Review

Generation of High Quality Biogenic Silica by Combustion of Rice Husk and Rice Straw Combined with Pre- and Post-Treatment Strategies—A Review

Hossein Beidaghy Dizaji ^{1,2,*}, Thomas Zeng ¹, Ingo Hartmann ¹, Dirk Enke ²,
Thomas Schliermann ¹, Volker Lenz ¹ and Mehdi Bidabadi ³

¹ DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH, 04347 Leipzig, Germany; Thomas.Zeng@dbfz.de (T.Z.); Ingo.Hartmann@dbfz.de (I.H.); Thomas.Schliermann@dbfz.de (T.S.); Volker.Lenz@dbfz.de (V.L.)

² Institute of Chemical Technology, Leipzig University, 04103 Leipzig, Germany; dirk.enke@uni-leipzig.de

³ School of Mechanical Engineering, Department of Energy Conversion, Iran University of Science and Technology (IUST), Narmak, 16846-13114 Tehran, Iran; bidabadi@iust.ac.ir

* Correspondence: hossein.beidaghy@dbfz.de

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Abstract: Utilization of biomass either as a renewable energy source or for the generation of biogenic materials has received considerable interest during the past years. In the case of rice husk (RH) and rice straw (RS) with high silica contents in the fuel ash, these approaches can be combined to produce high-grade biogenic silica with purities >98 wt % from combustion residues. The overall process can be considered nearly neutral in terms of CO₂ emission and global warming, but it can also address disposal challenges of rice husk and rice straw. For the resulting biogenic silica, several advanced application opportunities exist, e.g., as adsorbents, catalysts, drug delivery systems, etc. This article provides a comprehensive literature review on rice husk and rice straw combustion as well as applied strategies for raw material pre-treatment and/or post-treatment of resulting ashes to obtain high quality biogenic silica. Purity of up to 97.2 wt % SiO₂ can be reached by combustion of untreated material. With appropriate fuel pre-treatment and ash post-treatment, biogenic silica with purity up to 99.7 wt % can be achieved. Studies were performed almost exclusively at a laboratory scale.

Keywords: biogenic silica; rice husk; rice straw; ash quality; combustion

1. Introduction

According to the report of International Energy Agency (IEA) in 2017, the worldwide share of renewable energy reached 23.9% in the electricity sector, 10.3% for power production and 3.4% for transportation. A further increase to 29.4%, 11.8% and 3.8%, respectively, is expected until 2023 [1]. Besides solar, hydrothermal and wind energy, bioenergy, in particular the exploitation and valorization of agricultural side products and biogenic residues, will play an important role to enable this sustainable development.

Biomass needs to fulfill the following criteria as a sustainable resource of energy: (1) it should be readily available; (2) arable land for food resources should not be affected by biomass for energy generation; and (3) it should produce zero waste and have no negative impact on the environment [2]. In this regard, rice husk (RH) and rice straw (RS) as by-products in rice production and milling processes can fulfill these criteria. Rice represents the second largest share of any crop in the world based on the report of Food and Agriculture Organization of the United Nations (FAO) [3], and the amount is steadily increasing, Figure 1. The world capacity in production of paddy rice in 2015 and 2016 was around 739 and 755 million tons, respectively [4,5]. According to the FAO rice market

monitor [4], there are more than 50 countries with paddy rice production, with the largest cumulated production originating from Asia (681.8 million tons) followed by America (36.3 million tons) and Africa (32.6 million tons), while Europe and Oceania provide only marginal contributions of 4.1 million tons and 0.3 million tons, respectively.

Figure 1. Paddy rice production worldwide (data adapted from reports of FAO between 2006 and 2018 [4–16]); values for 2017 and 2018 are estimated and forecasted data according to the latest report of FAO [4].

Depending on the crop and harvesting method, approximately 20–25 and 40–60 wt % db (dry basis) of paddy rice are RH and RS, respectively [17,18]. RH and RS do not compete with food resources for land usage, and because of the abrasive structure and low nutritional value, they are not suitable for food and fodder, and usually are disposed [19–21]. Consisting predominantly of organic matter, i.e., cellulose, hemicellulose, and lignin, RH and RS are applicable for the use as sustainable fuel for energy generation [22–24]. After combustion of RH and RS, approx. 10–20 wt % of the initial fuel remains as ash rich in silica (i.e., “biogenic silica”). It can be an economically valuable material for various applications including the cement and concrete industry [25–27], an adsorbent to remove heavy metal ions such as lead (II), mercury (II), zinc (II) and nickel (II) ions from wastewater streams, as catalyst [28–38], for synthesis of zeolites and mesoporous silica [39–46] or for drug delivery systems [47,48]. Depending on the anticipated application, biogenic silica is required with different purities. For the utilization as pozzolan in concrete, a silica purity of at least 97 wt % db is sufficient [49]. In contrast, advanced applications such as electronics [50] and solar applications [51] require silica purity of up to 99.9 wt % db. Similarly, different characteristics are desirable depending on the desired application, e.g., negligible slagging tendencies [52], low carbon content and high silica purity for synthesizing advanced materials [53], whiteness and proper particle size for filler applications [54], amorphous structure and an optimized pore system (high specific surface area) [53,55].

Commonly, porous silica is produced on an industrial scale by precipitation from alkaline silicates [50]. Alkaline silicates (water glass) are typically obtained from carbonate powders reacting with silica sand, which is a very energy intensive process and requires very high temperatures (approx. 1400 °C) [50,56]. Water glass can also be produced by hydrothermal treatment of sand with lyes, which is also an energy consuming procedure [57]. The traditional process is not only expensive, but also it is

hazardous to the environment because during the production of 1 ton of silica, approximately 0.23 ton carbon dioxide, 0.74 ton sodium sulfate and 20 tons of waste water are produced, and it violates the principle of sustainable development [50]. Therefore, an economically feasible and environmentally benign route as an alternative method is required to produce silica. In this respect, a combined energy application and biogenic silica production from RH and RS under controlled conversion conditions would be a promising approach regarding climate protection and zero waste production. Currently, open burning and land filling are the common strategies for RH and RS disposal, which have their own challenges including air pollution, greenhouse gas emission, and large landfill space occupancy because of their low density [24,58]. Furthermore, uncontrolled open burning of these materials produces crystalline ash with high emissions [59], which is well recognized as a lung carcinogen as well as the health risk from silicosis caused by silica deposition in the lung tissue [60,61]. To overcome these issues, researchers have been investigated feasible, economical, and environmentally friendly strategies to convert RH and RS into pure biogenic silica via combustion based on various scientific publications [53,54,62–73] and patents [74].

Several studies have been carried out to review the field of biogenic silica production and combustion of RH and RS as raw materials [24,50,51,55,75–89]. Most of these studies have focused on applications of the rice husk ash (RHA), rice straw ash (RSA) and pure biogenic silica [50,75,81,88–90] or the synthesis of advanced materials from RHA and RSA [50,76,77,90], influence of RHA and RSA on concrete and cement properties [78,80,86,87] or energy and power generation using RH and RS [79,82,85]. However, to the best of our knowledge, there is no review highlighting the combination of pre-treatment strategies as well as post-treatment of the ashes with combustion in order to produce high quality biogenic silica from RH and RS. This review provides a comprehensive literature survey to cover both treatment and combustion for high quality biogenic silica production. First, fuel properties of RH and RS are reviewed and compared with clean wood. Subsequently, combination of several pre-treatment strategies to increase the quality of biogenic silica including chemical pre-treatment and combustion of the raw materials as well as post-treatment of RHA and RSA are discussed.

2. Fuel Properties of Rice Husk and Rice Straw

The organic matter of RH and RS consists predominantly of cellulose, hemicellulose, and lignin [91]. Table 1 lists organic contents, proximate and ultimate analysis as well as the ash compositions of RH and RS. Wood is included as a reference material for comparison. Fuel properties of high quality wood pellets fulfilling requirements of class A1 of the ENplus certification scheme were obtained from Pollex et al. [92]. According to Table 1, the ash obtained from wood uncontaminated by soil impurities is mainly composed of alkaline earth metals followed by silicon and potassium [93–97]. According to Table 1, since RH and RS have different ash forming elements than wood, they show completely different ash melting behavior. The ash content of RH and RS is one order of magnitude higher than the ash content of clean wood. Silicon is by far the most abundant element among the inorganic matter both in RH and RS [58,59,72,98–101]. Ca, Mg, K, Na, P, S, Cl, and Al are also included but to a far lesser extent [59,73,98,99,102–105]. Association of these ash forming elements as well as their distribution in the biomasses have a major impact on ash melting behavior [106] and consequently determine the remaining silica purity and quality [105,107–109].

Table 1. Fuel properties of RH, RS, and wood (data were taken from [23,59,99,102,110–155] for RH, from [105,109,112,119–121,125,135,136,145,156–175] for RS and from [92,110,176–178] for wood; n: number of data sets.

Characteristic	Rice Husk (RH)				Rice Straw (RS)				Clean Wood Pellet ¹ (W)			
Organic Type	CHL and HLC				CHL				CHL			
Inorganic Type	S Type				S Type				C Type			
Inorganic Sub-Type	HA				HA				LA			
	Mean	Minimum	Maximum	n	Mean	Minimum	Maximum	n	Mean	Minimum	Maximum	n
Moisture content (MC), wt %	8.79	4.64	12.08	21	8.74	5.58	13.06	12	6.90	3.30	10.80	249
Ash content (AC), wt % db	16.30	7.68	24.60	48	16.52	9.22	22.60	26	0.40	0.22	0.68	249
Volatile matter (VM), wt % db	65.77	51.98	81.60	43	67.82	49.00	80.20	18	83.75	82.00	84.90	4
Fixed carbon (FC), wt % db	15.92	12.40	25.10	41	15.18	6.62	28.40	17	15.59	14.07	17.20	4
C, daf ²	41.49	36.42	50.70	48	40.06	35.61	49.40	27	46.39	42.18	49.8	3
O, daf	38.51	29.33	53.70	48	38.01	29.23	53.64	26	46.95	43.7	50.54	3
H, daf	5.31	4.30	7.50	48	5.06	3.56	6.88	27	6.14	6.03	6.30	3
N, daf	0.84	0.09	4.26	47	0.76	0.17	1.41	27	0.11	0.05	0.51	174
S, daf	0.08	0.00	0.34	5	0.20	0.06	0.66	23	0.008	<0.005	0.037	249
Cl, daf	0.11	0.01	0.20	7	0.57	0.08	1.01	11	0.009	<0.005	0.042	249
Low heating value (LHV) (MJ/kg)	14.14	12.30	15.70	12	14.94	12.73	17.25	3	17.7	16.6	19.2	220
Cellulose, wt %	32.87	25.20	43.80	9	37.40	37.00	37.80	2	45.20	45.20	45.20	1
Hemicellulose, wt %	26.09	18.10	44.90	9	24.00	22.70	25.30	2	32.70	32.70	32.70	1
Lignin, wt %	21.73	13.60	34.80	9	18.45	13.60	23.30	2	22.10	22.10	22.10	1
Al ₂ O ₃ ³	0.34	0.17	0.78	7	0.59	0.07	1.94	14	3.63	4.43	2.65	81
CaO	1.23	0.24	3.21	8	2.99	1.60	10.12	13	37.94	<5.97	19.94	249
Cl	0.34	0.08	0.73	3	3.76	0.00	12.55	6	0.16	0.16	0.16	1
Fe ₂ O ₃	0.23	0.10	0.40	8	0.46	0.10	0.98	13	1.72	1.09	2.67	3
K ₂ O	4.31	2.29	8.30	8	13.85	11.30	20.92	14	19.84	<4.37	10.53	249
MgO	0.72	0.19	2.13	8	2.13	1.49	5.02	13	8.24	32.53	5.00	249
MnO	0.13	0.02	0.24	2	0.28	0.27	0.29	3	2.51	0.40	4.61	2
Na ₂ O	0.19	0.03	0.37	7	1.31	0.14	2.71	14	1.20	<1.15	8.64	249
P ₂ O ₅	1.05	0.43	3.70	7	1.65	0.61	2.65	12	4.68	3.76	6.39	208
SiO ₂	89.92	86.92	94.38	8	71.33	55.08	82.13	14	23.72	<45.61	42.90	249
SO ₃	0.68	0.34	0.96	5	1.56	0.84	4.95	10	3.38	0.80	5.30	3
TiO ₂	0.02	0.01	0.02	5	0.03	0.01	0.09	9	0.89	0.1	1.6	3

¹ wood uncontaminated by soil impurities. ² dry ash-free basis. ³ reported values are on ash bases.

Origin of the raw materials can have a significant impact on the inorganic composition of fuel ashes of RH and RS. For instance, as shown in Table 2, RH from Egypt, Cambodia, and Italy was evaluated in the same laboratory with the same measurement techniques [72,98]. Results highlight that Si, K and P contents of the fuel ash can vary significantly. Differences in compositions are due to a variety of factors, such as climate, soil types, harvesting season, the amount of fertilizers used during the rice cultivation, geographical and environmental aspects [53,179–181].

Table 2. Accompanying ash constituents of RH (wt % db) from different locations.

Location	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	SO ₃	Cl	Others ¹	Method	Ref.
Egypt	57.90	N.R.	14.60	2.30	3.40	1.00	1.00	13.80	3.20	2.30	0.50	XRF ²	[98]
Cambodia	80.18	N.R.	3.89	1.55	0.81	0.83	4.29	3.80	2.05	N.R.	2.60	XRF ²	[72]
Italy	83.20	N.R.	2.73	1.60	1.00	0.33	3.57	4.12	1.52	N.R.	1.92	XRF ²	[72]

¹ other measured inorganic oxides. ² X-ray fluorescence.

In Table 1, organic and inorganic types of biomass samples are defined according to Vassilev et al. [110,182–184]. Accordingly, Figure 2 illustrates a possible biomass classification based on the organic and inorganic composition. In Figure 2a, biomasses are arranged according to their relative share of cellulose, hemicellulose and lignin. For the majority of biomasses, cellulose is the predominant macromolecule based on the weight portion [110] followed by hemicellulose and lignin (Cellulose > Hemicellulose > Lignin, i.e., CHL). Marine organisms are usually characterized by hemicellulose as the predominant macromolecule and particularly low contents of lignin (Hemicellulose > Cellulose > Lignin, i.e., HCL). Nut shells and pits are often located in the LCH region based on their high lignin contents. RH and RS are usually located in the CHL region and in some cases also in the HLC region in Figure 2a [111]. Figure 2b shows fuel ashes dominated by components in the silicon, calcium, and potassium corners or between the calcium and potassium corners with S, C, K, and CK types, respectively [184]. Moreover, sub-types of HA, MA, LA represent high, medium, and low acid tendencies, respectively [184]. In Figure 2b, wood indicates the mean value of 249 datasets for evaluated wood pellet samples presented by Pollex et al. [92,185]. According to Figure 2b, both RH and RS have very low amounts of CaO + MgO + MnO in their fuel ash compositions compared to wood. On the other hand, the silica-based group of metal oxides (SiO₂ + Al₂O₃ + Fe₃O₄ + Na₂O + TiO₂) is higher in both RH and RS fuel ashes compared to wood fuel ash. Among the RS and RH fuel ashes, RH fuel ash has higher K₂O + P₂O₅ + SO₃ + Cl₂O in its inorganic composition. Figure 2b was defined based on empirical findings regarding ash melting tendencies of dedicated fuel assortments and can be divided into three distinct sections with low (<1100 °C), medium (1100–1300 °C) and high (>1300 °C) initial deformation ash fusion temperature (DT) [184]. RH is located close to the area associated with high DT, Figure 2b. Accordingly, it is expected that RH shows low melting tendency during the combustion process. In contrast, RS is located near the area associated with low DT; therefore, it is anticipated that RS shows a higher melting tendency during the combustion process than RH. However, some data points in Figure 2b are outside of the defined areas for which ash melt investigations are available, and it indicates some research gaps in knowledge. Therefore, scientific work must be carried out here to close the gaps.

According to Table 1 and Figure 2b, the silicon content of both RH and RS is high and suitable ash melting temperatures can be expected. However, there are several strategies to improve the purity of biogenic silica, which are discussed in Section 3.

Figure 2. Biomass classification systems based on data from (a) organic compositions; and (b) inorganic composition of the fuel ash and ash melting tendency (data were taken from [59,92,99,102,105,109–112, 114–116,156,157,186]).

3. Production of Biogenic Silica

Biogenic silica should have a low carbon content and high purity in order to be used in synthesizing advanced materials and for solar applications [50,51,53]. High specific surface area

(SSA) and pore volume are required for catalytic applications [53]. Furthermore, biogenic silica should also be amorphous with no slagging tendency for any applications. To optimize production of biogenic silica with high quality the following three steps may be addressed: (1) combustion of RH and RS, (2) additional pre-treatment of the raw materials and/or (3) post-treatment of RHA and RSA.

3.1. Combustion of Rice Husk and Rice Straw

During thermochemical processes, the temperature of the RH and RS is increased under either oxygen or air atmosphere (combustion, $\lambda \geq 1$), inert atmosphere such as nitrogen or argon (pyrolysis, $\lambda = 0$), or with stoichiometric amounts of air, oxygen, or CO_2 (gasification, $0 < \lambda < 1$) in order to decompose organic components. In general, combustion is typically applied to produce biogenic silica [20]. Therefore, the focus of the present work is on combustion of RH and RS.

For silica purity, temperature and residence time are two main influential factors. The purity of resulting silica increases by increasing the conversion temperature (CT) and residence time (RT) [20,69,187,188]. However, higher CT and RT can increase the risk of crystallization of the obtained biogenic silica [64,189]. According to Table 3, during the combustion process, the carbon content of RHA dramatically diminishes and the purity regarding residual carbon content sharply raises by increasing the CT from 300 to 600 °C [20]. By increasing the CT, carbon content and silica purity remain around the same until SiO_2 crystallization takes place [19,20,69]. On the other hand, higher CT and RT reduce specific surface area (SSA) and total pore volume of RHA [19,71]. Often, this is attributed to the reduction in the carbon content and ash agglomeration, resulting in diminished porosity [189]. According to Table 3, close to 600 °C, SSA and pore volume strongly depend on the CT, and they drastically decrease by increasing CT from 600 to 700 °C or above [19,71]. Therefore, to produce high quality silica, it seems that the optimum CT for combustion of untreated RH is around 600 °C. The quality of the resulting biogenic silica also depends on the combustion technology [179,190].

Sufficient air flow rate is required for complete combustion in order to produce pure biogenic silica; otherwise, the resulting ash will contain unburned carbon [67]. The heating rate (HR) during combustion also plays an important role in the quality of the remaining ash [54,188,191,192]. The purity of the silica and consequently the brightness of the resulting ash deteriorate when HR increases, although pore volume and SSA of the remaining ash increase at the same time [54,192].

Usually, a multi-step decomposition of RH and RS has been applied in lab-scale studies to obtain high purity biogenic silica with high SSA and low carbon [72,98,193]. For the decomposition of the individual macromolecules cellulose, hemicellulose, and lignin, as described in Section 2, different temperatures are used [72,98,100,193,194]. This strategy guarantees amorphous structure of the resulting silica since the maximum temperature never exceeds crystallization temperature [72]. The range of crystallization temperature is defined in Section 3.2. However, upscaling of such time-consuming sequential combustion processes at industrial and bench-scales is not feasible. A sequential combustion process can also be designed by pyrolysis of RH followed by an oxidization process (combustion). This strategy was shown to produce amorphous silica at low CTs with silica purity higher than 99.9 wt % with a very low carbon content [195]. Table 3 summarizes the result of different studies in the field of biogenic silica production using combustion of RH.

In conclusion, quality of biogenic silica can be adjusted by combustion parameters such as CT, RT and heating rate. To achieve purities exceeding approx. 97.2 wt %, further purification strategies have to be employed.

Table 3. Combustion of RH to obtain pure biogenic silica.

Input Material, Source, Silica Content in Fuel Ash	Combustion Process	Exp. Technique	Scale	Main Findings	Reference
Material: RH Source: Riceland Foods, Arkansas in the US ¹ . Silica content: N.R.	RH was combusted at different temperatures (700, 750, 800, 850, 900, and 950 °C). Atmosphere: air	TORBED reactor	The reactor used was 400 mm in diameter, and average fuel feed rate was 26.5 kg/h.	Resulting RHA had silica purity between 95.2 and 96.7 wt %. With low reactor RT ² of <10 min, RHA crystallization started at 950 °C. Loss of ignition (LOI) decreased from 1.8 to 1.0 wt % by increasing CT ³ from 700 to 900 °C. Furthermore, by raising CT from 700 to 900 °C, SSA ⁴ , pore volume and average pore radius decreased from 37 to 6 m ² /g, 0.11 to 0.02 cm ³ /g, and 1.9 to 1.2 nm, respectively.	Blissett et al., 2017 [19]
Material: RH Source: Heilongjiang province, China. Silica content: N.R.	RH was put in the furnace at 600, 700, 800, or 900 °C for 30 min. Atmosphere: air	Muffle furnace	Lab-scale	Silica purity in RHA obtained at 600 °C was 92.1 wt %. Both pore volume and SSA of the RHA drastically declined by increasing CT from 600 to 700 °C, and then slowly decreased by raising CT from 700 to 900 °C. SSA of the RHA was 145 and 25 m ² /g at 600 and 700 °C, respectively.	Chen et al., 2017 [71]
Material: RH Source: state of Rio Grande do Sul, Brazil. Silica content: N.R.	Combustion at around 700 °C Atmosphere: air	RH was combusted in three different combustion technologies: moving grate reactor, suspension/entrained combustion chamber, and fluidized bed.	The output electricity power capacity of the moving grate reactor, suspension/entrained combustion chamber, and fluidized bed were 3.8, 12.5, and 5 MWh, respectively.	Quality of the RHA (silica purity and carbon content, and the structure of the ash) was affected by combustion technologies. The highest silica purity (96.7 wt %) and the lowest LOI (2.96%) were obtained using fluidized bed technology. Consequently, SSA was 11, 27 and 39 m ² /g in fluidized bed, suspension/entrained combustion chamber, and moving grate reactor, respectively. XRD results indicated that the ashes from suspension/entrained combustion chamber are completely amorphous, while products from moving grate reactor and fluidized bed were completely or partially crystalline, respectively.	Fernandes et al., 2016 [179]
Material: RH Source: Harbin, Heilongjiang province, China. Silica content: N.R.	Heating RH at 5 K/min to 600 °C for 1 or 2 h, or to 700 °C for 1 h. Atmosphere: air	Muffle furnace with half-opened door for airflow control.	Lab-scale	Silica purity was 92.09, 93.00, and 93.42 wt %, LOI was 1.52, 1.48 and 3.24, and SSA was 86, 90 and 27 m ² /g for combustion at 600 °C for 1 and 2 h, and combustion at 700 °C for 1 h, respectively. Results indicated that RHA obtained at 700 °C was darker than RHA obtained at 600 °C. It was interpreted that when conversion temperature is higher than decomposition temperature of potassium oxide in the fuel sample K ₂ O melts and entraps the unburned carbon content. Therefore, remaining carbon in the ash is high for RHA obtained at 700 °C compared to the RHA produced at 600 °C.	Bie et al., 2015 [69]
Material: RH Source: Quzhou, Zhejiang, China. Silica content: N.R.	RH was combusted at 5 K/min from room temperature to 300 to 750 °C with RT of 2 h. Atmosphere: air	Muffle furnace	Lab-Scale	Silica purity of RHA increased from 29.7 wt % at 300 °C to 94.1 and 96.3 wt % at 600 and 750 °C, respectively. Consequently, the carbon content decreased from 48.8 wt % at 300 °C to 5.4 and 3.2 wt % at 600 and 750 °C, respectively. The structure of RHA remained amorphous up to 600 °C, and then a crystalline cristobalite peak appeared in XRD patterns. Results showed that SSA, total pore volume, micropore and mesopore volumes decrease by raising the CT. For instance, SSA decreased from 60 to 6 m ² /g by increasing the CT from 300 to 750 °C.	Chen et al., 2011 [20]
Material: RH Source: N.R. Silica content: N.R.	Combustion of RH was investigated with slow and fast heating rates. In slow heating, the furnace was heated from room temperature to 700 °C at 5 K/min with RT of 4 h. In fast heating, RH was transferred to the furnace at 700 °C for 3 h. Atmosphere: N.R.	Muffle furnace with steel trays with size of 15 × 10 × 2.5 cm.	Lab-scale	The purity of biogenic silica and the carbon content were around the same in both RHAs obtained from slow and fast heating. The value of the silica purity for slow and fast heating rates was 90.20 and 89.80 wt %, respectively; whereas, the carbon content was around 4.2 wt % for both heating rates. However, brightness of the RHA obtained in slow heating was higher than the brightness for the fast heating rate.	Krishnarao et al., 2001 [188]

¹ The rice husk provided was parboiled and dried prior to shipping. ² RT: residence time ³ CT: conversion temperature ⁴ SSA: specific surface area.

3.2. Combination of Fuel Pre-Treatment with Combustion

Since RH and RS are composed of organic matter such as cellulose, hemicellulose, and lignin as well as inorganic matter [50,53,91], washing or leaching the fuel samples with specified chemical solutions can alter the organic and inorganic composition of RH and RS as well as the composition of resulting RHA and RSA. Ash-forming elements can be divided into water soluble, acid soluble and insoluble parts [71,196,197]. In general, alkali metals (potassium, sodium) belong to the water soluble portion of the ash while alkaline earth metals (calcium, magnesium) and manganese are acid soluble. Silicon, aluminum and iron species remain insoluble. Pre-treatment of RS can change the concentration of ash-forming elements such as potassium. Consequently, the location of RS in Figure 2b can be adjusted to a position associated with higher DT. Figure 3 shows the melting behavior of the RS and tap-water washed RS during the combustion process. Accordingly, washing with water can prevent melting and slag formation during combustion of RS [198].

Figure 3. Rice straw: (a) before combustion; (b) untreated RS combusted at 700–800 °C; (c) untreated RS combusted at 900–1000 °C; (d) washed RS combusted at 900–1000 °C [198]. Reprinted from Waste Management, 33, N. Said, T. Bishara, A. García-Maraver, M. Zamorano, Effect of water washing on the thermal behavior of rice straw, 2250–2256, Copyright (2013), with permission from Elsevier.

As illustrated by Figure 4, the effect of pre-treatment is more prominent in RS than in RH. According to Figure 4, simple water washing can change the position of RS from close to low melting temperature region to a high melting temperature part. This shift is far less pronounced for RH, which shows that washing does not have a drastic effect on the melting tendency of RH. In Figure 4, data points for original and treated RH and RS are outside of the defined areas and it shows gaps in knowledge, which should be closed in future studies. Table 4 provides an overview of pre-treatment strategies which were used in Figure 4.

Table 4. Summary of fuel washing strategies for RH and RS used in Figure 4 [102,105,109].

Symbol	Fuel Pre-Treatment Strategy
WRH 1	RH was soaked in distilled water. No details have been reported for water washing.
WRS 1	RS was collected after having received a total of 451 mm/m ² of rain.
WRS 2	Laboratory washed, 100 g whole straw, hand sprayed for 1 min with tap water.
WRS 3	Laboratory washed, 100 g whole straw, submerged in 7 liters of distilled water for 24 h.
WRS 4	RS was collected after having received a total of 65 mm of rain (after first rain).

Figure 4. The effect of fuel washing strategies on the melting tendency of RH and RS (data were taken from [102,105,109]).

Another advantage of fuel pre-treatment is that it can reduce the risk of crystallization in the resulting biogenic silica [67,71,187,189,199]. Pre-treated RHs remained amorphous up to 1000 °C [200]. In contrast, untreated RH crystallized at temperatures between 600 and 900 °C depending on source of the RH and combustion conditions [19,20,66,189]. Pre-treatment was also shown to improve physisorption and pore structure characteristics of biogenic silica [53,71,73,100,200,201]. Accordingly, both SSA and pore volume are improved by pre-treatment of the fuels (Table 5), thus being a prerequisite for catalytic applications of biogenic silica.

Table 5 summarizes the results of combustion experiments performed with pre-treated RH and RS.

According to Table 3, the maximum silica purity, SSA and pore volume are about 97.2 wt %, 220 m²/g and 0.26 cm³/g, respectively, among the RHA obtained from combustion of untreated RH. According to Table 5, however, fuel pre-treatment improves purity of up to 99.77 wt %, increases SSA of 353 m²/g and doubling of the pore volume (0.52 cm³/g). The most effective fuel pre-treatment to remove impurities and to obtain biogenic silica with purity higher than 99.7 wt % has been reported by Umeda et al. [187]. In this strategy, RH was leached with 5 wt % of citric acid solution at 80 °C for 1 h followed by combustion in air atmosphere at 800 °C for 30 min. For further purification, ash post-treatment techniques may be applied, which are discussed in Section 3.3.

3.3. Combination of Fuel Pre-Treatment, Ash Post-Treatment and Combustion of Rice Husk and Rice Straw

Thermal treatment or acid leaching of RHA and RSA are considered a post-treatment. Table 6 provides an overview of ash post-treatments that were applied in combination with fuel pre-treatment and combustion of RH and RS.

Table 5. Combined fuel pre-treatment and combustion to obtain pure biogenic silica from RH and RS.

Input Material, Source, Silica Content in Fuel Ash	Fuel Pre-Treatment	Combustion Process	Scale	Main Findings	Reference
Material: RH and RS Source: Cambodia, Italy and Vietnam Silica content of the fuel ash: 50.7–83.2 wt %.	<ol style="list-style-type: none"> (1) 100 g of RH or RS was washed with water (solid-to-liquid ratio 1:13 wt./wt.) and agitated in a flask under stirring conditions at ambient temperature for one day followed by filtration. (2) Water-washed RH leached with 3.25 M citric acid (solid-to-liquid ratio 1:13) at 50 °C for one day followed by filtration. (3) Acid-leached RH was washed with water and dried for one day at 50 °C. 	<p>Multi-step sequential combustion at a heating rate of 10 K/min: 310 °C for 30 min, 450 °C for 60 min, 510 °C for 210 min and finally, 600 °C for 30 min.</p> <p>Atmosphere: air</p>	Muffle furnace	Both RHA and RSA showed silica purity higher than 99 wt %. Italian RHA had the highest purity which was around 99.7 wt %. SSA ¹ was higher than 260 m ² /g for all RHAs, and the highest value was for Cambodian RHA (300 m ² /g). As the maximum processing temperature was lower than normal crystallization temperature, all RHAs and RSA were completely amorphous. It was concluded that water washing, which is swelling of the cell walls and pre-hydrolysis the carbohydrates, allow citric acid to reach and contact with the inner parts and as a result, remove the inner inorganic matter effectively. Regardless of the silicon purity in the starting material, the process had a potential to produce biogenic silica with almost uniform quality.	Schneider et al., 2018 [72]
Material: RH Source: N.R. Silica content of the fuel ash: N.R.	<ol style="list-style-type: none"> (1) RH was washed with deionized water three times and dried at 60 °C for one day. (2) Sulfuric acid, hydrogen chloride, oxalic acid, and an ionic liquid (1-butyl-3-methylimidazolium hydrogen sulfate) were used as follows: Sulfuric acid treatment: RH was immersed in 72% sulfuric acid at 30 °C for 1 h. Then, concentration of the acid was adjusted to 4% using deionized water, and then RH was incubated at 121 °C for 1 h. Afterwards, the acid was removed and washed with hot deionized water. Hydrogen chloride treatment: RH was immersed in 10 wt % hydrogen chloride and incubated at 90 °C for 1 h. Then, it was washed with deionized water. Oxalic acid treatment: Reacting RH in 1 M of the acid under a carbon dioxide atmosphere with 20 psi at 200 °C for 3 h. Then, it was washed with deionized water. (3) Washed residue was dried at 60 °C for one day. 	<p>Combustion at 800 °C. Although it was called pyrolysis in the paper, but there is no indication for it. Furthermore, the results were compared with combustion studies.</p> <p>Atmosphere: N.R.</p>	Muffle furnace	XRD patterns showed that all RHAs were amorphous. Silica purity of RHA increased using fuel pre-treatment. The value for untreated samples and those treated with sulfuric acid, hydrogen chloride, oxalic acid, and ionic liquid was 94.7, 99.6, 98.0 and 99.5 wt %, respectively, whereas the carbon content for these ashes was around the same (between 0.02 and 0.08 wt %). Results indicated that ashes obtained from treated RH had no potassium content while untreated sample had around 1.7 wt % of K ₂ O. N ₂ sorption data showed that SSA and pore volume of untreated samples and treated with sulfuric acid, hydrogen chloride, oxalic acid, and ionic liquid were 99, 85, 66, 71 and 185 m ² /g and 0.17, 0.22, 0.18, 0.21 and 0.41 cm ³ /g, respectively.	Lee et al., 2017 [91]
Material: RH Source: Heilongjiang province, China. Silica content of the fuel ash: N.R.	<ol style="list-style-type: none"> (1) Original RH was dried at 105 °C for 2 h to completely remove moisture. (2) 30 g of RH was added to 500 mL of hydrochloric, sulfuric, or acetic acid solution for 1 h at room temperature. (3) Solid residue was filtered and washed with deionized water several times to reach a neutral condition, and then it was dried at 105 °C for 2 h in an oven. 	<p>As-received RH and acid-leached RH (LRH) were burned at 600, 700, 800, and 900 °C for 30 min while air flow was continuously fed in during the combustion process.</p> <p>Atmosphere: air</p>	Muffle furnace	<p>Result of inductively coupled plasma–optical emission spectrometry (ICP-OES) showed that silica purity in acid leached RHA (LRHA) samples, which were obtained at 600 °C, was in the range of 96.5–98.6 wt %. This range is much higher than the silica purity of untreated RHA 92.1 wt %.</p> <p>Furthermore, K₂O content was around 0.2–0.6 wt % in LRHAs; while, it was 4.0 wt % in untreated RHA.</p> <p>Both pore volume and SSA of the LRHA were higher than these values of original RHA. The maximum value of the SSA and pore volume obtained from sulfuric acid leached ash at 60 °C, which were 237 m²/g and 0.084 cm³/g, whereas these parameters were 145 m²/g and 0.051 cm³/g in untreated RHA, respectively. It is worth mentioning that the reported pore volumes are not reliable, as the authors did not measured the complete isotherm for their calculation.</p>	Chen et al., 2017 [71]

Table 5. Cont.

Input Material, Source, Silica Content in Fuel Ash	Fuel Pre-Treatment	Combustion Process	Scale	Main Findings	Reference
Material: RH Source: Selangor, Malaysia. Silica content of the fuel ash: N.R.	<ol style="list-style-type: none"> (1) RH was washed with sodium dodecyl sulfate solution under constant stirring for 10 min, and then washed with distilled water. (2) WRH was dried at room temperature and later at 110 °C for 24 h. (3) WRH was leached with hydrochloric acid or sulfuric acid at a concentration of 0.5 M for 30 min with constant stirring. (4) LRHs were washed with distilled water, and then filtered followed by air-drying. (5) LRHs were dried at 110 °C overnight. 	Combustion at 500, 600, 700, 800 and 900 °C for 2 h. Atmosphere: N.R.	Muffle furnace	Silica purity measured by XRF analysis, Brunauer–Emmett–Teller specific surface area (BET SSA) and total pore volume improved from 95.8 wt %, 116 m ² /g and 0.23 cm ³ /g in non-leached RHA to 99.1 wt %, 208 m ² /g and 0.31 cm ³ /g in sulfuric acid leached RHA and to 99.6 wt %, 218 m ² /g and 0.32 cm ³ /g in hydrochloric acid leached RHA, respectively. Moreover, crystallization temperature was decreased and impurities were drastically removed from the ash samples by using acid leaching strategy before the combustion.	Bakar et al., 2016 [199]
Material: RH Source: Jiangsu, China. Silica content of the fuel ash: N.R.	<ol style="list-style-type: none"> (1) RH was soaked in deionized water at 20–25 °C, and it was dried at 110 °C followed by pulverizing to approx. 60-mesh size. (2) WRH was leached with hydrochloric acid (8 wt %) in the ratio of 1:10 (g:mL) at 120 °C for 4 h. (3) pH of the solution was changed to 7 using distilled water, and then LRH was dried at 110 °C for 2–3 h. 	<p>A sequential burning process was applied as follows:</p> <p>(1) 5 g of LRH was pyrolyzed at 300–800 °C under nitrogen or carbon dioxide atmosphere with flow rate of 1 l/min at heating rate of 20 K/min for 30 min.</p> <p>(2) combustion of pyrolyzed RH (PRH) was carried out at 610 °C for 2–3 h under oxygen flow with the same flow rate at heating rate of 10 K/min.</p> <p>Atmosphere: Oxygen</p>	Tubular furnace	Silica purity, SSA and total pore volume of synthesized amorphous ashes were in the range of 95.8–99.6 wt %, 204–353 m ² /g and 0.35–0.52 cm ³ /g, respectively.	Gu et al., 2015 [195]
Material: RH Source: Kafr El-Daowar, Egypt. Silica content of the fuel ash: 57.9 wt %	<ol style="list-style-type: none"> (1) RH was washed with deionized water several times in order to remove adherent soil and dust. (2) RH was dried overnight at 110 °C followed by dry milling to obtain fine powder. (3) WRH powder was leached with 5 wt % of citric acid at 50 °C for 3 h, and then at 80 °C for 1 h. (4) Solid residue was filtered and washed with distilled water to become neutral. (5) LRH was dried overnight at 110 °C. 	Multi-step sequential combustion in air at a heating rate of 10 K/min: (1) 310 °C for 60 min, 400 °C for 120 min, 510 °C for 300 min and finally, 600 °C for 30 min. Atmosphere: air	Muffle furnace	XRF results indicated that silica purity increased by simply washing the RH from 57.9 wt % in the unwashed RH fuel ash to 85.6 wt % in washed RH fuel ash. In addition, selected multi-step temperature program improved silica purity to 97.7 wt % in LRHA. Nitrogen sorption analysis showed that both SSA and pore volume were increased from 220 m ² /g and 0.26 cm ³ /g in non-leached RHA to 313 m ² /g and 0.38 cm ³ /g in LRHA, respectively. Furthermore, internal structure analysis revealed that both RHA and LRHA had amorphous structure, since the maximum processing temperature (600 °C) was lower than the crystallization temperature.	Ahmad Alyosef et al., 2013 [98]

Table 5. Cont.

Input Material, Source, Silica Content in Fuel Ash	Fuel Pre-Treatment	Combustion Process	Scale	Main Findings	Reference
Material: RS Source: different regions in Spain and Egypt. Silica content of the fuel ash: N.R.	(1) RS was cut to 10 cm and washed with tap water following by drying at 105 °C to a constant weight. (2) Size of the unwashed RS and washed RS (WRS) was reduced to 0.5 mm.	RS and WRS was heated up from 30 to 1000 °C at a heating rate of 10 K/min. Air flow rate was 100 mL/min. Atmosphere: air	TG-DSC	Simply washing of RS with tap water reduced Na, K, Mg, P, S and Cl elements in the ashes with the removal percentages of 35.6–60.0, 26.1–49.5, 0.0–38.8, 0.0–34.8, 25.5–59.4 and 59.0–87.0%, respectively. As a result, water washing controlled slag formation during the combustion of RS from different regions.	Said et al., 2013 [198]
Material: RH Source: Wuyunjing, China. Silica content of the fuel ash: N.R.	RH was leached with deionized water at 25 ± 1 °C for 4 h.	RH and WRH was calcined and held at a maximum temperature (600, 700 and 800 °C) for 0.5, 1.5, 2.5 and 3.5 h. Atmosphere: air	N.R.	The effect of calcination parameters (CT ² and RT ³) on RHA content was studied in RH and WRH. It was shown that the ash content decreases by increasing CT in both RH and WRH samples. That is because some of the metallic elements show higher volatility at higher calcination temperatures. Results indicated that in the original RH, ash content was dramatically decreased by raising RT, which is because of the slow oxidation of carbon residues in original RH. On the other hand, WRH had no change in ash content when the RT is longer than 1.5 h, which implies no carbon residues in RHA, and it was interpreted as an indication for pure silica production from WRH. It was shown that increasing the CT and RT decreases the SSA of the WRHA, which is because of the agglomeration effect and diminishing porosity of the ash.	Shen et al., 2011 [189]
Material: RH Source: Niigata, Japan. Silica content of the fuel ash: N.R.	(1) 30 g of RH was added into 500 mL of citric acid solution with acid concentration of 1 to 7 wt % under different stirring conditions. The temperature of the solution was changed from 25 to 80 °C. The time of the stirring process was selected between 15 and 120 min under rotating speed of 960 rpm. (2) Water rinsing was carried out using deionized water at 20 °C for 15 min under stirrer condition. (3) The solution was dried at 373 K for 1 h in a muffle furnace.	LRH was burned at 800 °C for 30 min under airflow rate of 0.42 mL/s using a small air-compressor. Atmosphere: air flow.	Muffle furnace	XRF results indicated that leaching RH with citric acid solution and a concentration over 1 wt % produces RHA with silica purity higher than 99.5 wt %, whereas silica purity of untreated RHA was 97.2 wt %. Potassium oxide content was 1.39 wt % in untreated RHA. However, acid leaching process reduced its level into 0.01–0.03 wt % in LRHA samples. Furthermore, it was shown that silica purity is not sensitive to concentration of acid solution and temperature of acid leaching process, and only 1 wt % of citric acid leaching at room temperature was enough to remove potassium and carbon contents to produce pure biogenic silica. Maximum silica purity was obtained from RH leached with 5 wt % of acid solution at 80 °C, which was 99.77 wt % (compared to 99.47 wt % upon leaching with 1 wt % of citric acid at room temperature). XRD patterns showed that acid leaching improves LRHA resistance to crystallization.	Umeda and Kondoh 2010 [187]
Material: RH Source: Niigata, Japan. Silica content of the fuel ash: N.R.	(1) 20 g of RH was immersed in 500 mL of citric acid and sulfuric acid solution for 15 min with acid concentration of 5 wt %, and it was kept at 50 °C. (2) Water rising treatment after leaching process was repeated three and eight times. (3) It was dried at 100 °C for 1 h in an electric furnace to remove the acid.	As-received RH and LRH were burned in air (150 mL/min) at 600–1150 °C. Atmosphere: air	TG-DSC	Results of XRF analysis showed that silica purity was improved from 94.6 in untreated RHA to higher than 99 wt % in LRHA. Furthermore, LRHA with lower metallic impurities remained amorphous until 1050 °C, which is the highest value published in literature.	Umeda and Kondoh, 2008 [67]

Table 5. Cont.

Input Material, Source, Silica Content in Fuel Ash	Fuel Pre-Treatment	Combustion Process	Scale	Main Findings	Reference
Material: RH Source: Niigata, Japan. Silica content of the fuel ash: N.R.	(1) 20 g of RH was immersed in 500 mL of sulfuric acid solution for 15 min with acid concentration of 1–5 wt %, and it was kept at 44 °C during the leaching. (2) Water rinsing was carried out to remove acid from the sample, then it was dried at 100 °C for 1 h in a muffle furnace.	As-received RH and LRH were burned in air at 600 and 1000 °C. Atmosphere: air	TG-DTA	Leaching RH with only 1 wt % of sulfuric acid solution reduced calcium, potassium and sodium oxide impurities from chemical composition of LRHA drastically. Consequently, not only the silica purity improved, but also ash remained amorphous up to 1000 °C, whereas untreated original raw RH transformed into crystalline species at temperatures above 854 °C.	Umeda et al., 2007 [200]
Material: RH Source: Andhra Pradesh State, India. Silica content of the fuel ash: N.R.	(1) RH was washed with water to remove soluble impurities, and then it was dried in a muffle furnace at around 110 °C for 6–8 h. (2) Around 50 g of each RH was added to 500 mL of 0.1 N HCl acid and boil for 1 h under stirring condition. (3) Acid was decanted and LRH was washed with distilled water to reach to the neutral condition at 110 °C.	LRH was heated up from 300 to 1000 °C at an interval of 100 °C at different heating rates of 1, 2, 3, 5, 7 or 10 K/min and RTs of 2, 4 or 6 h. Atmosphere: N.R.	Muffle furnace	Acid leaching followed by combustion at 700 °C for 2 h increased silica purity from 89.5 wt % in ash from untreated RH to 97.8 wt % in the ash from LRH sample. Loss of ignition (LOI) test showed that in RHA obtained from untreated RH, in spite of the presence of some black particles compare to the ash from LRH, the value of LOI is almost the same with LRHA. It was concluded that the black particles contributes to fix carbon in RHA. It was shown that ash obtained from LRH switch from amorphous to crystalline form at higher temperatures compared to the RHA produced from untreated RH. Increasing the heating rate improved surface area and pore volume and decreased the brightness of the ash samples. It is because of higher carbon content in RHAs obtained at higher heating rates.	Chandrasekhar et al., 2006 [54]
Material: RH Source: Kerala state (KRH) and Andhra Pradesh state (APRH), India. Silica content of the fuel ash: N.R.	(1) Around 50 g of each RH was added to 500 mL of acetic, oxalic, hydrochloric and nitric acids of different concentrations for 90 min under stirring condition. (2) Sample was cooled and kept intact for around 20 h, and then supernatant liquid was decanted. (3) Sample was washed with distilled water until pH equal to neutral, and then it was dried at 110 °C.	LRH, WRH, as received RH samples were burned out at 5 K/min to 700 °C with RT of 2 h. Atmosphere: N.R.	Muffle furnace	Irrespective of CT and RT, black particles appeared in the ash obtained from APRH. In spite of visible black particles in ashes obtained from APRH source, LOI had around the same value all resulting ashes from two different sources, which was in the range of 1.8–4.6 wt %. Therefore, it indicates that there is no direct connection between black particles in the ash and the carbon content obtained by LOI. Further pre-treatment using different acids improved the silica purity, and the maximum reported value was 97.8 wt %. Nitrogen sorption analysis showed that RHA produced from RH with lower potassium content (KRH) had much higher SSA (approx. 150 m ² /g), while in the sample with higher potassium content (APRH), this value was less than 10 m ² /g for the same combustion conditions. Pore volume behaves in the same manner, and it was higher in the ash of KRH compared to the ash of APRH. Furthermore, acid leaching improved both SSA and pore volume in both samples.	Chandrasekhar et al., 2005 [53]

Table 5. Cont.

Input Material, Source, Silica Content in Fuel Ash	Fuel Pre-Treatment	Combustion Process	Scale	Main Findings	Reference
Material: RH Source: N.R. Silica content of the fuel ash: N.R.	(1) RH was washed with water. (2) WRH was leached with HCl acid under stirring condition at 100 °C for 1 h, and then it was filtered and washed with distilled water until neutralizing the acid. (3) LRH was dried at 100 °C for 24 h, and then it was pulverized to reach 323 mesh sizes for grains.	LRH was heated up from room temperature to 727 °C at heating rates of 5, 10, 15, and 20 K/min. Atmosphere: air	Thermogravimetric analysis (TG-DTG) in a form of tube reactor	The maximum silica purity, SSA and total pore volume in LRHA reached to 99.7 wt %, 235 m ² /g and 0.32 cm ³ /g for combustion at lower heating rate. All LRHA obtained from different heating rates were completely amorphous.	Liou, 2004 [191]
Material: RH Source: Trakya Region, Turkey. Silica content of the fuel ash: N.R.	(1) RH was washed with water, and then it was dried at around 110 °C overnight. (2) WRH was leached with 3% (v/v) hydrochloric acid and 10% (v/v) sulfuric acid at a ratio of 50 g WRH/l. (3) LRH was washed with distilled water following by drying at 110 °C.	20 g of RH, WRH and LRH was incinerated at 600 °C in four different ways: (1) combustion for 4 h in static air in muffle furnace; (2) incineration in tubular reactor under argon (1.5 L/min, for 3 h) and then supplying oxygen (1.0 L/min for 1 h); (3) combustion in tubular reactor under air flow (3 L/min, for 3 h) and; (4) combustion in tubular reactor under oxygen flow (1.0 L/min, for 2 h). Atmosphere: air and oxygen.	Muffle furnace & a tubular reactor placed horizontal inside the muffle oven	Incineration of untreated RH under oxygen atmosphere produced amorphous RHA with silica purity of 98.3 wt %. However, silica purity in the static air condition was 91.5 wt %. Result of RH, WRH, and LRH combustion under static air showed that silica purity increased from 91.5 wt % in the untreated sample to 95.5 wt % and 99.2 wt % in distilled water washed and HCl-leached samples, respectively. Furthermore, maximum purity obtained from sulfuric acid pre-treatment (99.6 wt %).	Yalçın and Secinç, 2001 [181]

¹ SSA: specific surface area; ² CT: conversion temperature; ³ RT: residence time.

Table 6. Combination of ash post-treatment with fuel pre-treatment and combustion to obtain pure biogenic silica from RH and RS.

Input Material, Source, Silica Content in Fuel Ash	Pre-Treatment Process	Combustion Process	Scale	Post-Treatment Process	Main Findings	Reference
Material: RH Source: Cambodia and Italy. Silica content of the fuel ash: N.R.	(1) RHs were sieved, washed with tap water at 50 °C for 2 h and dried. In some cases, RH was leached with 1 wt % citric acid at 50 °C for 2 h instead. Note: Prior to the bench scale experiments, different pre-treatment conditions including time, temperature, concentration and type of acid were investigated in lab-scale experiments using a muffle oven.	Combustion was carried out using ÖKOTHERM® boilers, and RH was continuously supplied into the boilers.	Muffle oven for lab scale studies and post-treatment and ÖKOTHERM® boilers with power up to 120 kW for bench-scale studies.	(1) RHA was leached with 0.5–2 wt % of citric acid or hydrochloric acid at 50 °C for 2 h. (2) Acid-leached RHA was heated up in air at 650 °C in a muffle oven.	This research is the first known attempt to consider both energy and material applications of agricultural residues in a real combustion unit. Some optimization for huge ash loading was done by modifying the conveying screw and using additional mechanical equipment to mobilize and transport the voluminous ash inside the boiler. As a result, the operation time was prolonged with no limit in fuel handling and ash discharged. Considering the principles of green chemistry by using less chemical resources, the cost of the process as well as the quality of the obtained biogenic silica, water washing and 2 wt % citric acid leaching at 50 °C for 2 h were selected, respectively, as the pre-treatment and post-treatment. The final product had an amorphous internal structure with BET SSA ¹ , specific mesoporous volume and silica purity of 185 m ² /g, 0.25 cm ³ /g, and >98 wt %, respectively.	Schliermann et al., 2018 [73]
Material: RHA was supplied by a local industry (Fumacense, Morro da Fumaça, SC, Brazil). Silica content: 72.1 wt %	-	N.R.	Electric oven with crucible of 24.5 cm diameter.	RHA was heated from room temperature to 400, 500, 600, or 700 °C for 3–6 h with heating rate of 10 K/min.	Simply heating the RHA to 700 °C for 6 h improved silica purity of the ash from 72.1 to 95 wt %, and RHA remained in amorphous form. However, SSA was changed from 177 m ² /g in the as-received RHA to 54 m ² /g in reheated RHA sample.	Della et al., 2002 [64]
Material: RH Source: Trakya Region, Turkey. Silica content of the fuel ash: N.R.	(1) RH was washed with water, and then it was dried at around 110 °C overnight. (2) WRH was leached with 3% (v/v) hydrochloric acid at a ratio of 50 g WRH/1 for 2 h. (3) LRH was washed with distilled water following by drying at 110 °C.	20 g of RH, WRH, LRH was incinerated at 600 °C. Atmosphere: air	Muffle furnace	RHA produced from untreated and acid leached RH was leached with 3% (v/v) HCl at a ratio of 50 g WRH/1 for 2 h.	The order of the silica purity was acid pre- and post-treated sample (99.7 wt %) > acid pre-treated sample (99.2 wt %) > water pre-treated sample (95.5 wt %) > acid post-treated sample (95.1 wt %) > untreated sample (91.5 wt %). SSA results revealed that the order of the SSA was untreated sample (63 m ² /g), water washed sample (194 m ² /g), acid pre- and post-treated sample (244 m ² /g), and acid pre-treated sample (321 m ² /g), respectively.	Yalçın and Secinç, 2001 [181]

¹ SSA: specific surface area.

Schliermann et al. [73,202] used pre-treated RH for combustion in a commercially available biomass boiler and applied post-treatment of the ash to improve the quality of biogenic silica. Thus, heat production was successfully combined with generation of biogenic silica considering also process cost and the principles of green chemistry. Amorphous biogenic silica was produced with purities exceeding 98 wt % and with satisfying SSA of approx. 185 m²/g as well as mesopore volume of 0.25 cm³/g. Furthermore, Schliermann et al. [73,202] improved the operating conditions of the combustion unit to reach to a continuous fuel supply with very low gaseous and particulate matter emissions.

4. Summary and Conclusions

In this comprehensive review, combinations of fuel pre- and ash post-treatment strategies with combustion of rice husk (RH) and rice straw (RS) have been discussed. With respect to the review objective, we conclude that:

- (1) By studying the ash melting tendency of original and treated RH and RS, it was shown that there is a gap in knowledge, and further investigation is required in this field.
- (2) Fuel pre-treatment has a significant impact on controlling ash melting issue in RH and RS, and it seems that at least water washing prior to combustion is essential in RS to avoid slag formation.
- (3) Increasing combustion temperature (CT) and residence time (RT) improves the purity of the biogenic silica with respect to the carbon content. At the same time, specific surface area (SSA) and pore volume of the biogenic silica decrease while the risk of crystallization is increased. The alternative strategy to improve all quality characteristics of rice husk ash (RHA) and rice straw ash (RSA) is using fuel pre-treatment prior to the combustion. Crystallization tendency of RHA possibly correlates with the alkali metal content, which facilitates formation of cristobalite. Crystallization temperature is around 600–900 °C in untreated RH and RS depending on the elemental composition, whereas pre-treated RH and RS remain amorphous up to higher temperatures of about 1000 °C.
- (4) In RHA from untreated RH, the maximum silica purity, SSA and pore volume are around 97.2 wt %, 220 m²/g and 0.26 cm³/g, respectively. However, these values can be improved to around 99.8 wt %, 353 m²/g and 0.52 cm³/g using fuel pre-treatment strategies prior to the combustion. Further improvement of silica purity is possible by a combination of fuel pre-treatment, combustion and ash post-treatment strategies.
- (5) Although high quality biogenic silica can be produced from RH and RS, most studies were performed in lab-scale muffle furnaces and investigations at a bench scale are scarce.
- (6) Economically feasible production of biogenic silica from RH was demonstrated at a bench scale though with silica purity limited to 98 wt %. For higher silica purities, a harsh pre- and post-treatment environment may be required, which could increase the technical efforts and thus the overall process costs.
- (7) Finally, it was shown that a preliminary practical study has been done to scale the production procedure up to a bench scale with the aim of developing an environmentally friendly and economically feasible process with coupled energetic and material utilization of RH. However, further investigations are required to understand the behavior of RH and RS in combustion. Moreover, there is no report in literature to predict the quality of biogenic silica as well as the ash melting tendency and gaseous emissions using thermodynamic calculations. By using thermodynamic calculations, the effect of chemical composition of input material can also be evaluated in order to transfer to other biomasses since there are limited experimental data available in literature. No information is available in literature on computational fluid dynamic (CFD) simulation of the combustion process of biomass to simulate their conversion mechanism to biogenic silica inside the boiler. If a CFD simulation is used, thermal efficiency of the combustion unit can also be evaluated and optimized. In addition, such a simulation will be valuable to

calculate the exact CT and RT of each singular biomass particle during the real operational condition of the combustion unit. In the literature, fundamental lab-scale studies are usually carried out in static airflow. However, the effect of dynamic airflow and air to fuel ratio on the quality of resulting ash have not been studied in the literature. Although many people have measured the biogenic silica purity and pore structure of the ash obtained from RH and RS, there is no information about the accuracy and repeatability of the measurements in the literature, and it seems this gap should be considered in future investigations. Sustainability, economic, and energetic analysis are essential once a commercial plant becomes available to produce biogenic silica from RH and RS in a process including the combination of pre- and post-treatment strategies with combustion.

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Conflicts of Interest: The authors declare no conflict of interest regarding the publication of this review.

Abbreviations

The following abbreviations are used in the manuscript:

DT	initial deformation ash fusion temperature
db	dry basis
LOI	loss of ignition
LRH	acid-leached rice husk
LRHA	acid-leached rice husk ash
LRS	acid-leached rice straw
LRSA	acid-leached rice straw ash
PRH	pyrolyzed rice husk
RH	as received rice husk
RHA	rice husk ash
RS	as received rice straw
RSA	rice straw ash
WRH	water-washed rice husk
WRHA	water-washed rice husk ash
WRS	water-washed rice straw
WRSA	water-washed rice straw ash
λ	excess air ratio

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