IMPROVING PADDY STRAW DIGESTIBILITY AND BIOGAS PRODUCTION THROUGH DIFFERENT CHEMICAL-MICROWAVE PRETREATMENTS

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ABSTRACT
Biofuel and Bioenergy generation from paddy straw offers a great potential as an alternative to fossil-fuels. Association of holocellulose with the protective structures such as lignin and silica adversely affects the conversion of paddy straw into the desired product. In this context, paddy straw was pretreated with different concentrations (0-10%) of various chemicals viz. NH3, Na2SO3, Na2CO3 and NaOH by soaking for 48h and by irradiating with microwave (720W, 180°C) for 60 min. Chemical-microwave pretreatment was found to be better than the chemical-alone pretreatment. Amongst the various chemical pretreatments, 4% Na2CO3-microwave and 4% NaOH-microwave was found to greatly enhance the paddy straw digestibility and biogas production where 44.3% and 65.6% increase in cellulose, 15.0% and 68.3% decrease in lignin, and 84.5% and 92.5% decrease in silica was observed resulting in 54.4% and 60.9% increase in biogas production, respectively.

Key Words: Biogas production, Chemical, Microwave, Paddy straw, Pretreatment.

INTRODUCTION
Disposal of paddy straw has been a big problem since time immemorial due to which the most common scene in the fields during harvesting season is paddy straw burning which causes soil erosion and emission of pollutants. Only a fraction of it is being used for composting, surface mulching, in situ incorporation, mushroom production, animal feed and the like. Annual production of rice is about 96.4 million tonnes (www.indiastat.com) and about 96.4-144.6 million tonnes of paddy straw is estimated to be produced annually. Lignocellulosic biomass generally has a high content of cellulose having combustion energy of 15kJ/g which when converted to methane, has a combustible energy of 50kJ/g (Khan et al., 1983). So, paddy straw can act as a very useful substrate for biofuel generation and can be well employed for biogas production, thereby controlling the environmental pollution caused by its burning and preventing soil erosion.

Anaerobic digestion is a biological process in which biodegradable organic materials are decomposed in the absence of oxygen to produce biogas. Biogas is a mixture of CH4 (50-60%), CO2 (30-40%), H2 (1-5%), N2 (0.5%), CO, H2S and water vapours (traces). The organic matter can be degraded by the sequential action of hydrolytic, acetogenic and methanogenic bacteria to produce biogas. However, paddy straw has high content of cellulose (35-40%), hemi-cellulose (20%), lignin (12%) and silica (8%). But, the lignin complex and silica incrustation shields the microbial action. So, the first step to utilize paddy straw is to remove/degrade lignin and silica.

Thus, different types of pretreatments i.e. physical (mechanical and thermal), chemical (acid, alkali, oxidising agents), physico-chemical (AFEX, CO2 and steam explosion) and biological using lignocellulosic microbes are being tried to increase the digestibility of rice straw. These pretreatment technologies either change or remove structural and compositional constraints to improve hydrolysis rate. Ammoniation of rice straw resulted in two-fold increase in gas production at 24 h of incubation.
(Eun et al., 2006). Yang et al. (2003) reported NaOH pretreated cotton stalks to produce 78.3% more biogas than untreated stalks and 13.2% more than the cotton stalks pretreated with Pleurotus florida. Zhang and Cai (2008) found that 2% NaOH pretreatment for 1 hour at 85°C could increase cellulose by 54.8% and decrease hemi-cellulose and lignin by 61.1% and 36.2%, respectively. Van Soest (2006) reported that NH₃ and urea simply crack the silicified cuticular layer of paddy straw but did not dissolve silica in contrast to the action of NaOH. An increase of 30.6% cellulose and 43.3% hemi-cellulose content of paddy straw by microwave pretreatment (680W; 24 minutes) has also been reported (Ma et al., 2009). Fox and Noike (2004) reported 3-4.5 times increase in methane production from newsprint waste after alkaline heat pretreatment. Microwave/alkali pretreated rice straw could achieve higher ethanol concentration and yield than that of the alkali alone pretreated rice straw (Zhu et al., 2005). Oxygen-sodium sulphite pulping method has been reported to be better than conventional alkaline pulping and oxygen-sodium hydroxide 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).

Although there have been many pretreatment methods, a few can be used on industrial scale based on economics and environmental consideration (Sun and Cheng, 2002). In this context, a wide range of concentration (0-10%) of various chemicals viz. NH₃, Na₂SO₃, Na₂CO₃ and NaOH have been employed to observe the comparative effect of all these chemical pretreatments on paddy straw digestibility and biogas production. Microwave irradiations were also supplemented to the chemical pretreatment so as to enhance/supplement the effect of chemical, thereby avoiding the adverse effects of higher concentration.

**MATERIALS AND METHODS**

**Pretreatment of paddy straw:** Washed and dried paddy straw was pretreated with different concentrations (0-10%) of different chemicals viz. NH₃, Na₂SO₃, Na₂CO₃ and NaOH and their effect on paddy straw degradation was studied. The paddy straw was soaked in different chemicals (for 24h and 48h) at room temperature and was irradiated with microwaves (for 30 min and 60 min).

**Chemical-soaking pretreatment:** Twenty gram paddy straw was soaked in two hundred ml solution of various concentrations (0-10%) of NH₃, Na₂SO₃, Na₂CO₃ and NaOH for 48 h. After the desired period of soaking, the solution was decanted off and paddy straw was washed with tap water until the washings were clean, colorless and neutral to pH. The paddy straw was then dried overnight in the oven at 100°C. Ground paddy straw was then used for chemical analysis of paddy straw i.e. total sugars, cellulose, hemi-cellulose, lignin and silica determination.

**Chemical-microwave pretreatment:** Twenty gram paddy straw was suspended in two hundred ml solution of various concentrations (0-10%) of NH₃, Na₂SO₃, Na₂CO₃ and NaOH as mentioned in Section 2.1.1 in 500 ml beakers. The beakers were then positioned in the centre of the rotating circular glass plate of the microwave oven and were irradiated with microwaves (180°C) for 60 min. Pretreated paddy straw was washed with tap water until the washings were clean, colourless and neutral to pH. Paddy straw was dried overnight in oven at 100°C, ground and analysed for its digestibility.

**Biogas production from pretreated paddy straw:** Biogas production experiments were carried out in glass biogas digesters of 2 litre capacity following monophasic method and biogas produced was measured by water displacement method. One hundred gram of the pretreated paddy straw was mixed with one hundred ml of the digested cattle dung slurry and one hundred ml of tap water. The mixture was fed to the biogas digesters which were incubated at 37±2°C.

**Analytical procedures:** The chemical analysis of paddy straw (cellulose, hemi-cellulose, lignin and silica content) was done according to the procedures given in the Standard methods (AOAC, 2000). Total sugars were estimated by phenol-sulphuric acid method using glucose as standard (Dubois et al., 1956).
RESULTS AND DISCUSSION

Effect of chemical-soaking pretreatment on paddy straw degradation: Fig. 1 depicts the change in paddy straw composition on soaking the paddy straw in various chemicals for a period of 48h. A wide range of concentration (0-10%) was taken for each chemical. Fig. I clearly depicts that 6% NH₃ and 4% Na₂SO₃, 4% Na₂CO₃ and 4% NaOH are the best concentrations with a significant enhancement in paddy straw digestibility after which the enhancement was not much significant and also, the higher concentrations are feared of the negative effects accompanied. So, the results of the best selected concentration of each chemical are shown in Table 1.

There was a drastic change in texture and physical appearance of Na₂CO₃ and NaOH pretreated paddy straw and about 65-70% weight loss was observed after these pretreatments. Pretreated straw became fragile and lighter in color with the increasing Na₂CO₃ and NaOH concentration. Similar results have also been reported by Zhu et al. (2005) and Xin and Kumakura (1993).

Results from the Table 1 indicate that there was 19.1% increase in total sugars in case of 4% Na₂SO₃-48h soaking (65.4 mg/g PS) whereas total sugars were found to decrease to the minimum of 31.5 mg/g PS in case of 4% Na₂CO₃-48h soaking from 54.9 mg/g PS (control) indicating a decrease of 42.6% than that of the control. Cellulose increased appreciably in case of 4% NaOH pretreatment with a maximum of 66.5% accounting to an increase of 52.5% compared to that of the control (43.6%). Hemi-cellulose was found to decrease in all the

![Graph showing the effect of different concentrations of various chemicals on paddy straw degradation](image)

**TABLE 1: Effect of chemical-soaking (48h) pretreatment on paddy straw degradation**

<table>
<thead>
<tr>
<th>Chemical composition of paddy straw (%)</th>
<th>Untreated PS (Control)</th>
<th>6% NH₃</th>
<th>4% Na₂SO₃</th>
<th>4% Na₂CO₃</th>
<th>4% NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total sugars (mg/g PS)</td>
<td>54.9</td>
<td>49.7±0.23 (9.4)</td>
<td>65.4±0.23 (19.1)</td>
<td>31.5±0.29 (42.6)</td>
<td>43.8±0.23 (20.2)</td>
</tr>
<tr>
<td>Cellulose</td>
<td>43.6</td>
<td>44.6±0.06 (2.4)</td>
<td>44.5±0.12 (2.1)</td>
<td>48.6±0.17 (11.5)</td>
<td>66.5±0.29 (52.5)</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>23.8</td>
<td>23.2±0.12 (2.7)</td>
<td>22.9±0.12 (3.6)</td>
<td>22.1±0.29 (7.1)</td>
<td>16.9±0.17 (29.0)</td>
</tr>
<tr>
<td>Lignin</td>
<td>6.0</td>
<td>4.7±0.17 (21.5)</td>
<td>5.0±0.29 (16.7)</td>
<td>5.9±0.52 (17.1)</td>
<td>2.8±0.12 (53.3)</td>
</tr>
<tr>
<td>Silica</td>
<td>5.3</td>
<td>6.3±0.29 (17.9)</td>
<td>4.7±0.17 (10.8)</td>
<td>3.1±0.35 (41.5)</td>
<td>2.1±0.23 (60.4)</td>
</tr>
</tbody>
</table>

PS: Paddy straw; ± values indicate Standard Error of the triplicate data
Values in the parenthesis indicate percent change (“!” or “!”) in paddy straw composition w.r.t untreated paddy straw
pretreatments. In case of 4% NaOH pretreatment, it decreased to 16.9% from 23.8% (control). Lignin was also found to decrease in all the pretreatments. More than 50% reduction in lignin was observed in case of NaOH pretreatment where it decreased to 2.8% from 6.0% in control. There was more than 60% reduction in silica in case of 4% NaOH pretreatment followed by a reduction of 41.5% in case of 4% Na$_2$CO$_3$ pretreatment. However, in case of 4% NH$_3$ treated paddy straw, an increase of silica by 17.9% was observed.

**Effect of chemical-microwave pretreatment on paddy straw degradation:** Fig. 2 depicts that the 6% of NH$_3$ is significant in enhancing paddy straw digestibility whereas 4% of Na$_2$SO$_3$, Na$_2$CO$_3$ and NaOH are the best combinations with microwave in enhancing paddy straw digestibility to an extent greater than that of their respective chemical-soaking combinations.

The weight loss, fragility and lightness in color of pretreated paddy straw increased with the microwave supplementation. Table 2 indicates that

**TABLE 2:** Effect of chemical-microwave (60 min) pretreatment on paddy straw degradation

<table>
<thead>
<tr>
<th>Chemical composition of paddy straw (%)</th>
<th>Untreated PS (Control)</th>
<th>6% NH$_3$</th>
<th>4% Na$_2$SO$_3$</th>
<th>4% Na$_2$CO$_3$</th>
<th>4% NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total sugars (mg/g PS)</td>
<td>54.9</td>
<td>68.3±0.17 (ʔ24.4)</td>
<td>77.2±0.23 (ʔ40.6)</td>
<td>30.5±0.29 (ʔ44.4)</td>
<td>38.3±0.17 (ʔ30.2)</td>
</tr>
<tr>
<td>Cellulose</td>
<td>43.6</td>
<td>44.9±0.23 (ʔ2.9)</td>
<td>470±0.23 (ʔ7.7)</td>
<td>62.9±0.17 (ʔ44.3)</td>
<td>72.2±0.12 (65.6)</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>23.8</td>
<td>21.7±0.17 (ʔ8.7)</td>
<td>21.3±0.17 (ʔ10.5)</td>
<td>20.9±0.24 (ʔ12.2)</td>
<td>11.4±0.23 (ʔ52.1)</td>
</tr>
<tr>
<td>Lignin</td>
<td>6.0</td>
<td>4.6±0.17 (ʔ22.6)</td>
<td>3.1±0.06 (ʔ48.3)</td>
<td>5.1±0.23 (ʔ15.0)</td>
<td>1.9±0.23 (ʔ68.3)</td>
</tr>
<tr>
<td>Silica</td>
<td>5.3</td>
<td>6.4±0.12 (ʔ21.4)</td>
<td>4.5±0.29 (ʔ15.4)</td>
<td>0.8±0.06 (ʔ84.9)</td>
<td>0.4±0.06 (ʔ92.5)</td>
</tr>
</tbody>
</table>

PS: Paddy straw; ± values indicate Standard Error of the triplicate data
Values in the parenthesis indicate percent change ("! or '!") in paddy straw composition w.r.t untreated paddy straw
Biogas production from pretreated paddy straw: Pretreated paddy straw (100g) was mixed with 100 ml digested biogas slurry (TS: 7-8%) and 100 ml tap water and the mixture was fed to the 2 litre capacity biogas digesters. C:N ratio of the feed was adjusted by adding biogas slurry (C = 28%; N = 1.8%; C:N = 15.6:1) to the paddy straw (C = 40%; N = 0.8%; C:N = 50.0:1). So, by mixing biogas slurry and paddy straw in the ratio of 1:1, the resultant C:N of the feed was 32.8:1 which is optimal for biogas production. pH of the feed fed to the biogas digester was 6.9. Biogas digesters remained almost ¾ empty after adding the Na₂CO₃ and NaOH pretreated paddy straw mixture to the digesters in comparison to those filled with untreated/Na₃H₃ pretreated/Na₂SO₃ pretreated paddy straw clearly indicating the weight loss and increased bulk density of paddy straw after pretreatment.

Results from the Table 3 indicate that biogas production from pretreated straw enhanced in a range of 36.1% (in case of 4% Na₂SO₃-24h soaking) - 60.9% (in case of 4% NaOH-60 min microwave) as compared to the control. A maximum of 309 litre biogas/kg PS was produced in case of 4% NaOH-60 min microwave pretreated straw. Pavlostathis and Gossett (1985) found a 100% increase in methane yield after an alkaline pretreatment of wheat straw. Yang et al. (2003) reported NaOH pretreated corn stalks to produce 78.3% more biogas than untreated stalks and 13.2% more biogas than the stalks pretreated with Pleurotus florida. Table 4 summarizes the biogas production data of the pretreated paddy straw at pilot scale (Fig. 1). Biogas produced at pilot scale was a little less than the amount of biogas produced at lab scale because of the uncontrolled temperature in the scale-up conditions.

Loss of fermentable sugars and production of inhibitory compounds makes the alkaline pretreatment less attractive for ethanol production.
TABLE 3: Biogas production from pretreated paddy straw at lab scale

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Chemical concentration</th>
<th>Biogas (l/kg PS)</th>
<th>Biogas (l/kg VS fed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>48h soaking</td>
<td>6% NH$_3$</td>
<td>263.0 (37.0)</td>
<td>249.7</td>
</tr>
<tr>
<td>60 min microwave</td>
<td>4% Na$_2$SO$_3$</td>
<td>261.3 (36.1)</td>
<td>305.0</td>
</tr>
<tr>
<td>48h soaking</td>
<td>4% Na$_2$CO$_3$</td>
<td>271.1 (41.2)</td>
<td>321.0 (34.3)</td>
</tr>
<tr>
<td>60 min microwave</td>
<td>4% NaOH</td>
<td>276.3 (43.9)</td>
<td>337.4 (35.1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>284.0 (47.9)</td>
<td>326.9 (30.9)</td>
</tr>
</tbody>
</table>

*Control: Untreated paddy straw; PS: Paddy straw; VS: Volatile solids
Values in the parenthesis indicate percent increase in biogas production as compared to control

TABLE 4: Biogas production from pretreated paddy straw at pilot scale

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Chemical concentration</th>
<th>Biogas (l/kg PS)</th>
<th>Biogas (l/kg VS fed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>48h soaking</td>
<td>6% NH$_3$</td>
<td>250.0 (35.1)</td>
<td>239.0</td>
</tr>
<tr>
<td>60 min microwave</td>
<td>4% Na$_2$SO$_3$</td>
<td>260.0 (40.5)</td>
<td>305.0</td>
</tr>
<tr>
<td>48h soaking</td>
<td>4% Na$_2$CO$_3$</td>
<td>271.0 (41.2)</td>
<td>321.0 (34.3)</td>
</tr>
<tr>
<td>60 min microwave</td>
<td>4% NaOH</td>
<td>280.0 (51.4)</td>
<td>337.4 (35.1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>284.0 (47.9)</td>
<td>346.6 (38.8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>287.4 (50.5)</td>
<td>368.8 (57.3)</td>
</tr>
</tbody>
</table>

*Control: Untreated paddy straw; PS: Paddy straw; VS: Volatile solids
Values in the parenthesis indicate percent increase in biogas production as compared to control

But the production of inhibitors is less severe to methanogens as compared to yeasts (Pavlostathis and Gossett 1985, Hendriks and Zeeman, 2009). It could be due to this fact that 60.9% increase in biogas production was achieved in case of 4% NaOH-60 min microwave. Interestingly, industrial scale microwaves can be utilized for the commercial exploitation of paddy straw for biogas production. Chemical-soaking combinations at ambient temperature are also good enough which increased the biogas production upto 47.9% in case of 4% NaOH-48h soaking. This soaking pretreatment which is simple and cost-effective can be utilized for biogas production from paddy straw at a small scale in rural areas.

CONCLUSIONS

Amongst all the pretreatments, a common increasing trend of cellulose was seen which is directly proportional to the biogas production as cellulose is a better substrate for anaerobic microflora to act upon which is why an increase of 60.9% and 54.4% in biogas production was seen in 4% NaOH-60 min microwave and 4% Na$_2$CO$_3$-60 min microwave pretreatment, respectively. Increase in biogas in the soaking combinations of these pretreatments was also
appreciable but was less than that of their respective microwave combinations. An appreciable decrease of 84.9% and 92.5% silica was observed in case of 4% Na₂CO₃-60 min microwave and 4% NaOH-60 min microwave pretreatment, respectively. Microwaves supplementation to the chemical alone pretreatment increased the biogas production to a greater effect than the chemical alone pretreatment and at the same time, it negates the need to go up to longer durations of chemical soaking. So, industrial scale microwaves can be utilized for the commercial exploitation of paddy straw for biogas production.

REFERENCES


