

Sodium carbonate pretreatment: an approach towards desilication of paddy straw and enhancement in biogas production

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Received: 22 April 2014/Revised: 4 January 2015/Accepted: 10 February 2015/Published online: 20 February 2015
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Abstract Lignocellulosic biomass is a useful but an inconvenient form of energy, and paddy straw (PS) is one of the most abundant lignocellulosic wastes on the earth. Lignocellulosics generally have a high content of cellulose having combustion energy of 15 kJ/g which, when converted to methane, have a combustible energy of 50 kJ/g. But lignin and silica are the main deterrents for the microbial action on the cellulose/hemi-cellulose component of PS. In order to break the protective shield made by lignin and silica and to enhance the PS digestibility, the PS was pretreated with different concentrations (2, 4, 6, 8 and 10 %) of sodium carbonate by soaking the PS in sodium carbonate solution for the periods of 24 and 48 h and simultaneously irradiating the other set with microwaves (power 720 W, temperature 180 °C) for 30 and 60 min. The change in chemical composition of PS was the factor determining the enhancement in PS digestibility. Sodium carbonate (4 %) + microwave (60 min) pretreatment was found to be the best amongst the other pretreatments with 84.9 % desilication of PS and 44.3 and 54.4 % increase in cellulose and biogas production, respectively.

Keywords Paddy straw · Pretreatment · Sodium carbonate · Microwave · Biogas production

Introduction

Biomass can be classified into three main categories: sugar-, starch- and cellulose-containing plants. Sugar- and

starch-containing plants are generally used as food sources, while cellulose-containing plants and their waste products (e.g., grasses, wood, bagasse and straws) are the most abundant form of biomass (Holtzaple and Davison 1999). Lignocellulosic biomass is defined as contemporary plant matter (Frank and Smith 1988) which is continually being replenished by the photosynthetic reduction of carbon dioxide (CO₂) by sun energy (Zhang and Lynd 2004; Ragauskas et al. 2006; Saratale et al. 2008). Lignocellulosic biomass/agricultural residue is a useful but an inconvenient form of energy. Lignocellulosic biomass generally has a high content of cellulose having combustion energy of 15 kJ/g which, when converted to methane, has a combustible energy of 50 kJ/g (Khan et al. 1983). It can be burnt, but the efficiency of combustion is reduced by the moisture content, if it is not dried. Alternatively, lignocellulosic biomass can be converted to methane via anaerobic digestion (Kashyap et al. 2003).

Anaerobic digestion is bioconversion of organic wastes such as sewage, animal manure, food wastes and municipal solid wastes to biogas. During the process, the biomass is transformed into biogas which is a clean fuel for energy generation. Biogas is composed of CH₄ (55–65 %), CO₂ (30–45 %), H₂ (1–5 %), N₂ (0.5–2.0 %), H₂S (0.1–0.5 %), CO (0–0.3 %) and traces of water vapours (Paus et al. 1987). Biogas generation involves consortium of microorganisms which is a group of hydrolytic, acidogenic and methanogenic bacteria. Paddy straw (PS), being a lignocellulose, consists of cellulose (35–40 %), hemi-cellulose (20 %), lignin (12 %) and silica (8 %). Although PS has high cellulose content, the lignin complex and silica incrustation shield the microbial action on it.

Therefore, the PS needs to be pretreated in order to enable cellulose/hemi-cellulose to be more accessible to the microbial/enzymatic attack for biogas generation.

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Accordingly, many physical (mechanical and non-mechanical), chemical (alkaline hydrolysis, acid hydrolysis, oxidative delignification and solvent extraction), physico-chemical (AFEX, CO₂ and steam explosion) and biological pretreatments (lignocellulolytic micro-organisms and enzymes) have been proposed in the recent years (Holtzapfle and Davison 1999; Saratale et al. 2008; Hendriks and Zeeman 2009). These pretreatment technologies either change or remove structural and compositional constraints to improve hydrolysis rate (Moseir et al. 2005). Ma et al. (2009) reported an increase of 30.6 % cellulose and 43.3 % hemi-cellulose content of PS by microwave pretreatment (680 W, 24 min). Microwave/alkali-pretreated rice straw could achieve higher ethanol concentration and yield than the alkali-alone-pretreated rice straw (Zhu et al. 2005). Some studies have shown that microwave irradiation could change the ultra-structure of cellulose (Xiong et al. 2000), degrade lignin and hemi-cellulose and increase enzyme susceptibility (Azuma et al. 1984; Ooshima et al. 1984; Kitchaiya et al. 2003). NH₃ and urea simply crack the silicified cuticular layer of PS but did not dissolve silica (Van Soest 2006). Wang et al. (2007) reported that NaOH and NH₄HCO₃, respectively, dissolves and cracks off the cuticle wax silica layer of rice stem epidermis resulting in the degradation of epidermis by rumen micro-organisms. Oxygen–sodium sulphite pulping method was reported to be better than conventional alkaline pulping with 95 % delignification and high retention of both cellulose and hemi-cellulose (Park et al. 2000). Lignin and cellulose degradabilities in cedar wood cultured with *Ceriporiopsis subvermispora* were found to be more in comparison to that cultured with *Lentinula edodes* (Okano et al. 2005). Sodium hydroxide-pretreated corn stalks were reported to produce 78.3 % more biogas than untreated stalks and 13.2 % more than the stalks treated with *Pleurotus florida* (Yang et al. 2003). Although there have been many pretreatment methods, few can be used at an industrial scale based on economics and environmental considerations (Sun and Cheng 2002). Variation in biogas yield from grasses is very much affected by the plant part used, harvesting frequency, plant age, clonal variations, nutrient addition, particle size reduction and various pretreatments (Gunaseelan 1997).

So keeping in view all these aspects and the importance of PS for energy and power generation along with combating the environmental pollution, the pretreatment of PS with sodium carbonate and microwave was investigated and its effect on PS composition and biogas production was studied.

Methods

Procurement of the materials

PS was procured from the research field of Punjab Agricultural University, Ludhiana, after the harvesting of the crop. The PS was chopped to 3–5 cm and was stored in polythene bags at room temperature. Digested biogas slurry was procured from a working biogas plant in Biogas Field Laboratory of School of Energy Studies for Agriculture, PAU, Ludhiana.

Chemical pretreatment of PS

PS was pretreated with sodium carbonate (Na₂CO₃) and its effect on PS degradation was studied. The PS was soaked in Na₂CO₃ solution for different durations as one set, and Na₂CO₃ solution-dipped PS was irradiated with microwave irradiations as another set.

Na₂CO₃-soaking pretreatment

Twenty gram of chopped, washed and dried PS was soaked in 200 ml Na₂CO₃ solution (2, 4, 6, 8 and 10 %) for different durations viz., 24 and 48 h. After the desired period of soaking, the chemical solution was decanted off and PS was washed with tap water until the washings were clean, colourless and neutral to the pH paper. The PS was then dried overnight in the oven at 100 °C. After drying, PS was ground. Ground, chemically pretreated PS was stored in polythene bags and was used for proximate [total solids (TSs), volatile solids (VSs), total organic carbon (TOC), and ash] and chemical (cellulose, hemi-cellulose, lignin and silica) analysis. Total sugars of the pretreated straw were also determined. A control (untreated PS) was analysed simultaneously in order to determine the extent of degradation of various components of PS.

Na₂CO₃-microwave pretreatment

Twenty gram of PS was suspended in 200 ml Na₂CO₃ solution of different concentrations as mentioned above in 500-ml beakers (in two sets). Two beakers of same concentration were positioned at the centre of the rotating circular glass plate in the microwave oven (MC-2681DS, LG Electronics India Pvt. Ltd.) at a time and were irradiated with microwave power of 720 W at the temperature of 180 °C for 30 and 60 min, respectively, for the two sets. Pretreated PS was washed with tap water until the

washings were clean, colourless and neutral to the pH paper. PS was dried overnight in an oven at 100 °C. Pretreated PS was then ground. To avoid drying and charring of PS in 60 min of pretreatment, the amount of chemical solution added was doubled. A control was also run simultaneously.

Scanning electron microscopy of the pretreated PS

The pretreated PS was analysed for structural changes through scanning electron microscopy at Electron Microscopy and Nanoscience Laboratory, PAU, Ludhiana, Punjab. The pretreated PS was processed for viewing under SEM which involved dehydrating the sample with the increasing alcohol series followed by mounting of the sample on the stub using carbon-tape, then sputter coating the sample with gold (Au) nanoparticles and finally viewing under the scanning electron microscope. The samples were viewed at the following working conditions:

- Accelerating voltage 15,000 V,
- Emission current 123,000 nA,
- Vacuum 15 kV,
- Magnification $\times 1.50$ K,
- Working distance 12.7 mm.

Biogas production from pretreated PS

Biogas production experiments were carried out in glass biogas digesters of 2 l capacity following monophasic method, and biogas produced was measured by water displacement method. Two different concentrations, i.e., 4 and 10 %, were selected on the basis of significant (for the former) and maximum (for the latter) increase in cellulose content and decrease in silica content. The selected pretreatments were taken up for biogas production. One hundred gram of the pretreated PS was mixed with 100 ml of the digested biogas slurry and 100 ml of tap water. The mixture was fed to biogas digesters which were incubated at 37 ± 2 °C. Biogas produced was measured daily for a period of 45 days. A control was also run where untreated PS was taken instead of pretreated PS.

Analytical procedures

The proximate (TS, VS, TOC and ash) and chemical (cellulose, hemi-cellulose, lignin and silica content) analysis of PS was done according to the procedures given in the Standard AOAC Methods (Thiex 2000). Total sugars were estimated by phenol–sulphuric acid method using glucose as a standard (Dubois et al. 1956).

Statistical analysis

All treatments were completed in triplicate. Critical difference at 5 % level was performed for proximate and chemical analysis of PS using programme Factorial Experiments in CRD of CPCS1 software (developed by Department of Statistics, PAU, Ludhiana, Punjab).

Results and discussion

Effect of Na_2CO_3 -soaking pretreatment on PS degradation

A significant weight loss was observed, and the pretreated sample became fragile and lighter in colour with the increasing Na_2CO_3 concentration. Results from Table 1 indicate a non-significant increase in TS and a significant increase in VS and TOC contents of PS with respect to increasing Na_2CO_3 concentration. TS, VS and TOC increased to 96.9, 92.1 and 51.2 % and 97.0, 92.6 and 51.4 %, respectively, for 10 % Na_2CO_3 -24 h soaking and 10 % Na_2CO_3 -48 h soaking. Ash content decreased to 7.9 and 7.4 % at 10 % Na_2CO_3 for 24 and 48 h, respectively.

Total sugars decreased significantly with the increasing Na_2CO_3 concentration and soaking period reaching almost half the value than that in the control. Total sugars were found to decrease from 54.9 mg/g PS in control to 29.4 and 27.4 mg/g PS in 10 % Na_2CO_3 -24 h soaking and 10 % Na_2CO_3 -48 h soaking, respectively. Cellulose increased significantly with the increasing Na_2CO_3 concentration and soaking period reaching a maximum of 49.9 and 50.2 % at 10 % Na_2CO_3 for 24 and 48 h of soaking period indicating an increase of 14.4 and 15.1 % in comparison to that of the control (43.6 %). Hemi-cellulose and lignin increased significantly with the increasing Na_2CO_3 concentration, but this increase was non-significant with respect to the increasing soaking period. Hemi-cellulose increased to a maximum of 26.1 and 26 %, while lignin reached a maximum of 6.5 and 6.9 at 10 % Na_2CO_3 -24 h soaking and 10 % Na_2CO_3 -48 h soaking, respectively. Silica decreased to such an extent that it remained only about half as compared to the control. This decrease in silica was significant with respect to the increase in Na_2CO_3 concentration and non-significant with the increasing period of soaking. Silica decreased to 2.8 and 2.5 % from 5.3 % in control accounting to a decrease of 47.2 and 52.8 % as compared to the control.

Decrease in total sugars might be attributed to the fact that either there was no conversion of cellulose/hemi-cellulose to fermentable sugars or if these components had undergone

Table 1 Effect of sodium carbonate-soaking pretreatment on paddy straw degradation

Proximate and chemical composition of paddy straw (%)	Untreated PS (control)	Soaking period (h)	Na ₂ CO ₃ concentration (%)						CD (Na ₂ CO ₃ concentration)	CD (soaking period)	CD (Na ₂ CO ₃ concentration × soaking period)
			0	2	4	6	8	10			
Total solids	96.7	24	96.6 ± 0.12	96.5 ± 0.06	96.7 ± 0.35	96.8 ± 0.23	96.8 ± 0.23	96.8 ± 0.23	96.9 ± 0.52	NS	NS
		48	96.5 ± 0.12	96.6 ± 0.06	96.7 ± 0.29	96.9 ± 0.23	97.0 ± 0.29	97.0 ± 0.29			
Volatile solids	89.2	24	89.4 ± 0.12	90.8 ± 0.35	90.9 ± 0.23	91.3 ± 0.40	91.7 ± 0.40	92.1 ± 0.35	0.65	NS	NS
		48	89.5 ± 0.12	90.2 ± 0.23	90.5 ± 0.35	91.9 ± 0.35	92.3 ± 0.40	92.6 ± 0.29			
Total organic carbon	49.5	24	49.7 ± 0.12	50.4 ± 0.35	50.5 ± 0.35	50.7 ± 0.40	50.9 ± 0.40	51.2 ± 0.35	0.65	NS	NS
		48	49.7 ± 0.12	50.1 ± 0.23	50.3 ± 0.23	51.1 ± 0.35	51.3 ± 0.40	51.4 ± 0.29			
Ash	10.8	24	10.6 ± 0.12	9.2 ± 0.35	9.1 ± 0.35	8.7 ± 0.40	8.3 ± 0.40	7.9 ± 0.35	0.65	NS	NS
		48	10.5 ± 0.12	9.8 ± 0.23	9.5 ± 0.23	8.1 ± 0.35	7.7 ± 0.40	7.4 ± 0.29			
Total sugars (mg/g PS)	54.9	24	56.8 ± 0.17	34.5 ± 0.29	31.8 ± 0.46	31.7 ± 0.35	29.7 ± 0.35	29.4 ± 0.23	0.62	0.36	0.88
		48	56.7 ± 0.12	33.3 ± 0.17	31.5 ± 0.29	30.3 ± 0.46	29.3 ± 0.29	27.4 ± 0.23			
Cellulose	43.6	24	43.6 ± 0.17	45.5 ± 0.12	47.8 ± 0.29	48.1 ± 0.29	49.1 ± 0.35	49.9 ± 0.23	0.47	0.27	NS
		48	43.7 ± 0.12	46.4 ± 0.23	48.6 ± 0.17	48.9 ± 0.23	49.7 ± 0.29	50.2 ± 0.12			
Hemi-cellulose	23.8	24	24.0 ± 0.23	24.5 ± 0.29	25.1 ± 0.23	26.9 ± 0.46	26.3 ± 0.17	26.1 ± 0.23	0.60	NS	NS
		48	24.2 ± 0.12	24.9 ± 0.52	25.5 ± 0.29	26.4 ± 0.23	26.0 ± 0.29	26.0 ± 0.29			
Lignin	6.0	24	5.6 ± 0.06	5.6 ± 0.35	5.7 ± 0.40	6.1 ± 0.40	6.3 ± 0.35	6.5 ± 0.23	0.69	NS	NS
		48	5.4 ± 0.23	5.9 ± 0.23	5.9 ± 0.52	6.4 ± 0.23	6.6 ± 0.35	6.9 ± 0.40			
Silica	5.3	24	5.3 ± 0.06	4.5 ± 0.35	3.5 ± 0.35	3.4 ± 0.06	3.5 ± 0.29	2.8 ± 0.35	0.71	NS	NS
		48	5.1 ± 0.12	3.6 ± 0.29	3.1 ± 0.29	3.0 ± 0.58	3.0 ± 0.35	2.5 ± 0.29			

PS paddy straw, NS non-significant, CD critical difference at 5 % level

Values depicted are mean ± standard error for n=3

hydrolysis, these might have got converted to acids, furfural, hydroxyl methyl furfural or other degradation products. Limited increase of cellulose was found to be the result of increase in lignin content which did not allow the profound exposure of cellulose. Increase in hemi-cellulose could be due to the breakage of the hemicellulose–lignin complex resulting in freely available hemi-cellulose. Enhancement in lignin content might be the result of re-precipitation or condensation of the soluble lignin components over the PS. Decrease in silica was attributed to the fact that silica got removed by the action of Na_2CO_3 .

Effect of Na_2CO_3 -microwave pretreatment on PS degradation

The weight loss, fragility and lightness in colour of pretreated PS get increased with the microwave supplementation in contrast to soaking. Results from Table 2 indicate a non-significant increase in TS with the increasing Na_2CO_3 concentration, but TS was found to decrease with the increase in soaking period. VS and TOC increased significantly to a maximum of 95.1 and 95.9 %, and 52.8 and 53.3 %, respectively, with the increasing Na_2CO_3 concentration and soaking period. Ash content decreased significantly to half of that of the control. A decrease of 54.6 and 62 % in ash was found at 10 % Na_2CO_3 -30 min microwave pretreatment (4.9 %) and 10 % Na_2CO_3 -60 min microwave pretreatment (4.1 %), respectively. Decrease in total sugars was also significant with respect to both the parameters. Total sugars decreased to 27.5 and 25.4 mg/g PS at 10 % Na_2CO_3 for 30 and 60 min of microwave duration, respectively, indicating a decrease of 49.9 and 53.7 % than that of the control (54.9 mg total sugars/g PS).

Cellulose increased significantly to 62.7 and 66.5 % at 10 % Na_2CO_3 with the increasing microwave durations showing an increase of 43.8 and 52.5 % than that of the control (43.6 %). Hemi-cellulose decreased significantly to 20.4 and 20.1 % at 10 % Na_2CO_3 -30 min microwave and 10 % Na_2CO_3 -60 min microwave, respectively, accounting to a decrease of 14.3 and 15.5 % in comparison to that of the control (23.8 %). Decrease in lignin and silica was found to be significant with respect to the increasing Na_2CO_3 concentration and non-significant with respect to the increase of microwave duration. Lignin get decreased to a minimum of 4.9 and 4.6 % for 30 and 60 min microwave, respectively, at 10 % concentration indicating a decrease of 18.3 and 23.3 % as compared to the control with 6 % lignin. Decrease in silica was profound and appreciable with 100 % silica removal at 8 and 10 % concentration.

Solubilization of some of the components might have led to the decrease in TS with the increasing microwave duration. Decrease in ash content was obvious because of the fact that VS gets increased. Decrease in total sugars

could be the result of conversion of hemi-cellulose to other degradation products as the hemi-cellulose content was also found to decrease with the increasing Na_2CO_3 concentration and microwave duration. Increase in cellulose was the clear-cut case of the decrease in lignin content which could be the result of solubilization of the lignin by the action of Na_2CO_3 in combination with microwave irradiation. Decrease in silica was the result of removal of silica by Na_2CO_3 which has also been confirmed by Jan and Alexandra (2006).

Change in surface properties of the pretreated PS

The change in surface properties of the 4 % Na_2CO_3 - and 10 % Na_2CO_3 -60 min microwave-pretreated PS with respect to that of the control is shown in Fig. 1. In Fig. 1a, the untreated PS was found to possess an intact epidermis covered with phytoliths which are actually silica-storing nodules, while in Fig. 1b, the surface of PS was seen partially broken and in Fig. 1c, the surface of the PS was seen completely broken with tearing of different layers of PS, thereby leading to the ultimate removal of silica and the recalcitrant lignin as well. These changes in the pretreated paddy are supposed to enhance the PS digestibility.

Effect of Na_2CO_3 pretreatment on biogas production

4 and 10 % Na_2CO_3 concentration were selected on the basis of significant and maximum enhancement in the digestibility of PS, respectively. Results from Table 3 indicate that the increase in biogas production in Na_2CO_3 -soaked PS ranged from 262 l biogas/kg PS (10 % Na_2CO_3 -48 h soaking) to 307 l biogas/kg PS (4 % Na_2CO_3 -48 h soaking) indicating an increase of 20.7 and 41.5 % than that of the control (217 l biogas/kg PS). TS and VS of the mixture were found to increase both with the increasing Na_2CO_3 concentration and soaking period reaching a maximum of 22.5 and 82.5 % (10 % Na_2CO_3 -48 h soaking), respectively, from 20.3 % TS and 71.9 % VS in control.

In case of microwave supplementation, the enhancement in biogas production from pretreated PS ranged between 274 l/kg PS (10 % Na_2CO_3 -60 min microwave) and 335 l/kg PS (4 % Na_2CO_3 -60 min microwave) corresponding to an increase of 26.3 and 54.4 % than that of the control (217 l biogas/kg PS). TS reached a maximum of 23.2 % while VS increased to 83.2 % in 10 % Na_2CO_3 -60 min microwave pretreatment.

Despite the maximum digestibility of 10 % Na_2CO_3 -60 min microwave-pretreated PS, the biogas produced was minimum which could be associated with the negative effects of the higher concentration of the chemical used. So 4 % Na_2CO_3 -60 min microwave pretreatment was found to be the best in terms of biogas production.

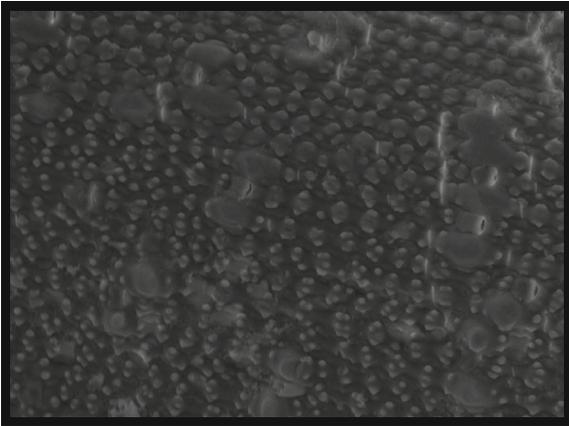
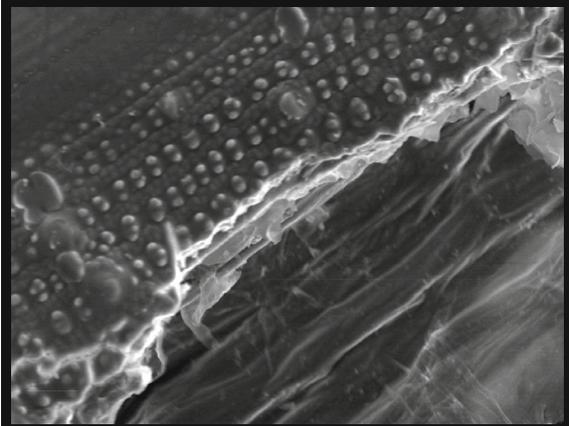
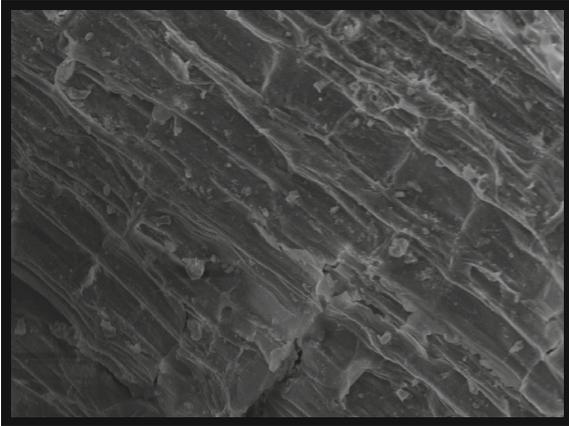
Table 2 Effect of sodium carbonate-microwave pretreatment on paddy straw degradation

Proximate and chemical composition of paddy straw (%)	Untreated PS (control)	Microwave duration (min)	Na ₂ CO ₃ concentration (%)							CD (Na ₂ CO ₃ concentration)	CD (microwave duration)	CD (Na ₂ CO ₃ concentration × microwave duration)
			0	2	4	6	8	10				
Total solids	96.7	30	96.6 ± 0.12	96.7 ± 0.40	96.7 ± 0.35	96.8 ± 0.35	96.7 ± 0.35	96.9 ± 0.35	96.7 ± 0.17	NS	NS	
		60	96.5 ± 0.12	96.6 ± 0.35	96.6 ± 0.29	96.7 ± 0.29	96.6 ± 0.35	96.7 ± 0.17				
Volatile solids	89.2	30	89.5 ± 0.12	92.1 ± 0.35	93.3 ± 0.17	94.2 ± 0.23	94.5 ± 0.29	95.1 ± 0.23	0.52	0.30	NS	
		60	89.6 ± 0.06	92.7 ± 0.23	94.1 ± 0.23	94.7 ± 0.40	95.3 ± 0.17	95.9 ± 0.35				
Total organic carbon	49.5	30	49.7 ± 0.12	51.2 ± 0.35	51.8 ± 0.17	52.3 ± 0.23	52.5 ± 0.29	52.8 ± 0.23	0.52	0.30	NS	
		60	49.7 ± 0.06	51.5 ± 0.23	52.3 ± 0.23	52.6 ± 0.40	52.9 ± 0.17	53.3 ± 0.35				
Ash	10.8	30	10.5 ± 0.12	7.9 ± 0.35	6.7 ± 0.17	5.8 ± 0.23	5.5 ± 0.29	4.9 ± 0.23	0.53	0.31	NS	
		60	10.4 ± 0.06	7.3 ± 0.23	5.9 ± 0.23	5.3 ± 0.40	4.7 ± 0.17	4.1 ± 0.35				
Total sugars (mg/g PS)	54.9	30	56.8 ± 0.12	32.3 ± 0.29	31.2 ± 0.29	30.3 ± 0.17	29.4 ± 0.23	27.5 ± 0.29	0.56	0.32	0.79	
		60	56.6 ± 0.06	31.9 ± 0.46	30.5 ± 0.29	28.9 ± 0.23	27.1 ± 0.35	25.4 ± 0.23				
Cellulose	43.6	30	42.6 ± 0.17	48.3 ± 0.17	59.2 ± 0.12	59.6 ± 0.17	61.3 ± 0.23	62.7 ± 0.40	0.50	0.29	0.71	
		60	43.7 ± 0.12	52.7 ± 0.35	62.9 ± 0.17	63.5 ± 0.29	64.4 ± 0.23	66.5 ± 0.29				
Hemi-cellulose	23.8	30	24.0 ± 0.12	23.8 ± 0.35	21.0 ± 0.29	21.3 ± 0.17	20.7 ± 0.40	20.4 ± 0.23	0.53	0.30	0.75	
		60	23.7 ± 0.06	23.5 ± 0.29	20.9 ± 0.24	20.6 ± 0.17	20.3 ± 0.17	20.1 ± 0.35				
Lignin	6.0	30	5.9 ± 0.12	5.6 ± 0.06	5.3 ± 0.17	5.2 ± 0.17	4.8 ± 0.35	4.9 ± 0.23	0.50	NS	NS	
		60	5.6 ± 0.17	5.5 ± 0.17	5.1 ± 0.23	4.9 ± 0.23	4.7 ± 0.40	4.6 ± 0.35				
Silica	5.3	30	5.3 ± 0.17	2.1 ± 0.23	1.1 ± 0.12	0.9 ± 0.17	0.3 ± 0.12	0	0.28	NS	0.39	
		60	6.1 ± 0.06	1.7 ± 0.23	0.8 ± 0.06	0.5 ± 0.12	0	0				

PS paddy straw, NS non-significant, CD critical difference at 5 % level

Values depicted are mean ± standard error for n=3

Fig. 1 Scanning electron micrograph(s) of the pretreated paddy straw

Fig. 1	Scanning Electron Micrograph	Description
(a)		Control/Untreated paddy straw
(b)		4%Na ₂ CO ₃ -60min microwave pretreated paddy straw
(c)		10%Na ₂ CO ₃ -60min microwave pretreated paddy straw

Conclusion

4 % Na₂CO₃-60 min microwave pretreatment was found to be the best pretreatment with significant enhancement in PS digestibility and 54.4 % increase in biogas production.

Although the maximum digestibility of PS was seen in case of 10 % Na₂CO₃-60 min microwave pretreatment, the increase in biogas production was not much appreciable which could be the result of inhibitory/toxic effects of higher concentration. Amongst the different parameters of

Table 3 Effect of sodium carbonate (soaking and microwave) pretreatment on biogas production

Parameters	Pretreatment	Control	Na ₂ CO ₃ concentration (%)	
			4	10
Total solids (%) of the mixture	24 h soaking	20.3	20.5 ± 0.75	21.9 ± 0.98
	48 h soaking		21.2 ± 0.69	22.5 ± 0.87
	30 min microwave		20.9 ± 0.81	22.5 ± 0.58
	60 min microwave		21.8 ± 0.46	23.2 ± 0.58
Volatile solids (%) of the mixture	24 h soaking	71.9	75.7 ± 0.40	80.3 ± 0.29
	48 h soaking		77.9 ± 0.52	82.5 ± 0.52
	30 min microwave		76.2 ± 0.58	81.1 ± 0.64
	60 min microwave		80.6 ± 0.35	83.2 ± 0.40
Biogas (l/kg PS)	24 h soaking	217.0	289.0 ± 22.5	278.0 ± 13.3
	48 h soaking		307.0 ± 24.8	262.0 ± 18.5
	30 min microwave		302.0 ± 24.2	297.0 ± 27.1
	60 min microwave		335.0 ± 20.2	274.0 ± 13.8
Percent increase in biogas production from control	24 h soaking	0.0	33.2	28.1
	48 h soaking		41.5	20.7
	30 min microwave		39.2	36.9
	60 min microwave		54.4	26.3

Control untreated paddy straw, *PS* paddy straw, Values depicted are mean ± standard error for n=3

proximate and chemical composition of PS, silica was found to be the most reliable factor in determining PS digestibility. The lesser the silica content, the higher the PS digestibility and biogas production. In nutshell, silica removal is the most crucial step in enhancement of PS digestibility and biogas production.

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