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Perspectives of the Silicon Dioxide Production from Rice Husk in Kazakhstan: an Overview

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Abstract

Rice husks (RHs) are the hard-protecting coverings of grains of rice. Considering the fact that this agricultural waste accumulates over the years, the need for prompt resolve for RH waste is readily apparent. As claimed by the Food and Agriculture Organization of the United Nations (FAO), the production of the global paddy rice in 2016 is considered to be 748.0 million tons. Based on this, the amount of RHs makes up about ~20% of paddy rice production by weight. Much of this production is treated as waste and either thrown into rivers or tossed on landfills, often causing pollution problems when it decays or simply returned to the fields where it can become airborne. This work presents synthesis routes for the production of SiO_2 from RH sourced in Kazakhstan. RH, chosen from Almaty, Kyzylorda and Turkystan regions, was utilized as the major silica source. The results shown verified that the highest purity (98.2–99.7%) amorphous silica with a certain surface area between 120–980 m^2 g^{-1} could be extracted during acid treatment and controlled calcination. The structure is amorphous, porosity diameter reduced from 26.4 nm to 0.9 nm, certain pore volume raised from 0.5 to 1.2 cm^3 g^{-1}.

1. Introduction

Rice is grown in many countries around the world. As reported by the data of the Food and Agriculture Organization of the United Nations (FAO), world rice production in 2016 was 748 million tons while it is 291 thousand tons in Kazakhstan (see Table 1).

There are three types of rice growing: irrigated, dry and estuary. The difference among these varieties lies in the nature of the flooding of the areas allocated for cultivation. The plots are divided into:

– irrigation (checks) – the plant grows in such a field in conditions of continuous being under water, only immediately on the eve of harvesting ripe rice the plot is drained. This is the most widespread method of cultivation (90% in the world);

– dry land – the crop is grown in places with an abundance of rainfall, without artificial irrigation. It should be noted that the yield when growing rice using this method is much lower than that of the irrigation method;

– estuary – the first of the emerging cultivation methods, is used in the countries of Southeast Asia. Rice with this method grows in river bays. It is worth noting the low efficiency of this method.

The world's largest rice production mainly belongs to China and India. Though its amount of rice harvested is smaller than India's, China's rice production is much bigger as a result of higher yields because almost all of China's rice area is irrigated, while more than half of India's rice area is not irrigated. After China and India, the third largest rice producers are Indonesia, Bangladesh, Vietnam, Myanmar and Thailand. All of these countries had an average production of more than 30 million tons of paddy rice in 2006-08 and make up more than

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Table 1
Major world producers of paddy rice 2016/2017 in tons [1]

Sr. no	Country	Paddy rice	Rice husk	Rice husk ash (estimated)
1	China	144.850.000	31.867.000	1.274.680
2	India	106.500.000	23.430.000	937.200
3	Indonesia	37.150.000	8.173.000	326.920
4	Bangladesh	34.578.000	7.607.160	304.286
5	Vietnam	27.861.000	6.129.420	245.177
6	Thailand	18.600.000	4.092.000	163.680
7	Burma	12.400.000	2.728.000	109.120
8	Philippines	11.500.000	2.530.000	101.200
9	Brazil	8.160.000	1.795.200	71.808
10	Japan	7.780.000	1.711.600	68.464
47	Kazakhstan	291.000	64.020	2.561
48	Nicaragua	290.000	63.800	2.552
49	Burkina	250.000	55.000	2.200
50	Mozambique	213.000	46.860	1.874

80% of world production altogether. The main rice cultivation developed in Kazakhstan mostly in the lower reaches of the Syr Darya, Kyzylorda Region such as Leader, Yantar, Marzhan, Novator, Favorit, Lazurny, KazNIIR-5, KazNIIR-6 and Ai Saule are grown.

The crop yield directly depends on the moisture content of the soil. This is a shade-loving tropical plant, when growing it is important to select the correct water regime at each phase of cereal cultivation. For example, as soon as seedlings emerge, the soil is saturated with water as much as possible. After transplanting the seedlings to a permanent place of growth, the field is covered with a layer of water.

Temperature conditions directly affect the swelling of grains:

– when germinating, the seeds rapidly absorb water within 5–6 days, the optimum temperature is +13 degrees;

– then the mode is set to +17 degrees for 2 days;

– then for 15 h +27 degrees;

– the grain will not sprout if the air temperature drops to +12 degrees.

The location of this region is below sea level, the state of the soil is ameliorative and agricultural conditions have become the reason for the creation of a special irrigation engineering system for watering rice fields. All the main regions in the territory of the Republic of Kazakhstan involved in rice production are in the south part of the country: Kyzylorda Region (78,4 thousand ha), Almaty Region (11,1 thousand ha) and South Kazakhstan Region (3 thousand ha) [2–3].

The agricultural waste provides about 33% of total biofuel use, supplying 39%, 29%, and 13% of biofuel use in Asia, Latin America and Africa, and 41% and 51% of the biofuel use in India and China. In most varieties, rice consists of about 20% of rice husk, which contains fibrous materials and silicon dioxide. It is estimated that from 1 t of paddy it is possible to produce 220 kg of rice husk. However, the amount of each component depends on the climate and the geographical location of the rice crop. Consequently, because of its high percentage in the composition of grain, the husk is considered a by-product in the mills and creates problems of recycling [4–5]. In the past decades, rice husk is extensively used as a construction material to produce concrete [6], or as an adsorbent for the removal of organic dyes, such as indigo carmine dye, and heavy metals such as lead, mercury, cadmium and zinc from wastewater metal ions [7–8]. Because of its high silicon amount, rice husk can be an economically-practical raw material for silicate production and silica materials. Every year the volume of rice cultivation increases that is why recycling the husks of this crop is an important task for the countries involved in the cultivation and processing of rice. The estimated annual harvest of rice in Kazakhstan is about 291 thousand tons, which produces roughly 64 thousand tons is rice husk [9].

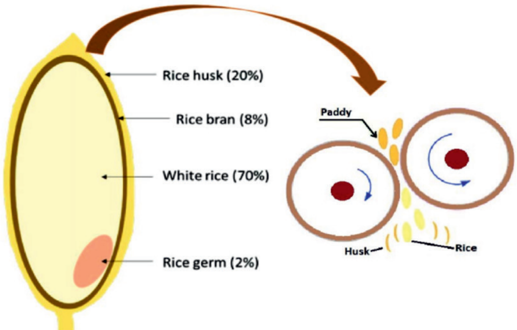


Fig. 1. Paddy rice grain (left) and its products after husking.

Rice husk is a fibrous substance containing lignin, carbohydrates, nitrogenous matters, vitamins, organic acids, mineral components, provided that their content depends on the variety of rice and can vary depending on the cultivation location and the agriculture technical methods of its cultivation [10]. The main carbohydrate component of the rice husk is cellulose, and hemicellulose (mainly pentosans) is contained in a smaller amount. Rice husk is still an agricultural residue in many countries that produce rice (Fig. 1).

Rice husk is distinguished by high abrasive properties, chemical resistance, low nutritional value, low bulk density and high ash content. Silicon dioxide is the major mineral component of rice husk determining its high ash content. Ashes also contain sodium, potassium, magnesium, iron, calcium, phosphorus, in much smaller quantities ash contains iron, copper, manganese and other elements [11]. A major part of husk obtained from the rice during the rice process is either burned or tossed as waste. Even if the rice husk is turned into finished products, such as raw materials and adsorbents, the major part of the husk is burned openly, leading to environmental pollution and health problems, especially in poor and developing countries [12–13]. Combusting of rice husk as a fuel interchange for power generation is one of the best solution used in many industrial fields. However, this leads to new wastes, called rice husk ash. Therefore, it is very important to find solutions for the full utilization of rice husk.

The two principal directions for the recycling of rice husk are the utilization of rice husk in agriculture and as a raw material for the production of various materials. In the first case, rice husk is used as a nutritional supplement to animal feed, bedding material, for soil treatment and mulching, and as a ballast material for sowing small seeds. In the second case, despite the potential, its preparation and processing are not always cost-effective [14]. Rice husk-derived materials are used in insulating, construction, road-building and mild abrasive materials for cleaning and polishing, production of paper and production of silica-containing and carbonaceous materials and other organic compounds (see Fig. 2) [15]. Also, rice husk ash (RHA) is largely used as raw material for various fields of application, such as the production of building materials and concrete. Ash can also be an adsorbent for the adsorption of organic dyes, metals, waste gases and as a catalyst carrier [16–17].

Many studies [18–19] have been conducted to change the composition of rice husk ash, depending mostly on many factors. These experimental studies contain practices in agricultural fields, such as the use of fertilizers in rice cultivation, the type of fertilizers used, and climatic or geographical factors. Therefore, depending on the geographical location, different authors have done different works characterizing the composition of the rice husk (see Table 2).

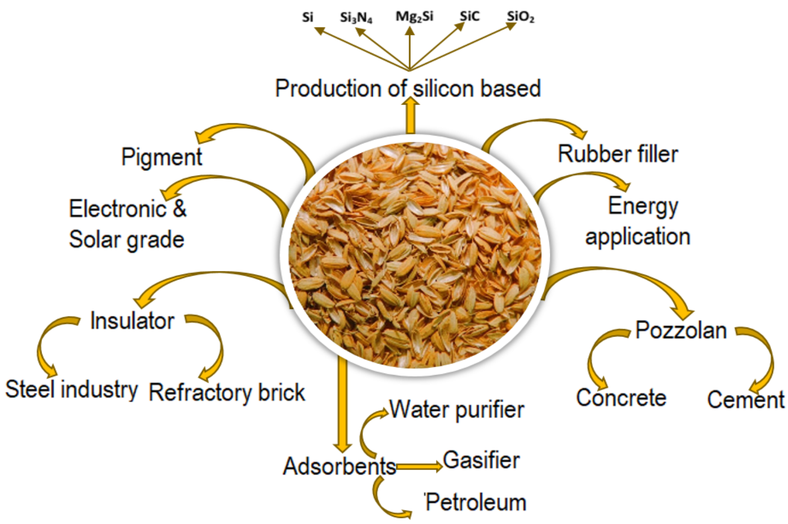


Fig. 2. Principal directions for the recycling of rice husk.

Table 2
The composition of elements in rice husk ash by different countries

Elemental composition of rice husk ash	XRF [20]	ICP [21]	XRF [22]	XRF [23]
	Canada	Egypt	Malaysia	Kazakhstan
SiO_2	91.56	91.5	91.25	91.39
K_2O	4.76	1.23	3.83	1.25
P_2O_5	-	2.30	2.45	0.5
CaO	0.78	2.57	0.88	2.62
SO_3	0.29	-	0.66	2.02
MgO	-	0.30	0.57	0.31
Al_2O_3	2.36	1.46	0.18	0.23
Fe_2O_3	0.11	0.42	0.09	0.57
MnO	0.07	0.04	0.07	0.14
Rb_2O	-	-	0.01	-
ZnO	0.01	-	0.01	0.04
CuO	0.06	-	-	0.29
Na_2O	-	0.18	-	0.36
Cl	-	-	-	0.28

It can be seen from Table 2 that although the composition of the rice husk depends on certain factors, the content of silicon dioxide in the ash range from 90–92%.

Due to the high silica content in the ash, the RHA (80–97%) can be a practical raw material for the silicate manufacturing of and silica materials [24–25]. Rice husk combustion gives ash, which contains a very heavy percentage of crystalline silica dioxides. Nevertheless, if it is combusted under controlled conditions at temperatures below 700 °C, an amorphous silica dioxide is obtained which has high reactivity. Transformation of this amorphous form into a crystalline form occurs if the ash is exposed to high temperatures above 850 °C [26]. Rice husk ash obtained by combusting rice husk can contain more than 90% silica dioxide and some metallic impurities. Metallic impurities like iron (Fe), manganese (Mn), calcium (Ca), sodium (Na), potassium (K) and magnesium (Mg) affect its purity and color of silica dioxide during the process and can be removed by pretreatment with hydrochloric acid, sulfuric acid or nitric acid before combusting [27]. As crystalline silica dioxide is utilized in ceramics [28] and the cement industry [29], amorphous silica dioxide has been used in more applications [30]. Therefore, this residue is believed to be a new practical raw material for silica dioxide production [31].

Rice husk is combusted straightly to manufacture silica dioxide to vary purity, with or without the pretreatment utilization [32–33]. The temperature of incineration, holding time and the applied pretreatment have an influence on the parameters of silica dioxide, especially on the surface and brightness (whiteness). As the temperature of incineration increases, some phase changes occur. It should be noted that the silica dioxide produced from rice husk at 500–650 °C with a combusting time of about 2.5 to 6 h is considered to be optimal to obtain white amorphous silica dioxide, whereas crystallinity is obtained as the temperature of incineration rises above 700 °C. The value for the working phase, whether cristobalite or tridymite, depends very much on the temperature variation and the impurity level contained in the rice husk. In addition, the temperature of incineration has a heavy influence on the surface area, consequently, the reacting capacity of the silica dioxide, obtained as a result of the direct combusting process. Silica dioxide, obtained from rice husk, can be utilized in cement and concrete structures as good pozzolan [34] and as an anticorrosive agent for other applications. Various improved products, such as aerogel [35], silica carbide, porous carbon [36], zeolites [37], high-purity silica [38], and other products can similarly be gained by applying the silica dioxide from rice husk.

Currently, there are various methods for the production of silica dioxide from the rice husk ash. The present paper explains a new synthesis method for the production of pure silica oxide from rice husks originated from the rice-producing regions of the Republic of Kazakhstan.

2. Materials and methods

2.1. Raw Materials and chemicals

Three different rice varieties were chosen for this research work: Regul, Lider, and 42. The RHs were collected from rice farms in Almaty, Kyzylorda, and Turkystan regions (Kazakhstan). All obtained Rice Husks were previously treated with DIW and dried in oven (Carbolite, PF 300, Keison, UK) at 105 °C and 8 h. Hydrochloric acid (37%, Sigma Aldrich, Germany) and sodium hydroxide (98%, Sigma Aldrich, Sweden), which were purchased from Sigma Aldrich, were applied in extraction procedure without further purification.

2.2. Sample characterization and analysis

The inorganic chemical composition of rice husk ash and extracted silica were analyzed using Axios mAX X-ray fluorescence spectrometer (PANalytical, Inc., USA). The phase composition and microstructure were checked by SmartLab X-ray Diffractometer (Rigaku Corporation, USA) with Cu Kα radiation (λ=1.540056 Å) at a scan rate of 0.02°θ s^{-1} in the 2θ variety of 10–90°. Thermal analysis was carried out by Simultaneous Thermal Analyzer (STA) 6000 (Perkin Elmer, Inc., USA) with a temperature of 10 °C min^{-1} in vary from 50 to 950 °C with nitrogen atmosphere. The surface structure and morphology of the obtained rice husk and rice husk silica were represented using Scanning electron microscopy of the brand Quanta 200i 3D (FEI Company, USA). The results of surface and pore size were obtained by utilizing the Brunauer-Emmett-Teller method (Autosorb-1, Quantachrome, UK) from nitrogen adsorption and desorption isotherms. The pore volume was taken at five points of P/P_0.

2.3. Extraction procedure

50 g of the raw RH was treated with 500 ml of 2 M HCl at 90 °C for 2 h. After that, it was constantly washed with water until the solution reach to pH=7 and separated from the solution via filtration. Thereupon, RH was dried at 105 °C overnight and then calcined at 600 °C for 4 h in a muffle furnace to produce white rice husk (WRH). 50 g of pristine RH produces about 8.71 g of WRH. Subsequently, the WRH was combined with 100 ml of 2M NaOH at 90 °C under constant intense blending for 2 h to extract the solid silica that could become water soluble sodium silicate (SS). The SS solution was then filtered to remove insoluble residues and converted into insoluble silicic acid by reaction for 30 min with concentrated Hydrogen chloride under intense blending. At last product was cleaned with hot water to remove by-products and then dried.

The mechanism of the silica particles formation from sodium silicate after treatment with HCl is as follows:

$$NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$$
$$(\Delta H^{773\ K} = -85\ kJ\ mol^{-1}).$$
$$Na_2SiO_3 + 2HCl \rightarrow H_2SiO_3\downarrow + 2NaCl$$
$$H_2SiO_3 \rightarrow SiO_2 + H_2O$$

The reaction of hydrochloric acid with sodium silicate promotes silanol (R_3Si–OH) groups formation and condensation causing the formation of lengthened three-dimensional Si–O–Si network [39].

3. Results and discussion

Preliminary acid treatment can influence the chemical composition of rice husk-obtained products but not the structural formation, whether crystalline formation or amorphous formation. The structure of SiO_2 depends on the temperature and duration of calcination and above 700–900 °C crystalline forms are produced. Several factors can cause the composition variation of the rice husk, like agricultural factors and climatic change or geographical factors. The main chemical elements in the samples of obtained RH ash (RHA) and silica are listed in Table 3. The chemical compositions of the RHA indicate that SiO_2 is the main part of the siliceous acceleration and the amount of metallic impurities is low. The samples of RHA without acid pretreatment contain from 73.9% to 84.4% SiO_2. After treatment with hydrochloric acid, the content increased to 99.7%. This proved that the application of the preliminary treatment method is useful for removing metallic impurities and improving the purity of silica. The major impurities of untreated RH ash are potassium oxide, calcium oxide, and iron oxide with 18.5%, 8.3%, and 2.5% contents, respectively. Oxides of potassium and calcium have been almost completely removed from the RH ash after pretreatment with HCl. All chemical treatments showed that the effective removal of oxides varies depending on the nature of the reagent used in the treatment of RH ash.

The X-ray diffraction patterns of silica samples are shown in Fig. 3. The noticeable broad halo with a maximum intensity rate at 23.0 2θ° correlates with the d-spacing of 0.36 nm and confirms the amorphous structure of SiO_2. The strong broad hump, between 15 and 30° (2θ) indicates that the silica SiO_2 that was extracted from the powder is amorphous and that no crystalline structure appeared and this is confirmed by the work of other researchers [40, 41].

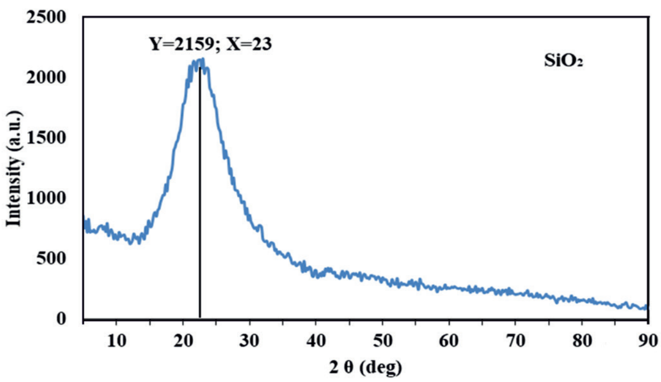
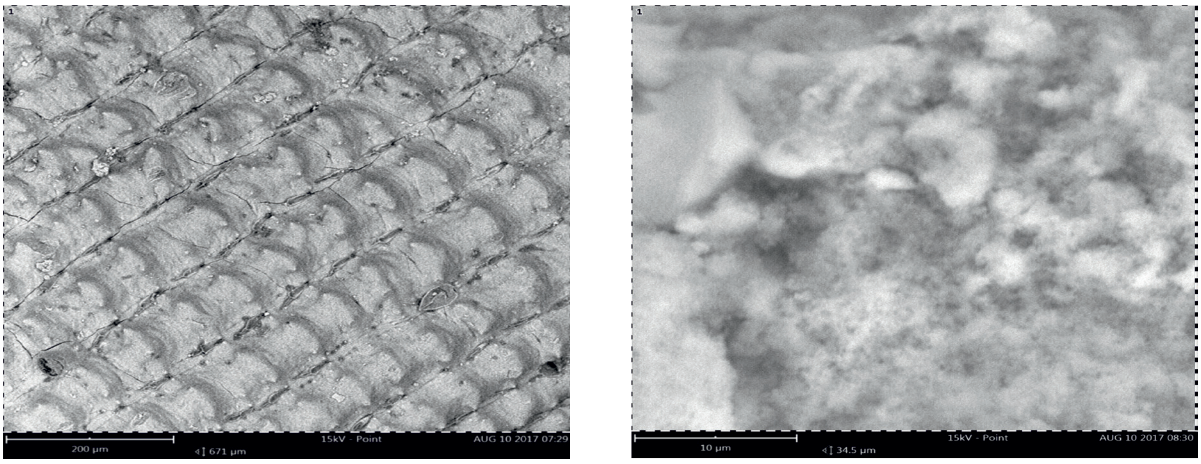


Fig. 3. X-ray diffraction pattern of silica.

Table 3
Results of X-ray fluorescent analysis of rice husk ash and silica samples

Elemental composition	Rice husk ash (untreated)			Rice husk ash (after treatment with HCl)			Pure SiO_2 sample		
	RHA*[1]	RHA*[2]	RHA*[3]	RHA*[1]	RHA*[2]	RHA*[3]	HCl*[1]	HCl*[2]	HCl*[3]
SiO_2	83.8	73.9	84.4	97.2		93.0	98.2	99.1	99.7
Na_2O	-	-	-	-	-	-	-		-
MgO	-	-	-	-	-	-	-	-	-
Al_2O_3	-	-	-	-	-	-	-	-	-
SO_3	-	-	-	-	-	-	-	-	-
Cl	-	3.1	-	0.9	6.1	2.8	1.8	0.8	-
K_2O	8.6	18.5	4.8	0.3	-	0.5	-	-	0.1
CaO	6.7	2.8	8.3	-	-	1.2	-	-	0.2
MnO	0.2	0.6	-	-	0.2	-	-	-	-
Fe_2O_3	0.6	0.6	2.5	1.2	3.7	2.2	-	0.02	-
CuO	-	-	-	0.3	0.3	0.1	-	-	-
ZnO	0.2	0.5	-	-	-	0.1	-	0.1	0.4
Cr_2O_3	-	-	-	-	0.01	-	-	-	-

*[1] Almaty region, *[2] Kyzylorda region, *[3] Turkystan region



(a) (b)

Fig. 4. SEM images of (a) rice husks before heat treatment (a) and (b) SiO_2.

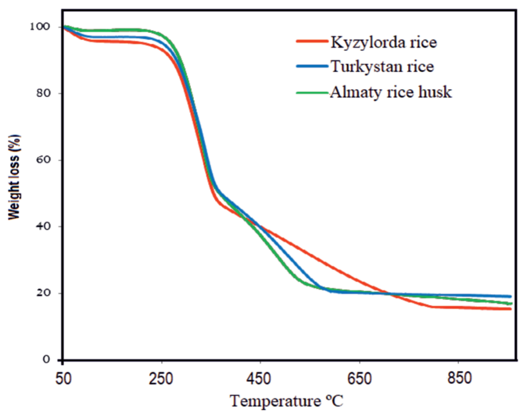


Fig. 5. TGA curves for rice husk.

SEM images of the original rice husks before heat treatment and silica are displayed in Fig. 4. The rice husk samples show a very dense and rough surface while the SEM image of the silica sample shows a nano-scale irregular surface coming from the morphology of silica nanoparticles, scattered in the big phase.

Figure 5 TG analysis was conducted to confirm the organic components existing in the rice husk. It can also be found that the initial loss of weight emerges within the variation of 50 to 250 °C. The second stage shows a fast and greater weight loss at the temperature range 300–450 °C. This is the main reason for the thermal decomposition of hemicellulose and cellulose as a major organic component in the rice husk. The third stage illustrates a weight loss of between 25–30% that could be mainly caused by lignin, a thermally more sustainable aromatic polymer that can undergo steady decomposition between 300 and 600 °C. The residue of ash is mostly the noncombustible silica (~15%, >600 °C).

The surface area and the pore characteristics of the silica samples were determined by the Brunauer-Emmett-Teller (BET) and density functional theory (DFT) methods. The specific surface area of the silica samples was observed to be 120, 150, and 980 $m^2 g^{-1}$, respectively. Compared to the surface area of the samples derived from RH 1 and RH 2, the surface area of the SiO_2 HCl 2 was indicated to be the largest specific surface area (980 $m^2 g^{-1}$) due to the smallest pore size of the extracted SiO_2 sample. The pore volume of the SiO_2 HCl_1, SiO_2 HCl_2, and SiO_2 HCl_3 silica samples were raised from 0.5 to 1.2 $cm^3 g^{-1}$ and the average pore diameter reduced from 26.4 nm to 0.9 nm. The specific surface areas, pore diameters, and pore volumes of the three silica samples are outlined in Table 4.

Table 4
The surface area and pore characteristics of the silica samples

Sample	BET surface area, $m^2 g^{-1}$	Pore characteristics (DFT method)	
		Pore volume, $cm^3 g^{-1}$	Pore size, nm
SiO_2_HCl_1	120	0.5	26.4
SiO_2_HCl_2	980	12.	0.9
SiO_2_HCl_3	150	0.8	18.4

The functional groups reveal in RHs and silica precipitate was determined by FTIR-ATR spectra (Fig. 6).

The notable peak in Fig. 6 (red) at about 3500 cm^{-1} correlates with the –O-H-extending vibrations of water molecules. The absorption peak at 2926 cm^{-1} can be associated with the symmetric and asymmetric extending vibrations of the aliphatic C-H bonds in $-CH_3$ and CH_2 groups in hemicellulose, cellulose and lignin, appropriately and 2114, 1423, 1383 cm^{-1} are associated with the C-H extended vibrations of the methylene groups. The peak at 1632 cm^{-1} can correspond to the –C=O stretching vibrations of the carbonyl groups in aldehydes and ketones. The peak at 1515 cm^{-1} is attributed to the C-O groups extending of carboxylates. The peaks at 1095, 898, 796, 662, 471 cm^{-1} are related to the stretching vibrations of the siloxane groups. The large absorption peak in Fig. 6 (blue) at 1055 cm^{-1} can be associated with the siloxane (Si–O–Si) network vibration modes, revealing a highly condensed silica network [42] and is in agreement with the literature [43]. The spectra of the produced SiO_2 illustrate no other band connected to organic or inorganic impurities.

4. Conclusion

The main rice cultivation developed in Kazakhstan mostly in the Kyzylorda region and a small amount in Turkystan. High purified amorphous silica samples (98–99%) with a surface area in the range from 120 to 980 $m^2 g^{-1}$ was successfully synthesized utilizing rice husk from various regions of Kazakhstan From different varieties Regul, Lider, and 42. The leaching under HCl pretreatment and controlled calcination at 600 °C for 4 h revealed decreasing in metal oxide content in the rice husk

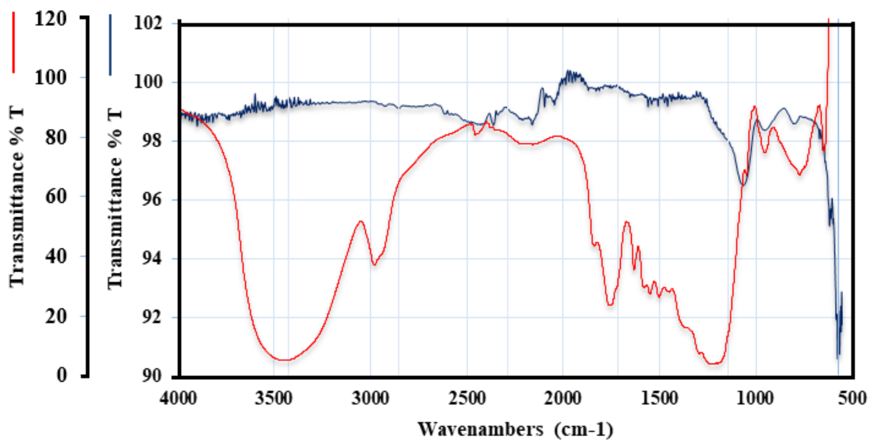


Fig. 6. FTIR spectra of RH (red) and SiO_2 (blue).

composition. The purity of the synthesized silica was observed by XRF analysis. With 99.7 pure silicon dioxide was synthesized from grade 42 from Turkestan, which was obtained by further purification. The current approach was compared with other studies, which also aimed to produce a silica sample from rice husk. The comparison was carried out to show the importance of parameters such as duration and temperature of thermal treatment, rice variety, geographical location, and concentration of used acid.

This research work shows the possibility of using the described simple chemical method in the production of large amounts of silica with lower costs in the rice-producing countries, which also solves the problem of the effect of burning rice husk in the open air on the environment. If extract silicon dioxide from rice husks only in Kazakhstan per year, we can get about 13 thousand tons of silicon dioxide, which can be further used in other industries.

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References

[1]. Crop Prospects and Food Situation – Quarterly Global Report, No. 1, March 2020. DOI: 10.4060/ca8032en

[2]. K. Askaruly, S. Azat, Z. Sartova, M. Yeleuov, A. Kerimkulova, K. Bekseitova, *Journal of Chemical Technology and Metallurgy* 55 (2020) 88–97. https://dl.uctm.edu/journal/node/j2020-1/12_19-76_p_88-97.pdf

[3]. B. Meyer, L. Lundy, J. Watt, I. Abdullaev, J.E. Capilla Roma, *Journal of Environmental Geography* 9 (2016) 33–42. DOI: 10.1515/jengeo-2016-0010

[4]. Y. Shen, P. Zhao, Q. Shao, *Micropor. Mesopor. Mat.* 188 (2014) 46–76. DOI: 10.1016/j.micromeso.2014.01.005

[5]. S. Nagrale, H. Hajare, P. Modak, *International Journal of Engineering Research and Applications* (IJERA) 2 (2012) 1–5.

[6]. N. Sapawe, N.S. Osman, M.Z. Zakaria, S.A. S.S.M. Fikry, M.A.M. Aris, *Materials Today: Proceedings* 5 (2018) 21861–21866. DOI: 10.1016/j.matpr.2018.07.043

[7]. A.R. Kerimkulova, S. Azat, L. Velasco, Z.A. Mansurov, P. Lodewyckx, M.I. Tulepov, M.R. Kerimkulova, I. Berezovskaya, A. Imangazy, *Journal of Chemical Technology and Metallurgy*, 54 (2019) 578–584. https://www.kaznu.kz/content/files/pages/folder21071/azat04.pdf

[8]. S. Azat, V.V. Pavlenko, A.R. Kerimkulova, Z.A. Mansurov, *Advanced Materials Research* 535–537 (2012) 1041–1045. DOI: 10.4028/www.scientific.net/AMR.535-537.1041

[9]. Statistic yearbooks. Agricultural, forest and fish in the Republic of Kazakhstan for each year 20002016 [Electronic source], 2016, URL: http://stat.gov.kz/faces/almatyobl/

[10]. S. Azat, Z. Sartova, K. Bekseitova, K. Askaruly, *Turk. J. Chem.* 43 (2019) 1258–1269. DOI: 10.3906/kim-1903-53

[11]. R.A. Bakar, R. Yahya, S.N. Gan, *Procedia Chemistry* 19 (2016) 189–195. DOI: 10.1016/j.proche.2016.03.092

[12]. I.J. Fernandes, F.A.L. Sánchez, José R. Jurado, A.G. Kieling, T.L.A.C. Rocha, C.A.M. Moraes, V.C. Sousa, *Adv. Powder Technol.* 28 (2017) 1228–1236. DOI: 10.1016/j.apt.2017.02.009

[13]. M.F.M. Zain, M.N. Islam, F. Mahmud, M. Jamil, *Constr. Build. Mater.* 25 (2011) 798–805. DOI: 10.1016/j.conbuildmat.2010.07.003

[14]. S. Kumar, P. Sangwan, R. Mor V. Dhankhar, S. Bidra, *Research Journal of Chemical and Environmental Sciences* 5 (2013) 126–129. https://www.huutokauppa.com/content/ad/file/13/96/139665.pdf

[15]. J. Alvarez, G. Lopez, M. Amutio, J. Bilbao, M. Olazar, *Bioresource Technol.* 170 (2014) 132–137. DOI: 10.1016/j.biortech.2014.07.073

[16]. Z.A. Mansurov, J.M. Jandosov, A.R. Kerimkulova, S. Azat, A.A. Zhubanova, I.E. Digel, A.S. Kistaubaeva, *Eurasian Chem.-Technol. J.* 15 (2013) 209–217. DOI: 10.18321/ectj224

[17]. A.R. Kerimkulova, S. Azat, Z.A. Mansurov, M.K. Gilmanov, S.A. Ibragimova, S.M. Adekenov, B.B. Rachimova, *Advanced Materials Research* 535–537 (2012) 284–288. DOI: 10.4028/www.scientific.net/AMR.535-537.284

[18]. Y.-B. Im, R. Wahab, S. Ameen, Y.-S. Kim, O-B. Yang, H.-S. Shin, *J. Nanosci. Nanotechno.* 11 (2011) 5934–5938. DOI: 10.1166/jnn.2011.4386

[19]. K. Kaviyarasu, E. Manikandan, J. Kennedy, M. Jayachandran, M. Maaza, *Adv. Mater. Lett.* 7 (2016) 684–696. DOI: 10.5185/amlett.2016.6192

[20]. Q. Tang, T. Wang, *J. Supercrit. Fluid.* 35 (2005) 91–94. DOI: 10.1016/j.supflu.2004.12.003

[21]. M. Ahmaruzzaman, V.K. Gupta, *Ind. Eng. Chem. Res.* 50 (2011) 13589–13613. DOI: 10.1021/ie201477c
[22]. R.M. Mohamed, R.M. Radwan, M.M. Abdel-Aziz, M.M. Khattab, *J. Appl. Polym. Sci.* 115 (2010) 1495–1502. DOI: 10.1002/app.31158
[23]. S. Azat, A.V. Korobeinyk, K. Moustakas, V.J. Inglezakis, *J. Clean. Prod.* 217 (2019) 352–359. DOI: 10.1016/j.jclepro.2019.01.142
[24]. H. Hamdan, M.N.M. Muhid, S. Endud, E. Listiorini, Z. Ramli, *J. Non-Cryst. Solids* 211 (1997) 126–131. DOI: 10.1016/S0022-3093(96)00611-4
[25]. B. Shi, Y.K. Shin, A.A. Hassanali, S.J. Singer, *Colloid. Surface. B* 157 (2017) 83–92. DOI: 10.1016/j.colsurfb.2017.05.048
[26]. I.J. Fernandes, D. Calheiro, F.A.L. Sánchez, A.L.D. Camacho, T.L.A. de C. Rocha, C.A.M. Moraes, V.C. de. Sousa, *Mat. Res.* 20 (2017) 512–518. DOI: 10.1590/1980-5373-mr-2016-1043
[27]. J.A.S. Costa, C.M. Paranhos, *J. Clean. Prod.* 192 (2018) 688–697. DOI: 10.1016/j.jclepro.2018.05.028
[28]. K.K. Larbi, Synthesis of high-purity silicon from rice husks. MS.C. thesis, University of Toronto, 2010.
[29]. F. Ledesma E., R. Acosta C., L. Garrido M., D. Polanco I., C. Guarnaluce D., *J. Mater. Environ. Sci.* 6 (2015) 114–118.
[30]. R.A. Bakar, R. Yahya, S.N. Gan, *Procedia Chemistry* 19 (2016) 189–195. DOI: 10.1016/j.proche.2016.03.092
[31]. I.B. Ugheoke, O. Mamat, *Maejo Int. J. Sci. Technol.* 6 (2012) 430–448.
[32]. K.A. Matori, M.M. Haslinawati, Z.A. Wahab, H.A.A. Sidek, T.K. Ban, W.A.W.A.K. Ghani, *MASAUM Journal of Basic and Applied Sciences* 1 (2009) 512–515.
[33]. G.R. de Sensale, *Cement Concrete Comp.* 32 (2010) 718–725. DOI: 10.1016/j.cemconcomp.2010.07.008
[34]. J. Prasara, S.H. Gheewala, *J. Clean. Prod.* 167 (2018) 1020–1028. DOI: 10.1016/j.jclepro.2016.11.042
[35]. R. Jauberthie, F. Rendell, S. Tamba, I. Cisse, *Constr. Build. Mater.* 14 (2000) 419–423. DOI: 10.1016/S0950-0618(00)00045-3
[36]. Z.A. Mansurov, M.K. Atamanov, Z. Elemesova, B.T. Lesbaev, M.N. Chikradze, *Combust. Explo. Shock* 55 (2019) 402–408. DOI: 10.1134/S0010508219040051
[37]. V. Kannan, *Constr. Build. Mater.* 160 (2018) 169–179. DOI: 10.1016/j.conbuildmat.2017.11.043
[38]. M.K. Atamanov, R. Amrousse, K. Hori, Z. Mansurov, *Combust. Sci. Technol.* 191 (2019) 645–658. DOI: 10.1080/00102202.2018.1498848
[39]. J. Alvarez, G. Lopez, M. Amutio, J. Bilbao, M. Olazar, *Ind. Eng. Chem. Res.* 54 (2015) 7241–7250. DOI: 10.1021/acs.iecr.5b01589
[40]. S. Wardiyati, W.A. Adi, Deswita, *IOP Conf. Ser.: Mater. Sci. Eng.* 202 (2017). DOI: 10.1088/1757-899X/202/1/012059
[41]. A. Mourhly, M. Khachani, A.El Hamidi, M. Kacimi, M. Halim, S. Arsalane, *Nanomat. Nanotechno.* 5 (2015). DOI: 10.5772/62033
[42]. H.I. Meléndez-Ortiz, Y. Perera-Mercado, J.A. Mercado-Silva, Y. Olivares-Maldonado, G. Castruita, L.A. García-Cerda, *Ceram. Int.* 40 (2014) 9701–9707. DOI: 10.1016/j.ceramint.2014.02.051
[43]. J. Umeda, K. Kondoh, *Ind. Crop. Prod.* 32 (2010) 539–544. DOI: 10.1016/j.indcrop.2010.07.002