

## Physical, Chemical and Biomethanation Characteristics of Stratified Cattle-Manure Slurry

H. K. Ong\*, P. C. Pullammanappallil<sup>1</sup> and P. F. Greenfield<sup>1</sup>

Malaysian Agricultural Research and Development Institute, P.O. Box 12301, 50774 Kuala Lumpur, Malaysia

**ABSTRACT** : In the quiescent state, cattle-manure slurry stratifies into three discernible layers, namely a floating scum layer, a bottom sludge layer and a watery middle layer. The proportions of top (scum), middle and bottom (sludge) layers were approximately 20, 60 and 20% respectively of the volume of the whole slurry. Particulate matter from the different stratified layers was characterised for particle size distribution and cellulose, hemicellulose and lignin composition. Total solids concentrations of top, middle and bottom layers were 12.7, 2.8 and 7.4% respectively. Larger particles were found in the top layer compared with the bottom. The top layer contained the highest amounts of Neutral Detergent Fibre (NDF), Acid Detergent Fibre (ADF), cellulose and hemicellulose, but the lowest amount of Total Kjeldahl Nitrogen (TKN). The bottom layer contained the highest amounts of Acid Detergent Lignin (ADL) and TKN. With increase in particle size, there were increases in NDF, ADF, cellulose and hemicellulose, accompanied by decreases in ADL and TKN. Biochemical methane potential of the three layers was also measured. The top layer was found to produce the most methane with the middle layer producing the least. Biomethanation rate from the top layer was also the highest. Differences in biomethanation rates and biochemical methane potential were attributed to differences in chemical composition of the particulate matter. About 48%, 23% and 30% of the total chemical oxygen demand (COD) in the top, middle and bottom layers respectively of the slurry was found to be degradable. (*Asian-Aus. J. Anim. Sci.* 2000. Vol. 13, No. 11 : 1593-1597)

**Key Words** : Cattle, Slurry, Biomethanation, Stratification, Particles, Composition

### INTRODUCTION

Cattle-manure slurry has a polluting effect on water and soils (Chantalakhana et al., 1999). It has been observed that in the quiescent state cattle-manure slurry stratifies into three discernible layers, namely a floating scum layer, a sludge layer at the bottom and a watery fraction low in particulate matter in the middle (Schofield and Rees, 1988; Kellner et al., 1990). Hence, it is generally considered that to enhance biomethanation, the slurry needs to be mixed to homogenise and to overcome mass transfer limitations during break down of particulate matter by promoting contact between enzymes (and/or microorganisms) and particulate matter. This has led to the development of digesters that incorporate auxiliary mixing devices. In developing countries implementation of such digesters may not be economically viable because of the increased capital and operating costs and the higher level of technical skill required to operate these systems. However, use of digesters without mixing devices could lower the biomethanation efficiency for the same loading rate (Murk et al., 1980; Hashimoto, 1982). To maintain the efficiency of biomethanation without sacrificing the throughput in unmixed digesters, it will be necessary to retain the

highly degradable fractions long enough to realise its methane potential. This would require incorporation of alternate features into the digester design and operation. With a view to developing alternatives for existing digester designs the degradability and biomethanation potential of the different fractions of cattle-manure slurry were studied. Specifically, the three layers of stratified cattle-manure slurry were physically and chemically characterised for its solids content, size distribution of particulate matter, degradable components and biomethanation potential.

### MATERIALS AND METHODS

The cattle from which the manure was collected for the experiments described here were fed approximately 12 kg/head/day of concentrate feed and 6 kg/head/day of oil palm frond. Cattle-manure slurry was prepared by blending 4 kg of fresh cattle faeces with 10 L of water. The slurry thus obtained was representative of slurry usually produced after routine cleaning of the cattle sheds. The slurry was allowed to settle and the different layers were manually decanted. A particle size distribution of fresh cattle-manure slurry and the decanted stratified layers were determined by a wet-sieving technique modified from those described by Jung et al. (1991) and Huhtanen et al. (1993). Slurries were sieved through test sieves of mesh sizes 2800, 1000, 600, 300, 106 and 45  $\mu\text{m}$ , using Endecotts Sieves Model EFL2 MK3 with shaker attached with wet-sieving kids. Samples of 1 L in volume were sieved in the shaker for 15 minutes.

\* Address reprint request to H. K. Ong. Tel: +60-3-8943-7285, Fax: +60-3-8945-6037, E-mail: keng@mardi.my.

<sup>1</sup> Advanced Wastewater Management Centre, Department of Chemical Engineering, The University of Queensland, Brisbane, St. Lucia, QLD 4072, Australia.

Received January 13, 2000; Accepted April 10, 2000

Particles retained on sieves were recovered on filter paper and dried at 60°C. Particle size distribution determinations were made in four replicates for each sample.

The solid fractions from the floating scum layer, the settled sludge layer, the mixed slurry and the various size fractions, namely those retained on sieve sizes of 2800, 1000, 600, 300, 106 and 45  $\mu\text{m}$ , within each layer were dehydrated at 60°C. These samples were analysed for cell wall components, Neutral Detergent Fibre (NDF), Acid Detergent Fibre (ADF) and Acid Detergent Lignin (ADL) following methods described by Goering and van Soest (1970) and van Soest and Robertson (1979). These methods are specific for plant cell walls and thus are useful for distinguishing between microbial and plant-derived residues. Total Kjeldahl Nitrogen (TKN) and Total Volatile Solids (TVS) analyses were also carried out according to methods of APHA (1985). All analyses were carried out in eighteen replicates except for the various size fractions which were analysed in triplicates. Data were analysed for variance and means and tested using Duncan's Multiple Range Test (Steel and Torrie, 1960). Total COD (TCOD) was determined by dichromate reflux method. Soluble COD (SCOD) was similarly determined using the supernatant portions of samples centrifuged at 1030 g's for 15 minutes.

Biochemical methane potential of each stratified fraction of settled slurry, viz. the floating scum layer, middle liquid layer and the settled sludge layer, and the whole slurry was determined. These samples were anaerobically batch-digested in four, 10 L perspex cylindrical tanks maintained between 26 and 27°C. The digester containing the whole slurry was stirred at 200 rpm for four times a day, each for duration of 30 minutes while the other digesters containing the stratified fractions were left unstirred. To each 9 L of sample, 1 L of digested slurry obtained from a full-scale anaerobic cattle-manure digester was added as seed material to initiate anaerobic digestion.

## RESULTS AND DISCUSSION

The proportions of top ('scum'), middle and bottom ('sludge') layers were approximately 20, 60 and 20% respectively of the volume of the whole slurry. The total solids content of the whole slurry, top, middle and bottom layer of stratified slurry were 7.4% ( $\pm 0.5$ ), 12.7% ( $\pm 3.7$ ), 2.8% ( $\pm 1.0$ ) and 7.4% ( $\pm 1.5$ ) respectively on a w/w basis. The volatile solids content ranged from 79-85% of the total solids. Among the three layers, the volatile solids content of the top layer was the highest at 85% ( $\pm 1$ ). 82% ( $\pm 0.5$ ) of the total solids in the bottom layer was volatile where as only 79% ( $\pm 0.7$ ) of the solids in the middle layer was volatile.

Particle size distributions of whole slurry as well as of the different stratified layers of slurry are shown in table 1. The patterns of distribution are significantly different among the three layers. In the top layer, 63.5% of particles were retained on a sieve mesh of 2800  $\mu\text{m}$  while in the case of middle layer; none were retained on that sieve size. In the bottom layer, the percentages of particles retained on sieve sizes 2800, 1000 and 600  $\mu\text{m}$  were 31.6, 30.4 and 13.2 respectively. Particles in the middle layer were mainly between 45 and 1000  $\mu\text{m}$ . Particles of whole slurry were mainly in the 300-2800  $\mu\text{m}$  range. Thus in a stratified slurry, higher amounts of the larger particles were found in the top layer compared with the bottom layer.

The compositions of cell-wall components of different fractions of cattle-manure slurry are shown in table 2. Results from the statistical analysis of the data are also indicated in the table. There were significant differences between fractions in contents of NDF, ADF, ADL, cellulose and TKN. The top layer contained the highest amounts of NDF, ADF, cellulose and hemicellulose, but the lowest amount of TKN. There were no significant differences in hemicellulose between the whole slurry and the top layer fractions, but both were significantly different from the bottom layer. The bottom layer contained the highest amounts

**Table 1.** Particles size distribution of whole and stratified fractions of cattle-manure slurry (mg/g of solid)

Mesh size ( $\mu\text{m}$ )	Whole slurry	Top layer	Middle layer	Bottom layer
>2800	287	635	nil	316
1000-2800	294	90	50	304
600-1000	148	72	332	132
300- 600	114	71	181	70
100- 300	42	63	173	59
30- 100	60	32	210	65
Losses	55	37	54	54

**Table 2.** Cell wall components and TKN of different strata of slurry (mg/g of solid)

Parameter	Mixed slurry	Top layer	Bottom layer
NDF	640 <sup>a</sup>	712 <sup>b</sup>	529 <sup>c</sup>
ADF	355 <sup>a</sup>	419 <sup>b</sup>	316 <sup>c</sup>
ADL	74 <sup>a</sup>	55 <sup>b</sup>	103 <sup>c</sup>
Cellulose	281 <sup>a</sup>	362 <sup>b</sup>	208 <sup>c</sup>
Hemicellulose	285 <sup>a</sup>	294 <sup>a</sup>	218 <sup>b</sup>
TKN	30.5 <sup>a</sup>	18.2 <sup>b</sup>	55.2 <sup>c</sup>

Figures on the same row bearing different superscripts differ significantly ( $p < 0.05$ ).

of ADL and TKN.

Cell wall components of different fractions of cattle-manure slurry in a quiescent state differ distinctively. The bottom fraction consisting of smaller particles was probably subjected to higher rate of digestion in the gastro-intestinal tracts of the animal, and therefore was lower in the contents of cellulose and hemicellulose. This relationship can also be seen from figure 1 in which smaller particles are shown to contain higher content of lignin, a refractory material. However, the top layer, which was made up of larger size particles, contained more cellulose and hemicellulose and lower lignin content. This indicated that this fraction could be digested further. The particles from the bottom layer contained more nitrogen. The source of this nitrogen could be proteinaceous compounds. Figure 1 shows a relationship between particle size and the cell wall components and TKN content of the slurry. Amounts of NDF, ADF, cellulose and hemicellulose decreased with decrease in particle size. On the contrary, amounts of ADL and TKN increased with decrease in particle size. Similar observations have been made on rumen content by Jung et al. (1990) and Huhtanen et al. (1993).

Chemical Oxygen Demand (COD) of the different fractions of the slurry as well as for the soluble and insoluble fractions were measured. The total COD of the whole slurry was 86 ( $\pm 4$ ) g/L with 9.5 ( $\pm 0.5$ ) g/L of the total COD being contributed by the soluble fraction of the slurry. The total COD of the top, middle and bottom fractions were 145.5, 37.5 and 86.0 g/L respectively. The contribution of the soluble fraction to the total COD was 9.5 g/L for each of these fractions.

Cumulative biogas production measured over eighty days of digestion from different fractions of stratified slurry is shown in figure 2. The figure shows the biogas produced from 10 L of the slurry. Biogas production from the bottom and middle fractions of the slurry dropped to zero (inferred from a leveling of the cumulative biogas production curve) after the initial increase after sixty days of digestion for the bottom fraction and forty five days for the middle fraction. However, even after eighty days of digestion the top fraction continued to produce biogas. It can be seen that the top layer exhibited the highest cumulative gas production (400 L after extrapolation), while the middle portion showed the lowest (50 L). The cumulative biogas production from the bottom fraction was 150 L. Low biogas production from the middle layer corresponded to low solids content of this layer. This indicates that during anaerobic digestion of cattle-manure slurry most of the degradable substrate is associated with the particulate matter. Even though the solids content of the top layer

was less than twice as much as the solids content of the bottom layer, cumulative biogas produced from the top layer was more than double of that produced from the bottom layer. This could be due to the higher amounts of degradable matter (cellulose and hemicellulose) in the top layer compared to that in the bottom layer. Based on the biogas production from the individual fractions the expected biogas yield from the whole slurry was estimated as 15.6 L/L slurry. The ultimate products of anaerobic digestion are methane and carbon dioxide and since COD of carbon dioxide is zero, the COD that is degraded appears as COD of the methane. Hence it is possible to estimate the extent of degradation as fraction of COD converted to

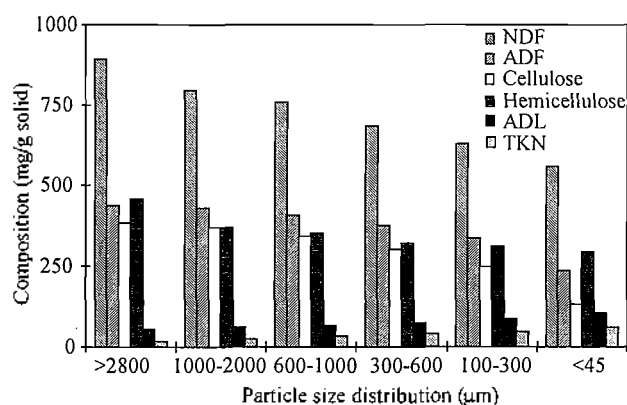


Figure 1. Relationship between particle size and chemical composition in cattle-manure slurry

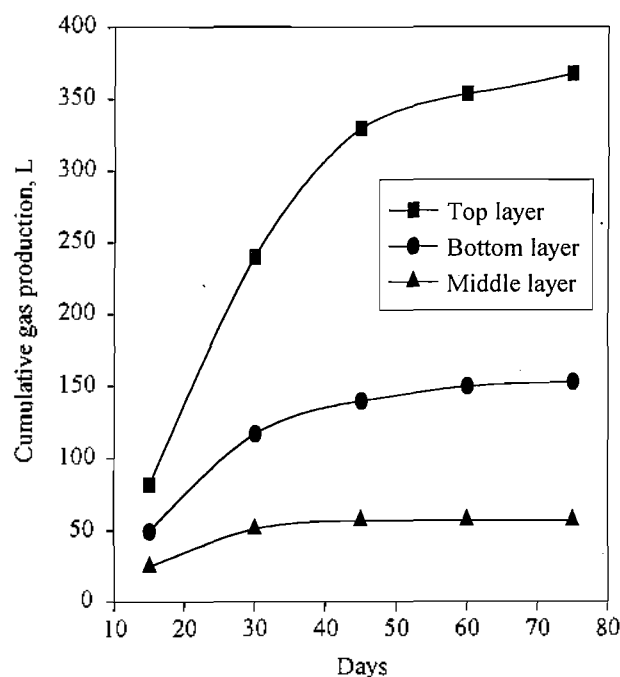


Figure 2. Cumulative biogas production from different fractions of slurry

methane. For the individual fractions of slurry, assuming 55% of biogas produced is methane, the COD of the methane captured in the biogas can be calculated to be 70 g COD/L slurry, 8.7 g COD/L of slurry and 26.2 g COD/L slurry for the top, middle and bottom fractions respectively. This means that 48%, 23% and 30% of the top, middle and bottom fractions respectively of the slurry can be degraded, which means that 29% of the COD in the whole slurry can be degraded based on the volume fractions of individual layers in the whole slurry.

The rates of biogas production also varied between the layers even though the slurries were seeded with the same material from an active full-scale, cattle-manure digester. The rate of biogas production from the top layer was higher than that produced from the bottom layer. This is indicated by the initial slope of the curves measured between 15 and 30 days in figure 2. During anaerobic digestion of particulate matter, the first step is the hydrolysis (or solubilisation) of the solids by enzymes secreted by the fermentative bacteria. Among other factors, the rate of this enzymatic step is affected by particle size. Smaller particles mean greater surface area per unit weight of the substrate, which in turn enhances hydrolysis rate. It would be expected that the bottom layer containing smaller particles would exhibit a higher rate of biomethanation than the top layer. The results obtained were contrary to that expected. This was probably because the degradable portions within the particles in the bottom layer were protected by lignin, making it more difficult to degrade. Moreover, the bottom layer also contained larger quantities of proteinaceous materials, which are known to degrade more slowly than carbohydrates like cellulose or hemicellulose (Pavlostathis and Giraldo-Gomez, 1991).

In cattle-manure slurry the top layer is the most active methanogenically. It contains the largest particles with the highest proportions of fibre, cellulose and hemicellulose but least proportion of lignin. In a continuously fed digester this fraction would have to be retained at least 30 days for it to produce 75-80% of its ultimate methane potential. The middle layer being poor in methane producing potential can be discharged in a shorter period thereby enabling the operator to increase the throughput of an existing digester or decreasing the digester volume for a given quantity to be treated. In a continuously mixed digester a segregation of the retention times of the three fractions is not possible. Intermittently mixed digesters or unmixed digesters afford this possibility.

### CONCLUSIONS

Upon storage, cattle-manure slurry stratifies into three layers namely, a floating "scum" layer, middle

liquid layer and a "sludge" layer at the bottom. The proportions of top ('scum'), middle and bottom ('sludge') layers were approximately 20, 60 and 20% respectively of the volume of the whole slurry. The chemical composition and particle size distributions were found to differ significantly among the three layers. Total solids concentrations of top, middle and bottom layers were 12.7, 2.8 and 7.4% respectively. The top layer was found to be made of larger particles compared to the bottom layer. About 64% of particles in the top layer were retained on sieve mesh of 2800  $\mu\text{m}$ . In the bottom layer, about 32, 30 and 13% of particles were retained on sieve mesh of 2800, 1000 and 600  $\mu\text{m}$  respectively. Particles in the middle layer were mainly between 45 and 1000  $\mu\text{m}$ . The top layer contained the highest amounts of Neutral Detergent Fibre, Acid Detergent Fibre, cellulose and hemicellulose, but the lowest amount of Total Kjeldahl Nitrogen. The bottom layer contained the highest amounts of Acid detergent Lignin and Total Kjeldahl Nitrogen. Thus, the top layer contains more carbohydrate than the bottom layer, while the bottom layer contains more nitrogen than the top layer. Higher Acid Detergent Lignin content was found in the bottom layer, although it consists of particles of smaller mesh size compared with the top layer. Particle size was found to have a significant effect on chemical composition of cattle slurry. With increase in particle size, there were increases in NDF, ADF, cellulose and hemicellulose, accompanied by decreases in ADL and TKN. Differential rates of biomethanation were found in different layers of slurry.

The top layer yielded the highest methane generating potential while the middle layer the lowest. This difference is attributed to the higher amounts of degradable matter in the top layer. The rate of methane generation was also found to be higher from the top layer compared to the bottom layer. The degradable substrates in the bottom layer were made up of proteinaceous compounds which are known to degrade slower than carbohydrates and cellulose which was protected from degradation by lignin. About 48%, 23% and 30% of the total COD in the top, middle and bottom layers respectively of the slurry was found to be degradable.

### REFERENCES

- APHA. 1985. *Standard methods for the examination of water and wastewater*, 16th edition. American Public Health Association, Washington, DC.
- Chantalakhana, C., R. Korpraditsakul, P. Skunmum and T. Poodusit. 1999. Environmental conditions and resource management in smallholder dairy farms in Thailand II: Effects of dairy wastes on water and soils. *Asian-Aus. J. Anim. Sci.* 12:220-225.
- Goering, H. K. and P. J. van Soest. 1970. Forage fibre

- analysis, Agric. Handbook No. 379, U.S.D.A., Washington, DC. pp. 1-20.
- Hashimoto, A. G. 1982. Effect of mixing duration and vacuum on methane production rate from beef cattle waste. *Biotechnol. and Bioengin.* 24:9-23.
- Huhtanen, P., P. Dakowski and A. Vanhatalo. 1993. Composition, digestibility and particle-associated enzyme activities in rumen digesta as influenced by particle size and time after feeding. *J. Anim. and Feed Sci.* 1:223-235.
- Jung, H. J. G., P. Aman and H. Graham. 1990. Profile of fiber composition in Lucerne hay and rumen digesta as influenced by particle size and time after feeding. *J. Sci. Food Agric.* 51:411-416.
- Kellner, C., E. Sasse and L. Sasse. 1990. Where the outlet should be: the distribution of slurry in a fixed dome plant. *Biogas Forum*, Vol. 4, No. 43. pp. 4-7.
- Murk, J. S., J. L. Frieling, L. D. Totorici and C. C. Dietrich. 1980. Use of bench-scale digesters to evaluate full-scale digester performance. *J. Water Pollution Control Fed.* 52:2709-2716.
- Pavlostathis, S. G. and E. Giraldo-Gomez. 1991. Kinetics of anaerobic treatment: A critical review. *Critical Rev. in Environ. Control.* 21:411-490.
- Schofield, C. P. and Y. J. Rees. 1988. Passive separation and the efficiency of anaerobic digestion of cattle slurry. *J. Agric. Engng. Res.* 40:175-186.
- Steel, R. D. G. and J. H. Torrie. 1960. Principles and procedures of statistics. McGraw-Hill Book Co. Inc., New York.
- van Soest, P. J. and J. B. Robertson. 1979. Systems of analysis for evaluating fibrous feeds. In: *Standardization of analytical methodology for feeds*. IDRC document 134e, Ottawa. pp. 49-60.
- Varel, V. H., A. G. Hashimoto and Y. R. Chen. 1980. Effect of temperature and retention time on methane production from beef cattle waste. *Appl. Environ. Microbiol.* 40:217-222.