Nano Powder SiO_2 from Rice Husk and its Industrial Applications: A Concept of Wealth from Waste

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ABSTRACT

The rice Husk (RH) is a renewable biomass product and through thermochemical processes like pyrolysis and gasification, silica-rich RH is transformed into biofuels (such as bio-oil, vapors, and charcoal) and biochar at the same time. RH catalysts can convert bio-oil into more renewable biofuel (biodiesel). Using RH silica materials to purify gas or undergo catalytic reforming, vapors from the breakdown of organic waste can be transformed into syngas, which have more value and can be utilized to create energy or make chemicals. Biochars created from RH are usually used to produce materials for silicon batteries, mend soil, clean up pollutants, and accomplish other things. This study looked at recent improvements in how RH silica products are created and how they can be used in the future, notably in manufacturing materials that benefit the environment and save energy. RH-silica compounds have environmental benefits, can eliminate organic and heavy metal contamination through integrated processes and adsorption, and are used as a catalyst in fertilization, and water purification, including gas cleaning. Lastly, biomass with a lot of silica could be a source of cheap starting materials for creating high-value silica/silicon compounds that can be employed in the actual world.

1. Introduction

Silicon (Si), the second largest element within the earth's crust behind oxygen (O), is liberated in the soil through chemical or biological mechanisms. Plants have a significant effect on the biogeochemical silicon cycle within the chemosphere. Within silicic acid, which is dissolved in water, silicon is extracted from soil (H_4SiO_4), polymerizing and forming amorphous silica (SiO_2) along the transpiration channel. When a plant dies, SiO2 goes back into the ground, and the breakdown of the plant creates humic acid, which speeds up the weathering of the soil. The activity of fungus, bacteria, and actinomycetes additionally aids the bicycling of SiO_2 in the earth (Akhila Subash., 2020). Plants and microorganisms play a significant role in the global silicon cycle because they interact with soil minerals. Plants often retain silicon as phytoliths, typically including 5-15% amorphous hydrated silica (SiO_2). Plant-derived proteins, including carbohydrates, could play a role in the polymerization synthesis of biologically active silica. Amorphous silica, like that found in opal or silica gel, is a common cause of silica within the biosphere (Hafez A. I., 2022).

2. Rice Husk (RH) and Silica Production

As a member of the Gramineae family, rice (*Oryza sativa*) typically makes up 20–22% of total production as RH, which is thrown away by the rice mill industry. It's vital to note that rice husk has the most SiO_2, ranging from 8.7% to 12.1% and an average of roughly 10.6%. However, it is amorphous and hydrated, like most other biosphere species. Biominerals are complex forms of inorganic materials (like silica) created by living beings (Di Costanzo, L. F., 2022). Recent advances in synthesizing RH-derived silica complexes, including their ecologically sustainable use, are discussed, focusing on their application in catalytic, energy, and environmental-friendly materials.

3. Silica and Silicon Materials

Silica is an excellent example of an essential inorganic substance used in many industries (including adsorbents, catalysts, and electrical & medical instruments). Low density, thermoplastic polymer particles, and solid architectures for encapsulation were three reasons why inorganic microstructures containing pores seem relevant. Making silica materials chemically is complex since it is expensive, polluting, and requires precise conditions. However, bio silicification can occur under more benign physiological conditions in living creatures, including microalgae, cyanobacteria, sponges, and plants. It generates a variety of complex as well as hierarchical nano-structural structures made of biogenic silica.

RHA (Rice Husk Ash) is preferable to RH in the vast majority of cases. Generally speaking, any ash produced by RH is referred to as RHA. The appearance of the produced RHA is drastically altered by temperature. The silica's structure shifts in response to the RHA's combustion conditions (time, temperature, etc.): time, weather, and other variables. Crystalline silica is created at greater temperatures than the amorphous kind, which forms around 550 - 800°C (Rahim, N. A., *et al* 2023). Due to their varied characteristics, different applications call for different RH silica formulations. RH silica's structure and properties are typically sensitive to how it is manufactured. Depending on the temperature or the chemicals used to treat it, RH silica can take several shapes, from amorphous to distinct crystal phases. Figure 1 depicts how silica is typically manufactured from RH. One of the easiest and most effective ways to create ultrafine SiO2 nanoparticles from RHA is simple acid leaching followed by post-annealing uses the chemical process to utilize.

The hydrolysis of the hemicelluloses and cellulose in RH could be accelerated. Still, most metal impurities were removed by leaching the material and heating the mixture at varying temperatures and for different amounts of time. Because of this, white silica composites are feasible.

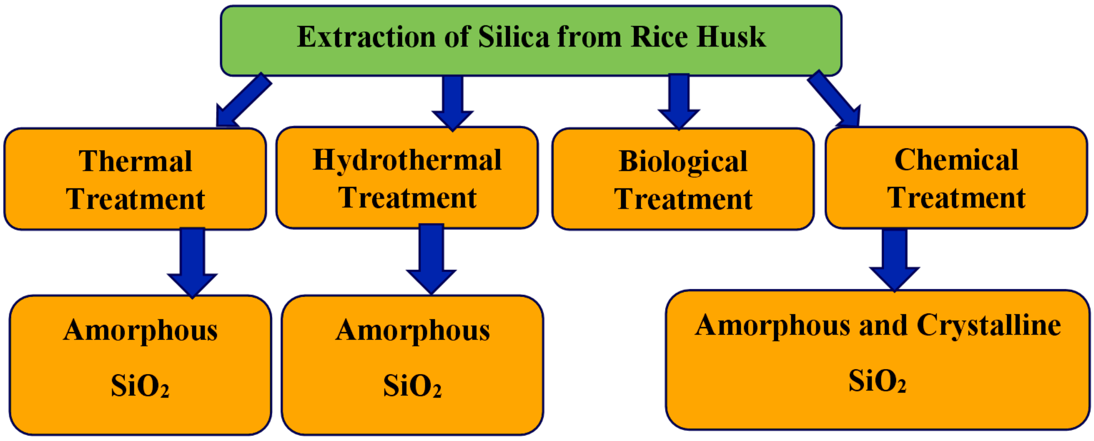

Fig. 1. demonstrates distinct structural silicas treatment from RH.

The properties of silica materials can be modified by the types of biosilica precursors and how they are manufactured. generated biogenic silica nanopowders from different sources of RH. The silica nanoparticles that were created were smaller than 50 nm (sticky RHA) and had a homogeneous surface shape and size distribution (brown RHA) (brown RHA). The brown RHA mesoporous silica nanopowder has the largest surface area and the narrowest range of particle sizes. Also, RH might be used to generate amorphous spherical silica particles with diameters from nanometers to the micrometer, which could be exploited in various ways (Sankar S., *et al* 2016).

When burned, RH produces bio-oil and syngas, which can be converted into usable forms of energy. Elevated amorphous silica can be made by combining pyrolysis char with chemical extraction. Activated charcoal, biofuels, lignocellulosic constituents, and silica appear straightforward ways to monetize RH.

Rice grows when it takes in silicic acid, CO_2, water, and several minerals. The amorphous silica builds up on the cell walls of rice. On the plant's leaves, branches, & husks, it produces two layers of silica—a silica-cuticle and a silica-cellulose. Amorphous silica upon the RH cell walls could be used as a spontaneous template for recycling porous carbon (PC) and silica. They did this by bringing together several types of RH structural cells. Notably, when steam was utilized to activate the PC, the meso- and micro-pores expanded. This resulted in the invention of HPC, which has good qualities in living creatures and negligible toxicity. Additionally, it serves as adsorbent materials, drug development and bio-interface materials, scaffolding for incubation cells, and other critical therapeutic activities (Tabata S, *et al* 2020). The electrical and industrial areas aren't the only ones that can leverage these applications.

The pore sizes in the semi-crystalline highly porous structures that could be modified were created by adding K+ cations to the silica nanoparticles and adjusting the pyrolysis conditions. Synthesized porous silica frameworks are more beneficial and work better than amorphous porous silica because they are more crystalline and have greater structural integrity (Wang W, *et al* 2012). Fig.2 depicts RHA, rice, RH, the rice plant, and synthetic silica nanoparticles depicted in digital & SEM photos.

Fig.2. RHA, rice, RH, the rice plant, as well as synthetic silica nanoparticles are depicted in digital & SEM photos.Copyright with permission from ref (Sankar S., *et al* 2016).

4. Catalysts for Processing Bio-Oil and Vapor

Like a renewable supply of raw materials for producing platform chemicals, including biofuels, biomass is growing in appeal. The price of the catalyst could be one of the most expensive aspects of a process, mainly if waste biomasses are used as the first raw material. When both the goal product and waste materials are employed to manufacture the catalysts, the process becomes cheaper and better for the environment. Individuals have been more interested in producing catalysts using heterogeneous biomass waste in the past few years. Since the characteristics of the waste feedstock influence how well the catalyst performs, triggers for a particular application are usually created from groupings of similar components by applying thermochemical procedures such as pyrolysis and gasification, RH biowaste to bio-oil, vapors, as well, and biochar. Biochar is used to manufacture things out of carbon and silica, but the mists and bio-oil it creates could be improved to be used as biofuels (Shen Y., *et al* 2014).

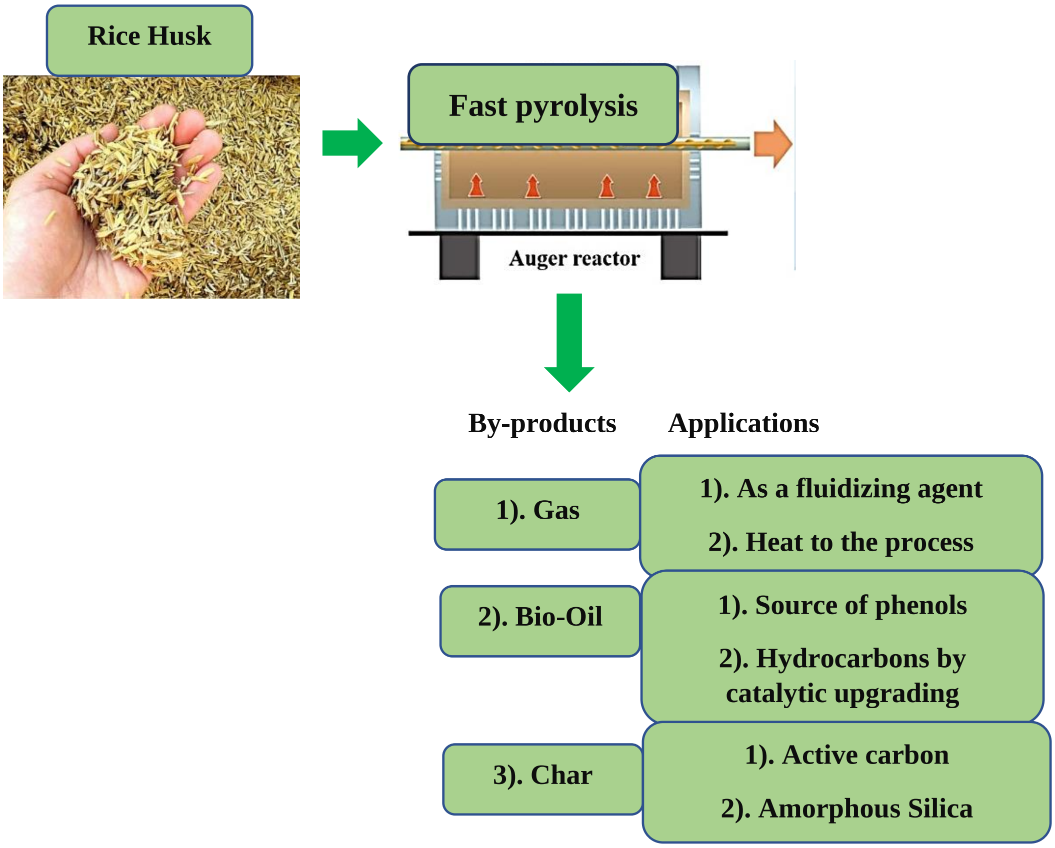

Fig.3. Activated carbon and amorphous silica production from RH.

A silica-rich RHA can nearly instantly transform into a catalyst or support for bio-oil and vapor processing, as shown in Figure 3. Researchers looked into RHA's potential as a solid acid catalyst for producing biodiesel, and their findings were fascinating. Byproducts such as plant matter, algae, eggshells, animal bones, clay, and ash have all been used to produce solid acid catalysts. Most catalysts generated from waste have been put to use in the synthesis of biodiesel. There is no need to worry about heating or cooling the room for either process (TAGs). Esterification was once performed using solid acid catalysts. These catalysts comprise pyrolyzed or carbonized activated carbons that have been sulfonated. Calcium oxides (CaO) make up the bulk of solid-base transesterification catalysts. Calcium oxides are commonly produced from shells. Extensive reports (Nurfitri I, *et al* 2013) have shown that solid acid catalysts derived from garbage can be used to produce biodiesel. Biodiesel can be made with the help of solid acid catalysts. Heterogeneous solid bases have far faster TAG transesterification rates than solid acids. Calcium is commonly found in landfill debris, so CaO has been used as a transesterification catalyst. The byproducts of bio-oil extraction can be utilized to make catalysts, lowering the price of biodiesel production. The potential for recycling old shells into a catalyst and calcium oxide supply has boosted the worth of trash. CaO is feasible and becomes hydrated and carbonated when exposed to air at average temperatures. Extremely high atmospheric water and carbon dioxide levels are responsible for these shifts.

The RHA-derived Li_2SiO_3 catalyst for biodiesel generation was developed by using a solid-state approach.Li_2CO_3 was employed as the activation agent (Chen *et al.* 2013) Methyl esters were used by (Hindryawati *et al.*2014) to create alkali metal silicates. And so, alkali metal silicates were born. Using RHA as a starting material, (Zeng *et al* 2014*)* developed a silica-based solid acid catalyst for producing biodiesel from soybean oil and methanol. Recently, waste materials like eggshells and RHA have been repurposed by (Chen G *et al.* 2015) into effective catalysts for application in palm oil transesterification. This particular solid base catalyst was made by combining calcined eggshells with RHA.

Tar in vapors from the thermal conversion of biomass, such as pyrolysis and gasification, must be removed before syngas can be used for energy production or chemical synthesis. Before using syngas, this must be accomplished first. Historically, RHA-based catalysts used in the conversion of tar and vapor were developed by RH pyrolysis. Catalytically, RHA excels in tar conversion because of the minerals it contains.

Mountingtransition metals, including iron, nickel, and copper, on silica support improve their catalytic activity. Incorporating metal precursors (such as Ni2+) into biomass (step 1), catalytic pyrolysis of biomass (step 2)), in situ, generation of highly dispersed catalytic active nanoparticles in the biochar matrix (step 3), and catalytic conversion of primary tars (step 4) are all crucial reaction steps in the integrated approach for catalytic biomass pyrolysis or gasification. Nanoscale biomass pyrolysis or gasification processes can be made more efficient and ecologically friendly with a thorough understanding of the concepts underlying each phase of the reaction process. As a result, state-of-the-art conversion technologies must be developed before more complex gasification systems. This is only the first stage of a multi-stage process for obtaining the metal nanoparticles in ash for practical applications. (Braga *et al.*, 2016) by catalytically increasing the vapor produced while elephant grass pyrolysis, WO3 hosted on RHA and RHA-MCM-41 was constructed. Silica catalysts generated from RHA may also be used in chemical syntheses. These investigations show that enhancing the bio-oil and vapor quality produced through the thermochemical valorization of biomass is a realistic prospect. To make these catalysts, RHA is used.

5. Batteries and their Components

For the production of battery technologies, silicon in high precision and crystallized forms is typically needed. The conventional method of making silicon is highly pricey. Significant efforts are being made to develop a high-volume, low-cost manufacturing technique for producing silicon in large quantities for use in electrical applications (Acharya H, *et al* 1980). One of these is the transformation of RHA towards silicon. It has been possible to make silicon from RH in several ways. For instance, a carbothermal conversion can change amorphous silica into silicon at very high temperatures. As even a biogenic partial substitute for cement,(Marchal *et.al* 2015) created solar-grade silicon using RHA that is 99.9999% clean. An experimental 50 kW electrical arc furnace (EAF) operating in the batch system at 1700-2100 °C would first subject RHA to acid grinding, boiling wash, powder metallurgy, and carbothermal reduction. How amorphous silica changes into silicon when exposed to metal has also been studied extensively. With lower temperatures, the transition metals Mg, Ca, Al, and Ti can reduce SiO2 and produce mixtures of the following modes of products. The total reactions, free energy variations, and adiabatic temperatures per mol of silicon are all displayed in Table 1.

Table 1. Silica-metal reaction thermodynamicdata

Reaction	Temperature (ºC)	ΔH (kJ/mol)	ΔGº (kJ/mol)	Adiabatic Temperature (ºC)
$SiO_2+2Ca=Si+2CaO$	650	−363	−333	2348
$SiO_2+2Mg=Si+2MgO$	650	−312	−261	1906
$SiO_2+4/3Al=Si+2/3Al_2O_3$	650	−210	−180	1477
$SiO_2+Ti=Si+TiO_2$	650	−34	−33	407

Carbothermal, magnesiothermic, aluminothermic, and calciothermic reduction are all possible thermochemical reduction pathways for SiO2. Silicon is typically produced in the metal industry using carbothermal drop, which employs EAF at 2000°C. However, this method typically involves much energy and silicon melting, which modifies SiO2's natural state. Magnesiothermic reduction is gaining popularity since it may be performed at temperatures as low as 650°C. It is common practice to combine Mg powder with SiO2 powder before burning the mixture in a furnace to the point when the Mg turns to vapor. Due to this method of reduction, the composition shifts at various locations. Close to the magnesium powder, Mg2Si is formed, whereas Si and unreacted SiO2 is formed further away. According to (Luo *et al.* 2013) using NaCl in the reduction process helps dissipate the byproduct of this highly exothermic reaction: tremendous heat. If the combustion temperature increased during melting to more than 801°C, silicon would melt, but NaCl prevents this by lowering the temperature—acquaintances and fellow employees. The porous nano-silicon was produced using a repeatable magnesiothermic sand reduction technique supported by heat scavengers (Favors Z, *et al* 2014).

To clean silicon, (Mishra *et al.*1985) suggested the calcium reduction of RHA. Following stoichiometric guidelines, they combined the required quantities of calcium with 500°C RHA. Next, we lowered the mixture's temperature to 720°C. Multiple acid leaching processes were performed using HF, H2SO4, and HCl after reducing RHA with magnesium at 800°C to produce silicon with a purity of 99.9999%. Byproducts, including magnesium oxide, magnesium disilicate, and unreacted magnesium, can be neutralized by adding an acid. Heating RHA pellets at 900°C in flowing argon, with Mg concentrations 5% wt higher than what the stoichiometry asks for, will produce the highest silicon yield, according to Larbi (Larbi KK *et al 2010*). "magnesiothermic synthesis" was used as an additional method to create ultra-fine silicon nanocrystals. The ability of magnesiothermic reduction to produce copies of Si that are organized in three dimensions from SiO_2 diatoms has contributed to the rise in popularity of the technique of reducing SiO_2 to Si.

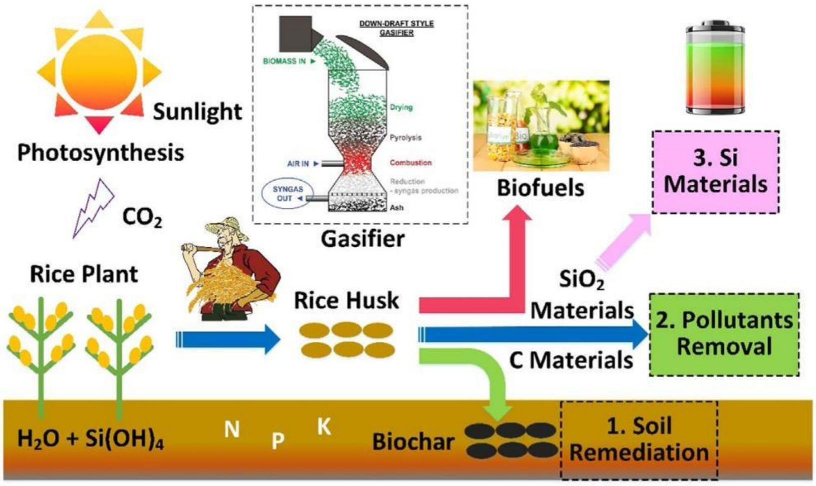

Fig. 4. Integrated approach to valorizing agricultural wastes (such RH) for said manufacture of carbon, silica/silicon products, and biofuels.Copyright with permission from ref [21].

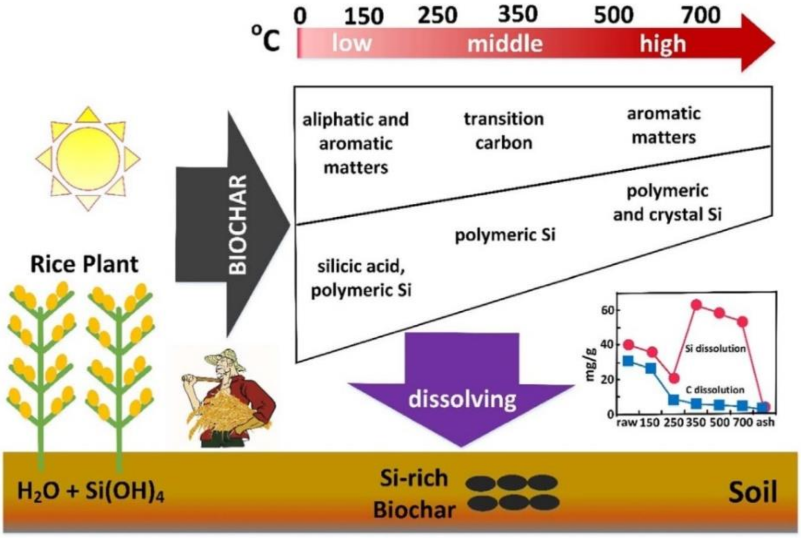

Fig. 5. Diagram illustrating the shape, solubility, and change of carbon and silicon in biochar made from pyrolyzed rice trash.Copyright with permission from ref (Xiao X, *et al* 2014).

Silicon/carbon composites and SiC are popular in lithium-ion applications. Magnesium disulfide (Mg2Si) may connect silicon and silicon dioxide in magnesiothermic reduction of silicon dioxide (SiO2). Silicon can become a kinetic product if silicon dioxide (SiO2) is converted to silicon before silicon intermediates are exposed to carbon. Si can be created by slowing Si intermediates toward carbon.

Using abundant biogenic silica supplies, the unique nanostructures of amorphous silica can be silicon or silicon-carbon compounds turned into elevated LIBs technologies (like RH). The investigation of RH-derived semiconductor materials used throughout LIBs applications is summarised in Table 2, which can be seen below. In most cases, the potential for utilization of silicon-based substances as LIBs anodes is greater than silica composites. The magnesio-thermic reduction process of (Jung *et al* 2013) was employed to generate nanostructured Si from RH. Using a two-step acid etching procedure, 3D porous silicon was then manufactured. This study produced Si with the optimal porosity with high-capacity LIB anode nanostructure using RH. With the help of its connected nanoporous structure, the efficiency of Si anodes could be significantly improved, leading to better cycle and power efficiency. Si anodes were created over years of gradual progression for effective rice production.

Table 2. Comparison of RH-derived Si materials in LIBs applications

Si Materials	Properties	Capacity (mAh/g)	LifeCycle	Ref.
Si nanoparticles	10–40nm	2790	86% (300	[27]
			cycles)	
Nanoporous Si	40–60nm	1553	100% (200	[22]
Mesoporous Si	150.10m^2/g	1221.20	cycles) 1000mAh/g	[28]
Carbon-SiO_2 **composite**		500.0	100% (40 cycles)	[7]
Si-graphene		1000	100% (300	[29]

An efficient magnesiothermic reduction process was developed by (Liu *et al*. *2013)* to convert RH into nano-Si. Initially, RH was changed to nano-SiO2 by using thermal techniques and then into nano-Si using geothermic means. There are many advantages to this novel approach, such as its ease of implementation, low energy requirements, and scalability. There is no need for costly silica precursors or reagents, either. By sharing the same nanostructure as RH silica, recycled silicon improves battery performance with less grinding. Electrolysis, a low-cost production process, also produces magnesium (Mg). Mg can be synthesized from MgCl2 using electrolysis. Therefore, this process is environmentally friendly because it requires no toxic chemicals beyond HCl, which is electrolyzed to produce Cl2 by a simple chemical reaction.

The production of silicon nanoparticles using RH silica was accomplished by (Wong et al. 2014) using a magnesiothermic decomposition method. In the end, silicon nanoparticles being utilized in LIBs as such photoanode made it possible to create a Si-graphene composite without using it, making it possible to develop a Si-graphene composite without a binder. The maximum capacity of said Si-graphene composite is 1000 mA h/g at a current density of 1000 mA/g, which is a muchmA/g, which is a significantly higher electrical density. Last but not least, the findings of these experiments show that waste products from agricultural practices, such as RH, have quite a promising future with high-tech applications (Praneetha S, *et al* 2015).

6. Environmental Consequences

RH is rarely utilized because of its bulk, tenacity, and inability to break down into nutrients. Open field burning and landfilling are the most prevalent disposal methods because waste has a low bulk density. Both disposal methods waste energy, greenhouse gases, air pollution, and landfill space, but they are still the most popular. Because of this, researchers have been searching for cost-effective RH-using technologies. RH has been used to make agricultural waste, cement, bricks, insulating fillers, and controlled-burning power (controlled burning). Many silicon-based chemicals have been studied recently as potential RH-increasing techniques. This scientific field has also grown significantly. Extracting silica or silicon from agricultural waste, particularly RH increases its commercial value and reduces its environmental impact. Gasification and pyrolysis are the best ways to convert RH into biofuels like bio-oil, syngas, and biochars (Manya JJ.2012).

Refining bio-oil with RH catalysts produces renewable biofuels like biodiesel . Gas cleaning and catalytic reformation using RH silica materials convert organic matter vapors into syngas. Syngas can be utilized for energy or chemical synthesis. Figure 4 shows the many uses of RH biochars, including pollution reduction and silicon formation. Biochar is being studied to reduce greenhouse gas emissions and improve soil health and agricultural productivity. Biochar promotes soil pH, carbon stability, water and fertilizer retention, organic pollutants, and heavy metal absorption. Due to its low cost and environmental impact, biochar is a promising option for soil pollution and carbon storage. Biochar can be used as a soil supplement due to its porous structure, which increases water retention and soil surface area. Charred wood became biochar. Biochar also improves soil nutrient use. Biochar may include nutrients or physical-chemical mechanisms that enhance nutrient uptake from soil or fertilizers. Biochar's biological integrity is intriguing. Charcoal from natural fires and ancient humans has shown that biochar has been stable over millennia. Photosynthesis removes CO2 from the atmosphere, turning biomass into regular soil carbon species that generate a longer-lived carbon sink. Biochar may also remove carbon dioxide from the environment. Biochars can boost soil amendment, waste biomass value, and energy generation. Biochar from agricultural waste can help farmers sequester carbon and generate renewable energy (Liu N, *et al 2013*). Biochar stores carbon and generates sustainable energy.

Pyrolyzing silica-rich biochar, Chen and colleagues examined silicon and carbon form, solubility, and modification. Figure 5 shows that higher temperatures generated crystalline silicon. Aliphatic organic compounds become aromatic. Rice cultivation produces amorphous silicon and carbon-rich biowaste. At 250 degrees Celsius, silica acid polymerizes and brings silicon and carbon closer together. Carbon components cracked extensively, revealing silicon inside the tissue around 250–350 degrees Celsius. Silicon crystallization and carbon aromatization caused biochar to condense at 500–700 degrees Celsius. This reduced the amount of carbon released into the water, unlike when the rising temperature increased both the amount and the pace. The size of particles and silicon protection also affect biochar stability and aromatic structures. Now that we understand how silica and carbon interact, we can study biochar's potential to sequester carbon in the soil. Biochar's silica-carbon construction may slow physicochemical oxidation. This may extend soil turnover and carbon sequestration. Silicate-rich biochars may provide a unique slow-release supply of physiologically accessible silicon in agricultural soils with low silicon levels if silicon dissolution kinetics can be predicted. RH biochars, high in nitrogen, phosphorus, and potassium (N, P, and K), are used as a source of nutrients, affecting the carbon, nitrogen, and phosphorus biogeochemical cycle. RH biochar and silica can remove metals and organic pollutants through adsorption, catalysis, and integrated methods(Shaheen, S. M., *et al* 2022).

7. Conclusion and Prospects

Both the control of waste and the preservation of energy are developing into increasingly pressing concerns. Therefore, waste RH biomass is a form of renewable energy that possesses tremendous potential as a low-cost input in creating high-quality end products. Removing silica or silicon from the environment can reduce the adverse effects on the environment while simultaneously increasing the RH resource's value. The simultaneous conversion of RH to biofuels by utilizing thermochemical reactions like pyrolysis and gasification is the most promising of the available options (such as bio-oil, vapors, and biochars). RH catalysts can convert bio-oil into renewable bio-fuels like bio-diesel, which are then used (like bio-diesel). Steam may be cleaned up and turned into high-quality syn-gas with the help of RH silica materials, which can then be used in energy production or chemical synthesis. Bio-chars derived from RH can be applied in a broad number of settings, such as improving soil quality, eliminating contaminants (such as heavy metals and organic compounds), and producing silicon for use in various types of battery technology. There is a significant chance that silicon compounds produced from RH will eventually be utilized in LIBs. If porous silica could be obtained quickly and at a reasonable cost from a reliable source, the distribution method might be significantly improved. It is possible to create crystal silicon from RH amorphous silica using either the carbothermal reduction or the magnesia reduction procedures, which is suitable for usage in battery materials (such as Lithium-ion batteries). Last but not least, the RH's abundance of amorphous silica makes it feasible for it to have the ability to serve as a source of low-cost raw materials, making it possible for it to be used in the creation of high-value silicon and amorphous-silica-based goods that have practical applications.

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