VTI Thüringer Verfahrenstechnisches Institut
für Umwelt und Energie e. V.

Process, Environmental and Energy Engineering Institute of the State of Thuringia
for industry-related research, process development and technology transfer

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Report no. 069/03

Subject	**Fermentation tests modeled on DIN 38 414 using treated/untreated liquid pig manure**
Order no.	069/03 – 845 – 3
Client	BioAktiv-Pulver Produktions- und Vertriebs GmbH Hauptstr. 67 D – 06712 Würchwitz
In charge	Dipl.-Ing. D. Telschow
Distribution list	2 x BioAktiv-Pulver 1 x VTI Saalfeld e. V.

Saalfeld, Dec. 12, 2003

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When using results in other contexts please indicate report no.

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Bibliography

List of Enclosures

List of abbreviations

CH_4	Methane
CO_2	Carbon dioxide
COD	Chemical oxygen demand
VOA/TIC	Volatile organic acids/Total inorganic carbon
H_2S	Hydrogen sulfide
L_N	Normal liter (0°C, normal pressure)
L_S	Standard liter (25°C, normal pressure)
O_2	Oxygen
OS	Original substance
DOM	Dry organic matter
DM	Dry matter

1 Purpose

The tests aimed at evaluating the fermentation behavior of untreated liquid pig manure and comparable liquid pig manure pretreated with a product made by BioAktiv GmbH Würchwitz.

Samples were to undergo simultaneous monofermentation modeled on DIN 38414 part 8 in mesophile conditions over a period of at least 25 days using three minibatches (1 l container capacity) of untreated/treated manure each. A blank experiment and activity test were to be conducted in parallel.

Fermentation behavior was to be assessed by measuring the amount and composition of biogas produced, and by determining VOA/TIC and pH for process control.

In order to characterize the material, determination of DOM and COD was planned for both the raw material and fermentation residue.

2 Materials and methods

2.1 Sampling

Samples of untreated/treated liquid pig manure were taken in a staggered procedure and under comparable conditions by Dr. Reinhold from TLL (Thüringer Landesanstalt für Landwirtschaft Jena - Agricultural Establishment of the State of Thuringia at Jena) and kept in TLL's cold store at Jena.

Approx. 5 l of each type of sample was made available for fermentation testing which began immediately after the samples had been handed over.

Seed sludge was provided by the test establishment.

2.2 Fermentation tests

For each type of manure, three minibatch fermentation tests (container capacity 1 l) were prepared by mixing 50% by vol. of untreated/treated liquid pig manure with 50% by vol. of seed sludge.

To facilitate the start of fermentation, seed sludge containing bacteria desirable for biogas formation was added to the batches. To eliminate the effect on gas yields from seed sludge, its gas formation without additives was determined in a blank experiment, the results of which served to correct the results of fermentation tests. In addition, a test with microcrystalline cellulose was conducted to monitor seed sludge activity. There was double determination for the blank and activity tests.

Biogas was collected in bags and analyzed for quantity and CH_4, CO_2, O_2 and H_2S content.

To monitor the fermentation process, pH and VOA/TIC were measured at the beginning and end of each test. VOA/TIC determination to instructions issued by Bundesforschungsanstalt für Landwirtschaft (Federal Agricultural Research Establishment) at Braunschweig involved titration of a centrifugate with sulfuric acid. The reading obtained for a normal fermentation process should not exceed 0.3.

Fermentation tests in the biogas lab were conducted under identical conditions at a temperature of 37°C and broken off after 30 days because biogas formation was severely reduced.

3 Results of fermentation tests

Prior to fermentation, the DM and DOM content of substrates had to be defined as a basis for measuring biogas yield. The former was determined by drying the sample at 110°C to constant weight, the latter by measuring ignition loss at 550°C.

In addition, COD was determined photometrically using a cuvette test to DIN 38409 H41 to measure degradation processes during fermentation.

The samples for COD determination were not identical to the ones used to measure DM and DOM. Characteristics of raw materials are shown in Table 1:

	DM content, %	DOM content relative to DM, %	COD, g/l
Untreated liquid pig manure			
Sample 1	3.28	62.6	65.70
Sample 2	3.50	63.3	46.80
Sample 3	3.29	63.9	64.89
Sample 4	3.30	64.4	57.46
Sample 5	3.40	62.4	62.10
Sample 6	3.40	62.4	-
Average	**3.36**	**63.15**	**59.39**
Treated liquid pig manure			
Sample 1	2.67	58.62	28.28
Sample 2	2.72	58.86	30.85
Sample 3	2.70	59.36	27.22
Sample 4	-	-	27.69
Sample 5	-	-	27.95
Sample 6	-	-	27.97
Average	**2.69**	**58.95**	**28.33**

Table 1: Raw materials analysis

The very low DOM content in the two raw materials was remarkable but had to be accepted in the absence of detailed information on the samples. To ensure accurate readings, DOM contents were determined for a variety of samples and must actually be assumed to be very low for the two samples in Table 1 because there is little fluctuation around the average.

COD differed widely for the two raw materials and, again, was determined for a number of samples to ensure accurate results. There was a confirmed trend in that the COD of treated material was approximately only half that of the untreated variety.

Input/output materials (fermentation residue) were the result of mixing the raw materials with seed sludge (1:1). Analytical values are summarized in Encl. 1.

Results of process control are shown in Encl. 2, with pH readings (7.3 – 7.9) consistently in the neutral and slightly basic range and VOA/TIC values of less than 0.3.

The amount and composition of biogas was determined with an instrument type Biogas 401 made by ADOS.

Fermentation tests gave the following readings (averages from three test batches each, corrected with blank test results):

Parameter	Unit	Untreated manure (without seed sludge)	Treated manure (without seed sludge)
Biogas volume	L_N	5.35	4.23
Biogas yield	L_N/kg DOM_{added}	549.19	544.23
Biogas yield	L_N/kg OS_{added}	11.13	9.19
Methane volume	L_N	3.41	2.63
Methane yield	**L_N/kg DOM_{added}**	**352.35**	**336.38**
Methane yield	L_N/kg OS_{added}	7.10	5.71
Average methane content	%	63.81	62.17
Average H_2S content	**ppm**	**483.33**	**92.81**
DOM degradation	%	30	26
COD reduction	%	22	16

Table 2: Results of fermentation tests

The following table gives individual readings for methane yield, other values for biogas formation and gas composition are listed in Encl. 3.

	Methane yield, L_N/kg DOM	
	Untreated liquid pig manure	**Treated liquid pig manure**
Test 1	327.11	373.81
Test 2	360.68	326.54
Test 3	369.26	308.79
Average	**352.35**	**336.38**
Fluctuation, L_N/kg DOM (approx.)	+/- 20	+/-30
Fluctuation, % (approx.)	6	9

Table 3: Individual readings for methane yield per fermenter

4 Summary, assessment

Readings can be interpreted as follows:

- The initial values for COD showed significant differences for the two samples.
  COD for the untreated sample was about twice that for the treated sample.

- Untreated liquid pig manure yielded 4.5% more methane than the treated variety. When allowance was made for ranges of fluctuation in individual test batches, the deviation was within the range of variation.

- The average methane content for the two samples (between 62 and 64%) was comparatively high.

- Conversion of organic compounds into methane reduced the DOM content in both samples.
  In keeping with greater biogas formation, the DOM degradation rate was higher for the untreated sample than for the treated variety.

- The conversion of easily degradable organic compounds into methane was also reflected in a lower COD after fermentation.
  As expected, COD reduction was greater in the untreated sample than in the treated variety.

- The hydrogen sulfide content in the untreated sample was comparatively high, which is not unusual in liquid pig manure.
  It was remarkable, however, that the H_2S reading for biogas from the treated sample was considerably less at only 20% of that found for the untreated sample. This trend has been confirmed throughout individual measurements.

- Organoleptic assessment of untreated and treated liquid pig manure by several test persons showed no clear difference between the two samples.
  Fermentation residues from the two samples were naturally less malodorous than the input material, but again no clear differences were found.

Summarizing, it may be said that treated liquid pig manure produced somewhat less methane than the untreated variety. The differences were, however, within the range of variation for individual batches so that more tests will be necessary to corroborate this statement. On the other hand, it was absolutely surprising to find a clearly lower hydrogen sulfide content in the treated sample. Since no chemical analyses showing sulfur content were available for the raw material samples, this is a phenomenon which can only be stated but not explained. Again, more extensive studies will be needed to clarify this effect. Confirmation of a significantly lower H_2S content in the biogas from treated liquid manure would be important and extremely interesting in terms of cost reduction for gas cleaning and/or ensuring a longer life for the gas engines of district heating power stations.

The present minibatch tests modeled on DIN 38414 used very small quantities in equilibrium conditions and are therefore not directly applicable to the dynamic conditions prevailing in practice.

VTI has facilities for enlarging the scale of testing in equilibrium conditions to a fermenting container capacity of 20 l, or conducting quasi-continuous fermentation trials on a 150-l scale under quasi-practical conditions. It is therefore recommended to confirm the trends observed and optimize fermentation, possibly in conjunction with co-substrates, by continuing trials on a 150-l scale under dynamic and quasi-practical conditions. Information on the test setup and other services available from VTI in the biogas sector are attached (see Encl. 4).

VTI stores the fermentation residues from trials for a period of 4 weeks and then discards them if they are not claimed by clients.

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Encl. 1

Analyses of input/output material (with seed sludge)

	Input material			Output material		
Material	**DM content, %**	**DOM content rel. to DM, %**	**COD, g/l**	**DM content, %**	**DOM content rel. to DM, %**	**COD, g/l**
Untreated liquid pig manure (+ seed sludge)						
Sample 1	3.39	58.77	43.06	2.88	54.31	23.17
Sample 2	3.26	59.54	40.12	2.84	54.26	27.96
Sample 3	3.26	59.35	41.80	2.85	54.73	25.47
Average	**3.30**	**59.22**	**41.66**	**2.86**	**54.43**	**25.53**
Treated liquid pig manure (+ seed sludge)						
Sample 1	3.08	57.80	37.80	2.68	54.78	26.95
Sample 2	3.02	57.94	40.60	2.71	54.22	22.46
Sample 3	3.12	58.82	38.31	2.71	54.25	24.96
Average	**3.07**	**58.19**	**38.90**	**2.70**	**54.77**	**24.79**

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Encl. 2

Process monitoring results

Fermenting untreated liquid pig manure

	Batch	**pH**	**VOA/TIC**
Beginning of test	Sample 1	7.32	0.293
	Sample 2	7.34	0.284
	Sample 3	7.4	0.295
End of test	Sample 1	7.76	0.033
	Sample 2	7.76	0.053
	Sample 3	7.78	0.049

Fermenting treated liquid pig manure

	Batch	**pH**	**VOA/TIC**
Beginning of test	Sample 1	7.44	0.228
	Sample 2	7.57	0.221
	Sample 3	7.47	0.234
End of test	Sample 1	7.85	0.050
	Sample 2	7.89	0.062
	Sample 3	7.91	0.057

Biogas formation as a function of VOA/TIC

- VOA/TIC untreated
- Biogas volume (uncorrected) untreated
- VOA/TIC treated
- Biogas volume (uncorrected) treated

Probe - Sample
Beginn - Beginning
Ende - End

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Encl. 3

Individual fermentation test readings

Fermenting untreated liquid pig manure with seed sludge

Test days	Batch	O_2	CO_2	CH_4	H_2S	Volume
		% by vol.	% by vol.	% by vol.	ppm	L_N
	1	2.8	28	46	1,100	0.37
0 – 3	2	3.2	29	47	1,400	1.84
	3	2.9	27	51	910	1.55
	Average	**3.0**	**28**	**49**	**1,137**	**1.72**
	1	2.5	21	63	940	1.24
4 – 8	2	2.6	20	62	170	0.82
	3	1.6	22	66	580	1.49
	Average	**2.2**	**21**	**64**	**563**	**1.17**
	1	2.4	19	69	180	2.69
9 - 30	2	1.9	20	70	30	3.51
	3	1.7	20	70	60	3.07
	Average	**2.0**	**20**	**70**	**90**	**3.09**

Fermenting treated liquid pig manure with seed sludge

Test days	Batch	O_2	CO_2	CH_4	H_2S	Volume
		% by vol.	% by vol.	% by vol.	ppm	L_N
	1	0	33	45	0	1.11
0 – 3	2	4.9	26	41	490	1.62
	3	4.6	25	41	360	1.00
	Average	**3.2**	**28**	**42**	**283**	**1.25**
	1	3.8	20	56	180	0.81
4 – 8	2	2.8	22	61	140	0.86
	3	2.9	21	60	50	0.71
	Average	**3.2**	**21**	**59**	**123**	**0.79**
	1	0	21	71	0	3.20
9 - 30	2	2.5	19	67	0	2.49
	3	1.8	20	70	0	2.69
	Average	**1.4**	**20**	**69**	**0**	**2.82**

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Blank experiment gas formation (average)

Test days	Batch	O_2	CO_2	CH_4	H_2S	Volume
		% by vol.	% by vol.	% by vol.	ppm	L_N
30		3.4	16	51	0	1.26

Activity test

Test days	Gas formation rate GF_{21}	O_2	CO_2	CH_4	H_2S	Volume
	$L_N/kg_{DM, cellulose}$	% by vol.	% by vol.	% by vol.	ppm	L_N
21	633.3	3.9	23	43	90	1.9
21	966.7	3.7	24	42	70	2.9
Average	800.8	3.8	24	42.5	80	2.4

Activity test positive as biogas volume > 1.2 L_N or > 400 $L_N/kg_{cellulose}$