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Anaerobic co-digestion of poultry manure and waste kitchen oil

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1.0 Introduction

Agro – food industry is a huge producent of wastes that can be for energetic purposes used. Excrements of animals as poultry, swines, livestocks are one of them. Their energetic content is still sufficient for composting or anaerobic digestion. Annual animal excrement production in Slovak Republic is about 13 700 000 t what can be used for **1,03 TWh$_e$** (3,7.10^{15} J) electric energy and **2,8 PJ$_t$** (2,8.10^{15} J) heat energy production. For this aim 258 biogas stations are needed.

Tab.1Basic technologic parametres for different animal excrements anaerobic digestion [1]

Parameter	***Dimension***	***Swine***	***Beef***	***Poultry***
Minimal digestion time	*d*	*13 – 17*	*16 – 21*	*25 – 30*
Temperature	*^{0}C*	*38 – 42*	*38 – 42*	*38 – 42*
Maximal loading of biosludge	*kg VS/m^3/d*	*5*	*4*	*3*
Biogas production	*m^3/kg VS/d*	*0,35*	*0,20*	*0,40*

Very perspective method of agro – food wastes utilization is co-digestion, where different biodegradable wastes are together anaerobic treated. At choice of treated wastes many factors take into account is needed. The most important are price and access of wastes, their composition (organic mass and mineral content), methane yield from organic mass, price of needed digestion technology etc. Co-digestion has in comparison with single anaerobic fermentation several advantages.

- increased biogas production with single fermentation of wastes comparison
- minimal green house gases producing
- disposition of wastes, which occupy large planes
- contamination's restraint of ground waters
- destruction of pathogenous germs in raw waste
- smell removal
- digested waste is perfect bio-organic fertilizer

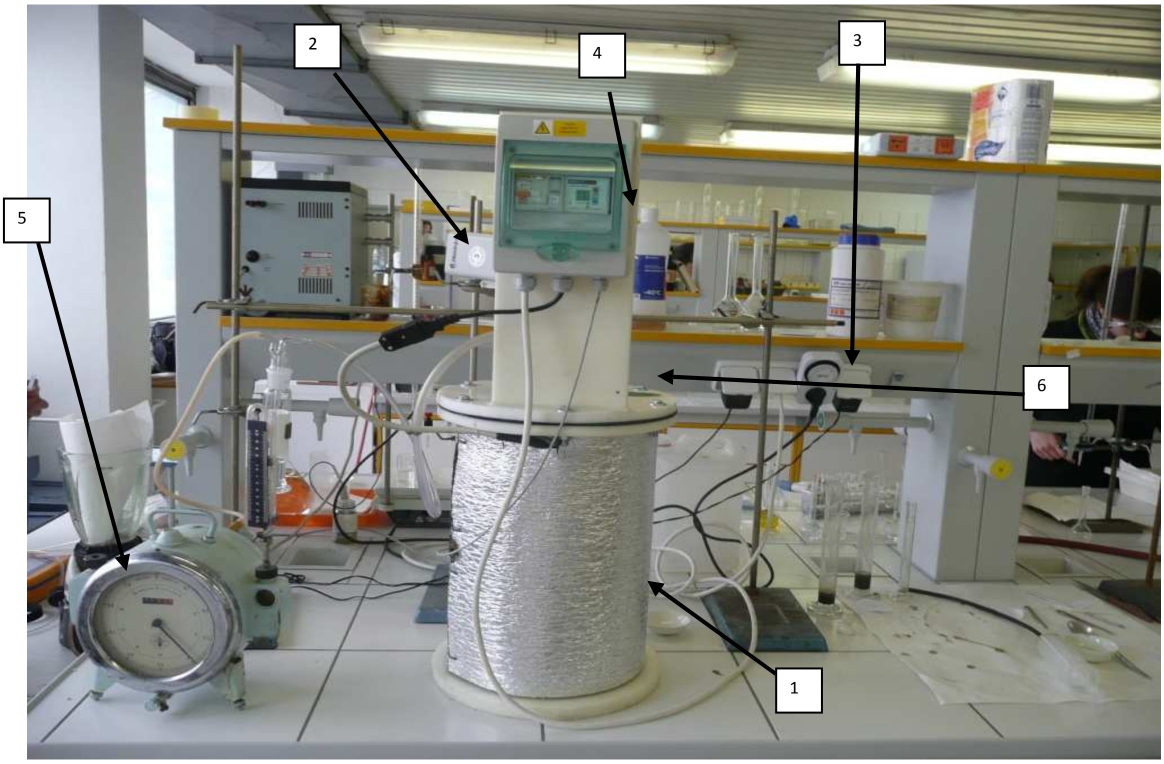
In this presented work poultry manure as a animal waste and waste kitchen oil as a restaurant waste were chosen. Poultry manure was chosen due to its biggest methane yield related to 1 kg volatile solids (VS) (Tab.1) and waste kitchen oil due to its high energetic content (Tab.3). This experiment is only part of big study where intensification methods to anaerobic process are aplicated.

2.0 Experimental

Aim of this work was monitoring of biogas production and its composition from agro-food wastes. The first of all, anaerobic digestion of poultry manure and wasted kitchen oil was investigated. Organic fraction ratio of poultry manure and wasted oil in this presented work was *9:1*.. Temperature value of this anaerobic process was maintaining in mesophilic scale i.e. 37^oC. As an anaerobic laboratory apparatus, semicontinuous reactor was used. Substrates feeding and excess sludge removal was every day and biosludge loading by volatile solids was inceasing gradually untill fermentation colaps . Periodically biogas composition by the mobile *IR spectrophotometer* was measured. As an anaerobic stabilized inoculum waste water sludge was used. Average input substrate's parameters, resp. inoculum like *COD*, *ammonia* concentration, *pH* and *organic fraction (OF)* is in table2.

Tab 2. Basic parameters of inocculum – stabilized waste water anaerobic sludge

COD [mg/l]	1370
NH_4^+ [mg/l]	231
VFA [mg/l]	369
X_c [g/l]	7,5
pH	7,8



Pic.1 1-isolated laboratory reactor, 2-stirrer with electromotor, 3-time switch, 4-electric heating with regulation, 5-drum gas gauge, 6-feeding open

Total reactor volume was approximately *17 l*, where anaerobic mixture occupied *15 l*. Therefore, remaining space about *2 l* as an improvised gasholder serviented. From there, excess gas through the bubbler to flow-meter was led away. Mixing of anaerobic mixture by propeller blender was secured. Process temperature was measured by thermometer, which the mixture's heating was regulating.

3. Results and discussions

3.1. Poultry manure – waste kitchen oil anaerobic digestion

Aim of this experiment was monitoring biogas production and its composition at graduated organic mass loading and also measuring of processing parameters that characterize anaerobic processes (pH, NH_4^+, VFA (volatile fat acids), X_c (dry mass content)). For anaerobic systems these parameters are indical and change one of them cause change the other. Experiment was running until system began be collapsing. Poultry manure and waste kitchen oil as a co-fermentation system was chosen.

Co-digestion started with initial organic mass (VS) loading on the level 0.3 kg VS/m^3/d and gradually was increased until final value 1.2 kg VS/m^3/d. Feeding by manure and oil was at every loading to constant VS ratio both substrates , it means 9:1. First **12 days** organic mass loading was **0.3 kg VS/m^3/d**, 13 – 23. day 0.5 **VS/m^3/d**, 24 – 120. day **0.7 VS/m^3/d**, 121 – 143. day **1 VS/m^3/d** and finally 144 – 305 day **1.2 VS/m^3/d**. In generally anaerobic system stabilization is long – time process that take several weeks till months. It depends on many factors (intensity of organic mass loading, temperature and composition of input substrates).

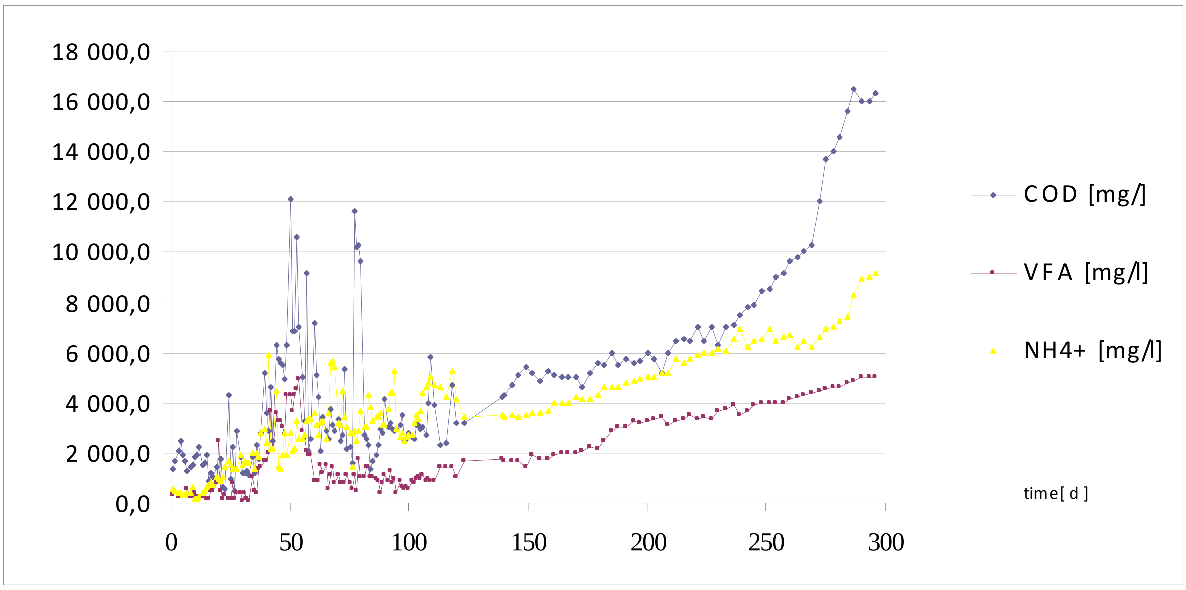


Fig.1 Anaerobic process parameters time development (COD, VFA, NH_4^+)

Organic mass loading is mostly expressed two ways – loading by volatile solids (VS) and loading by COD. Because different substrates has different organic mass composition, it means different COD related to 1 kg VS , better and for anaerobic processes more valuable parameter COD should be. Typical example studied co-digestion system poultry manure – waste kitchen oil was. Chemical oxygen demand (COD) for poultry manure was **0.9 g COD/kg VS**, eventually **2340 COD/kg VS** for waste kitchen oil (Tab. 3).

Poultry manure was periodically taken from near farm and subsequently stored in fridge. Waste kitchen oil was taken from university canteen and also stored in fridge. Average stored time for poultry manure was 2 – 3 weeks. If stored time overreached 3 weeks, manure started decompose. It was indicated by ammonia smell. If so particularly decomposed manure was dosing, always unstability in anaerobic process was happened. As can be shown in Fig.1, every dosing of particularly decompose manure caused increasing COD, NH_4^+ and VFA. After 125th co-digestion days stored time of manure was decreasing to 10 days. As a result was stabilizing of anaerobic process.

Tab.3 Organic mass and COD biosludge loading through the anaerobic digestion poultry manure - waste kitchen oil

Total organic mass loading [kg VS/m^3/d]	Organic mass loading - manure [kg VS/m^3/d]	Organic mass loading - oil [kg VS/m^3/d]	COD loading - manure [g COD/m^3/d]	COD loading - oil [g COD/m^3/d]
0,3	0,27	0,03	0,243	70,2
0,5	0,45	0,05	0,405	117
0,7	0,63	0,07	0,567	163,8
1	0,9	0,1	0,81	234
1,2	1,08	0,12	0,972	280,8
COD - manure	0,9	g COD/kg VS		
COD - oil	2340	g COD/kg VS		

Optimal pH value for anaerobic process is in interval 6.5 – 7.5. For holding this value existence of acid – basic buffer system is needed. In anaerobic system co-exist two basic buffer system (*ammoniac* $NH_3 + H^+ \leftrightarrow NH_4^+$ and *carbonate* $CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$). However if substrate with high total nitrogen content is digested (poultry manure), inhibition of anaerobic processes can happen. For example if swine manure is digested, upper limit free ammonia value is **1,1 g NH_3 – N/l.** Ammonia is generated from nitrogenous matters as proteins and urea [3]. Free ammonia and NH_4^+ are two main inorganic nitrogenous forms in aqueous solutions. Free ammonia toxicity is caused its freely membrane-permeability and consequently causing proton imbalance or potassium deficiency [4]. From all anaerobic types of microorganisms, the methanogens are the least tolerant and the most likely to cease growth due to ammonia inhibition [5]. There are many different maximum free ammonia concentrations for methanogens on literatures. For example , as ammonia concentrations were increased in the range of **4051–5734 mg NH_3–N/l**, acidogenic populations in the granular sludge were hardly affected while the methanogenic population lost **56.5%** of its activity [6]. In our present work , after **175th digestion day** free ammonia inhibition started be significant, if concentration **4000 mg NH_4^+/l** was overreached (Fig.1). According [11] free ammonia if concentration of NH_4^+ is known can be counted as follows: **$pH = (TAN/(1+10^{(pKa - pH)})$.**
In 175th day pH = 8,4, pKa = 8,95 [11] a therefore concentration of free ammonia **NH_3 = 1130 mg/l.**

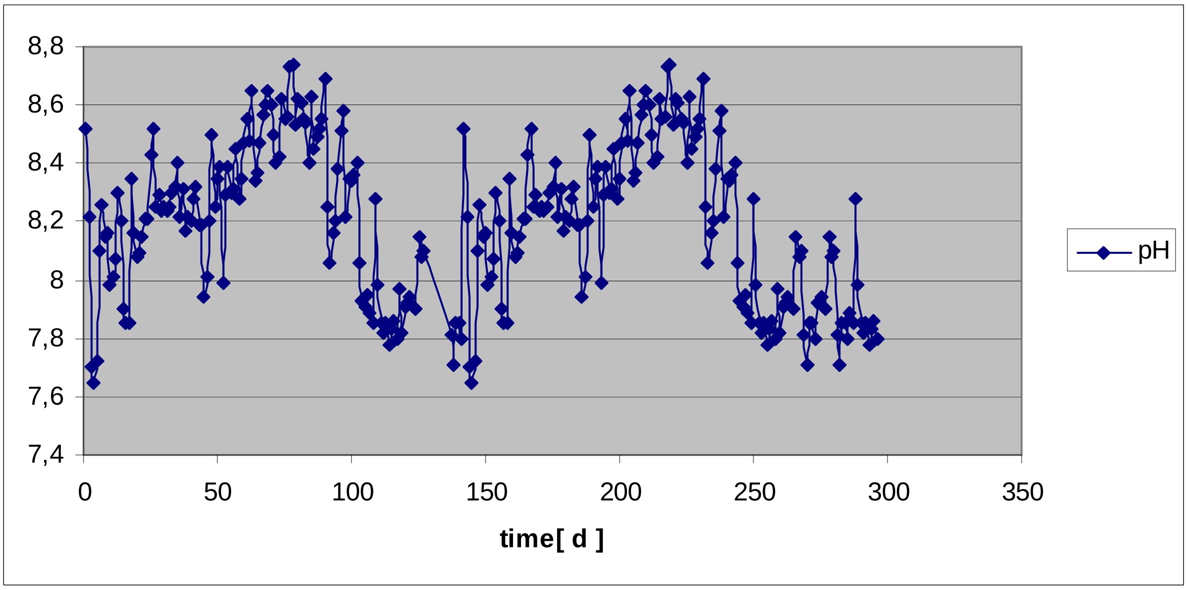


Fig.2 pH development during anaerobic digestion of poultry manure – waste kitchen oil

During treatment of waste containing high concentrations of TAN (total ammonia nitrogen), pH affects the growth of microorganisms as well as the composition of TAN [7]. Process instability due to ammonia often results in volatile fatty acids (VFA) accumulation, which again leads to a decrease in pH and thereby declining concentration of free ammonia FA. The interaction between FA, VFAs and pH may lead to an "inhibited steady state", a condition where the process is running stably but with a lower methane yield [8]. In our presented work this situation occurred after 175th co-digestion day, where pH value due to free ammonia started increase (Fig.2) and consequential rise of COD and VFA concentration (Fig.1).

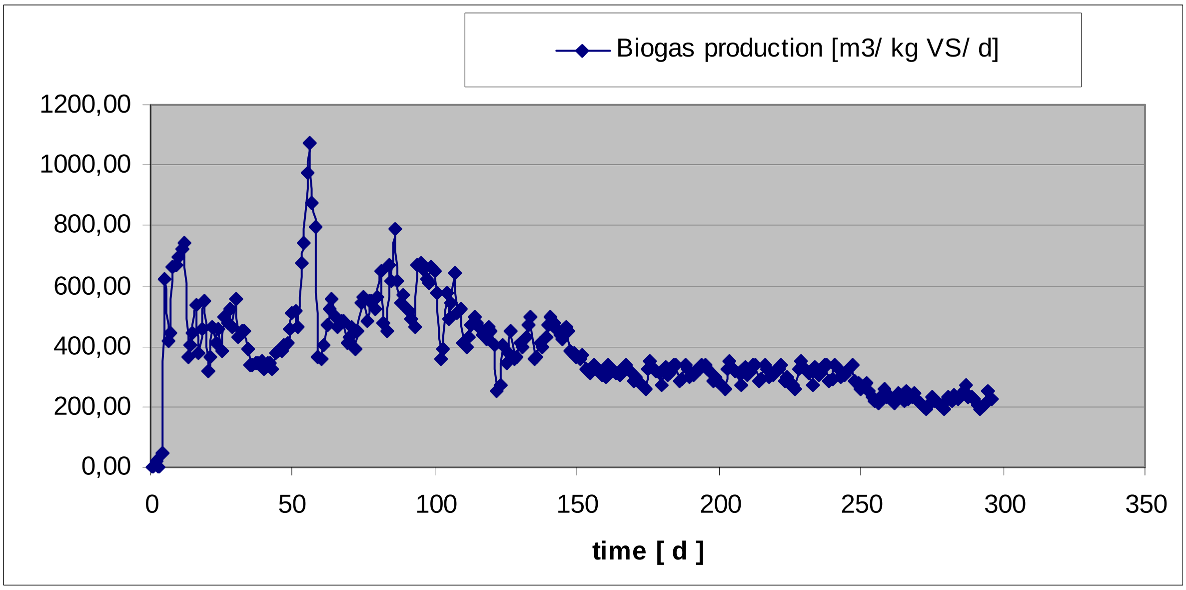


Fig.3 Biogas production related to 1 kg added VS

This free ammonia inhibition caused decrease of biogas production (Fig.3). System was pseudo – stable, it means that biogas production was stabilized and oscillated between **200 – 300 m^3/kg VS/d.** However in comparison with biogas production before inhibition (before 175th day , **400 - 600 m^3/kg VS/d**) it was only 50 % yield (Fig.3). Toxic influent of free ammonia caused also decrease in methane content in biogas (Tab.4). Therefore the most important if substrates with high nitrogenous matters are anaerobic digested (poultry manure) is decrease of free ammonia concentration. There are two main physical–chemical methods to free ammonia removal, air stripping and chemical precipitation [9]. For ammonia precipitation magnesium ammonium phosphate can be used. Another posibility is dilution of manure to a total solid level of **0.5–3.0%** . This approach is joined with economic unattractivity due to high waste volume [10].
Various types of inhibition can be counteracted by increasing the biomass retention in the reactor. It was found that the methane yield in a CSTR could be increased by switching off the stirrer half an hour before and after substrate addition [11]. Ammonia inhibition can be reduced using different types of inert material (clay, activated carbon, zeolite) or adding of ionic exchanger or adsorbants (natural zeolite, glauconite) [12]. Another parameter that can affects to free ammonia concentration temperature is. As is known , higher temperature has positive impact to microorganism's growth and metabolic rate, on the other side higher temperature leads to higher free ammonia concentration, thus to inhibition. Several authors have found that anaerobic treatment of waste with high ammonia is less stable in thermophilic conditions in comparison with mesophilic digestion [13]. It was discovered that some ions as Na^+, K^+, Ca^{2+} and K^+ have anti – inhibition effects, mainly joined with free ammonia inhibition.

Tab.4 Biogas composition (poultry manure – waste kitchen oil)

Digestion day	*14*	*22*	*34*	*41*	*57*	*71*	83	91	111	127	147	165	187	210	235	251	270	294
Organic mass loading [kg VS/m³/d]	0,3	0,5	0,7	0,7	0,7	0,7	0,7	0,7	0,7	1	1,2	1,2	1,2	1,2	1,2	1,2	1,2	1,2
componets	Biogas composition																	
CH_4 [%]	60,4	56,6	53,9	45,2	70,7	58,8	55,8	57,8	56,2	55,5	52,3	51,4	52,4	50,3	49,8	50,1	46,4	48,3
CO_2 [%]	33,3	36,8	40,1	48,7	24,4	33	38,9	37,1	37,5	37,6	40,1	41,6	43,1	45,3	44,3	42,3	47,3	45,9
O_2 [%]	1,1	1,4	1,3	1,6	0,9	1,2	1	1	1,1	1	0,9	1,1	1,2	1,1	1	0,9	1,1	1,2
H_2S [ppm]	104	137	740	1210	515	169	806	455	1069	1152	1005	1054	1003	989	1052	1035	989	1105
H_2 [ppm]	165	42	55	51	85	100	80	80	68	80	95	101	125	114	131	145	167	195

4.0 Conclusions

1. Co - digestion of poultry manure and waste kitchen oil was occurred. Initial organic mass loading was **0,3 kg VS/m³/d** and consequently gradually increased up to **1,2 VS/m³/d.** Organic mass ratio between poultry manure and waste kitchen oil was during all co-digestion on constant level 9:1.

2. It was found that high concentration of free ammonia has very negative influence to anaerobic process and for co-digestion of poultry manure – waste kitchen oil upper limit concentration of free ammonia on level **1130 mg NH_3/l** was detected.

3. Free ammonia inhibition caused decrease in biogas production, where from origin production before inhibition (up to 175th co-digestion day) **400 – 600 m³/kg VS/d** declined to **200 – 300 m³/kg VS/d** (after 175th co-digestion day)

4. It was discovered, that if storage time of poultry manure is very long (2 weeks and longer), its decomposition happened to ammonia production. It led to high concentration of ammonia in dosing batch and subsequently to inhibition of anaerobic process.

5. The most important if substrates with high nitrogen content are digested is reduce concentration of free ammonia. However maximum acceptable free ammonia concentration is for various anaerobic microorganisms different and for every substrate individual. Determination of this concentration by experiment is necessary

6. Free ammonia remove by different methods can be reached. The most important are air – striping and chemical precipitation by magnesium ammonium phosphate.

5.0 Literature

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