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STUDIES ON THE BIOMETHANATION OF RICE STRAW

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ABSTRACT

The biomethanation of rice straw which was subjected to different pretreat ment modes and fortified with pig manure was studied. The volume and quality of the biogas produced were monitored as well as the changes in the composition of the substrate.

The anaerobic digestion of crop residues has been posed as an option towards the utilization of these lignocellulosic residues. At present, the farmer feels that the most practical way of using this resource is to return them to the soil.

The amount of lignocellulosic crop residues generated in the Philippines annually is of significant volume and comes mainly from sugarcane bagasse, rice straw, rice husk and coconut husk. Table 1 and Table 2 show the volumes and compositions of their residues (Del Rosario, 1978).

The figures show that as of 1975, the amount of rice straw produced was 5 million tons. Thus the quantities are large and other uses for this residue must be explored.

There is not much published work on the detailed analysis of the constituents of rice straw, but a representative analysis of the proximate composition of the straw IR-8, a variety of rice, is shown in Table 3. The organic portion of rice straw, especially cellulose and hemicellulose are potential substrates for microbial action. However, lignification, silicification and the highly crystalline structure of cellulose reduce the biodegradability of rice straw. A proper understanding of the effects of these factors on the biomethanation of rice straw will allow the utilization of this crop residue in biogas production.

Background Information

Badger and co-workers (1979) have noted that all their test crops produced twice as much biogas as did cattle manure. Further studies on the feasibility of the biomethanation of crop residues have also been conducted by Clausen and co-workers (1979). Boersma and co-workers (1981) noted the need to fortify crop residues with manure to improve the carbon: nitrogen ratio.

The nature of cellulose, in association with lignin, pectins, tannins, etc. makes it difficult for microorganisms to degrade. Gaden (1975) suggested that the degree of crystallinity and the extent of lignification of cellulosic materials determine their accessibility to hydrolytic action. The presence of silica as another

Table 1. Production estimates of some crop residue in the Philippines.

Crop Residue	*Amount Generated Million Mt/Yr.*	*Year*
Sugarcane bagasse	5.3	1975
Rice straw	5.0	1975
Rice hulls	1.0	1975
Coconut coir dust	2.1	1977

Source: Del Rosario (1978)

Table 2. Approximate composition of some lignocellulosic materials.

Material	*Cellulose %*	*Hemicellulose %*	*Lignin %*	*Ash %*
Sugarcane bagasse	40-50	20-30	18-20	4
Rice straw and rice hulls	35-45	20	20-30	15-20
Coconut coir dust	24.2	27.3	54.8	6.2

Source: Del Rosario (1978)

encrusting substance further increases the indigestibility of the cellulosic material (Han, 1975). Rice straw has an extremely high silica content of up to 16.5% of its dry matter (Han, 1975).

Thus, in order to improve the degradability of lignocellulosics, various physical and chemical pretreatment modes have been proposed (Han and Callihan, 1974; McManus and Choung, 1976; Ghedalla and Miron, 1981).

In view of the above-mentioned information, studies were conducted to determine the factors that influence the biomethanation of rice straw.

Materials and Methods

The experiment was conducted using the set-up in Fig. 1. Gas slides volumes were measured by water displacement and the digester bottle was shaken twice a day to allow for the mixing of the contents.

pH was monitored using pH paper moistened with the fermentation medium. Gas quality was determined using the flammability test and gas chromatographic

Table 3. Proximate composition of the rice straw from IR-8.

Constituent	*Per cent*
Crude Protein	3.21
Crude Fiber	28.59
Crude Fat	3.10
NFE	46.86
Total Ash	18.24
Ca	0.46
P	0.14

Source: Mohammed and Ravi, 1969.

analysis on a Shimadzu GC3B using a stainless steel column packed with 60/80 mesh activated carbon and nitrogen as carrier.

Volatile solids was determined using the standard AOAC methods and the analysis of rice straw by sequential fractionation was based on the method of Datta (1981) and shown on Fig. 2.

The fermentor slurry was prepared using chopped rice straw (5 cm) and ground rice straw (40 mesh) mixed with the starter and enough water to make up 2.1 liters final volume.

The following chemical treatments were used:

1. Sodium Hydroxide – Rice straw was soaked in 4% sodium hydroxide solution at room temperature for 4 hrs. Straw was washed until neutral with distilled water after soaking.
2. Sodium hydroxide with neutralization using hydrochloric acid. After the alkali treatment period as in 1, excess alkali was neutralized with hydrochloric acid overnight and subsequently washed with distilled water.
3. Ammonia – Rice straw was soaked in 0.1 ammonia water solution at room temperature for 20 days. Excess ammonia was washed off until neutral.
4. Hydrochloric acid – Rice straw was soaked in 0.1 N hydrochloric acid for six hours at 60°C with constant stirring and subsequently washed with distilled water until neutral.
5. Steaming – Premoistened rice straw was autoclaved at 15 psi for 1.5 hrs.
6. Coconut Coir Dust Ash Solution – Rice straw was soaked for 3 days at room temperature with coconut coir dust ash solution at varying concentrations and washed with distilled water until neutral.

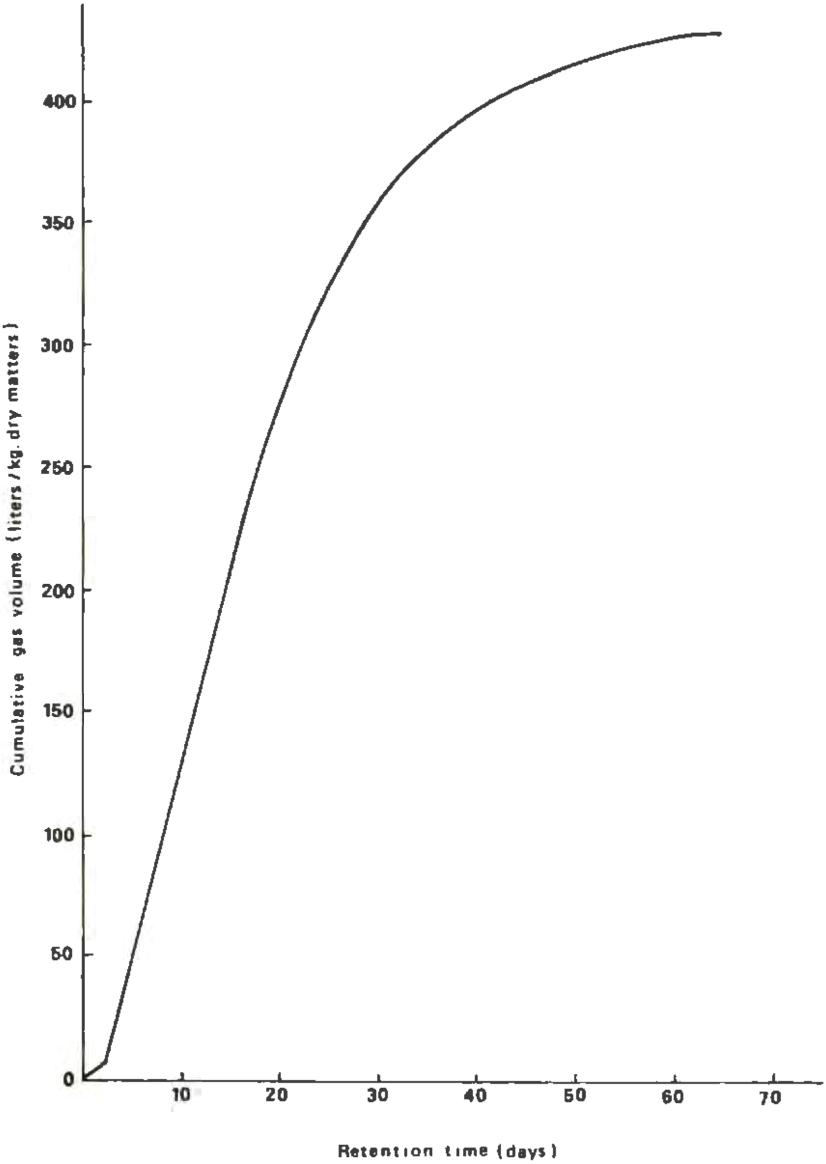

Figure 1. Typical gas production curve.

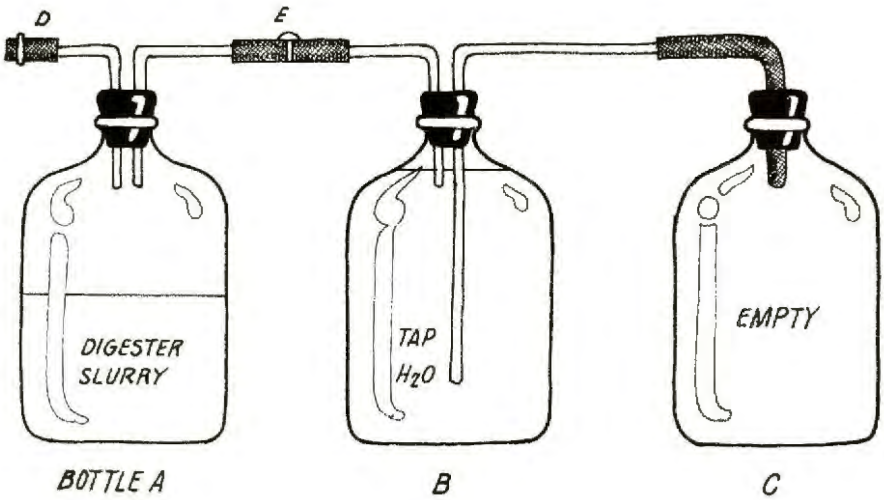

Figure 2. Biodigester set-up.

Discussion of Results

Ground rice straw (40 mesh) proved to be a better substrate than chopped rice straw (5 cms).

The results are summarized in Tables 4-10. The different treatments had various effects in the removal of the dry matter contents of rice straw. The treatment using bases showed an average weight loss of between 33% and 39%. Negligible changes were observed with the steam treated samples. Major losses in the water soluble fractions were also observed using the base treatments. Likewise, the bases were able to extract more hemicelluloses than hydrochloric acid.

The lignin portion of the rice straw was effectively removed by the bases. The cellulose fraction seem to be the least susceptible to loss during chemical treatment.

The silica content could be lowered by about 75% using the bases.

It has been shown that after 70 days of fermentation, only 50% of the volatile solids has been converted to biogas.

Chemical treatment of rice straw before fermentation showed varying degrees of improvement except for the hydrochloric and sodium hydroxide enhanced biogas production and shortened the active growth phase, but treatment with ammonia and hydrochloric acid even slowed down gas production within the first two weeks.

Methane concentrations in the different treatments range from 49% to 75% as the fermentation progressed. Fluctuations were observed during the first 30 days, the methane levels becoming more stable after the first month. High levels of methane were observed in both the neutralized and unneutralized sodium hydro-

Table 4. Average values of % volatile solids and % ash of control and treated rice straw.

	% Volatile Solids	*% Ash*
Rice Straw (5 cm)	77.49	22.51
Ground Rice Straw	77.5	22.47
Treated Ground Rice Straw		
NaOH	73.95	26.05
NH_3	74.82	25.18
NaOH-HCl	74.65	25.35
HCl	75.90	24.10
Steam Pressure	77.57	22.44

Table 5. Ashfree values of the different components of rice straw using fractionation method of analysis.

Treatment	*% Water Solubles*	*% Hemi-Cellulose*	*% Cellulose*	*% Lignin*
Ground Rice Straw	16.51	16.39	34.45	10.18
Treated Ground Rice Straw				
NaOH	5.76	7.04	30.95	1.63
NH_3	7.50	8.55	31.04	2.31
NaOH-HCl	8.44	7.00	30.82	1.68
HCl	10.66	8.36	32.98	9.93
Steam Pressure	16.81	16.29	34.25	10.21

xide treatments from 16-32 days of fermentation giving methane levels above 70%. Both the hydrochloric acid and steam treatment did not improve gas quality compared to untreated ground rice straw and untreated chopped straw.

The flame tests showed bluish luminous color whose persistence was proportional to the rate of biogas production.

Regression analysis shows that gas production is enhanced by the levels of water solubles, hemicelluloses and cellulose contents and inhibited by lignin and alkali soluble silica contents. This confirms findings of other workers.

Preliminary results using coconut coir dust ash as an indigenous source of alkaline material shows very encouraging results with cumulative gas volumes of

Table 6. Ash analysis of treated and control rice straw after ignition at 550°C.

Treatment	*% Sand*	% Alkali Soluble Silica
Ground Rice Straw	75.07	10.15
Treated Rice Straw		
NaOH	88.90	2.63
NH_3	86.45	2.83
NaOH-HCl	88.02	2.82
HCl	78.68	10.62
Steam Pressure	75.18	10.12

Table 7. Percentage of the volatile solids converted to biogas (Trial 1).

Treatment	*Day 7*	*Day 14*	*Day 21*	*Day 28*	*Day 36*	*Day 70*
Rice Straw	8.75	19.59	25.42	28.19	31.57	35.96
Ground Rice Straw	16.82	27.64	32.95	37.10	40.70	48.57
Treated Rice Straw						
NaOH	36.02	49.20	51.69	52.76	54.12	55.58
NH_3	16.97	43.43	49.65	51.70	52.64	55.26
NAOH-HCl	29.96	48.00	51.69	53.92	54.89	57.45
HCl	5.60	13.60	22.45	33.89	39.14	45.85
Steam Pressure	22.38	30.8[illegible]	35.92	37.67	40.48	46.35

400 liters at 67 days fermentation time and methane levels of up to 69% at three weeks fermentation time.

Detailed investigations are being undertaken to understand the reasons for the above-mentioned trends and observations. Likewise, a search for indigenous sources of treatment schemes is being undertaken. This is crucial for the technology to be moved to the countryside.

Table 8. Cumulative gas production (liters per kg. dry matter) for each treatment.

TREATMENT	*3*	*6*	*15*	*DAYS* *21*	*28*	*36*	*70*
Rice Straw (5 cm)	12	50	143	174	192	216	246
Ground Rice Straw (40 mesh)	53	96	200	225	254	278	332
Treated Rice Straw							
NaOH	82	164	244	252	257	264	271
NH_3	19	56	230	254	265	270	283
NaOH-HCl	21	119	246	260	271	276	289
HCl	10	25	91	132	200	231	270
Steam Pressure	75	143	218	245	257	276	316

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Table 9. Concentration of the biogas produced in trial 2 (in % by volume methane)

TREATMENT	DAYS														
	5	8	12	15	19	22	26	33	36	40	43	48	54	63	69
Ground Rice Straw	56.80	49.90	51.52	57.74	52.47	51.82	52.20	54.28	54.26	55.31	54.19	53.88	58.52	54.73	56.47
Rice Straw	60.68	54.31	53.08	58.51	55.22	49.90	49.75	51.66	55.83	51.84	52.21	53.14	60.40	56.95	56.28
Treated Rice Straw															
NaOH	49.95	48.59	47.07	50.09	64.26	74.69	73.59	70.43	60.90	58.81	58.48	57.10	56.33	57.96	65.07
NH_3	50.22	47.24	50.15	55.16	70.49	63.74	65.41	63.67	62.04	59.08	59.43	56.32	58.44	60.11	59.55
NaOH-HCl	44.37	50.01	56.79	51.55	73.84	76.71	70.50	70.70	64.40	61.79	60.22	61.08	65.17	65.89	66.23
HCl	55.07	61.26	55.49	55.39	56.60	47.21	50.96	54.20	53.78	53.61	53.69	55.02	57.83	58.48	57.40
Steam Pressure	53.16	56.10	60.77	55.46	52.66	50.76	53.00	56.31	57.46	53.12	55.76	55.52	53.93	53.52	53.13

Table 10. Mean cumulative volume of gas produced and gas chromatographic analysis of pretreated rice straw.

TREATMENT	*GAS VOLUME (l/kg. DRY MATTER)*	*GAS COMPOSITION DAYS* 9		16		23	
		$\%CH_4$	$\%CO_2$	$\%CH_4$	$\%CO_2$	$\%CH_4$	$\%CO_2$
6% Coir Dust Ash	398	54	46	57	43	58	42
9% Coir Dust Ash	413	54	46	60	40	51	49
12% Coir Dust Ash	353	54	46	61	39	59	41
15% Coir Dust Ash	430	50	50	68	32	69	31
Control	311	56	44	51	49	64	36

Julian A. Banzon, Discussant

This study on biomethanation of rice straw is probably the only lengthy Philippine contribution on the subject so far. The authors have taken advantage of the much-studied caustic soda treatment of straw to increase digestibility of the straw for animal feeding.

Anaerobic digestion of waste biomass resulting in methane-rich biogas is one of the ways to meet the petroleum fuel problem. This gas serves to replace LPG in the kitchen; in N.Z., methane is separated from CO_2 (as both occurs in biogas) and the CH_4 is compressed and commercially used to run taxi cabs, cars and tractors. The potential purefulness of straw as a source of a very versatile fuel is thus obvious. A little over 1/2 of the biomass of the mature rice plant consists of straw, the grain comprise the remainder, hence the magnitude of the available rice straw for biomethane procedure while the experiments reported are in the laboratory stage where costs may be of secondary importance, experimenters however should keep a sharp eye on keeping procedures simple and inexpensive, if the lab results are any nearer to succeed in field trials. Water has become a very precious and scarce commodity in most any place; distilled water should be mentioned most prudently.

Some information relevant to the subject of biomethanation was discussed in an Australian-Asian Symposium on utilization of fibrous materials last May 1981 and which was held in the UPLB Campus; it appears that the authors missed this symposium.

Summing up, the authors deserve congratulation for pioneering in this area of straw utilization via biomethanation.

Romeo V. Alicbusan, Discussant

When the paper was submitted to me for review it is the first time that I have read such kind of work that discussed in details some studies in the bioconversion of rice straw to methane. There are some publications from other countries you can come across but these are more of a passing reference rather than a detailed report on what happens with the rice straw as it produces the biogas, how much amount is needed, what kind of pre-treatment must be done. There is no such study before and so this work is very pioneering as far as the magnitude and the nature of the research is concerned. In a way that this is going it is answering the question why rather than the how. The study, however, should be geared towards rural adaptation taking into consideration the economic situation of the people. I think the simplest way by which we can adopt the technology is to make it more practical yet efficient. It may only be 50% efficient but if easier and cheaper to make people will accept it. I would say that maybe in the years to come when a lot of these uncertainties about rice straw conversion to methane has been resolved, the Biotech Institute will go down to the level of simplifying the procedure of methane production so that it will be highly adaptable for rural communities. Hand in hand with this development, I think engineering study must be done so that the digester could be adapted to the kind of raw material that it is going to receive. The report of Dr. Padolina is something that has look beyond the objectives. I am recommending that you study the microbiological aspect especially the anaerobes. I know that Dr. Barril studied quite extensively in Australia on this aspect and probably his expertise could be tapped. Methane generation can be done only with appropriate raw materials and the microorganisms under favorable conditions.

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