Influence of nutrient composition on methane production from animal manures and co-digestion with maize and glycerine

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Introduction

Biogas production from animal manures and co-digestion of energy crops and agricultural wastes is a very promising option to generate renewable energy in the Ukraine. Biogas plants require a targeted nutrient supply to make optimum use of animal manures, energy crops and agricultural wastes. The research project aimed at finding basic principles and data on the metabolic and energetic turnover during anaerobic digestion of animal manures, energy crops and agricultural wastes in agricultural biogas plants. The influence of animal diet and milk yield on the composition of cattle manure and on the methane yield through anaerobic digestion was investigated.

Materials and Methods

Substance and energy turnover during anaerobic digestion of cattle manure, energy crops and agricultural wastes were measured in eudiometer batch experiments at 40 °C that were conducted according to DIN 38 414 (1985, fig. 1). A detailed methodology description can be taken from AMON ET AL. (2003).
The Federal Research Institute for Agriculture in Alpine Regions (BAL Gumpenstein) conducted feeding trials with dairy cows at contrasting milk yields and feeding intensities. The animal diets are listed in table 1.

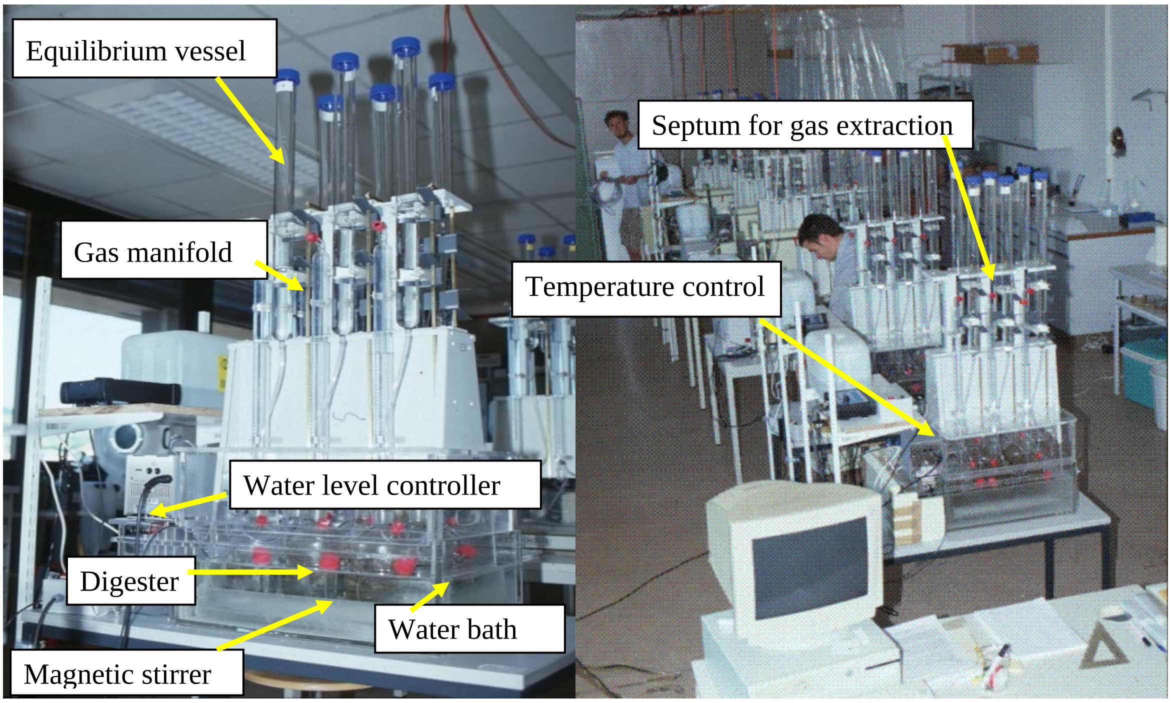

Fig 1. *Eudiometer batch equipment*

Table 1. *Diet and milk yield of dairy cows and other cattle that delivered the manure for the digestion experiments*

Treatment	Description	concentrate [kg DM]	hay [kg DM]	grass silage [kg DM]	maize silage [kg DM]	milk yield/ consumption [l day^{-1}]
Dairy_1	dairy cow	0	5.2	10.4	0	11.2
Dairy_2	dairy cow	0	5.4	6.4	5.8	11.2
Dairy_3	dairy cow	4.6	4.0	4.8	5.2	17.6
Dairy_4	dairy cow	5.8	5.0	10.0	0	16.0
Dairy_5	dairy cow	11.0	3.2	3.8	3.6	29.2
Dairy_6	dairy cow	10.0	3.0	6.2	0	29.2
Ox_1	ox young	0.9	0.8	5.0	0	0
Ox_2	ox old	1.3	1.5	9.0	0	0
Bulls_1	fattening bull	2.3	0	6.5	4.5	0
Bulls_2	fattening bull	1.0	1.0	0	7.0	0
Calf_1	calf young	0.4	1.0	0.5	0.5	max. 8 l
Calf_2	calf up to 200kg	1.3	2.0	1.0	1.0	0
Y.Cattle	young cattle	0.0	2.0	4.0	0	
Heifers	heifers	0.4	5.0	3.0	0	0
S.Cow	suckler cow	1.0	6.5	6.5	0	0

To explore the influence of co-digestion of glycerine with energy crops and pig manure on the methane yield, a basic mixture (BM) was digested that consisted of 31 % fresh masse (*FM*) maize silage, 15 % (*FM*) corn maize and

54 % (*FM*) swine manure. To this basic mixture 3, 6, 8 and 15 % (*FM*) of glycerine were added. Raw glycerine was supplied by the “Energy and Protein Supply Company South Styria” (SEEG). The chemical composition of the glycerine was analysed by MITTELBACH (2000).

Results and Discussion

Dairy cow manure

Table 2 gives the nutrient composition of the contrasting dairy cow manures: pH, dry matter (DM), crude protein (XP), crude fibre (XF), cellulose (Cel), hemi-cellulose (HCel), lignin (ADL), crude fat (XL), ash (XA), gross energy (GE). Biogas and methane yield per norm litre of volatile solids are listed as well.

Table 2. *Composition of dairy cow manures and specific biogas and methane yield*

composition of dairy cow manure [g (kg DM)$^{-1}$]											gas yield [Nl (kg VS)$^{-1}$]	
treatment	pH	DM	XP	XF	Cel	HCel	ADL	XL	XA	GE [MJ]	biogas	methane
Dairy_1	6.95	143.7	162.6	265.9	194.7	144.0	162.1	46.4	157.1	15.8	208.2	136.5
Dairy_2	6.79	128.8	154.3	265.8	227.3	175.9	128.2	34.5	155.0	17.3	213.1	131.8
Dairy_3	6.60	135.0	156.6	310.1	250.8	190.3	124.7	23.8	131.7	14.6	245.8	166.3
Dairy_4	6.60	159.6	150.6	279.5	164.1	187.9	183.3	29.1	162.8	19.3	222.5	143.1
Dairy_5	6.70	148.5	180.2	273.3	161.8	208.7	190.4	28.5	148.4	15.6	238.9	125.5
Dairy_6	6.66	157.3	296.5	248.5	210.1	195.5	121.7	30.3	167.8	16.8	267.7	159.2

The dairy cows of the treatments *dairy_1* and *dairy_2* had a low milk yield, *dairy_3* and *dairy_4* had a medium milk yield and *dairy_5* and *dairy_*6 had a high milk yield. In each level of intensity, manures with contrasting crude protein levels were produced. The manures with the higher crude protein levels (*dairy_1, 3, and 6*) gave higher methane yields during anaerobic digestion.
Lignin in the manure reduced the specific methane yield. The higher the feeding intensity and the milk yield, the greater was the reduction in methane yield through an increase in lignin content.

Manure of the treatment *dairy_3* was received from cows with medium milk yield that were fed a well balanced feeding ration. Forage consisted of hay, grass silage and maize silage. Concentrate was supplemented according to the cows` requirements. Manure of the treatment *dairy_3* produced the highest specific methane yield of 166.3 Nl CH_4 (kg VS)$^{-1}$ (fig. 2).

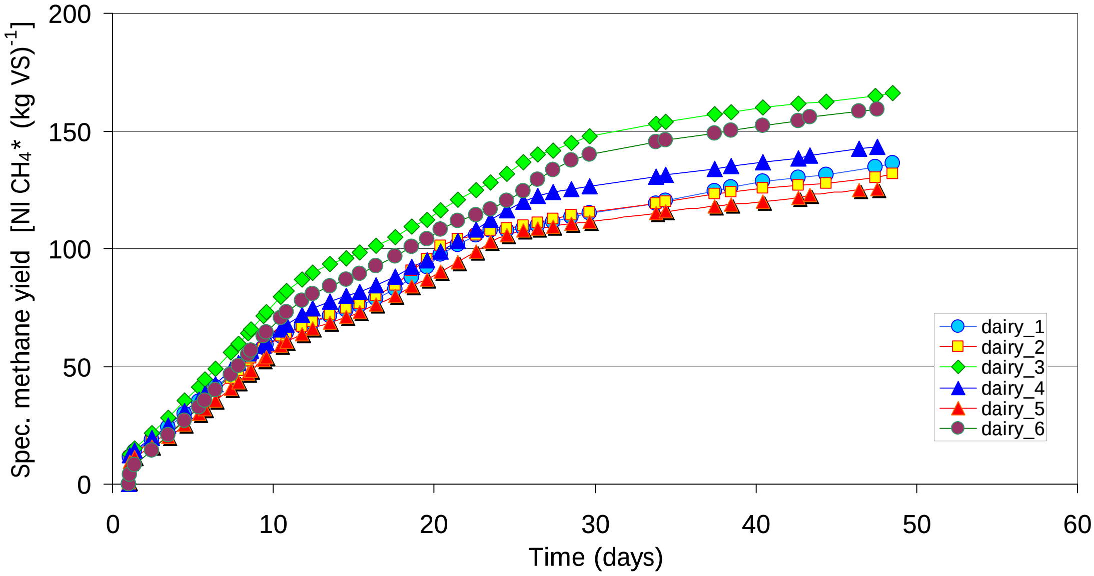

Fig. 2. *Cumulated specific methane yield of dairy manures and regression equations*

Cattle manure

Table 3 gives the nutrient composition of the contrasting cattle manures: pH, dry matter (DM), crude protein (XP), crude fibre (XF), cellulose (Cel), hemi-cellulose (HCel), lignin (ADL), crude fat (XL), ash (XA), gross energy (GE). Biogas and methane yield per norm litre of volatile solids are listed as well.

Table 3. *Composition of dairy cow manures and specific biogas and methane yield*

composition of dairy cow manure [g (kg DM)$^{-1}$]											gas yield [Nl (kg VS)$^{-1}$]	
treatment	pH	DM	XP	XF	Cel	Hcel	ADL	XL	XA	GE [MJ]	biogas	methane
Ox_1	6.50	127.84	193.6	219.9	211.5	121.9	119.0	44.5	173.5	18.6	268.6	153.9
Ox_2	7.05	134.12	155.9	230.0	204.7	118.1	143.3	33.2	179.0	16.6	207.0	112.9
Bulls_1	6.59	182.52	181.7	229.3	195.8	191.7	104.4	35.7	197.7	16.1	246.8	138.3
Bulls_2	6.30	174.64	129.6	316.7	288.7	232.6	118.4	23.9	101.9	16.3	192.6	110.4
Calf_1	6.70	203.52	182.8	244.3	216.0	190.5	106.3	35.4	125.3	17.3	208.4	113.4
Calf_2	6.40	184.32	148.8	244.7	223.0	181.3	107.2	37.8	154.0	17.6	230.7	131.4
Y.Catle	6.89	120.52	176.7	215.0	194.0	119.8	130.6	36.7	190.1	15.9	230.9	129.9
Heifers	6.80	150.82	135.5	226.8	215.5	157.6	104.8	32.9	219.5	18.4	297.3	172.2
S.Cow	7.15	162.04	144.9	286.3	193.3	180.3	158.4	36.1	192.1	16.7	167.1	98.7

As can be seen from figure 3, the treatment *Heifers* gave the highest methane yield. The slurry of the treatment *Heifers* had the highest gross energy (GE) content and the lowest lignin (ADL) content. The highest ADL content was observed with the treatment suckler cow (*S.Cow*). This was probably the reason for the low biogas and methane yield that was measured from this treatment. The treatments fattening bulls (*Ox_2*) and young cattle (*Y.Cattle*) confirm this assumption. Net total methane yield is likely to be limited by the ADL content in animal manures. When the ADL content is low, then the amount of other components as cellulose, crude protein (XP) and crude fat (XL) has a significant influence on the methane yield.

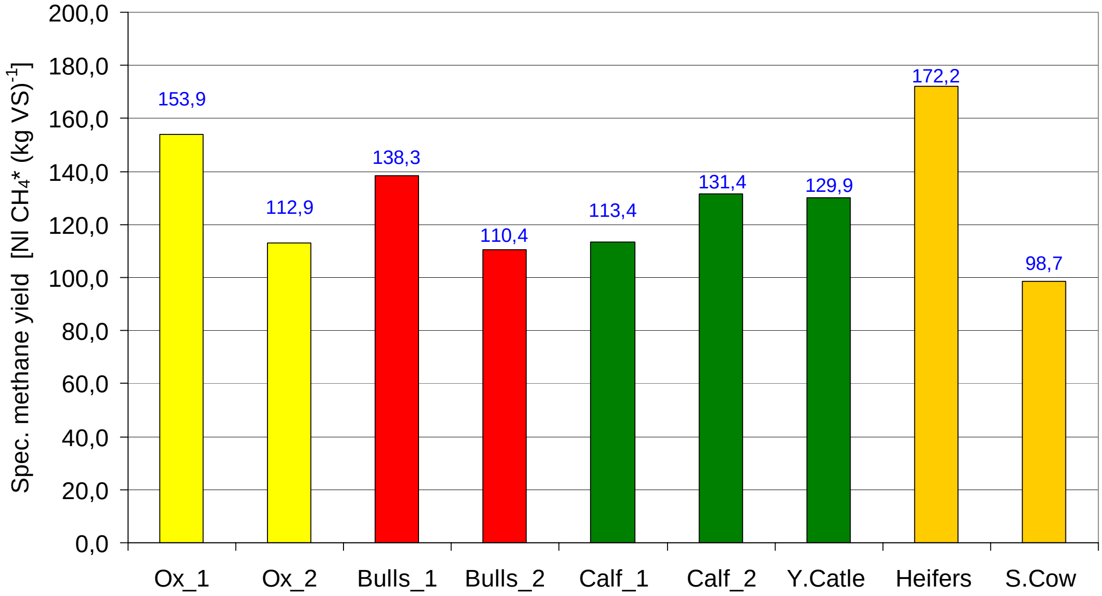

Fig. 3. *Cumulated specific methane yield of contrasting cattle manures*

Manure from young oxes (Ox_1) had 20 % more crude protein (XP), *c.* 20 % more crude fat (XL) and 20 % less ADL compared to manure from elder oxes (Ox_2). This resulted in an increase in methane production of *c.* 30 %. Younger animals excreted more nutrients then elder cattle.

The manures from the two fattening bull treatments (Bulls_1 and Bulls_2) yielded significantly different amounts of methane. This can be explained through the different feeding ratios that the bulls received. Bulls_1 were fed a well balanced diet. Bulls_2 received a non balanced, energy rich diet. The resulting difference in methane yield was more than 20 %.

Co-digestion of pig manure, maize and glycerine

Figure 4 shows methane yields resulting from various amounts of glycerine that were added to a basic mixture (BM) which included: 31 % (FM) of maize silage, 15 % (FM) of corn maize and 54 % (FM) of pig manure.
The line with "▲"on the Fig. 4 shows the methane yield from the "basic mixture" without glycerine addition. The methane yield amounted to 335 Nl CH_4 (kg VS)$^{-1}$.
Addition of 3 % (*FM*) of glycerine increased the methane yield by 20 % and achieved 411 Nl CH_4 (kg VS)$^{-1}$. The addition of 6 % (FM) of glycerine resulted in the highest methane yield of 440 Nl CH_4 (kg VS)$^{-1}$. Addition of more than 6 % glycerine to the basic mixture had only a low positive influence on the methane yield.
Addition of 15 % glycerine to the basic mixture decreased the methane yield to 400 Nl CH_4 (kg VS)$^{-1}$. At the same time, duration of fermentation increased. Methane formation at the start of the experiments was delayed.

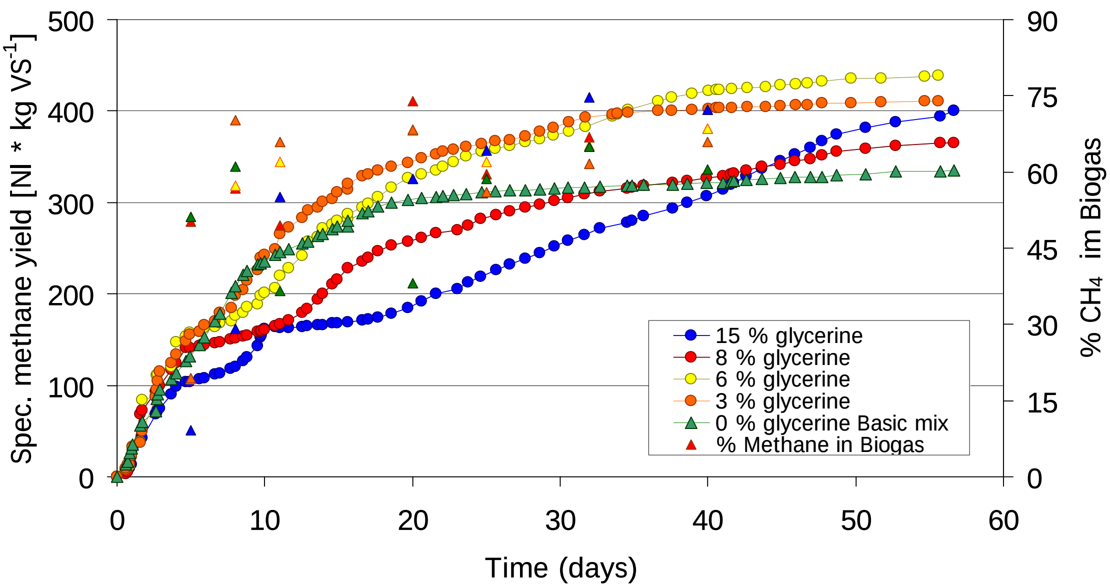

Fig. 4. *Cumulated specific methane yield of the basic mixture with various levels of glycerine addition*

To identify the possible causes of inhibition of methane formation the concentration of volatile fatty acids at the start, in the middle and at the end of the experiment was analysed (table 4). The volatile fatty acid concentration in the mixtures with more than 6 % glycerine increased rapidly at the beginning of the digestion. The concentration of acetic acid in the mixture with 15 % glycerine was 15 times higher than in the basic mixture without glycerine. But it still did not reach the level where the inhibition of methane formation begins. After Weiland 2001 the inhibition of methane formation could break out if more then 2000 mg/l of acetic acid in substrate is available. The pH-Values were in the optimum range (7.5-8pH) with all treatments as well. The amount of propionate acid in the mixtures with 15 % glycerine was 272 times higher than in the mixture without glycerine addition and 30 times higher than in the mixtures with 6 % glycerine. The presence of large amounts of propionate and butyric acids is the cause of inhibition of the methane formation. The large amount of propionate and butyric acids were build during decomposition of methanol. This hypothesis is confirmed through the comparatively low content of acetic acid.

Table. 4 *Content of acetic acid (HAC), propionate (PRO), i-butter- (i-BUT), n-butter- (n-BUT), i-valerian- (i-VAL), n-valerian (n-VAL) acid and acetic / propionate acid-ratio in the mixtures with 0, 3, 6, 8 and 15 % glycerine*

Treatment	HAC	PRO	i-BUT	n-BUT	i-VAL	n-VAL	HAC/PRO
BM + glycerine 15%	446.13	141.49	21.99	4.06	34.58	2.63	3.15
BM + glycerine 8%	45.03	2.15	0.00	0.24	0.60	1.16	20.94
BM + glycerine 6%	29.42	4.77	0.00	0.00	1.30	0.00	6.17
BM + glycerine 3%	28.81	0.87	0.00	0.00	0.00	0.63	33.25
BM + glycerine 0%	29.96	0.52	0.00	0.28	0.19	0.71	58.08

BM - basic mixture (in % FM): (31 % maize silage, 15 % corn maize and 54 % pig manure), acid concentrations are given in [mg l^{-1}]

Conclusions

- The animal diet, animal performance and the animals´ age have a great influence on the methane yield from cattle slurry. The slurry from young cattle’s has significantly higher methane potential as the slurry from older cattle’s.
- Methane production from manures received from cows with contrasting milk yields and feeding intensities differs considerably. The highest methane yield is achieved from dairy cows that have a medium milk yield and are fed a well balanced diet.
- Addition of 3 – 6 % glycerine to a mixture of pig manure and energy crops results in the highest methane yield. The maximum co-digestion effects were reached in the mixtures with addition of 3 and 6 % of glycerine which amounts between 18 and 22 % compare to the each separate digested substrate. This could greatly improve profitability of biogas production.

Acknowledgements

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