## STUDIES ON BIOCONVERSION Part I. On the Effect of Urea for Improving Biogas Yield

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On analysis, chemical constituents of bufallo dung varied from barn to barn and season to season. This variation may possibly be related to the age of animal and diet consumed. 0.05 and 0.1% urea/kg raw materials were found to be adequate doses for mixing with dung without altering optimum C/N value of fermentation. Addition of urea for prolonged periods though improved biogas yield by 34%, it also increased carbon dioxide value with passage of time. It is, therefore, suggested that either urea should be added periodically, or a single shock dose may be given for improving the efficiency of biogas digester.

Key words: Biogas, Urea, Cow dung.

### INTRODUCTION

In order to improve efficiency of biogas digesters during winter, farmers in Northern India cover gas holders with plastic sheets after sunset [1]. Devkota [2] used heat, generated from compost, for heating digesters. In a review, entitled. "A multidisciplinary Review on Biogas Technology in the Third World" edited by Barnett, Pyle and Subramanian [1] it has been reported that urea, urine algae and molasses have been used for improving gas yields.

Studies carried out on biogas generation by the authors generally showed an average production of 0.032 - 0.035 m<sup>3</sup> gas/kg bufallo dung in summer. This yield, however, reduced to 0.021 - 0.024 m<sup>3</sup> gas/kg in winter. Investigations, therefore, were carried out to determine the effect of urea on biogas yield during the year and more so in winter under local environmental conditions. As reported in the review under reference, this may not be totally true and applicable in climatic conditions of Karachi.

Results on chemical analysis of bufallo dung collected at different times of the year from several barns; effect of addition of various concentrations of urea on chemical composition of bufallo dung (so as to establish proper dosage of urea) needed for preparing feed having optimum Carbon/Nitrogen (C/N) ratio; and finally evaluation and comparison of biogas yields after addition of appropriate amount of urea, have been reported here.

### MATERIALS AND METHODS

Bufallo dung from different barns in Karachi was collected at different times of the year and analyzed.

Moisture content and volatile solids were estimated according to the standard methods of analysis [3]. Nitrogen was determined using micro kjeldahal techniques [4] and carbon percentage calculated by dividing percentage volatile solids with factor 1.8 [5]. pH of the material was checked on a pH meter.

It may be pointed out that these experiments were conducted in Karachi, where mean average temperature in summer generally ranges between  $26.5 - 33^{\circ}$  and occasionally rises to  $38 - 40^{\circ}$  whereas in winter the average temperature range varies between  $11 - 26^{\circ}$ 

Urea in concentrations of 0.0 - 0.2% was thoroughly mixed with measured amounts of bufallo dung and the mixture analyzed for C/N ratio and pH estimated. To determine the effect of urea on biogas yield, vertical Indian type cement biogas digester with metallic floating gas holder of 4  $m^3$  gas holding capacity was used (Fig. 1). Slurry using 3000 kg bufallo dung and an equal weight of water was prepared and fed to the digester. This preparation contained approximately 10% total solids, had pH 7.0 - 7.2 and 28.5/1 C/N ratio. Digester remained in continuous operation from January to December. After retention time (30 days); 100 kg feed/day was fed to the digester and gas, thus, evolved was measured daily. Gas was analysed weekly by carbon dioxide absorption on potassium hydroxide solution using Orsat technique [6]. Methane was calculated by difference in volume of gas after absorption and confirmed by visual gas test [7]. In the subsequent year, 0.05% urea/day mixed with the dung prior to feeding, and again the digester was kept in continuous operation for one whole year. Gas was measured and analyzed as previously.

#### **RESLULTS AND DICUSSIONS**

Chemical analysis of 12 bufallo dung samples collected from different locations showed great variation (Table 1) from season to season, and barn to barn depending on the age of the animal and diet consumed. pH of bufallo dung samples varied between 6.75 - 7.8; moisture content 71.4 - 86%, volatile solid 65% - 85% and nitrogen 1.28 - 2.35%; carbon values ranged between 36 - 47%, whereas C/N varied between 17.8/1 - 36.0/1. Average values of the chemical composition have also been calculated and given in Table 1.

The reason for slightly higher C/N ratio of bufallo dung as noticed in experiments may be due to the fact that As concentrations of urea increased, pH value and C/N ratio decreased (Table 2). At 0.2% urea concentration C/N level reached (26/1) near the lower side of the optimum range. Most suitable dose selected for mixing with dung were 0.05 and 0.1% urea/kg dung. To avoid the risk of gradual over dosing, 0.05% urea/kg was used for adding to the above mentioned digester.

It was noted that bufallo dung yielded, on an average (of one year),  $0.032 \text{ m}^3$  gas/kg raw material with 34 - 35% carbon dioxide. Gas yield increased to average 0.043 m<sup>3</sup> gas/kg raw material with 38 - 40% CO<sub>2</sub> on addition of 0.05% urea/kg./day raw material. i.e. 34% increase in yield of biogas was noted on addition of urea along with an increase in carbon dioxide content. Table 3 shows

Table 1.	Chemical	composition of	various sample	of bufallo dung.

	1	2	3	4	5	6	7	8	9	10	11	12	Avg.
pH	7.7	7.45	7.0	7.35	6.75	7.75	7.1	7.35	7.0	6.9	7.20	7.4	7.80
Moisture %	79.5	80.00	80.00	71.40	79.00	78.0	73.0	77.70	86.0	75.00	75	75.50	77.50
Total solid %	20.5	20.00	20.00	28.60	21.00	22.0	24.0	23.30	14.0	25.0	25.00	24.5	22.20
Volatile solids %	77.0	83.00	85.00	75.40	84.50	79.5	65.0	74.00	82.0	74.0	73.50	79.0	71.80
Carbon %	44.0	46.00	47.00	42.00	47.00	44.0	36.0	41.00	45.6	41.0	41.00	44.0	43.20
Nitrogen %	1.6	1.85	2.35	1.99	1.28	1.9	1.8	2.30	1.5	1.8	1.45	1.5	1.77
C/N	27.5	24.90	20.00	21.00	36.00	23.0	20.0	17.80	30.4	22.7	28.30	29.3	25.00

Concentration of urea $\%$	pH	C/N	
0.0	6.9	31.8	
0.05	7.10	30	
0.1	7.2	29.2	
0.2	7.25	26	

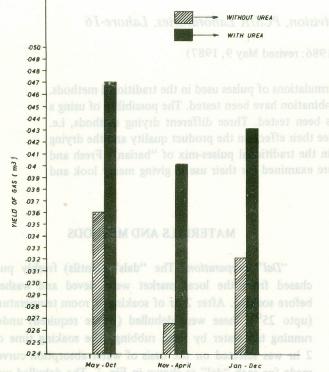
in Pakistan animals generally consume proportionately more cellulosic than proteinaceous diet. Besides, dung sometimes also gets mixed with straws fed to animal, C/N obtained from most of the analyzed samples was found to be within the optimum range (25/1 - 35/1) as required for biogas fermentation.

Prior to addition of urea to biogas digesters (for improving gas yield) experiments were conducted on laboratory scale to determine the optimum dose of urea required for adding to the dung without imbalancing appropriate C/N requirement for biogas fermentation. Initial pH and C/N ratio of fresh samples of bufallo dung before adding urea was evaluated along with urea added samples and it was found to have pH of 6.9 and C/N ratio of 31.8. Table 3. Effect of urea on yield of gas during January – December.

	Average m <sup>3</sup> gas/kg raw material + no urea	Average m <sup>3</sup> gas/kg raw material + 0.05% urea
January	0.021	0.036
February	0.029	0.036
March	0.030	0.043
April	0.031	0.042
May	0.033	0.048
June	0.043	0.055
July (rain)	0.028	0.038
August	0.036	0.054
September	0.037	0.047
October	0.039	0.041
November	0.029	0.043
December	0.024	0.0387
Average yield of gas	0.032	0.043
Average CO <sub>2</sub> value recorded	34-35%	38-40%

yield of biogas throughout the year in different months, before and after adding urea.

During summer (May – October) yield of gas varied between  $0.028 - 0.043 \text{ m}^3$  gas/kg raw material without addition of urea (Avg.  $0.032 \text{ m}^3$ ). Whereas in winter



AVERAGE YIELD OF GAS DURING SUMMER (May - Oct) WINTER (Nov - Aprial) & THROUGHOUT THE YEAR Jan - Dec

Fig. 1. Indian type vertical biogas cement digester with moving steel drum gas holder – showing (right) feed inlet and (left) sludge outlet.



Fig. 2. Average yield of gas during summer (May - Oct) winter (Nov - April) and through out the year (Jan - Dec).

through a meat mincing machine with sieve holes size of about 2 mm dia. The minced meat so obtained is mentioned as "minced meat" in the tables of results. The fibre type (November – April) biogas yield reduced by 10 - 25%. Addition of urea improved biogas yield by 21 - 28% in summer; however in winter instead of reduction, gas increased in yield as compared with that obtained in summer where no urea was added (Fig. 2). Increase in cabron dioxide (38 - 40%) after addition of urea most likely may be due to the fact that decomposition of urea results in release of carbon dioxide and since this carbon dioxide is not being fully utilized in methane conversion, it slowly accumulates in the digester. If urea is continuously fed, with passage of time CO2 level may reach an alarming stage, thus lowering methane ratio, and reducing biogas digester's efficiency. It is, therefore, suggested that urea should be added periodically or a single shock dose may be employed to the biogas plant from time to time for improving gas efficiency in general, and particularly before onset of winter when yield generally falls off due to cold weather.

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