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Energy Recovery Together with Amorphous Nanosilica Production from Rice Straw *via* Dry Anaerobic Digestion

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Rice straw burning is the most widely used industrial process for silica production, resulting in the loss of carbohydrate energy and environmental pollution. In this study, dry anaerobic digestion was applied to convert an organic fraction of rice straw into biogas while generating a solid digestate rich in silica. The methane yield obtained from the dry digestion was 119 L per kg of volatile solids of the straw. The silica content in the ash of the digested straw was 20.7% higher than that of the ash from raw rice straw. The X-ray diffraction pattern revealed the existence of amorphous silica in the ash of the digested straw. The Fourier transform infrared analysis dispelled concerns about the addition of silica impurities by the anaerobic digestion process. The transmission electron microscopy results revealed the formation of nanosilica with particle sizes between 15 nm and 30 nm. It was concluded that high-quality nanosilica can be obtained from anaerobically digested rice straw. The application of this process can decrease the annual global greenhouse gas emissions by 10.5 million tons.

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INTRODUCTION

Silica can be obtained from various sources, *e.g.*, quartz sand, rock, clay, volcanic soil, phytoplankton, and rice hull and straw (Barik *et al.* 2008), and it exists in both crystalline and amorphous (non-crystalline) forms (Lyon 1994). Crystalline silica is hard, chemically inert and has a high melting point. Amorphous silica is highly reactive in nature and can be a source for preparing advanced materials like silicon carbide, silicon nitride, elemental silicon, and magnesium silicide (Chandrasekhar *et al.* 2003). Its main applications are in thermal insulation, building materials, and polymer composites (Lee *et al.* 2006; Hosseini *et al.* 2011).

Rice straw, as an agricultural waste biomass, is one of the most abundant byproducts produced in paddy fields (Yuvakkumar *et al.* 2014). Approximately 731 million tons are produced globally per year, with distribution in Africa (20.9 million tons), Asia (667.6 million tons), and Europe (3.9 million) (Wi *et al.* 2013). Rice straw contains a considerable amount of silica (7% to 20%). In addition to silica, rice straw contains remarkable amounts of lignocellulose, which consists of cellulose (32% to 47%), hemicellulose (19% to 27%), and lignin (5% to 24%) (Hu and Hsieh 2014). Like other lignocelluloses, rice straw is a renewable resource that can be used to produce sustainable

energy (Taherzadeh and Karimi 2008). However, in most previous studies on the preparation of silica from straw materials (Table 1), the organic fractions/lignocelluloses in the straw were burnt (Chen *et al.* 2010, 2012; Amutha and Sivakumar 2013), which resulted in the waste of lignocelluloses and the generation of CO_2. Therefore, it is of great environmental and economic importance to utilize both carbohydrates and silica in rice straw.

Table 1. Previous Studies on Preparation of Silica from Agricultural Wastes

Feed	Product	Procedure	Reference
Rice straw Maize stalk	Nano-biosilica	Calcination at 650 °C; Dissolution in NaOH solution; Precipitation by HCl solution	Amutha and Sivakumar 2013
Semi-burned rice straw	Silica nanosphere	Dissolution in NaOH solution; Precipitation by H_2SO_4 solution	Hessien *et al.* 2009
Rice husk	Silica nanoparticles	Dissolution of lignocellulose in ionic liquids; Pyrolysis at 700 °C	Chen *et al.* 2012
Rice husk	Silica nanoparticles	Boiling in HCl solution; Pyrolysis at 700 °C	Wang *et al.* 2011
Rice straw	Amorphous silica nano-disks	Pyrolysis (heating and holding at certain temperatures up to 575 °C); Dissolution by NaOH solution; Precipitation by H_2SO_4 solution	Lu and Hsieh 2012
Rice husk	Amorphous silica	Air combustion at 800 °C; Citric acid leaching	Umeda and Kondoh 2010
Rice husk	Nanosilica powder	Pyrolysis at 973 K; Washing with HCl solution; Boiling with NaOH solution; Precipitation by H_2SO_4; Sintering at 973 K	Yuvakkumar *et al.* 2014
Rice husk	Nanosilica	Heating in acidic solution; Dissolution in NaOH solution; Precipitation by an organic acid solution; Calcination at 500 °C	Noushad *et al.* 2014
Rice husk	Nanosilica	Acid treatment at 150 °C; Calcination at 650 °C	Carmona *et al.* 2013
Wheat straw	Nanosilica	Combustion at 500 °C; Acid treatment using nitric-sulphuric acid aqueous solution; Burning at 400 °C to 700 °C	Chen *et al.* 2010
Semi-burned rice straw ash	Silica nanoparticles	Dissolution of ash in NaOH solution; Precipitation by H_2SO_4 solution	Zaky *et al.* 2008

Anaerobic digestion (AD) is one of the alternatives for energy recovery from rice straw (Zhang and Zhang 1999; Kabir *et al.* 2015), which can be performed under wet (total solid (TS) < 15%) or dry (TS > 15%) processes. Wet AD is the most common method; however, it needs a large reactor, consumes a lot of energy, and generates a high amount of wastewater. Dry AD is a promising alternative method that can overcome these problems and is also compatible with the dry nature of rice straw as an agricultural waste (Brown *et al.* 2012; Yang *et al.* 2015). With the removal of digestible parts, the solid residues contain enriched silica which can be further processed to high purity silica with various industrial applications. Therefore, the proposed process of dry AD is a promising

approach for both energy recovery and silica preparation from rice straw. However, little to no research has been done for this purpose.

In this study, dry anaerobic digestion was applied to produce biogas as a form of bioenergy from rice straw, whereas the digested residue was used for silica preparation. The methane yield from the straw along with the degradation of cell wall components was investigated. The ash samples of both the raw and digested straw were characterized for their physicochemical properties.

EXPERIMENTAL

Materials
Rice straw and inoculum preparation

The rice straw used in this study was collected from Lenjan field (Isfahan, Iran). The straw was cut by a knife to approximately 1 cm in length. Particles that were larger than 0.85 mm (mesh-20) were stored in a sealed plastic bag at room temperature until use.

The inoculum for AD was prepared by concentrating the digester effluent using centrifuge according to a previously described procedure (Mirmohamadsadeghi *et al.* 2014). The effluent was obtained from an industrial-scale mesophilic anaerobic digester at Isfahan Municipal Sewage Treatment Plant (Isfahan, Iran). After centrifugation, the inoculum was well mixed and kept at 37 °C for one week prior to use. The total solid (TS) and volatile solid (VS) of the inoculum were 7.9% and 4.5%, respectively.

Methods
Dry anaerobic digestion

Approximately 5 g of rice straw was mixed with 30 g of inoculum in a 118 mL batch reactor to obtain an initial TS content of 20% and a feed-to-inoculum ratio (F/I) of 3 based on VS contents. The reactors were purged with pure nitrogen gas for approximately 2 min to obtain anaerobic conditions (Hansen *et al.* 2004) and then incubated at mesophilic conditions (37 °C ± 1 °C) for 60 days. The inoculum without any feedstock addition was also run as a control. The AD tests were performed in triplicates. Gas samples were periodically taken and analyzed for biogas production during the 60 days. Afterwards, the solid digestate was collected and used for silica preparation and further analysis.

Silica preparation

The 60-day anaerobically digested rice straw was thoroughly washed with tap water on an 80-mesh sieve to remove the sludge. The solid fraction was collected, dried at 60 °C, and weighted for calculating the recovery percentage by digestion. The dried digested rice straw (DRS) was calcined at 550 °C for 8 h along with the raw rice straw (RS). The resulting rice straw ash (RSA) and digested rice straw ash (DRSA) were collected for further analysis.

Biogas analysis

Methane and carbon dioxide contents in the produced biogas were analyzed using a gas chromatograph (GC; Sp-3420A, TCD detector, Beijing Beifen Ruili Analytical Instrument Co., Beijing, China) equipped with a packed column that was 3 m in length and

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3 mm in internal diameter (Porapak Q, Chrompack, Germany). Nitrogen was used as the carrier gas at a flow rate of 45 mL/min. The column, injector, and detector temperatures were 40 °C, 100 °C, and 150 °C, respectively. A 0.250-mL pressure-lock syringe (SGE Analytical Science, Australia) was used for gas sampling and injection to the GC. To avoid high-pressure build-up in the reactors, the excess gas was discharged after each gas sampling. The biomethane yield was calculated based on the total VS of the mixture fed into the digester and was reported at standard conditions (0 °C, 1 atm), after subtracting the methane yield of the control sample.

Characterization of RS and DRS

The rice straw samples and inoculum were dried at 105 °C for 4 h (Sluiter *et al.* 2008a) and combusted at 575 °C for 24 h (Sluiter *et al.* 2008b) to reach a constant weight to determine the TS and ash contents, respectively.

The digestate was analyzed for the pH, alkalinity, and volatile fatty acids (VFA). The samples were prepared by mixing 2 g of the digestate with 20 g of distilled water. The supernatants were then separated by centrifugation and collected for analysis. A two-stage titration technique using a H_2SO_4 solution was performed to obtain the total VFA and alkalinity (Lossie and Pütz 2008).

The RS and DRS were analyzed for lignin, hemicellulose, and cellulose contents according to the National Renewable Energy Laboratory (NREL) method (Sluiter *et al.* 2008c). Concentrations of the released sugars were quantified by high-performance liquid chromatography (HPLC), equipped with a refractive index detector (RID) (Agilent 1100, Agilent Technologies, Palo Alto, CA), and an Aminex HPX-87P column (Bio-Rad, Richmond, CA, USA). The temperature of the column was 80 °C, and the mobile phase was HPLC-grade water eluting at a flow rate of 0.6 mL/min. The acid-soluble and acid-insoluble lignin contents were measured using a UV–Vis spectroscope (Rayleigh UV-1601, Braic, Beijing, China) at 320 nm, and after calcination of the samples at 575 °C, respectively.

The main functional groups presented in the samples were identified by a Fourier transform infrared (FTIR) spectrometer (Rayleigh WQF-510A, Braic, Beijing, China), obtained using KBr pellets with a resolution of 2 cm^{-1} from 4400 cm^{-1} to 400 cm^{-1}.

Nanosilica characterization

The chemical contents of RSA and DRSA were determined using an energy dispersive X-ray fluorescence (XRF; Bruker S4 Pioneer, Bruker AXS, Karlsruhe, Germany) spectrometer. The X-ray diffraction (XRD) patterns of the samples were recorded by an X-ray diffractometer (Philips, X'pert, The Netherlands). The patterns were measured at 40 kV and 30 mA in the scan range of $2\theta = 5°$ to $80°$. The microstructure of the RSA was observed by a scanning electron microscope (SEM; XL30, Philips, Eindhoven, Netherlands). The dried sample was gold coated (BAL-TEC SCD 005, Bal-Tec AG, Liechtenstein) and analyzed at 7.5 kV. A transmission electron microscope (TEM; EM208S, Philips, Eindhoven, Netherlands) operating at 100 kV was used to investigate the approximate particle sizes of the DRSA. The TEM microphotographs were analyzed using ImageJ software (ImageJ 1.42q Wayne Rasband, National Institute of Health, Bethesda, MD). The FTIR analysis was also performed on the ash samples as described in the 'Characterization of RS and DRS' section.

RESULTS AND DISCUSSION

Anaerobic Digestion of Rice Straw

The microbial consortia in the anaerobic digester converted cellulose and hemicellulose in the lignocelluloses to biogas through a series of biochemical reactions (Cui *et al.* 2011). In this study, rice straw was subjected to anaerobic digestion, which not only recovered energy from organic fraction, but also generated silica-rich residues. A dry batch of anaerobic digestion with a TS content of 20% and an F/I ratio of 3 was conducted to produce biomethane from the rice straw. The cumulative methane production from the rice straw is shown in Fig. 1. The methane yield was 119.1 L.kg^{-1} VS at standard conditions (0 °C and 1 atm). Based on the organic composition, the theoretical methane yield of rice straw (Li *et al.* 2013) is 459 L.kg^{-1} VS. Therefore, the anaerobic biodegradability of rice straw counts for 26%. The results were consistent with a previous study on rice straw (115.9 L.kg^{-1} carbohydrate equal to 99.2 L.kg^{-1} VS), which was performed at a TS of 21% (Mirmohamadsadeghi *et al.* 2014). The methane yield from the rice straw can be enhanced using different pretreatment methods (Taherzadeh and Karimi 2008) or using a leach bed reactor (Li *et al.* 2018). These methods have the ability to improve the silica quality, but further investigation is needed to prove this. The final pH and VFA/alkalinity ratio of the digested rice straw were 8.2 and 0.7, respectively, which were in the range of a healthy performance for dry AD (Brown and Li 2013).
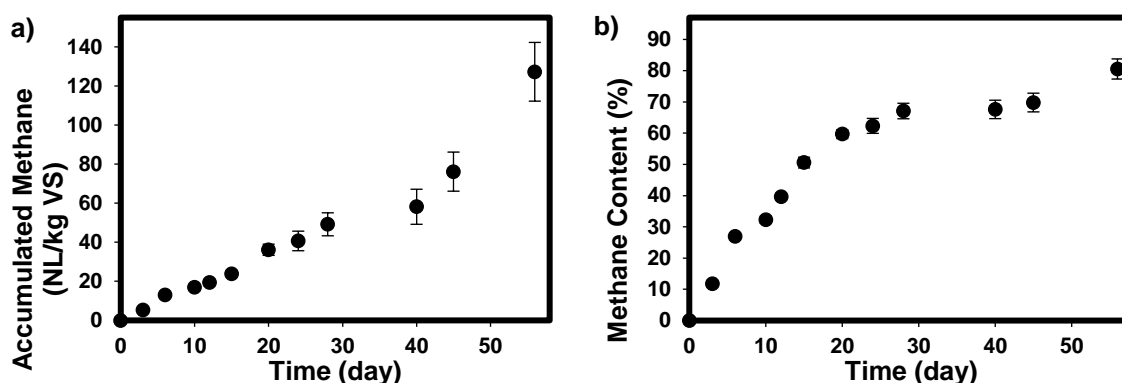

Fig. 1. (a) Methane production yield and (b) methane content from dry AD of rice straw

Table 2 shows the composition of the rice straw before and after digestion as well as the degradation results of lignocellulose after the 60-day anaerobic digestion. The highest degradation (39.2%) was observed for cellulose and followed by hemicellulose (36.3%). The results showed that lignin was not considerably degraded by the digestion. Unlike holocellulose, lignin is generally difficult to degrade by the microorganisms in anaerobic digesters (Taherzadeh and Karimi 2008). The ash content of DRS (12.5%) was higher than that of RS (8.6%) as a result of the partial removal of digestible organic parts. Furthermore, the differences between the morphologies of digested rice straw and raw rice straw were visible. The rice straw was yellow with a smooth texture, whereas the digested straw was dark with a rough texture. The rice straw recovery was 75.2% after anaerobic digestion, indicating that 24.8% of the straw was digested and converted to biogas.

Table 2. Compositional Analysis and Anaerobic Degradation of Rice Straw

Sample	Composition (%)				Degradation (%)		
	Cellulose	Hemicellulose	Lignin	Ash	Cellulose	Hemicellulose	Lignin
Rice Straw	37.5 ± 0.3	34.0 ± 0.1	14.1 ± 0.8	8.6 ± 1.1	-	-	-
Digested Rice Straw*	30.3 ± 0.5	28.8 ± 0.8	18.5 ± 0.5	12.5 ± 0.5	39.2	36.3	1.1
* Anaerobic digestion conditions: 60 days, F/I = 3, and TS = 20%							

Nanosilica Characterization

The ash obtained from the digested rice straw was a white material (Fig. 2), which was indicative of a relatively pure silica as compared to the raw rice straw ash. In contrast, the ash from the untreated straw was black and gray and contained more impurities. The physicochemical properties of RSA and DRSA were compared and discussed further in detail below.
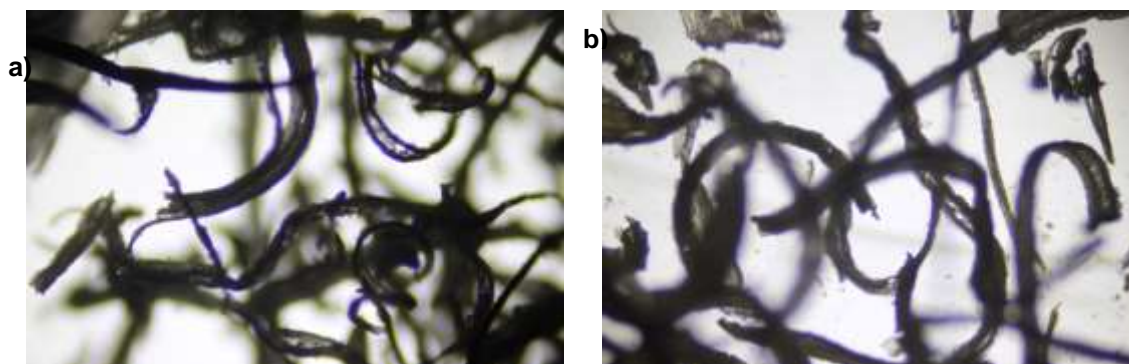
Fig. 2. Microscopic image of (a) raw rice straw ash and (b) digested rice straw ash

Chemical Analysis

Table 3 illustrates the inorganic components of the RSA and DRSA samples. The DRSA contained 58.4% silica, which was approximately 20% higher than that in RSA. Another remarkable change was the reduction in potassium oxide, which changed from 30.40% to 0.92% after digestion. It has been shown that potassium ions, due to the eutectic phenomenon with SiO_2, are responsible for the melting of silica nanoparticles at relatively low temperatures during burning (Real *et al*. 1997). This leads to the aggregation of silica nanoparticles, an increase in crystallinity, and a dramatic decrease in the specific surface area. Therefore, the absence of K^+ is crucial for the synthesis of high-quality silica nanoparticles (Umeda and Kondoh 2010). Acid treatments are a common way to remove K^+ ions prior to burning to obtain silica nanoparticles with high purity and surface area and low crystallinity (Wang *et al*. 2011). However, acid treatments require expensive corrosion-resistant reaction equipment and may raise pollution issues. Therefore, they are undesirable for commercial production. The results of this study indicated that anaerobic digestion could effectively remove most potassium cations, which would eliminate the need for acid leaching for potassium ion removal before burning.

Table 3. Chemical Analysis of Ash Samples by X-ray Fluorescence

| Sample	Chemical Content (%w/w)										
	SiO_2	K_2O	CaO	Cl	SO_3	P_2O_5	MgO	Na_2O	Fe_2O_3	MnO	Al_2O_3
RSA*	37.70	30.40	10.40	10.20	3.94	3.42	1.93	0.70	0.51	0.44	0.13
DRSA**	58.36	0.92	23.66	0.30	7.54	4.01	1.62	0.21	1.50	0.21	1.25
* Raw straw ash; ** Digested RSA; chemical compounds: SiO_2- silicone dioxide, K_2O- potassium oxide, CaO- calcium oxide, Cl- chloride, SO_3- sulfur trioxide, P_2O_5- phosphorus pentoxide, MgO- magnesium oxide, Na_2O- sodium oxide, Fe_2O_3- iron (III) oxide, MnO- manganese, and Al_2O_3- aluminum oxide											

XRD Patterns

The XRD results indicated that the DRSA sample contained amorphous silica (Fig. 3). A broad peak was observed at 2θ ranging from 15° to 28°, which confirmed the presence of amorphous silica. This peak was also observed in the XRD pattern of the silica obtained from burning of rice straw followed by a base dissolution and an acid precipitation process (Lu and Hsieh 2012). However, this peak was not observed in the XRD pattern of RSA, which demonstrated that there was no amorphous silica in the untreated sample.
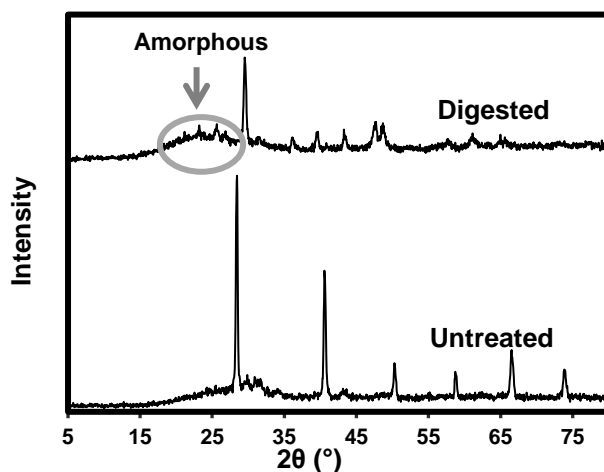
Fig. 3. XRD spectra of ash samples

FTIR Spectrum

An FTIR analysis (Fig. 4) was performed for the RS, DRS, RSA, and DRSA samples to compare their functional groups. The spectra of RSA and DRSA were similar in the number of peaks and wavelength; however, the peak intensities were entirely different. The much lower peak intensities of RSA was probably due to the dark color of the sample that caused a dark pellet and less transmittance of the IR beam, in comparison with the DRSA sample. The transmittance bands and their corresponding functional groups are summarized in Table 4. The existence of silica was confirmed by the three peaks at 1110 cm^{-1} to 1040 cm^{-1}, 790 cm^{-1}, and 470 cm^{-1}. The broad peak between 1110 cm^{-1} and 1040 cm^{-1} indicated the stretching vibration of a Si-O-Si siloxane bond. The sharp peaks at 790 cm^{-1} and 470 cm^{-1} represented the amorphous silica of the Si-O-Si bending mode and in-plane bending vibrations of O-Si-O bond, respectively. The increase in the intensity of these three peaks was clearly apparent in the DRSA sample, which was evidence of the

increase in the silica content of the sample. The presence of peaks at 2920 cm^{-1} and 2850 cm^{-1} demonstrated the polysaccharide groups in RS and DRS, which was almost omitted in the RSA and DRSA samples. It was confirmed that silica was the main component in the DRSA and RSA samples. However, there were carbonate impurities in both samples, which can be removed using common methods. In general, it was concluded that silica and biogas can be simultaneously produced from rice straw without any concern about the addition of extra impurities to the straw by the anaerobic digestion process.
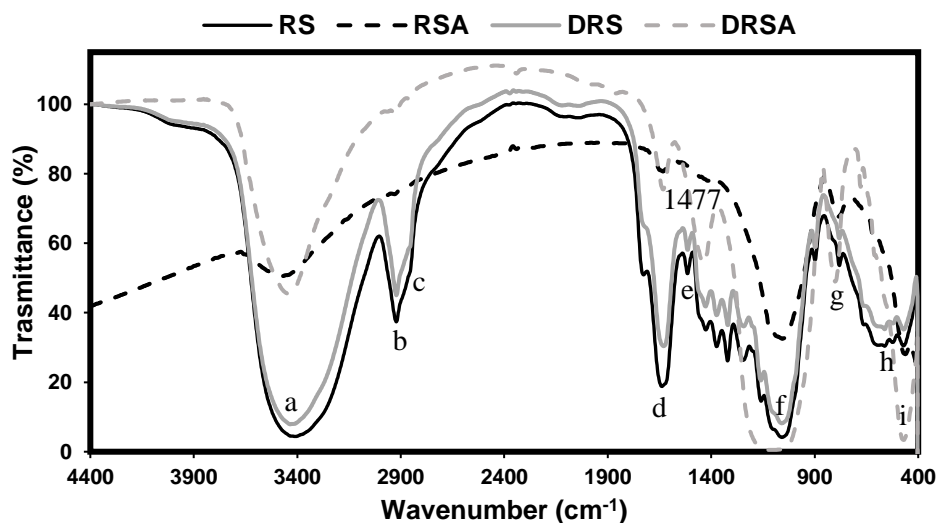
Fig. 4. FTIR spectra of rice straw (black line), rice straw ash (black dotted line), digested rice straw (gray line), and digested rice straw ash (gray dotted line)

Table 4. Transmittance Bands and Corresponding Functional Groups in FTIR Spectra

Symbol	Band (cm^{-1})	Assigned Functional Group	Assigned Components
a	3780 to 3000	SiO–H	Silanol
b	2920	CH$_2$	Polysaccharides
c	2850	CH$_2$	Polysaccharides
d	1690 to 1550	H–O–H	Water
e	1480 to 1410	CO$_3^{2-}$	Carbonate
f	1110 to 1040	Si–O–Si	Silica, siloxane
g	790	O–Si–O	Amorphous silica
h	620	Cristobalite	Crystal structure of silica
i	470	O–Si–O	Silica

Scanning and Transmission Electron Images

Figure 5 shows the SEM images of the ash sample obtained from the raw rice straw. The SEM images of RSA (Fig. 5a) showed the silica crystals with the cubic shape, distributed on the surface of the RSA. By contrast, silica was observed in the amorphous form for digested rice straw ash (Fig. 5b), accumulated as larger particles rather than that of the RSA. The TEM images of the DRSA sample confirmed the existence of silica particles at the nanoscale (Fig. 6). The estimated particle size of amorphous silica in the DRSA was between 15 nm and 30 nm.
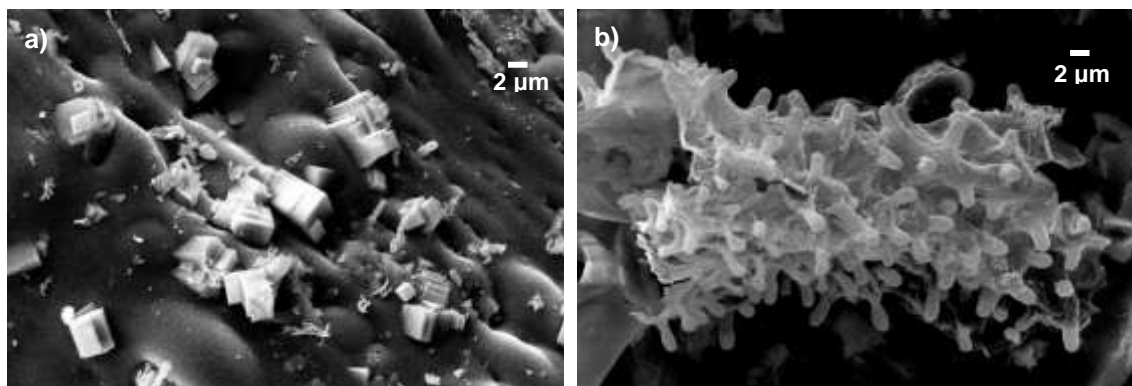
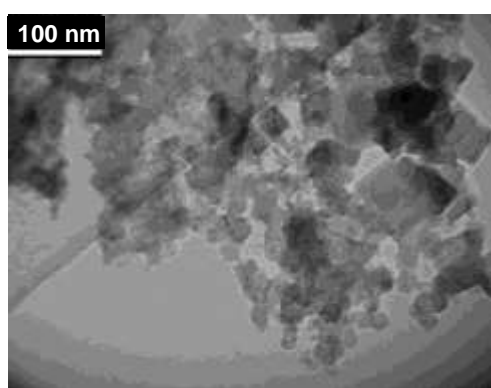**Fig. 5.** SEM images of ash samples of (a) raw and (b) digested rice straw

Fig. 6. TEM image of silica nanoparticles of DRSA sample

Mass Balance

Applying mass balance on the whole process showed that the use of 1 kg rice straw as the feed yielded the production of 99 L methane and 94 g nanosilica.

Reduction of CO_2 Emissions

The collectible residue from rice harvesting in Iran is annually 1.38 million tons (Alavijeh and Yaghmaei 2016). Its average amount of greenhouse gas emissions is approximately 275.4 g/kg of rice straw, which results from straw burning that includes CO_2, CO, CH_4, and N_2O (Miura and Kanno 1997). Thus, the annual amount of gas emissions from rice straw burning is approximately 0.38 million tons in Iran. Considering Iran's global contribution to crop residue production (0.9%) (Alavijeh and Yaghmaei 2016), the global greenhouse gas emissions from rice straw burning is around 42.2 million tons annually. Regarding 24.8% conversion of the straw to biogas, biogas production from straw prior to the silica production process will decrease 10.5 million tons of greenhouse gas emissions per year. The reduction in greenhouse gas emission can be even more than the predicted amount if a more efficient process would be applied for AD. The amount of gas emissions from biogas burning is not considered because biogas will be utilized as a substitute of fossil methane, which is currently used and emits the same amount of greenhouse gases emitted by biomethane. Therefore, combining biogas and silica production processes will help to decrease the greenhouse gas emissions by 10.5 million tons annually.

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CONCLUSIONS

1. This study demonstrated that dry anaerobic digestion is an effective route to recover energy from rice straw while leaving a silica-rich residue for industrial applications.

2. Nanosilica was recovered from digested rice straw with particle sizes of 15 nm to 30 nm with higher purity than that of untreated straw. Thus, the concern about the addition of extra impurities to silica *via* anaerobic inoculum was dispelled. This process can improve the process economy by converting the digestible organic parts of the straw to biogas.

3. Using this process, the greenhouse gas emissions can be decreased by 10.5 million tons annually.

4. Furthermore, the amorphous silica was represented in the XRD pattern of the digested straw ash but not in that of the raw straw ash.

ACKNOWLEDGMENTS

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