

Slutrapport

Djupströgödsel i gårdsbiogasanläggningar, sönderdelning och blandningsförhållanden

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Hushållnings sällskapet i Sjuhärad 2011



1 GENOMFÖRANDE

1.1 Personal och arbetsmetoder

Projektet initierades hösten 2010 av Hushållningssällskapet Sjuhärad, främst för att få tydligare värden på biogaspotentialer för djupströgödsel i förhållande till biogassatsningarna i Gäsene där ett biogasprojekt pågår, men också för att lära sig mera om den halmbaserade djupströgödseln som är ett vanligt substrat på Sjuhärads mjölkgårdar.

Gödseln som användes i batchförsöken kom från Gudmundstorps Gård som är en av gårdarna i projekt "Gäsene biogas" där en etablering av biogasproduktion för närvarande utreds. Karin Eliasson var projektledare i samverkan med Ilona Horwath. Batchförsöken genomfördes på uppdrag av Högskolan i Borås av Enikö Szabo som mycket noggrant och detaljerat rapporterat projektets resultat vilket ligger som bilaga till denna slutrapport.

1.2 Resultat

Projektets mål och syfte var att ge lantbrukare och rådgivare en struktur till att bedöma vilka parametrar som styr värdet av halmbaserad djupströgödsel i kontinuerliga biogasprocesser samt att utvärdera blandningsförhållanden för biogasprocesser avseende (VS/m³) för substratet nötflyt och djupströgödsel från mjölkgårdar i Gäsene.

Projektets mål och syfte anses vara uppfyllda för de parametrar som angivits i projektet. Utrötningsförsöken har tydligt visat på betydelsen av djupströgödseln möjligheter till utökad gasutbyte. Parametrar som **kol kvävekvot** och påbörjad **hydrolys** har en inverkan på resultatet. Resultaten visar på att **mängden djupströgödsel och blandningsförhållandena** (VS/m³) har en stor betydelse på biogasutbytet där 10-30% bättre resultat uppmättes i försöken. VS halten i de substratblandningar som hade högst andel djupströgödsel utgjorde 12,9 % och ca 15% TS vilket i sig möjliggör en **pumpbar** fraktion med viss spädning vilket också är en viktig parameter för teknisk utformning.

1.3 Aktiviteter

Projektets aktivitet har varit att genomföra batchförsök enligt bifogad försöksrapport "Methane production from mixtures of liquid manure and deep litter manure"

1.4 Tidsplan och budget

Projektets tidsplan och budget har följts såsom den angivits i projektplanen.



2 FORTSÄTTNING OCH DISKUSSION

Inblandning av djupströgödseln i kontinuerliga gårdsbiogasanläggningar innebär en möjlighet till förhöjd gasproduktion. Men beroende på hur biogasanläggningen är utformad kan resultatet bli olika. I försöken användes en simulering av blandningstank som värmdes till 37 C och leder till att hydrolyssteg startar. Denna höga temperatur är inte relevant i de biogasanläggningar som nu är i drift och har en blandningstank, där temperaturen oftast är lägre. Men försöken visar vikten av blandningstanken och att det i vissa fall kan vara intressant att använda den som ett hydrolyssteg (vilket är den ”riktiga” benämningen för en tvåstegsrötning, det vill säga att den första tanken verkligen fungerar som en hydrolystank).

Ett annat viktigt resultat, som också redovisas i tidigare försök (Eliasson, Halmbaserad djupströgödsel i kontinuerliga biogasprocesser på gårdsnivå, 2011) är att den biogaspotential som anges för gödselmedel i Substrathandboken (Carlsson & Udal, 2009) inte ska hanteras okritiskt. Vilket kan vara ett problem då den används för dimensionering och i rådgivning av biogasanläggningar. I substrathandboken beräknas biogasutbytet till 213 Nm³ CH₄/ton VS (Carlsson & Udal, 2009) och i detta experiment visas skillnader mellan 190 Nm³ CH₄/ton VS för den obehandlade flytgödseln till 280 Nm³ CH₄/ton VS för den förbehandlade flytgödseln vid 26 dagars uppehållstid, en skillnad på 35%. Tillexempel påverkar detta beräknade gasnivåer vilket i sin tur ofta ligger till grund för tillstånd m.m.

Vidare påverkar sönderdelningen resultatet vilket även det visat sig i tidigare studier. En del av detta arbete pågår i det försök med fastgödselinmatning som sker på Sötåsens biogasanläggning samt i förstudier genomförda i Skaraborgsgas (Eliasson, Djupströgödsel i kontinuerliga gårdsbiogasprocesser -Sönderdelningsutrustning och biogasutbyte, 2010).

Ytterligare studier inom djupströgödsel kan vara växtnäringsfrågorna, tillgången till mineraliserat kväve i förhållande till ej behandlad djupströ gödsel. En del av detta kan hanteras i projektet ”Utvärdering av gårdsbiogasanläggningar” där rötrest analyser genomförs. Även utsläppen av växthusgaser i samband med hantering av djupströgödsel är intressant.

Det som detta projekt och försök viktigast visar är att vi behöver mera kunskaper om teknik och dimensionering dels av sönderdelsutrustning innan matning men också för vilka substrat och blandningsförhållanden tvåstegsrötning (hydrolys) på gårdsanläggningar kan vara aktuella.

Resultaten av detta projekt kommer även att redovisas vid en workshop vid Sötåsens biogasanläggning den 27 oktober i samverkan med de två ovan nämnda projekten.

Slutligen vill jag rikta ett stort tack till Enikö Szabo och Ilona Horwath som varit med i utförandet av projektet.



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Methane production from mixtures of liquid manure and deep litter manure

Enikö Szabo



1. 1. Objective

The aim of this study was to determine the biogas yield and the methane potential attainable from different mixture ratios of liquid manure and deep litter manure.

Deep litter manure is manure mixed with straw or sawdust, with high TS content of above 20%. Deep litter manure represents a significant portion of manure produced in animal farming.

However, farm-scale biogas production in Sweden treats today in most cases liquid manure (with TS content of about 5-10%) within continuous processes. To make these processes economically more feasible, an improved methane yield is required, which can be achieved by operating the plants at higher solid levels. Deep litter manure is used today as fertilizer, when the straw content of the deep litter adds carbon to the soil and helps to maintain the humus content of arable land. On the other hand, some disadvantages occur by this type of utilization of deep litter manure, namely the great nitrogen losses resulting in a bad nitrogen economy for the farm.

It is therefore of high agricultural interest to examine the deep litter manure in biogas processes. It allows both a higher gas production and also a good treatment producing a fertilizer with better quality.



2. Materials and methods

2. 2.1. Experimental set-up

3. 2.1.1. Batch digestion

The experiments were carried out in 2000 ml glass bottles, under mesophilic conditions (37°C). The liquid volume was 500 ml (100ml substrate and 400 ml inoculum), with 1.5 % VS concentration (it means 7.5 g VS in 500 ml cultivation mixture). The feedstock material was cattle manure (the different mixtures of liquid manure and deep litter manure are presented in chapter 2.1.2.) The inoculum was obtained from a pilot-scale anaerobic biogas plant that treats cattle manure (Sötåsen, Sweden).

After the appropriate experimental setup each bottle was sealed with rubber plugs and aluminium screw-caps and then flushed with a gas mixture of N₂ (80%) and CO₂ (20%) to provide anaerobic conditions. To determine background gas production, blanks were also performed using 100 ml water and 400 ml inoculum as cultivation mixture. Each experimental setup was conducted in triplicates.

4. 2.1.2. Substrate mixtures

The substrate used in these experiments was cattle manure: liquid manure (slurry) was mixed with deep litter manure at three different ratios, there portions of liquid manure were 100%, 90% and 75%, respectively (Table 1).

Table 1. Composition of the manure-mixtures

	100% slurry	90% slurry	75% slurry
Liquid manure (grams)	1500	1350	1125
Deep litte rmanure (grams)	0	150	375



5. 2.1.3. Total solid, volatile solid and COD content

The total solid and volatile solid content of the inoculum and of the substrate-mixtures were determined and the data is presented in Table 2.



Table 2. TS and VS content of the inoculum and of the substrate

	inoculum	100% slurry	90% slurry	75% slurry
TS (%)	6.2	11.8	13.1	14.9
VS (%)	4.8	9.9	11.2	12.9

To achieve the 7.5 g VS / 100 g substrate the manure-mixtures were diluted as presented in Table 3.

Table 3. Dilution of the manure-mixtures

	100% slurry	90% slurry	75% slurry
Manure-mixture (grams)	750	750	750
Water (grams)	237	369	543

To model the conditions of the mixing tank (where the substrate is mixed before it is pumped in the main digester) the diluted manure-mixtures were stored in locked plastic bowls at 37°C for 3 days. The dissolved COD content of the mixtures was measured before and after this three-day long pretreatment period (Table 4.)

Table 4. Dissolved COD content (mg/L) before and after the 3-day long pretreatment period

	100% slurry	90% slurry	75% slurry
Before	25300	20700	15000
After	23300	25800	18000



6. 2.2. Analysis and calculations

7. 2.2.1. TS and VS measurement

Total solids (TS) and volatile solids (VS) content of the substrates and inoculums were determined, to be able to set the correct inoculum to substrate ratio in the reactors.

Total solids are by definition all solids present in the sample. It can be determined directly by drying a known amount of a sample in an oven at 105°C. First an empty evaporation dish (crucible) was dried at 105°C overnight, and then cooled down in a dessicator and measured precisely. Accurately measured amount (usually between 10-15 grams) of samples were filled in the evaporation dish and placed back to the oven at 105°C for 24 hours. During that time, all of the water has evaporated, and the dish together with the sample was taken out and cooled down in a dessicator. The weight of the dish plus the remaining solids from the sample could be then determined. Finally, the TS content can be calculated with the following equation:

$$TS(\%) = \frac{x_3 - x_1}{x_2} * 100$$

where x_1 is the weight of the dried (105°C) crucible,

x_2 is the amount of sample, and

x_3 is the weight of the dish together with the remaining solids after drying at 105°C.

Volatile solids correspond to the organic content of a sample and can be determined by measuring solids that can be removed by ignition of the dried sample at 550°C in a muffle furnace. The crucibles containing the dried samples were therefore placed into a furnace at 550°C for 4 hours after the determination of total solids. The samples were then cooled down in a dessicator and weighted. The VS content can be calculated with the following equation:

$$VS(\%) = \frac{(x_3 - x_1) - (x_4 - x_1)}{x_2} * 100$$

where x_1 is the weight of the crucible,



x_2 is the amount of sample,

x_3 is the weight of the dish plus the remaining solids after drying at 105°C, and

x_4 is the weight of the dish plus the remaining solids (ash) after ignition at 550°C.

8. 2.2.2. COD measurement

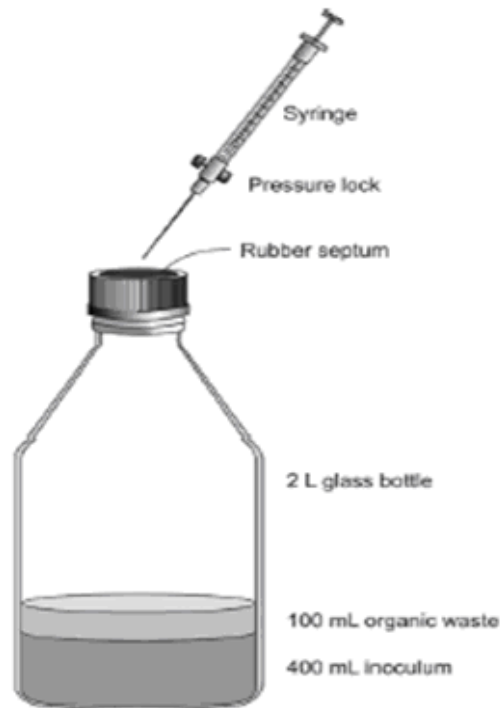
Soluble chemical oxygen demand (sCOD) was used to estimate the solubilized organic materials after the pretreatment, using a HACH apparatus with Digestion Solution sCOD vials (operating range 0-15000 mg COD/L) and equipped with a UV-Vis Spectrophotometer (HACH, Germany). The samples were previously centrifuged at 12500×g for 5 minutes, and the COD content of the supernatant was measured colorimetrically.

9. 2.2.3. Gas chromatography

To obtain the rate of biogas production during the digestion, gas samples of 100 µl were withdrawn regularly from the headspace of each batch reactor. Sampling was carried out with a 250 µl pressure-tight syringe (VICI, Precision Sampling Inc., USA), making it possible to take gas samples at the actual pressure (Figure 1.).

Figure 1. Batch reactor and sampling (adapted from Hansen et al 2004)





The amount of methane and carbon dioxide was then determined in each sample by direct measurement using a gas chromatograph (Varian 450-GC). The GC was equipped with a packed column (J&W Scientific GS-GasPro, 30 m x 0.320 mm, Agilent Technologies, USA) and a thermal conductivity detector (Varian) with inject temperature of 75°C. The carrier gas was nitrogen operated with a flow rate of 2 ml/min, the temperature of the oven was 100°C and that of the detector was 120°C.

Assuming ideal gas mixtures and using the ideal gas law, the methane and carbon dioxide content in the reactor headspace can be calculated using the data from the GC measurements without measuring the actual pressure in the bottle [Hansen et al. 2004]. Pure methane and carbon dioxide gas with known volume, temperature and pressure was used as standard in each measuring occasion. Then the amount of substance can be calculated with the equation below:



$$n_{\text{sample}} = \frac{A_{\text{sample}}}{A_{\text{standard}}} \times n_{\text{standard}} \times \frac{V_{\text{headspace}}}{V_{\text{standard}}}$$

where n_{sample} is the mole number of the sample,

A_{sample} is the area of the peak of the sample on the chromatogram

A_{standard} is the area of the peak of the standard

n_{standard} is the mole number of the standard

$V_{\text{headspace}}$ is the volume of the headspace in the reactor

V_{standard} is the volume of the standard injected (100 μl)

Excess gas was removed to avoid pressure higher than 2 bar, directly after sampling, followed by a second gas sampling and GC-measurement. The amount of gas produced between two subsequent sampling was calculated from the difference of the amount of the gas determined after releasing the overpressure and the amount of gas determined at next sampling time before the release.

All the results of methane and carbon dioxide volumes are presented at conditions of 101325 Pa and 25°C.

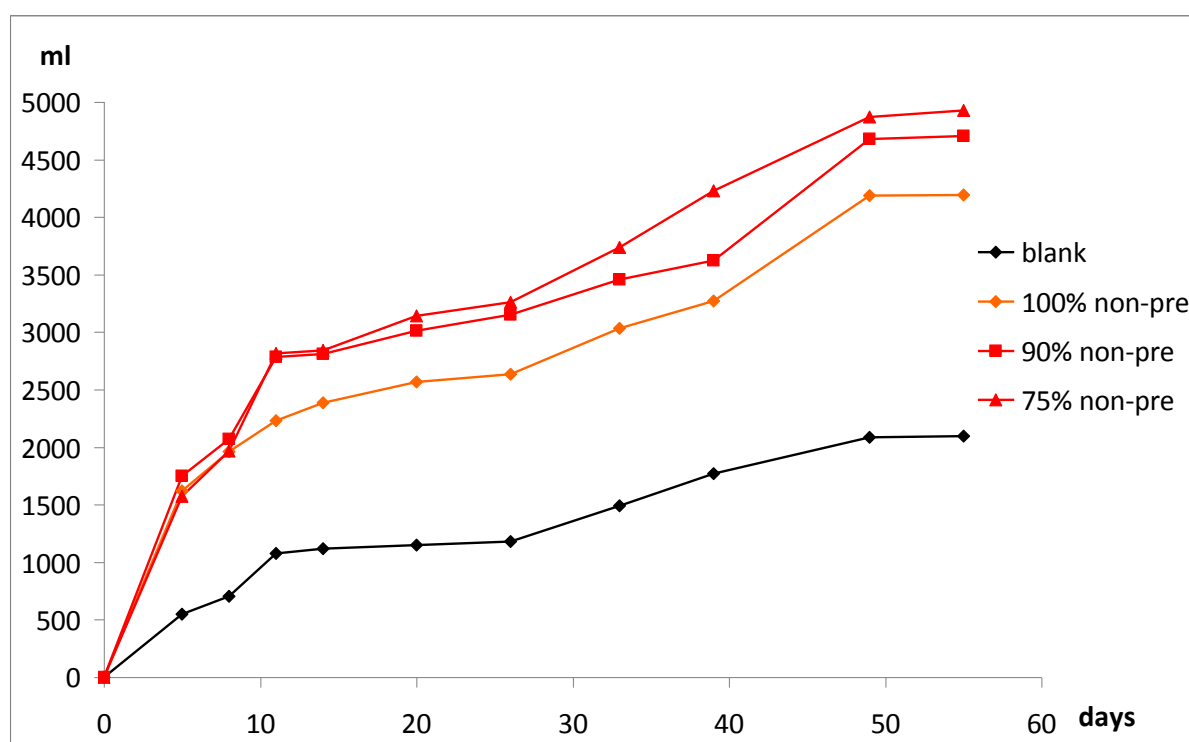


10. 3. Results and discussion

11. 3.1. Effect of the deep litter manure

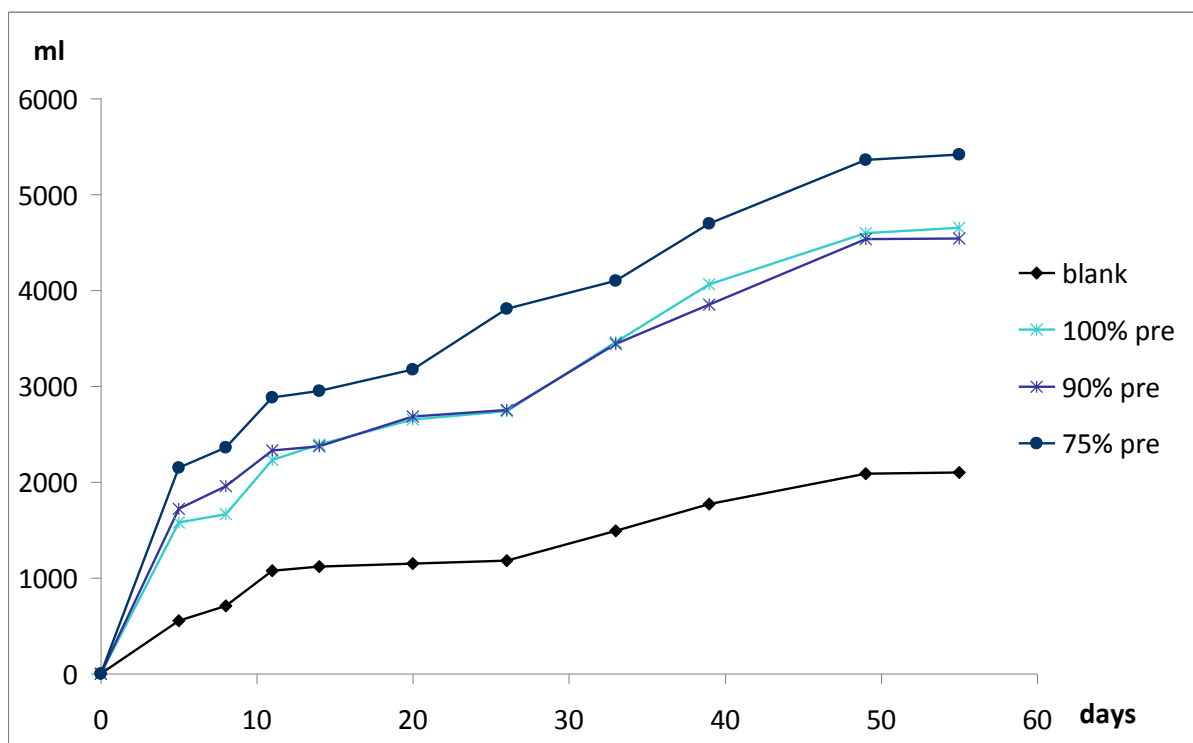
Figure 1 shows the results obtained from samples with no pretreatment (no „mixing tank”). This is the case when the deep litter manure is directly screwed into the main digester, and it is mixed with the liquid manure inside the main reactor. The results show that the addition of deep litter manure has no inhibitory effects on the biogas process. There were higher methane yields, corresponding to an increase with 11 and 29%, observed, when mixing deep litter manure of 10 and 25%, respectively, with liquid manure compared with digesting pure liquid manure. This can be explained by achieving a better carbon to nitrogen ratio in the substrate as a result of the addition of carbon rich deep litter manure, since the nitrogen content in the liquid manure is too high.

Fig. 2. Methane yields (ml) of the non-pretreated manure mixtures (averages of the triplets)



The second three triplets (Fig.3) model the case where deep litter manure is mixed with the liquid manure in a mixing tank prior to pumping the mixture into a digester. The retention time in the mixing tank is set to 3 days. In this case, addition of low amount of deep litter manure (10%) did not result in higher methane yield compared to that of the pure liquid manure. However, addition of higher amount, i.e. 25% of deep litter manure was admixed, resulted in an increased methane yield (39% after 26 days and 16% after 39 days of incubation).

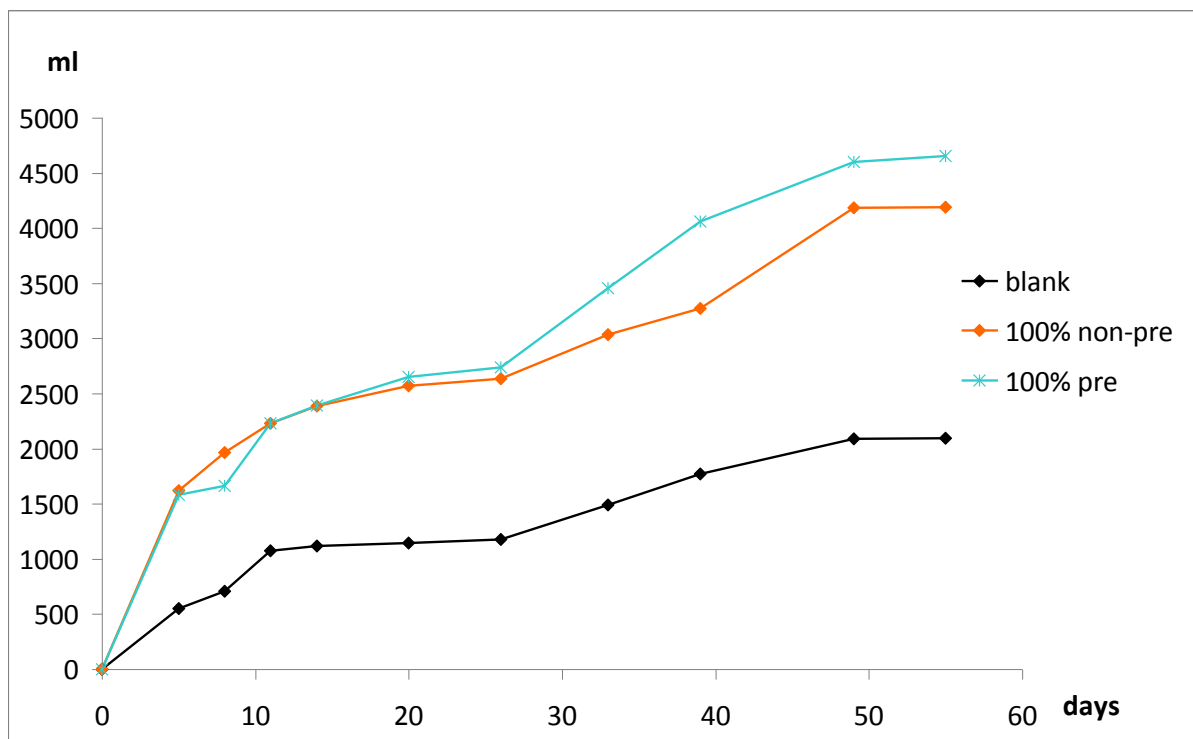
Fig. 3. Methane yields (ml) of the pretreated manure mixtures (averages of the triplets)



12. 3.2. Effect of the three-day long pretreatment period

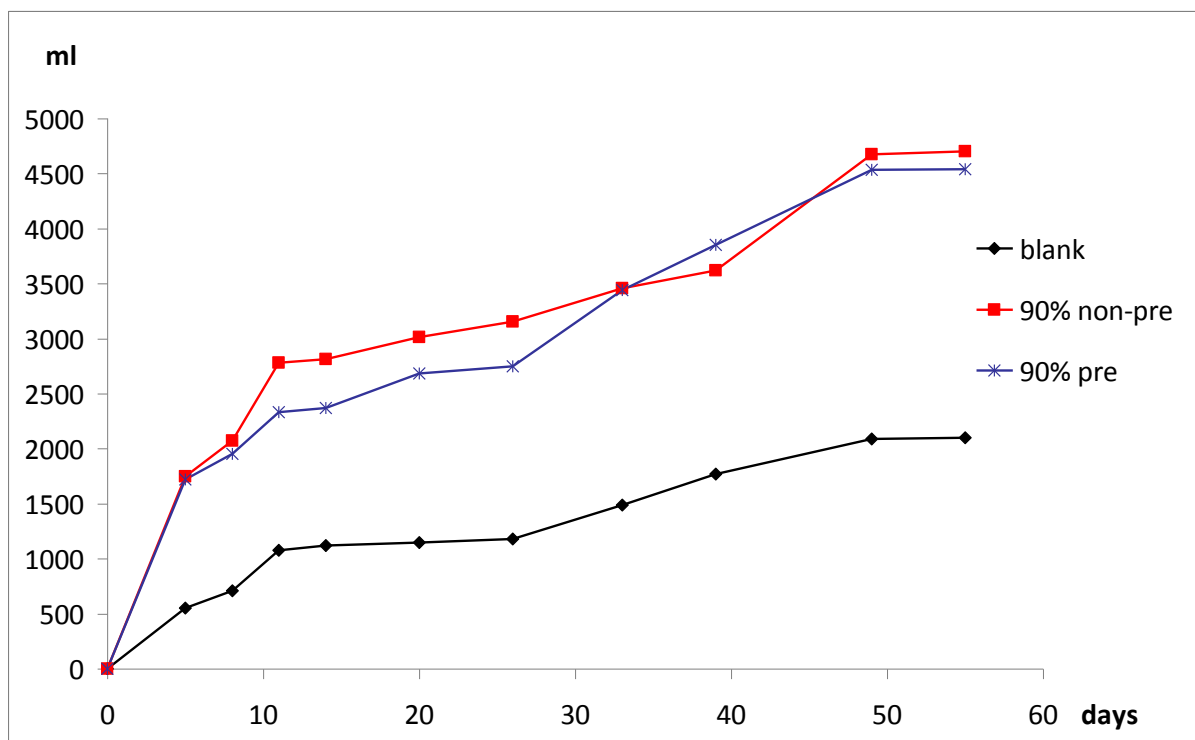
The methane yields achieved from the pure liquid manure with and without pretreatment are shown on Fig. 4. In case of 100% liquid manure the pretreatment has no significant effect on the biogas yield. The reason for this might be that the liquid manure is already easily degradable, there are no components that would require hydrolysis to make them soluble during the pretreatment. This is in accordance with the results of the COD measurements, there the sCOD values of the samples were about the same both prior and after the pretreatment (Table 4).

Fig. 4. Methane yields (ml) of the 100% liquid manure with and without pretreatment (averages of the triplets)



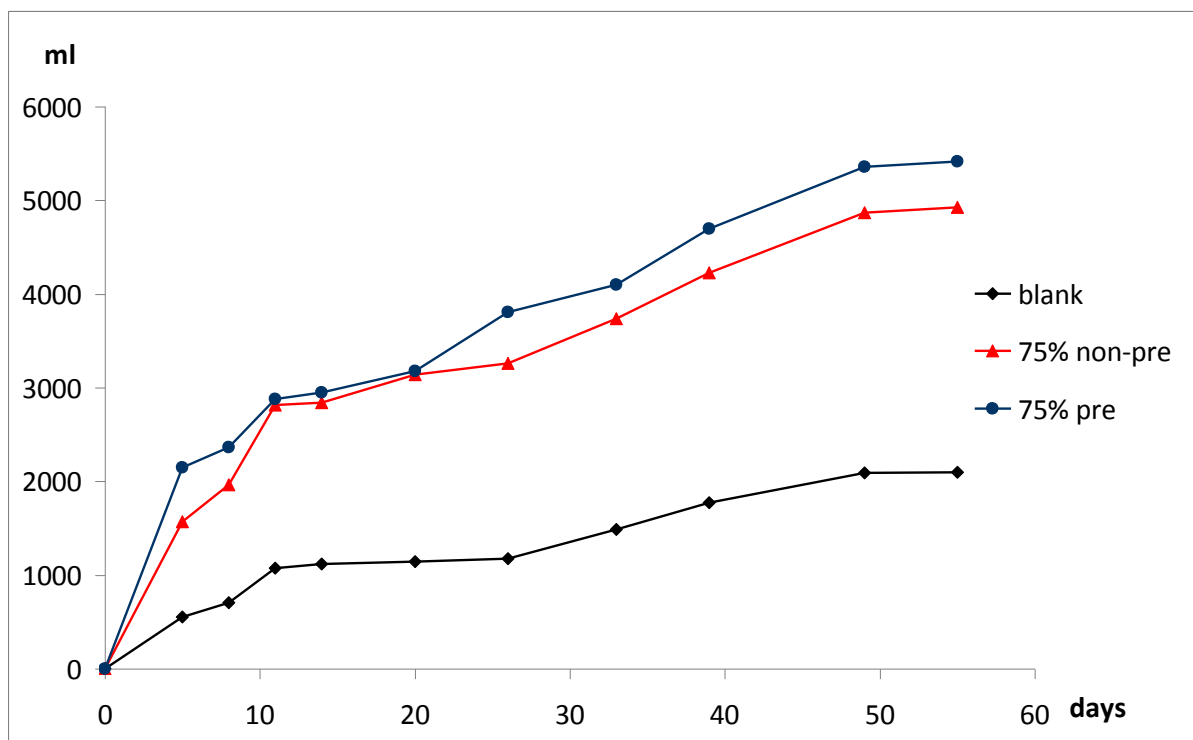
The methane yields achieved from the mixture of 90% liquid manure and 10% deep litter manure are shown on Fig. 5. In this case the pretreatment seemed to have a negative effect on the methane production during the first 30 days when pretreated samples gave less methane as the non-pretreated ones. The reason for this might be that the small amount of straw could be hydrolyzed during the pretreatment, resulting in too high dissolved substrate concentrations and consequently causing substrate inhibition. The COD measurements confirm this theory, showing an increase in the amount of dissolved COD content after the pretreatment (Table 4). However, towards the end of the digestion period of 55 days, same accumulated methane yields were obtained in both cases.

Fig. 5. Methane yields (ml) of the 90% liquid manure with and without pretreatment (averages of the triplets)



The methane yields achieved from the mixture of 75% liquid manure and 25% deep litter manure are shown on Fig. 6. In this case the pretreatment had a positive effect: pretreated samples gave more methane than the non-pretreated ones. Assumedly the 3-day pretreatment was not long enough to hydrolyze completely the straw content of this sample, therefore there was no inhibitory effect due to too high substrate levels. Moreover, the addition of straw increased the carbon to nitrogen ratio, which resulted in a more stable system with higher methane yield. The soluble COD measurements, can confirm this theory, showing that the sCOD content increased from 15000 mg/L to 18000 mg/L during the pretreatment (Table 4).

Fig. 6. Methane yields (ml) of the 75% liquid manure with and without pretreatment (averages of the triplets)



13. 3.3. Specific methane production rates

The specific accumulated methane production obtained after 55 days of incubation are shown in Table 5. It can be seen that the addition of deep litter manure without pretreatment resulted in increased methane production of 0,35 m³ CH₄ / kg VS and 0,38 m³ CH₄ / kg VS for mixtures containing 90% and 75% liquid manure, respectively, compared with 0,28 m³ CH₄ / kg VS production of the 100% liquid manure. The pretreatment resulted in higher methane productions in two cases i.e. mixtures containing 100% and 75% liquid manure. However, the pretreated sample of the mixture containing 90% slurry and 10% deep litter manure had slightly lower production rate during the first period of the digestion process, compared with the non-pretreated sample. Nevertheless the accumulated methane production in the end of the digestion of 55 days was the same for both samples (Table 5). The highest methane production rates were achieved with high amount (25%) of deep litter manure added, where 0,38 m³ CH₄ / kg VS was obtained from the non-pretreated sample and 0,45 m³ CH₄ / kg VS from the pretreated one (Table 5).

Table 5. Specific methane production rate (m³ CH₄ / kg VS) after 55 days of incubation

100% non-pretreated	0,28
90% non-pretreated	0,35
75% non-pretreated	0,38
100% pretreated	0,34
90% pretreated	0,34
75% pretreated	0,45



14. 4. Conclusion

It can be concluded that addition of deep litter manure to the liquid manure can increase the methane yield by 10-30%. If there is low amount of deep litter manure available (10% of the total amount of substrate) it is better to feed it directly into the main digester, to avoid hydrolysis in the mixing tank, which may result in substrate inhibition. If higher amount of deep litter manure can be utilized as substrate, it is better to feed it into a mixing tank and let it stay for a pretreatment for a couple of days, when hydrolysis of the solids can occur, increasing the biodegradability within the following digestion step .



15. Appendix

Methane yield (ml)

	0	5	8	11	14	20	26	33	39	49	55
blank	0	550	706	1077	1117	1147	1178	1490	1772	2088	2097
100% non-pretreated	0	1621	1964	2229	2386	2568	2637	3034	3271	4185	4192
90% non-pretreated	0	1748	2071	2783	2812	3012	3154	3457	3623	4677	4704
75% non-pretreated	0	1572	1965	2818	2844	3140	3263	3739	4227	4872	4925
100% pretreated	0	1580	1664	2231	2393	2649	2739	3458	4062	4599	4652
90% pretreated	0	1719	1955	2330	2372	2682	2750	3444	3851	4533	4538
75% pretreated	0	2149	2362	2880	2949	3175	3809	4101	4697	5359	5416

Carbon dioxide yield (ml)

	0	5	8	11	14	20	26	33	39	49	55
blank	0	666	727	1171	1194	1284	1259	1478	1832	1917	2312
100% non-pretreated	0	1307	1512	1737	1939	2148	2161	2311	2578	3169	3500
90% non-pretreated	0	1415	1549	2158	2209	2457	2508	2703	2901	3560	3940
75% non-pretreated	0	1357	1559	2241	2297	2579	2615	2859	3308	3591	3853
100% pretreated	0	1261	1268	1812	1938	2495	2647	3159	3657	3829	4119
90% pretreated	0	1273	1351	1740	1755	2116	2138	2591	3006	3315	3669
75% pretreated	0	1777	1857	2246	2300	2561	3080	3201	3744	4016	4262

