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Rice Husk Nanosilica Preparation and Its Potential Application as Nanofluids

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Abstract

The fast development in the extraction technique of silica from biomass has resulted in the signification use of silica in the industry. Rice is one of the world's most significant plants, which serve as a carbohydrate intake for humans. Rice husk is one of the main agro-wastes comprising big quantities of silicate. This chapter presenting the review on rice husk nanosilica production techniques by thermal and chemical methods. A direction on efficient and sustainable nanosilica extraction method will be discussed. Apart from that, method on nanofluids preparation will be accumulated with respect to the end application. Moreover, the influence of nanoparticle in nanofluids in terms of heat conductivity, rheological properties, and stability will be discussed. The potential application area of silica nanofluids such as solar, automobile, electronic cooling, and biomedical application will be explored.

Keywords: rice husk nanosilica, chemical method, thermal method, industrial application

1. Introduction

The surface area and porosity of the nanosilica are large and can be commonly used in products such as fillers [1], pharmaceuticals [2], catalysts [3], and chromatography [4]. Industrial silica production uses sodium silicate as the main ingredient of silicone. Nevertheless, a large amount of energy is required to produce sodium silicate via melting the quartz sand and sodium carbonate at 1300°C [5]. In the future, fossil fuel energy may not be viable. Thus, it is also fascinating to create a technique for producing nanosilica from a silicon-containing biomass content that will be economically feasible. Biomass is a significant resource for renewable energy and represents 15% of the worldwide power supply [6]. Rice husk (RH) is one type of biomass, which is effective heat deliver and lignocellulose rich for biological oils [7]. The global annual product of RH is about 100 million tons [8]. RH is rich in silica content (~20 wt%) and abundant in rice milling as waste. RH is not widely known due to lack of commercial utilization. Nanosilica precursor is an exciting future application for the preparation of advanced materials, such as carbon/silica composites [9], photocatalysts [10], hydrogen production as well as CO₂ capture materials [11, 12], and metal ion removal adsorbents [13]. Nanosilica with porous RH composition can be prepared by various methods [14–16].

Kalapathy et al. [17] explored sodium hydroxide dissolved xerogel formation utilizing RH as raw resources. They discovered that combining the rice husk ash (RHA) acid with xerogel's washing step can efficiently improve nanosilica sample purity. Following a pre-treatment with acid, Zhang et al. [18] utilized RH as a forerunner to acquire superfine 30–200 nm diameter nanosilica the pretreated sample. In the latest studies, biotransformed nanosilica with *Fusarium oxysporum* fungus [19] or via a bio-digestion process using worms [20]. Witoon et al. [21] utilized RHA as raw resources for the preparation of bimodal porous nanosilica and Chitosan as a template.

Meanwhile, nanofluid is comprised of nanometer-sized particles (nanoparticles) and fluids. Water, engine oil, ethylene glycol, and so on are usually used for base fluids in many industries including transport, power supply, manufacturing, and electronics [22]. Conventional base fluids suffer from low heat transfer performance, which limits its application [23]. In order to overcome the drawbacks, nanosized particles suspended in the base fluid can improve the transfer of heat and rheological properties, acting as property enhancer [24]. Moreover, most of the nanofluid studies underline the nanoparticle preparation methodology. A research from Rao et al. [25] found that nanofluids have greater thermal conductivity than conventional fluids, strongly nonlinear temperature dependence on effective thermal conductivity, improve or decrease heat transfer in single-phase flow, improve or decrease nucleate pool boiling heat transfer, and yield higher critical heat flows under pool boiling conditions. To the best of our knowledge, RH-derived nanosilica has not been reported elsewhere. In this context, the method of preparing nanosilica will be deliberated. Moreover, the method of nanofluid preparation from nanoparticle and the potential applications of nanofluids will be discussed.

2. Method of preparing nanosilica

Thermal and chemical methods are the two major methods that have been widely adopted for silica production from biomass. **Figure 1** illustrated the methods used for producing nanosilica from biomass/agricultural waste.

2.1 Thermal methods

Thermal methods involve the utilization of furnace muffles, fixed bed furnace, fluidized bed reactor, and other thermal methods that consist of inclined step-grate furnace, cyclone furnace, and rotary kiln. The thermal technology does have a number of disadvantages such as required more time for reaction, hot spot formation, the absence of free-flowing air for full carbon oxidation, and many others [26].

2.1.1 Electric/muffle furnace

Nanosilica is extracted from agricultural waste in a laboratory scale by electric/muffle furnace. The biggest disadvantage in using this technology is the long reaction time and a lower production rate. Patil et al. [27] investigated the biggest RH nanosilica extraction, consisting in thermal treatment with electric oven for 6 hours at 700°C at different temperatures. XRD and FTIR were used to characterize the sample. XRD information showed that the nanosilica acquired was amorphous in nature. About 95.55% pure nanosilica obtained from RHA with acid leaching preceded by the treatment of thermal heating with muffle oven at 600°C [28]. According to Bogeshwaran et al. [29], silica extracted from RH is highly

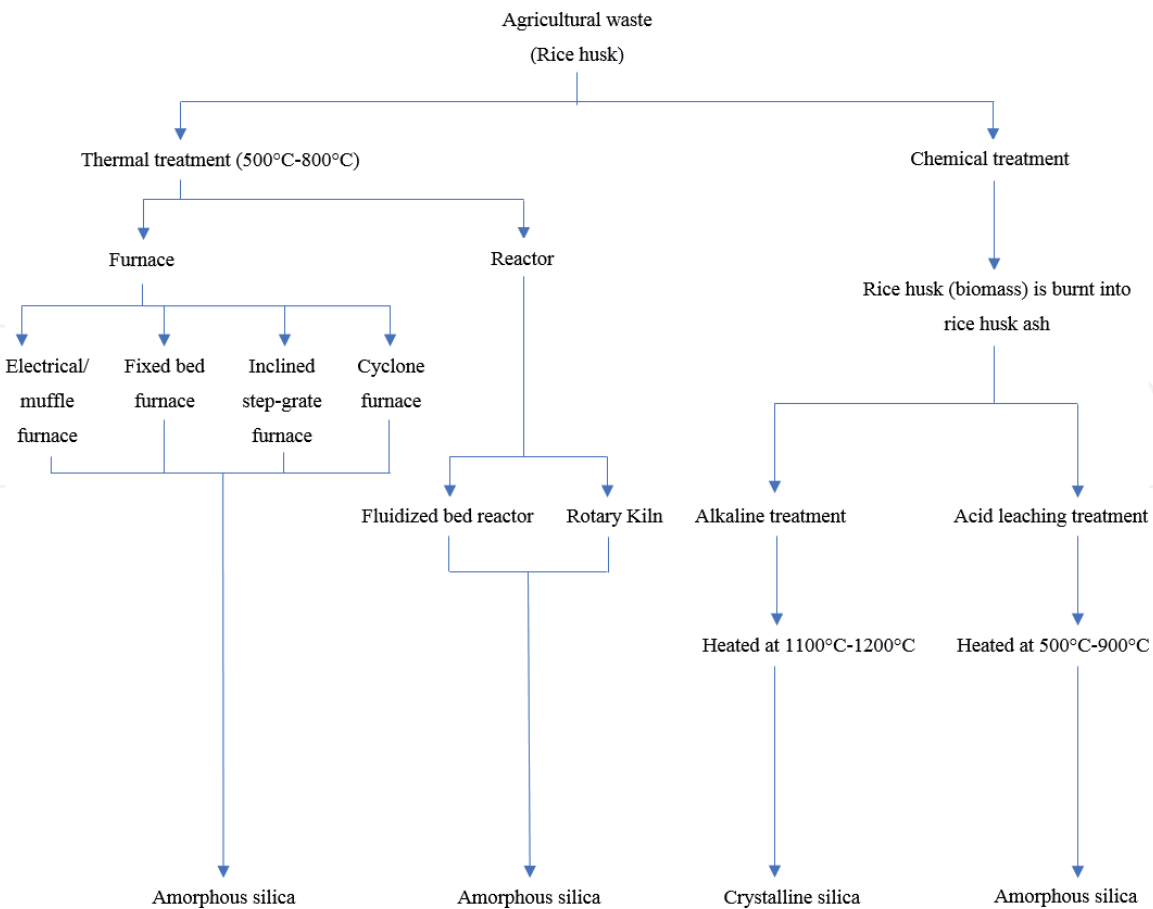


Figure 1.
Various treatments used to produce nanosilica from agricultural waste.

pozzolanic when burned in the muffle furnace. By thermal treatment, Chen et al. [30] utilized wheat straw to effectively produce nanosilica products. The combustion of wheat straw ash was kept at 500°C for 8 hours. The collected sample was washed with distilled water after the combustion and followed by calcination at the temperature from 400 to 700°C in a muffle furnace. Nano-amorphous silica was characterized by using XRD, TEM, EDX, FTIR, and BET. Ahmad Alyosef et al. [31] investigated the use of thermo-chemical treatment for meso/macroporous biogenic silica (3–1500 nm) from biomass such as miscanthus, wheat straw, and cereal remnant pellets. The biomass (wheat straw) was leached by concentrated H_2SO_4 (5 M). The wheat straw proportion of H_2SO_4 was controlled at 1:10 (gmL^{-1}). The treatment was performed under continuous stirring (1000 rpm) at 353 K for 24 hours. The ash of silica generated at various temperatures and times after heating by furnace. The combustion and acid leaching therapy of RH obtained pure amorphous silica. HCl , H_2SO_4 , and HNO_3 leached the husk with different concentrations. The wheat-husk ash samples were positioned inside the muffle furnace at the temperature from 300 to 700°C for 24 hour after leaching treatment. The research proves that hydrochloric acid leaching treatment was more effective than any other acid to remove metal ions. Pure amorphous silica from acid-treated wheat husk ash was obtained at 500–700°C [32]. Yalcin and Sevinc [33] manufactured amorphous silica RH successfully at 600°C in a tubular stainless steel reactor for 4 hours in an electronic laboratory muffle furnace. In particular, electric/muffle furnace can increase the purity of silica contents obtained from incineration. Except that, amorphous silica structure can be obtained by incineration up to 425°C for 90 minutes. The structure of silica varies on the incineration temperature and time required [34].

2.1.2 Fixed bed furnace

The manufacturing of RH silica was also carried out using a fixed bed furnace. By using fixed bed furnace, Yang et al. [35] obtained amorphous silica in burst nano size. In this process, RH treated with raw and acid was conducted in fixed bed furnace for pyrolysis at 600–1200°C. The amorphous silica transforms into crystalline at 1000°C. Hamad [36] discovered RHA silica successfully using the 500–1150°C muffle furnace and fixed bed reactor.

2.1.3 Fluidized bed reactor

The advantages of fluidized bed reactor are the distribution of uniform temperature, fast reaction time, efficiency of carbon conversion, low temperature operating range, high intensity of combustion, elevated reaction of gas-solid mixtures, and outstanding mixing characteristics [37, 38]. Huang et al. [39] manufactured RH silica white by utilizing fluidized bed reactor. RH amorphous silica can be obtained by using fluidized bed bubbling pilot plants at different temperatures and at different speeds [40]. Genieva et al. [41] obtained RH silica material that is produced by the rice-milling phase, and it is a large agricultural waste product by using and characterizing the fluidized bed reactor throughout the nitrogen atmosphere. Luan and Chou [42] found RH silica in a modified fluidized bed reactor throughout the existence of pilot flame. Therefore, outcome revealed that the high-activity silica product was acquired.

2.1.4 Other thermal method

Inclined step-grate furnace is commonly used in the manufacturing of RHA. It consists of feeding component, chamber of combustion, and chamber of ash precipitation. The disadvantage of using this RHA manufacturing methodology is low yield quality and elevated unburnt carbon content. RH was provided from the upper part of the reactor as air flows from the lower part [43]. Moreover, cyclonic furnace was developed by Singh et al. [44]. In this furnace, the air kept the husk spinning and accelerated the combustion in the chamber. The benefit of using cyclone furnace to make husk ash is that the product has less carbon content. Subsequently, rotating kiln is a pyro-processing tool used in the ongoing process to increase calcination materials. Sugita [45] patented active RHA generated from rotary kiln. In this process, RH has been carbonized by an upstream rotary kiln that is heated at 300–400°C by electric heaters, burners, or other heat sources. Carbonized RH is supplied into rotating oven and burnt at 600°C after carbonization. These techniques effectively produced the husk ash. The disadvantage of using this technique was the need for additional fuel to avoid ash from being crystallized, longer reaction time, and high energy required.

2.1.5 Discussion on thermal method

Thermal method is one of the initial initiatives to obtain silica nanoparticle derived from RH biomass (**Table 1**). Muffle furnace helps in incineration of RHA to form nanosilica. The crystalline of nanosilica is dependent on the temperature and before incineration process takes place. Utilizing temperature around 500–700°C will form amorphous nanosilica. Alternatively, crystalline structure of nanosilica obtains above temperature of 900°C [46]. Chemical pre-treatment is vital to avoid any unburned material that leads to reduce the nanosilica's purity. Fixed bed furnace has an ideal temperature of 600–700°C to obtain white RHA. Complete combustion

Electric/muffle furnace								
No	Method	Material	Time	Temperature (after getting silica gel)	Size	Purity	Yield	References
1	Furnace in which the subject material is isolated from the fuel and all of the products of combustion, including gases and flying ash	RH	700°C	6 hours	—	95.55%	—	Patil et al. [27]
2		RH	500°C	8 hours	—	—	—	Chen et al. [30]
3		RH	80	24 hours	3–1500 nm	—	—	Ahmad Alyosef et al. [31]
Fixed bed furnace								
1	Material is heaped onto a grate, and preheated primary air (called under fire air) is blown from under the bed to burn the fixed carbon	RH	600– 1200°C	—	1–10 nm	—	—	Yang et al. [35]
		RH	500–1150°C	—	—	—	—	Hamad [36]
Fluidized bed reactor								
1	A simple fluidized reactor consists of a room, which is assisted by a distributor plate, and contains a bed of inert particles like sand	RH	800–950°C	4–8 hours	—	92–96%	—	Pitt [37] and Soltani et al. [38]
2		RH	100°C	4 hours	20 nm	—	—	Genieva et al. [41]
3		RH	60–860°C	4 hours	—	—	—	Luan and Chou [42]

Table 1.
List of thermal method and its parameters.

of carbon content is the major benefit of this furnace. However, the heat loss during the process could affect the temperature, which leads to unstable production of silica structure [36]. Fluidized bed reactor has many benefits such as high combustion intensity, lower operating temperature range, simple operation and quick start-up, and easier ash removal. However, it appears hard to fluidize RH and husk char or otherwise blended with sand, mold, and ash to produce a multi-structure [47–49]. Inclined step grate furnace is simple in construction and process, but it is inefficient in combustion and separation of ash resulted smoke and spark partially drawing into the dryer plenum [43]. The rotary kiln carbonizes RH first by burning without flaming and transforms the carbonized RH into ash. This method easily produces white RHA, which has excellent chemical reactivity [45]. This furnace requires new improvement to the capacity part due to low production along the process. Soponronnarit et al. [50] prove that cyclone furnace able to increase the furnace efficiency by 16% rises the air by 90%. Observation made proves that the height of ash on the grate does not affect the efficiency of the furnace. However, incomplete combustion may occur because of too high airflow rate in tertiary duct that did not support combustion since the burning RH fell quickly from the grate. Among them, fluidized bed reactor suites the best requirement for producing silica due to its better purity (92–96%) and operating at optimum temperature (800–950°C), which is also in agreement with Soltani et al. [38].

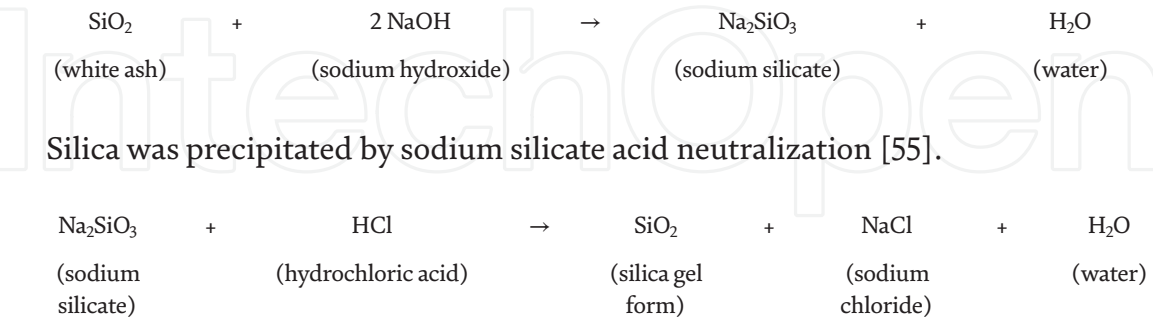
2.2 Chemical method

Chemical techniques include techniques of alkaline extraction used to achieve pure and high silica quantities. However, this method is costly due to a slightly longer reaction time (24–48 hours) and involves different measures with the use of different sorts of chemicals. Usually, RH will go through thermal process (incineration) to obtain RHA before proceeding to any chemical process involvement.

2.2.1 Alkaline extraction

Alkaline extraction and acid neutralization are an effective and easy technique of extracting amorphous silica from agricultural waste. Zulkifli et al. [51] utilized alkali extraction technique from RH to extract silica particles in order to remove metallic impurities. In a water bath, RHA was initially treated with HCl for 4 hours at 75°C. The filtration took place by constantly washing using distilled water until neutral state was reached and dried at 110°C for 12 hours. The NaOH was used to prepare a constantly stirring solution of sodium silicate for 1 hours at 90°C. The silicate sodium solution was then reacted to ethanol, and a steady 10-minute water mix was added. The whole mixture has been titrated 3 M H_3PO_4 until gel formation is carried out. The product after centrifugation of yellowish gel was washed with distilled water to clear away residual sodium silicate and phosphate, followed by calcination to produce silica nanoparticles. Hassan et al. [52] prepared nanosilica from rice husk in high surface area using the NaOH (alkaline extraction method). In their study, analyses of characterization of nanosilica were investigated by using FTIR, XRD, SEM, and TEM. The impact from their study states that more than 95% of nanosilica obtained. Liou and Yang [53] investigated various variables of silica derived from RHA processing via the alkali-extracted method. Acid and alkaline concentrations, gelation pH, aging time, and temperature have been optimized to prepare SiO_2 nanoparticles from RHA. The effects on the surface area from various acids and silica particle size have also been assessed. Rehman et al. [54] synthesized nanosilica using silica source from RHA. Silica nanoparticles were obtained from RH through the use of NaOH alkaline sol-gel method.

The application of H₂SO₄/water/butanol to pH 4 precipitated the silica. Thuc and Thuc's [55] technique was used to obtain nanosilica particles with high-specific surface area. Their study continues to prepare zeolite Y in sodium form (NaY) derived from nanosilica. Awizar et al. [56] produced and used nanosilica as a green corrosion inhibitor by alkaline extraction. Haq et al. [57] obtained RHA silica with reflux condition for a varying period of time by NaOH solution. The RHA reaction mechanism mixed with NaOH was given as follows:



Low surface microsphere silica can be achieved by alkaline and acid precipitation from wheat husk ash. Nano amorphous silica with a specific surface area of 8.23 m²/g was achieved after alkaline extraction with NaOH [58]. Masnar and Coorey [59] prepared silica nanoparticles by following the same step as Liou and Yang [53]. Silica nanoparticles obtained at 80°C for 48 hours after solids have been dried.

Selvakumar et al. [60] prepared silica from RHA by adopting pre-treatment process (acid process). Pre-treatment of acid was used to enhance the silica purity with the effective removal of the majority of metallic impurities and to produce silica (white color). From their study, RHA was pre-treatment by various acids (pH 1, 3, 5, or 7 using 6 N hydrochloric acid, nitric acid, and sulfuric acid). RHA amorphous nanostructured silica was produced using alkaline extraction technique with NaOH solutions (2.0–3.0 N). Their research showed that treatment with 2.5 N NaOH produced RHA containing 90.44% silica. Rungrodnimitchai, Phokhanusai, and Sungkhaho [61] prepared RHA silicate materials using 2.0 M of sodium hydroxide with the help of microwave (800 W) for 10 minutes. Zhang et al. [62] synthesized silica nanoparticles from RHA by involving acid pre-treatment. Na₂CO₃ solution was added after the pre-treatment to obtain nanosilica slurry. The precipitation was then cleaned with distilled water and dried for 24 hours in the vacuum oven at 120°C. Adam et al. [63] obtained spherical nano size silica from RH by using nitric acid (65%) and sodium hydroxide. No calcination for ash formation was required in this treatment.

2.2.2 Acid extraction

Faizul et al. [64] prepared amorphous nanosilica with the size of 181.2 nm with mild acid solution (citric acid, acetic acid, and phosphoric acid) obtained from rice husk. Carmona et al. [65] used acid leaching to synthesize nanosilica of two kinds of rice husk, namely the agulhinha and the catetus. They believe that their method can be efficient in removing impurities (Zn, MN, Ca, K, Mg, Cu, and Al). Mahmud et al. [66] used hydrochloric acid for acid leaching to obtain high purity and high surface area of nanosilica. Rafiee and Shahebrahimi [67] prepared nanosilica from rice husk with high surface area by acid leaching treatment. The average size of nanosilica is 6–7 nm supported by the catalyst. Bakar et al. [68] prepared high purity silica by acid treatment followed by combustion. Pre-combustion rice husk

was leached with hydrochloric acid and sulfuric acid to achieve pure silica. Thus, XRF confirmed the purity of amorphous silica over 99%.

2.2.3 Other chemical extraction methods of silica from agricultural waste

Many chemical treatments exist for the production of silica from bio-waste. Faizul et al. [69] obtained amorphous silica and activated carbon by three effective procedures by using toluene/ethanol, NaClO_2 , and KOH. The method of calcination was used in the production of nano amorphous silica (100–120 nm). The manufacturing of amorphous silica was carried out using organic acid leaching instead of strong acid [70]. Ionic liquid was also used in the manufacturing of silica from agricultural waste by Kumar et al. [71].

2.2.4 Discussion on chemical method

Chemical method is advisable to obtain high purity of amorphous nanosilica due to its effective chemical reaction (**Tables 2 and 3**). Basically, there are two types of extraction methods (alkaline extraction and acid extraction). In this review, alkaline extraction method is predominantly compared to acid extraction method in terms of nanosilica properties obtained. Hassan et al. [52] produced the preparation of silica nanoparticle by alkali treatment and obtained more than 95% purity of nanosilica. Furthermore, Liou and Yang [53] prepared nanosilica and obtained 99.48% of silica content throughout alkali treatment. For further improvement, Selvakumar et al. [60] used pre-treatment and result in high purity (85%) of silica contents. Similarly, Adam et al. [63] also reported acid pre-treatment before conventional alkaline method, where ~95% purity of nanosilica was obtained. As for pre-treatment is use to enhance silica purity and remove metallic impurities. Meanwhile, Rungrodnimitchai et al. [61] used 2.0 M sodium hydroxide assisted by microwave (800 W) to obtain high purity of nanosilica from RHA. The modification could enhance the properties of the nanosilica obtained from the conventional method in terms of morphology, size, and purities as presented in **Table 2**. Furthermore, acid leaching method has been presented in **Table 3**. It was found that acid leaching method produced high purity of nanosilica as reported by Bakar et al. [68], where 99% purity of nanosilica was obtained with 500–700 nm. Similarly, Mahmud et al. [66] also reported that acid leaching method produced 99% high purity of nanosilica using HCl. Referring to above, acid leaching improves the other metal removal and increases the purity of nanosilica. It is noticed that single method like alkaline extraction and acid leaching method required high temperature thermal process to acquire nanosized silica. While combination of acid leaching and alkaline method could provide high purity of nanosilica without high temperature thermal process, in another words, mild condition, as reported by Adam et al. [63] and Selvakumar et al. [60].

2.2.5 Discussion for method

As mentioned above, two major methods that have been widely adopted by researcher in nanosilica production are thermal and chemical methods. Fluidized bed reactor could produce high purity of nanosilica at 92–96% using thermal process at 800–950°C for 4–8 h [38]. While chemical method modified alkaline method showed promising properties, produced 95% purity nanosilica with 110°C (mild condition) [63]. It is noticed that thermal method used a lot of energy (high temperature and long reaction time) to acquire nanosilica, whereas chemical method required high usage of chemicals (acid and alkaline solution), which

Alkaline extraction method								
No	Method	Material	Time	Temperature (after getting silica gel)	Size	Purity	Yield	References
1	Using alkali solution and followed by acid neutralization and undergo thermal process (calcination)	RH	30 minutes	550°C	98–272 nm	—	—	Zulkifli et al. [51]
2		RH	4 hours	700°C	20–25 nm	>95%	—	Hassan et al. [52]
3		RH	48 hours	80°C	20–30 nm	99.48%	91.91% @pH 3	Liou and Yang [53]
4		RH	24 hours	50°C	10–20 nm	—	—	Awizar et al. [56]
6		RHA	24 hours	60°C	—	—	80% (NaOH concentration of 1.0 mol dm ⁻³)	Haq et al. [57]
7		Wheat husk ash	1 hour	550°C	227 nm	—	—	Cui et al. [58]
8		RHA	48 hours	80°C	—	50.15%	—	Masnar and Coorey [59]
Alkaline modification method								
1	Acid pre-treatment before conventional alkaline extraction	RHA	1 hour	130°C	—	85% (1.0 N NaOH)	—	Selvakumar et al. [60]
3		RHA	24 hours	120°C	47 nm		69–73% (250 ml Na ₂ CO ₃ solution)	Zhang et al. [62]
5		RH	overnight	110°C	15–91 nm	~95.5%	—	Adam et al. [63]
2	Separating rice husk ash silica gel from microwave heating	RHA	48 hours	150°C	—	—	—	Rungrodnimitchai et al. [61]

Table 2.
List of alkaline technique based on its parameters.

Acid leaching method								
No	Method	Material	Time (h)	Temperature (after getting silica gel)	Size	Purity	Yield	References
1	Raw material undergoes acid leaching at mild condition and followed by thermal process (calcination)	Palm ash	30 minutes	800°C	—	92% (6% citric acid)	—	Faizul et al. [64]
2		RH	1 hour	650°C	181.2– 294.7 nm	—	—	Carmona et al. [65]
3		RH	2 hour	700°C	53–55 nm	99.761% (HCl), 99.760% (citric acid)	—	Mahmud et al. [66]
4		RH	48 hours	50°C	6 nm	98.801%	—	Rafiee and Shahebrahimi [67]
5		RH	2 hours	600°C	500–700 nm	>99%	—	Bakar et al. [68]

Table 3.
List of acid leaching method based on its parameters.

resulted in cost intensive. Moreover, high thermal and chemical methods also contributed some bad impact on environment due to releasing of nonfriendly gases and waste materials produced, respectively. Thus, low cost and environmental friendly method is required to idealize for industrial application. In recent year, Mor et al. [72] reported a low-cost method in preparing nanosilica using green technology. Initially, the RHA was dissolved in NaOH and placed to autoclave at 100°C for 2 h to obtain the mixture slurry and followed dilution with distilled water for phase separation. The supernatant proceeds for silica extraction with filtration process. The filtrate precipitated with HCl and followed by washing and oven dried at 50°C where high purity of nanosilica (99%) was obtained.

3. Method of nanofluid preparation

There are two main methods for preparing nanofluids, which are one-step and two-step methods. One-step method combines between synthesis and dispersion of nanoparticles into base fluid in one step. Several differences exist in these methods. In one of the conventional techniques called the one-step method of direct evaporation, the nanofluid is obtained inside the base fluid by solidifying the nanoparticles that are originally in the gaseous phase. Akoh et al. [73] created the one-step direct evaporation method and are referred to vacuum evaporation on the method of running oil substrates. The concept of this method was originally developed the nanoparticles in order to obtain dry nanoparticles. Particles are difficult to differentiate from liquids. The technique of laser ablation to obtain alumina nanofluids is another one-step technique [74]. Zhu et al. [75] used one-step technique to prepare copper nanoparticles in the medium of ethylene glycol.

The two-step method is widely utilized for nanofluid preparation, and most of the cases used nano powders (solid) during the preparation. The technique first produces nanoparticles; thereafter, the nanoparticles will be dispersed into the base fluids. Jena et al. [76] used hydrogen reduction techniques to prepare nanoparticles from the chemical precursor and dispersed them into fluid via two-step methods. The use of ultrasonic technique to disperse the nanoparticles into deionized water, which containing sodium lauryl sulfate (SLS) during nanofluid preparation, is also one of the widely adopted technique [77].

Wei and Wang [78] synthesized copper nanofluids by using a constant flow microfluidic microreactor. Through this technique, the microstructure copper nanofluids can be synthesized continually by changing parameters such as additive and flow rate and reactant concentration. Using a new precursor conversion technique, ultrasonic and microwave irradiation can be used to synthesize CuO nanofluids with a better solid volume fraction (~10 vol%) [79]. Under microwave irradiation, the $\text{Cu}(\text{OH})_2$ precursor will entirely converted into CuO nanoparticles in H_2O . The ammonium citrate stops nanoparticles from growing and aggregating, resulted in stable CuO nanofluid with a better heat conductivity than the ones produced by using other dispersive techniques. The easier way to acquire colloids of monodisperse noble metal is by using the technique of phase transfer [80]. The two-phase cyclohexane system, aqueous formaldehyde, is transmitted to cyclohexane in water through the dodecyl amine response to cyclohexane as an intermediate form reduction. Cyclohexane solution intermediates can reduce Ag or Au ions in aqueous solution to form dodecyl amine-protected Ag and Au nanoparticles at room temperature. Feng et al. [81] used phase transfer method in preparing Au, Ag, and Pt nanoparticles based on a reduction in solubility of PVP in water at increased temperature. The technique of phase transfer is also used to prepare stable Fe_3O_4 nanofluids based on kerosene. Oleic acid is effectively grafted in chemisorbed

fashion on the surface of Fe_3O_4 nanoparticles, enabling Fe_3O_4 nanoparticles to be well compatible with kerosene [82]. The phase-transfer technique prepared Fe_3O_4 nanofluids not showing “time reliance of the characteristic of heat conductivity” as reported previously. The main problem is the production of nanofluids with a controllable microstructure. It is well recognized that nanofluid characteristics are highly dependent on nanomaterial structure and shape. Recent study demonstrates the improvement in conductivity and the stability of nanofluids when synthesized using chemical solution compared to other techniques [83]. This technique is differentiated by its controllability from others. The microstructure of nanofluids can be differed and manipulated by regulating the factors of synthesis, including acidity, radiation from the microwave and ultrasonic, temperature, acidity, concentrations, and types of reactor and the order of additives added to the solution.

Silica is widely used as both precursor and material for ceramic product manufactures. Silica has high abrasion resistance, high thermal stability, and electrical insulation [84]. Fazeli et al. [85] dispersed nanosilica into the distilled water, and the suspension was sonicated for at least 90 min in an ultrasonic bath. They discovered that silica nanofluids remained stable without visible settlement for 72 hours. Pang et al. [86] used ultrasonic to mix SiO_2 -pure methanol by ultrasonic (750 W, 20 kHz) and Al_2O_3 -pure methanol to break the agglomeration through vibration during 2 hours. They examined the impact of the zeta potential and pH of methanol-based nanofluids in nanoparticles. They proved that the zeta potential is closely connected with the pH of the suspension. Al_2O_3 nanofluids have zeta potential >60 mV; meanwhile, SiO_2 nanofluids have zeta potential >30 mV, which indicated that both nanofluids were well stable. The visualization and Tyndall effect (light dispersion study in nanoparticles) images show that nanofluids based on methanol are well dispersed. Bolukbasi and Ciloglu [87] have been using magnetic stirrer to prepare SiO_2 nanofluids. The suspensions were continuously sonicated for 2 hours into an ultrasonic vibrator (600 W and 40 kHz). The researcher confirmed that no sedimentation was traced throughout the experimental period. Darzi et al. [88] applied distilled water to the specified quantity of SiO_2 nanoparticles and mixed for half an hour with a magnetic stirrer. Afterward, the ultrasonic vibrator was dispersed for 2 hours to have the stable suspension. During the synthesis method, no surfactant/dispersant additives were added, otherwise affecting the thermophysical characteristics of nanofluid. Silica nanoparticles were used to function through grafting silanes directly on the silica nanoparticles surfaced by Yang and Liu [89]. For the functioning method, silane of (3-glycidoxylpropyl) trimethoxysilane has been used as the reacting silane and silica nanoparticles with a mass ratio of 0.115. Nanoparticles were successfully dispersed into water. Meanwhile, the solution was stored at 50°C for 12 hours of ambient temperature. Functional nanoparticles were discovered to continue to disperse even when the nanofluid remained at a mass concentration of 10% for 12 months. In addition, no sedimentation has been reported. They prepared traditional nanoparticles by dispersing and oscillating them to water. Powder of silica nanoparticles was first dissipated into deionized water and then oscillated in an ultrasound bath for 12 hours. Sedimentation was found after a few days. Anoop et al. [90] dispersed SiO_2 nanoparticles with an ultrasound bath in deionized water for 30 minutes. In addition, the application of a sonicator type probe to the nanofluids intensified this colloidal suspension. The suspension was provided by cyclic ultrasonic pulses for around 15 minutes in order to obtain maximum particle de-agglomeration. By adding nitric acid reagent grade from the isoelectric pH value, the pH value of the suspension was kept at 4.5. Nanofluids have been indicated to show excellent stability over period. Qu and Wu [91] developed nanofluids Al_2O_3 and SiO_2 water. The pH value of the nanofluids was modified as a first step to a value that was far from the respective isoelectric point

(IEP) of silica (with pH ~ 3) or alumina (with pH ~ 9), then added to the water nanoparticles (with pH ~ 9) and with pH ~9. The dispersion solution was vibrated in an ultrasonic bath for about 4 hours afterward. Alumina nanoparticles have been discovered to be better dispersed. Hwang et al. [92] generated CuO, MWCNT, and SiO₂ nanofluids by using an ultrasonic disruptor. For SiO₂ and CuO nanoparticles, they acquired stable suspensions. Nevertheless, sodium dodecyl sulfate (SDS) has been used as a surfactant to produce MWCNT nanofluids as the MWCNTs are entangled and aggregated into aqueous suspension.

4. Potential application of nanofluids

Nanofluids have been proved in experiment and theory in enhancing heat transport and energy efficiency for various manufacturing purposes such as mechanical applications, electronic cooling, transportation, and many more in a range of thermal exchange technologies. In all applications, nanofluid performs a key position in creating the next device generation for various medical and engineering applications. Some of the following applications are discussed below.

4.1 Solar applications

The temporal difference between energy supply and energy requires rendered storage system design. Stocking of thermal electricity as in solar thermal installations as sensitive and latent heat, with an emphasis on an effective use as well as preservation of wastewater and solar energy in buildings and manufacturing, has become a significant element in energy planning [93]. Compared to the basic material, the PCMs contained extremely high thermal conductivity. Liu et al. [94] synthesized a new type of nanofluid phase change material (PCM) with a tiny portion of TiO₂ nanoparticles suspended in aqueous saturated BaCl₂ solution. The PCM nanofluids had relatively better thermal conductivity compared to base material. The cool storage/supply rate and the cool storage/supply capability have risen significantly compared with aqueous solution of BaCl₂ without the need of additional nanoparticles. The greater thermal characteristics of PCMs show that in cool storage applications, they have the ability to replace standard PCMs. Copper nanoparticles are the additives that are efficient to enhance PCM cooling and heating levels. Shin and Banerjee [95] recorded an anomalous increase in nanofluid-specific heat capacity of high temperature. The researcher discovered that 1 wt% SiO₂ nanoparticle-doped alkali metal chloride salt eutectic improves the specific thermal capacity of nanofluid by ~15% to be used in solar thermal energy storage facilities. One of the methods used to store solar energy is the use of PCMs. Paraffin is the most appropriate of many accessible PCMs because of its attractive features, including large latent heat capacity, insignificant super cooling, and low cost. The intrinsic low thermal conductivity (0.21–0.24 W/mK), however, avoids possible applications [96]. Wu et al. [96] numerically researched Cu/paraffin nanofluid PCM melting procedures. Their findings showed that the melting time with 1 wt% Cu/paraffin is saved by 13.1%. The study found that the addition of nanoparticles is an effective way for increasing the heat transfer of latent heat energy storage system.

Solar energy is an important factor in energy use because of a shortage of electricity generation. Lack of fossil fuel and environmental factors will limit future use of fossil fuels. Researchers are encouraged to discover alternative energy sources. This became even more widespread as fossil fuel prices continue to increase. In latest years, solar energy has had a notable advantage. In just 1 hour, the earth gets more sun energy than the world consumes for a year [97, 98].

Solar collectors are specific types of heat exchangers that convert solar energy to transport medium internal energy. This equipment absorbs incoming sunlight, which is converted into heat and transmitted the heat to a fluid that flows through the collector (generally oil, air, and water). The energy is collected directly from the working fluid to the hot water or space conditioning or thermal energy storage tank, for night or on cloudy days [99].

Taylor et al. [100] found that the use of the graphite/therminol VP-1 nanofluid with volume fractions around 0.001% or less could be of benefit for 10–100 MWe energy crops. In combination with a solar thermal power tower with 100 MWe of capacity in a solar resource such as Tucson, Arizona, the researchers estimated that \$3.5 million more could be achieved each year. The supply of fresh water is more crucial arid distant areas of the globe. Solar desalination technologies are possible to overcome portion of the issue in these areas, where solar energy is accessible. The absence and untrustworthy drinking water is a main issue in developing countries. Global dryness and desertification are estimated to make drinking water a major problem in the world [101].

Greenhouse gas emission from fresh water production can be prevented by solar stills [102]. Many experts have researched solar stills and used different techniques to enhance their productivity. Gnanadason et al. [103] found that the productivity of solar system was influenced by nanofluids. The implications of putting carbon nanotubes (CNTs) to the water in a single solar basin were investigated. The findings have shown the addition of nanofluids that will enhance the efficiency by 50%. However, the quantity of nanofluid added to the water inside the solar was not yet mentioned. In addition to solar nanofluids, the economic growth should be perceived. Certain works in the literature disclosed the addition of dyes to solar stills could increase the efficiency. Nijmeh et al. [104] investigated that adding violet color to the solar water still improves the efficiency significantly by 29%. Furthermore, nanofluids (especially the CNTs) are more expensive, and this might therefore be a difficult task for the use of nanofluids in solar stills because the nanofluids in solar stills do not flow in a closed loop in order to recover them.

4.2 Automobile applications

Adding nanotubes and nanoparticles to the conventional engine coolants (ethylene glycol and water mixture), nanofluid lubricants can boost their thermal conductivity and enhance heat change rates and fuel economy [105]. Tzeng et al. [106] have studied the impacts of nanofluids on automatic transmission cooling. They spread CuO and Al₂O₃ nanoparticles and antifoams into the transmission fluid and then used four-wheel automatic transmission on a real-time basis. The findings indicate that CuO nanofluid has the lowest temperature distribution and the highest heat transfer impact on the rotating speeds [107]. CuO and nanofluids based on aluminum oxides were developed with the arc-submerged nanoparticle synthesis system along with the plasma charging arc system [108, 109]. Both types of nanofluids have increased the characteristics, including a greater boiling point, a greater viscosity, and a greater conductivity than conventional brake fluid. With greater viscosity, conductivity, and boiling point, the brake oil nanofluids reduce the vapor lock from occurring and offer greater safety in driving condition [110].

4.3 Electronic cooling

As IC (embedded circuit) and microelectronic parts decrease in size, the energy dissipation has risen dramatically. Better thermal management and cooling liquids are necessary for secure operation, with enhanced heat transport characteristics.

Nanofluids were regarded as working liquids for electronic cooling applications in heat pipes. Tsai et al. [111] used water-based nanofluid as the operating channel for circular heat pipe. It was intended as a heat diffuser and applied in CPU of notebook or desktop PC. The findings exhibited that the nanofluid heat pipes have considerably lower thermal resistance than deionized water. The findings showed that the thermal strength of a vertical meshed heat tube differs respectively with nanoparticle size. Ma et al. [112] examined the impact of nanofluids toward oscillating heat pipe transport capability. The experimental results reveal that the temperature difference between the evaporator and the condenser decreased from 40.9 to 24.3°C at an input energy of 80 W by 1 vol% nanoparticles. Lin et al. [113] examined nanofluids using silver nanoparticles in heat pulsating pipes and found supportive outcomes. The silver nanofluid enhanced the thermal transfer properties of the heat pipes. Vafaei et al. [114] found that nanofluids are efficient in engineering surface wettability and potentially surface tension. With a goniometer, the presence of a very small bismuth telluride nanofluid concentration significantly affected the wetting features of the surface. Concentrations as low as 3×10^{-6} improved the contact angle to more than 40°, showing clearly nanoparticles affect the force balance triple line vicinity. Experimental, numerical, and theoretical studies on nanofluid prove numerous prospective applications of nanofluids are present such as electronic cooling, displays, micro devices, cameras, thermal exchangers, military, spacecraft equipment, boats, medicine, atomic reactors, fuel cell and sensor applications. The stability of nanofluids is a major challenge for nanofluid commercialization. By solving the problems, significant developments are anticipated in many applications. Further study should be conducted on numerous heat and fluid applications.

4.4 Biomedical applications

Some special types of nanoparticles possess antibacterial activity or drug delivery properties, so that nanofluids that contain these nanoparticles have certain relevant properties [110]. Organic antibacterial products, especially at high temperatures or pressures, are often less stable. Consequently, inorganic materials such as metal oxides and metal have received considerable attention in the previous decade because they are able to resist severe process circumstances. ZnO nanofluid antibacterial behavior indicates that ZnO nanofluids are bacteriostatic to *Escherichia coli*. With the growing concentration of nanoparticles, antibacterial activity rises and the particle size decreases. Measurements of electrochemical show a direct interaction between ZnO and elevated ZnO levels of bacterial membrane (L. [115]). Jalal et al. [116] created ZnO nanoparticles with a green technique. An estimation of the reduction ratio of ZnO-treated bacteria was made on ZnO suspension activity of nanoparticles with *E. coli*, the bacteria's survival ratio reduces with increased nanofluid ZnO levels and time. Silver nanoparticles were discovered to depend on the size of silver particles for their antibacterial activity. Antibacterial efficiency was achieved by the very small silver concentration of 1.69 µg/mL Ag [117]. Lyon and Alvarez [118] suggested that C60 suspensions exhibit ROS-independent oxidative stress in bacteria that show protein oxidation, modifications in cell membrane potential, and cellular respiration interruption. The mechanism needs direct contact between bacterial and nanoparticles as well as contrast from nanomaterial antibacterial processes earlier reported involving ROS generation (metal oxides), or leaching of toxic components (nanosilver).

4.5 Discussion for applications

It was found that nanoparticles added to the base fluid improve the characteristics of fluids such as structure, thermal conductivity, viscosity, convective heat

transfer, density, and specific heat. In our review, we have narrowed down the application of nanofluids such as solar, automobile, electronic cooling, and biomedical application. It is noticed that the physical properties of nanoparticles such as size and crystallinity are influencing the nanofluid performance during its application. For instance, Micali et al. [119] explored the possibility to reduce temperature up to 13.6% on the exhaust valve seat and up to 4.1% on the exhaust valve spindle by 2.5% volume concentration on the cylinder head and the spindle of the exhaust valve. Al-Jethelah et al. [120] discovered improvements of solar thermal applications in terms of melting process through numerical and experimental by adding nanofluids into PCM. Said et al. [121] prepared 0.3% volume fraction of Al_2O_3 nanofluids and dispersed into distilled water and ethylene glycol as base fluid (ratio of 50:50) and discovered that it enhances the thermal performance by 24.21%. We believe that RH-derived nanosilica will provide similar performance compared to other semiconductor nanoparticles as mentioned above. Akilu et al. [122] attained ~27% thermal conductivity enrichment at 21.1% disparagement of specific heat by using hybrid nanofluids, and SiO_2 -CuO (0.5–2 vol%) dispersed into base fluid (Glycerol/EG). Yao et al. [123] did the research on the boiling efficiency of Al_2O_3 , SiO_2 , and their mixture with water at the ratio of 1:1. The significance of their study was its impact of pressure on the performance of boiling nanofluids. Based on the outcomes, nanofluid efficiency increased the pressure reduction. Authors also regarded the effects of nanoparticle size on the heat flux posed tiny rise while raising the nanoparticle size between 30 and 50 nm.

5. Conclusion

This book chapter collectively reviews the preparation method of rice husk nanosilica, its application as nanofluids, and nanofluid application in the industry. There are two main methods in preparing nanosilica, namely thermal and chemical methods. It is noticed that chemical method is more preferable than thermal method in terms of nanosilica purity, which is critical. The popular chemical methods widely used by the researcher are alkaline extraction and acid leaching method. It has found that utilizing solely single chemical method must follow high thermal treatment and high operating cost, which is not feasible. Thus, a combination or modification of the chemical method is required to improve the purity of nanosilica. Pre-acid treatment followed by conventional alkaline extraction presented better purity of nanosilica. The purity of nanosilica is a crucial property in nanofluid preparation, which will affect the performance of the nanofluids. There are one-step and two-step methods, which are widely adopted by the researcher in preparing nanofluids. One-step technique combines the production of nanoparticles and dispersion of nanoparticles into the base fluid with a single step. Meanwhile, in two-step method, nanoparticles are first produced and then dispersed into the base fluids. However, two-step method is preferable for rice husk nanosilica-based nanofluid preparation, which involves ultrasonic method. The application of the nanofluids has been explored such as solar application, automobile application, electronic cooling application, and biomedical application. It was found that nanofluids could improve the base fluid performance due to the additional of the nanoparticles. Even though the review focused on semiconductor-based nanofluids, we believe that rice husk nanosilica-based nanofluids could also have the similar trends of performance. Gradually, the awareness on the usage of “green” material in the product is rising, and rice husk nanosilica could be an ideal candidate as nanoparticle and nanofluid application.

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