogen comprised by the vitamins contained in rice hull. Organic acids contained in rice hull include acetic, citric, fumaric, oxalic, and succinic acids, as well as some aromatic acids.

The predominant mineral component of rice hull, responsible for its high ash content, is silica. The ash also contains potassium, sodium, magnesium, calcium, iron, and phosphorus, as well as considerably smaller quantities of copper, iron, manganese, etc.

The content of rice hull components, wt %, varies extensively as follows [1]: water 2.4–11.35, crude protein 1.7–7.26, crude fat 0.38–2.98, nitrogen-free extractive substances 24.7–38.79, raw cellulose 31.71–49.92 (34.34–43.8, according to other sources), pentosans 16.94–21.95, ash 13.16–29.04; other substances (lignin) 21.4–46.97. It should be noted that data reported by different researchers can differ considerably.

Silica occurring in the outer epidermis imparts to rice hull its steady humidity, high hardness (5.5–6.5 on Mohs scale), and abrasivity. Some other characteristics of rice hull can be summarized as follows: true density 0.735 g cm^{-3}, bulk weight 0.1 g cm^{-3}, packed bulk density 0.4 g cm^{-3}, and calorific value 13827–15084 kJ kg^{-1}. The thermal conductivity of rice hull is identical to, or even lower than, that of some insulating materials (asbestos, mineral wool) [1].

Rice hull accounts for ~20% of the mass of unhulled rice, on the average. With steadily growing amounts of rice cultivated, rice hull utilization has become of much importance for countries involved in rice cultivation and processing. Among them, China and India, with 33 and 22% of the global rice harvest, respectively, are the major producers; other large producers include the United States, Pakistan, South Korea, Egypt, and Cambodia, as well as some counties of Africa and South America. As to former USSR countries, the main producers are Russia, Uzbekistan, and Kazakhstan [2].

There are two major options for rice hull utilizetion: in agriculture and in preparation of various materials and valuable chemical products. In agriculture, rice hull is used as an additive for animal feed, as well as a bedding material, soil treatment and mulching agent, and ballast for fine seed sowing. Soil application of rice hulls results in enhancement of the resistance of plants to galling and to insect pests through phosphorus and silica uptake. Rice hull ash, which is also a source of silica, possesses properties identical to those of rice hull. This fact is of much importance for rice cultivation, because a significant amount of silica is carried away from fields with rice harvest. Some sources report [1] that an increase in productivity due to soil application of rice hulls is paralleled by delayed appearance of sprouts and slowed down initial growth of plants. High-temperature steaming of rice hulls, followed by mixing with a special impregnating solution, yields a humatized organic fertilizer [3], and bioconversion of organic waste (rice hulls) under certain conditions gives a biofertilizer [4].

As mentioned above, rice hull can also be used as a feedstock for preparation of various materials and valuable chemical products.

Owing to its low thermal conductivity coefficient, rice hull possess good insulating properties, but due to a number of reasons has only limited application as insulator. First, rice hulls settle down with the course of time, which leads to violation of heat insulation. Further, rice hulls need special treatment to make them fire-resistant, as well as treatment with pesticides to prevent the emergence of various insects, rodents, and other pests. Also, there is a need in hermetic sealing to exclude water vapor condensation inside the insulating layer. Though giving positive results, all these activities are not always economically justified [5]. Good insulation properties and lacking steel-contaminating impurities make ash suitable as a material for covering the upper part of just-cast steel ingots, aimed to reduce shrinkage holes and waste produced.

A large number of studies were dedicated to rice hull and rice hull ash application of in manufacture of various building and road-building materials: concrete, concrete blocks, bricks, tiles, structural panels, etc. [6–10]. Unmodified rice hull-filled concretes typically do not satisfy relevant strength criteria and are susceptible to weather influences. Good results were shown by rice hull ash mixed with rice hull and cement (2:1:1). Concrete blocks manufactured from these mixtures are softer than normal concrete (though possess a permissible strength), which enables their saw cutting, as well as driving and screwing nails therein. These concretes possess good heat insulation and fire resistant properties, but their production was terminated due to the lack of burnt rice hulls [1].

Milled rice hulls or rice hull ash can be used as fillers for different composites: polymeric materials, including linoleum and plastics for tableware manufacture, rubber for tire manufacture, etc. [11–13].

Abrasive properties of rice hulls (soft abrasives) can be profitably used in tumbling, polishing, and soft blasting. Rice hulls perform better than sand in tumble polishing of cast-iron, aluminum, and brass items and are suitable for polishing and smoothing of small plastic items and precious stones [14].

Rice hulls were tested in paper production, but the resulting material proved to be fragile and brittle due to a low content of α-cellulose and insignificant length of its fibers. High ash content of rice hulls constituted another negative factor [14].

Another, peculiar, application of rice hulls as press aids to facilitate extraction of juice was reported at the UNIDO Conference on Rice Processing (India, 1971). When added in amount of 1% of the weight of fruit and berries being pressed, hulls provide drain channels for the expressed juice. As a result, the latter is more efficiently forced out of the pulp, and pressing goes faster. However, the rice hulls need preliminary refining to prevent soluble substances from contributing off-flavors and color changes [1].

A nearly identical application of rice hulls was suggested for oil and fat industry: It was recommended that 3–10% rice hull be added to oil seed in oil production to improve oil quality [15].

Also, rice hull is known to be extensively applied as raw material for production of silicon- and carbon-containing materials and of some organic compounds.

As mentioned above, rice hull is distinguished by high silica content and has an advantage over silicon-containing materials (sand, bentonite, diatomaceous earth), traditionally used as silica source, in terms of a minimum of impurity elements it contains.

The first patents belonging to the field of rice hull processing into silica date back to 1970s, but the procedures suggested therein still undergo improvements and constitute a patentable subject matter. The leaders in this field are India and Japan [16].

Various procedures were proposed for silica preparation from rice hull, in particular [16–25]: oxidative calcination at ~800°C; acid leaching of the product of oxidative calcination of rice hull; acid leaching of the raw material and calcination of the insoluble residue; enzymatic treatment followed by calcination; and alkaline hydrolysis followed by silica precipitation with acid. The resulting silica products vary in the content of the basic substance and associated impurities, aggregation state, particle size, specific surface area, pore volume, and other characteristics. The SiO_2 content in the rice hull processing products ranges from 40 to 99.99%, and the oxides of impurity metals occur in the following concentrations, %: iron 0.5–0.02, aluminum 0.7–0.02; calcium 0.9–0.005, magnesium 0.8–0.03; zinc 0.03–0.003, manganese 0.2–0.01, copper 0.002 – 0.0007, and silver < 0.002. The yields of black ash (with 36–88% SiO_2) and white ash (with 90–99.99% SiO_2) are 36–44% and 9–21%, respectively. Depending on the treatment conditions, the resulting silica particles are characterized by the specific surface area of 80 – 454 $m^2\ g^{-1}$, specific pore volume of 0.196–0.390 $cm^3\ g^{-1}$, and average pore radius of 1.69–2.3 nm. Heating rice hull to 1000°C causes the amorphous to crystalline transformation of silica with the specific surface area decreasing to 8–10 $m^2\ g^{-1}$ [16, 24, 25].

Silica derived from rice hull can be used in many fields that need pure amorphous silica: pharmaceutical and perfume industries, column chromatography, and electronics, as well as rubber, porcelain, glass, textile, and other industries. For example, upon preliminary chemical and heat treatment, rice hull-derived silica (99.1±0.1% SiO_2, impurities ~0.8%, bulk weight 0.264 g cm^{-3}, specific surface area 1.3±0.1 $m^2\ g^{-1}$, specific pore volume 1.6±0.1 $cm^3\ g^{-1}$, pH of aqueous suspension 7.0) is suitable as support for gas-liquid chromatography [26, 27] alongside the widely used Chromaton N-AW. Unlike the latter, the silica-based material is characterized by an inert and a more homogeneous surface, which makes it suitable for separation of highly polar (methanol, acetone, acetic acid, etc.) on nonpolar liquid phases without preliminary silanization of the support.

Treatment of carbonized silica (black ash) with an Au(III) salt solution, followed by elimination of carbon from the material, gave a sorbent efficient in mercury vapor concentration and removal. This sorbent is suitable for demercuration of air in rooms and for treatment of gases, as well as a collector column for mercury vapor in mercury analyses [27, 28].

Heat treatment of rice hull, followed by alkali treatment of the resulting ash containing 50–99% silica, gives water-soluble silicates [29, 30]. By varying the process conditions (alkali concentration, hydromodule, stirring speed, temperature, pressure, etc.) it is possible to prepare water-soluble silicates ranging in color from dark to colorless, which are characterized by different silicate modules essential for liquid glass properties. These silicates can be used in soap, fat, chemical, textile, and paper (in particular, for cardboard container manufacturing) industries, as well as in machine building and steel industry for production of welding electrodes, and also as binders in manufacture of moulds and cores in foundry, as flotation reagents in mineral beneficiation, and for other purposes.

In 1980–1990, increased researchers' interest, in particular, in Kazakhstan, was focused on rice hull and its hydrolysis product, hydrolytic lignin. The latter is economically attractive as a raw material for synthesis of silicon carbide and silicon nitride [31–55] by technologies that could constitute alternatives to existing highly energy-intensive and expensive procedures.

Published data [31–49] suggest that all the technologies proposed for silicon carbide synthesis from rice hulls are basically identical. They all include the following stages: pretreatment of the raw material (hydro treatment, pyrolysis); high-temperature synthesis of SiC in an inert gas medium; separation of filamentous crystals from dispersed powder (the synthesized product is comprised of a mixture of 10–50% fibrous material and dispersed powder of β-SiC modification); and removal of impurities (burning-off the residual carbon). The yield, morphology, and size of the resulting silicon carbide particles depend on the hydro treatment conditions, the preliminary pyrolysis temperature, and the type of catalyst used.

As shown in [46], synthesis of silicon carbide from rice hull-derived hydrolytic lignin gives a homogenous dispersed powder. When a catalyst (FeO, 3 wt %) is introduced into the process, the resulting product is comprised by a mixture of filamentous crystals (10–15%) and dispersed β-SiC particles [55].

The syntheses of silicon nitride from rice hulls and rice hull-derived hydrolytic lignin follow the same routes as in the case of silicon carbide, except for the fact that the high-temperature synthesis stage is carried out in a nitrogen atmosphere [50–55]. The resulting silicon nitride is comprised of a mixture of filamentous α-Si_3N_4 crystals and α- and β-Si_3N_4 modification powder [55]. Compared to rice hulls, rice hull lignins give thinner and shorter filamentous crystals: 0.1–0.5

against ~1 μm (in diameter) and 10–15 against 15–40 μm (in length).

The growing demand for pure silicon from electronic industry can be satisfied through the use of advanced organic synthesis technologies as applied to preparation of pure silicon and tetrachlorosilan from rice hulls. The production of silicon from rice hull or lignin is based on preparation of silica or silicon carbide for subsequent electrothermal reduction [56, 57]. This method offers an advantage in terms of high purity of the resulting silicon due to minor amounts of impurity elements in the raw material and its pyrolysis products, above all, negligible quantities of boron and arsenic adversely affecting the electrical properties of silicon. Pure tetrachlorosilan $SiCl_4$ can be synthesized by chlorination of rice hull or of amorphous silica preliminarily isolated therefrom [16].

Of no less importance and scale is utilization of rice hull as a raw material for production of carbon sorbents via heating under conditions of limited, or lacking, air access. This procedure yields, along with carbon, an aqueous distillate of liquid resins, from which it is possible to recover acetic acid, methanol, acetone, and other chemical products [58–62]. In general, studies dedicated to complex processing of plant-based waste materials are very scarce; they mainly concern the preparation of sorbents from rice hull and their applications [63–67].

Carbonized silica was shown [27] to display high sorption capacity (exceeding that of active carbons commonly used for these purposes) with respect to metals: copper, lead, cadmium, and nickel. The optimal metal sorption proceeds in neutral medium (pH 6.7–7.5). The sorption capacity of the sorbent with respect to metals decreases as $Cu^{2+} > Pb^{2+} > Cd^{2+} > Ni^{2+}$, specifically: copper 12.0, lead 10.0, cadmium 9.1, and nickel 6.3 mg g^{-1}. The sorbent can be regenerated in hydrochloric acid (1:1).

As shown in [63–68], rice hull-derived carbonaceous sorbents are promising for tap water treatment, gold concentration, and copper and cadmium sorption, as well as for medicinal and pharmaceutical applications. These sorbents very efficiently remove oils, petroleum, and petroleum products from water surface and wastewater [69–72]. Specifically this finding has underlain the development of the concept of an ecological complex to be established in Krasnodar krai [73]. The aim was to integrate enterprises engaged in paddy culturing and rice processing, production and application of sorbents, and oil production and oil refining, as well as other subjects involved in liquidation of the consequences of emergencies from spills of petroleum and petroleum products, soil reclamation activities, etc., and also enterprises utilizing spent sorbent (road building enterprises, heat power plants, oil refineries), etc. Based on an integrated approach to regional ecosystem management, this project does not provide, however, for integrated rice hull processing: It seeks to obtain only one product to be variously used within the specific region.

Boiling rice hulls in an aqueous solution of sulfuric acid, followed by steam distillation, yields furfurol, and this process has found industrial application. For example, the furfurol production consumes ~2% and 12% of the total amount of rice processing waste in the United States and Italy, respectively [1]. However, the yield of furfurol from rice hulls (4–5%) is not very high compared to that achieved with other plant-based waste materials (~17.5, ~19, and ~30% in the case of cotton seed hulls, corn cobs, and clean oat hulls). Therefore, preparation of furfurol as a single product from rice hulls is economically unjustified. This raises the issue of development of a low-waste technology that avoids environmental pollution to which end it is necessary to ensure that the rice hull hydrolysis residue and highly siliceous ash will find application. In this context, it was suggested [74] that the hydrolysis residue be used as an ingredient of a carbon-based self-lubricating material to be applied to end seals and sliding bearings. The will ensure reliable performance under variable conditions, boundary friction, also in media containing abrasive particles, e.g., in pumps for pumping water and chemical solutions, in centrifugal pumps of ship installations, and in chemical and petrochemical industry facilities.

It was found [75] that rice hull hydrolyzates have a good biological quality and can be recommended for use in growing fodder protein yeast; the yield of absolutely dry yeast from reducing substances under laboratory (no-loss) conditions is 58–66%. A method was developed for percolation hydrolysis of agricultural plant waste with the use of rice hulls as the filtration aid to increase the hydrolysis efficiency via improving the process hydrodynamics. This technique was implemented at a number of enterprises.

The hydrolyzate obtained by the procedure described in [76] displays bactericidal and bacteriostatic activities and improves the crude protein digestibility.

An attempt was made to develop a complex procedure for rice hull hydrolysis into two products: xylite (intended as sugar substitute in medicine) from hydrolyzate and amorphous silica from hydrolysis residue [25, 77].

With the list of procedures available for rice hull processing so long it might seem that rice hull utilization would be no problem. However, due to a number of economic, social, and political factors, the vast majority of the proposed technologies have not been implemented. As regards industrial implementation, of prime importance among these factors is the focus that most of these technologies place on preparation of a single product (either inorganic or organic). Hence, these technologies may not always be justified economically; there also can be environmental objections, etc. This causes further aggravation of the rise hull utilization problem, which can, however, be removed by development of a technology suitable for complex processing of rice hulls.

The Laboratory of Silicon-Carbon Composites, National Center for Integrated Processing of Mineral Raw Materials of the Republic of Kazakhstan, Republican State Enterprise, has developed an integrated technology for thermal processing of rice hulls [78]. It this procedure, the raw material is dried to residual moisture content of 3–5% and heat-treated at 600–650°C for 30 min. The resulting solid product is continuously unloaded into the receiving bunker; the gas/vapor mixture is condensed into a liquid organic products, and noncondensable gases are released.

The black solid product is silicon-carbon nanocomposite; this is a macroscopic object constituted by densely packed and evenly distributed carbon (~500 Å) and silica (100–200 Å) nanoparticles occurring in virtually identical amounts of 50–55 and 32–35 wt %, respectively. The organic product is represented by an aqueous solution of carboxylic acids (22%), phenols (14%), ketones (12%), cyclic aliphatic hydrocarbons (4.5%), heterocyclic compounds (4%), and alcohols and ethers/esters (4.5%) [79].

The products yielded by thermal processing of rice hulls have a wide range of applications. For example, a silicon-carbon filler for elastomers [80, 81] and a feed additive for farm animals [82] can be prepared from rice hulls. Through activation and/or modification of silicon-carbon it is possible to obtain a sorbent for extraction of noble and rare metals [83].

The organic product is a highly selective collector for lead minerals in lead-zinc ore beneficiation [84]. Its 1% aqueous solution is suitable as plant growth stimulant [85] and disinfectant (at >50% concentrations) [86]. A mixture of noncondensable gases (CH_4 25–38%, C_2H_4 2–8%, CO_2 10–38%, CO 26–50%, and H_2 2–3%) can be used for production of carbon black and high-calorific gaseous fuel.

Thus, the thermal processing method developed enables maximal utilization of rice hulls. It opens up new prospects for production of polyfinctional materials from renewable plant-based feedstock.

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