Feasibilities of anaerobic digestion of agricultural and food-processing industry wastes

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Keywords: co-fermentation, biogas, wastes, manure, agricultural, food-processing industry

Abstract
Permanent decrease of fossil fuels reserves like oil, natural gas and their very fast cost increase cause that in near future primary energetic carriers renewable sources will become. Problems with wastes removal are actual also. Agricultural plant and animal manufacturing as well as food industry produce enormous amounts of wastes qua cow, hen, pig, horse and sheep manures further straw, hewed grass, leaves and of course molasses, whey, beer yeast, distillery pot ale, etc. All these undesirable products contain still a big quantity of unused chemical energy. By operation of methane bacterium on these matters in oxygen absence biogas mixture very similar to natural gas is produced. For maximum achievement of anaerobic stabilization effect their joint digestion is necessary. This process is called co-fermentation alternatively co-digestion. Generally, co-fermentation substrates consist of solid or liquid animal excrements that have stability and buffering functions (mainly cow manure) and additives like phytoid and dendroid mass, kitchen and municipal organic waste otherwise waste from food-processing industry. Overall these additives are called co-substrates. Co-fermentation has in compare with individual digestion several advantages. It can be reached higher energetic yield, higher organic dry mass decay. Likewise important is ecological aspect. Annually energetic potential in Slovak republic expressed as biogas production, is 241 mil. m$^3$, for cow manure, 58 mil. m$^3$ for pig manure and cca 36 mil. m$^3$ for hen excrement, which means that, overall annual biogas production in our country 367 mil. m$^3$ can be. Aim of all research is monitoring of biogas production and its composition from agro-food wastes. The first of all, anaerobic digestion of hen’s manure and wasted kitchen oil is investigated. Organic fraction ratio of hen’s manure and wasted oil in this presented work is 9:1. Temperature value of this anaerobic process is maintaining in mesophilic range i.e. 37°C. In spite of that anaerobic co-digestion of hen’s manure – waste kitchen oil mixture is still running, it can be said, that ash content in hen’s manure and reactor’s loading have a big influence for methanogenesis.
1. Introduction

1.1 Anaerobic process

Anaerobic degradation, resp. anaerobic digestion or methane fermentation is a big group of biochemical reactions, which by the symbiotic operation of different bacterial cultures are performing. Biogas as a main product of this process is produced. In generally, except methane like a major compound many others gases are forming, for example $CO_2$, $H_2S$, $H_2$, $N_2$, $NH_3$ etc. Next product of anaerobic digestion is solid residue – digestat, as well as. Biological decomposition of organic substances in anaerobic conditions into four phases can be split.

- Hydrolysis – hydrolytic fracturing of polymer organic compounds (polysaccharides, proteins, lipids) to low molecular matters (mono-saccharides, amino-acids, fat acids and glycerol)
- Acidogenesis – degradation of hydrolytic’s products onto basic organic substances (alcohols, acids, $H_2$, $CO_2$). Finally, anaerobic environment is created.
- Acetogenesis – oxidation of fat organic acids into $CO_2$, $H_2$ a acetic acid
- Methanogenesis – ending phase of anaerobic digestion, when methane from accessible substrates (methanol, formic acid, $CO$, $CO_2$, $H_2$ and $CH_3COOH$) is generated.

1.2 Co-fermentation

Co-fermentation or co-digestion is joint liquidation of wastes, which from agro and food-processing industry are produced. The biggest benefits of co-fermentation anaerobic process in following points can be summarized.

- 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

According work [1], annually energetic potential in Slovak republic expressed as biogas production, is $241 \text{mil.} m^3$, for cow manure, $58 \text{mil.} m^3$ for pig manure and cca $36 \text{mil.} m^3$ for hen excrement. To correct prediction of biogas production from animal excrement was determined, many parameters known have to be, namely dry mass, organic fraction (OF), pH value, proteins, lipids, saccharides contents and others. There are some informations about animal excrements in tab.1, resp. amount beef-cattle, swines and poultry in Slovakia ,tab.2

<p>| Tab. 1 Nutritional composition of domestic animal excrement [2] |
|---------------------------------|-----------------|-----------------|-----------------|
| <strong>Substrate</strong> | <strong>Beef-cattle</strong> | <strong>Swine</strong> | <strong>Poultry</strong> |
| | <strong>Liquid manure</strong> | <strong>Solid manure</strong> | <strong>Liquid manure</strong> | <strong>Manure</strong> |
| Dry mass [%] | 7 - 17 | 25 - 40 | 2,5 - 13 | 20 - 34 |
| OF/dry mass [%] | 44 - 86 | 52 - 84 | 70 - 80 |</p>
<table>
<thead>
<tr>
<th>pH value</th>
<th>6.2 - 8</th>
<th>6.5 – 7.6</th>
<th>7 - 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw fibre in dry mass [%]</td>
<td>12 - 24</td>
<td>17</td>
<td>12</td>
</tr>
<tr>
<td>Raw fat in dry mass</td>
<td>2 -5</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td>Raw proteins in dry mass [%]</td>
<td>10 - 18</td>
<td>24</td>
<td>26</td>
</tr>
<tr>
<td>Raw hydrocarbons in dry mass [%]</td>
<td>20 - 43</td>
<td>32</td>
<td>27</td>
</tr>
<tr>
<td>Total nitrogen [g/l]</td>
<td>3.3 – 9.9</td>
<td>3.9 – 8.0</td>
<td>17</td>
</tr>
<tr>
<td>Biogas production [l/kg OF]</td>
<td>176 - 520</td>
<td>220 - 637</td>
<td>327 – 722</td>
</tr>
</tbody>
</table>

Tab. 2  Slovak republic – number of animal in agro industry, amount of excrement production [1]

<table>
<thead>
<tr>
<th>Region</th>
<th>Beef-cattle [t.y⁻¹]</th>
<th>Swine [t.y⁻¹]</th>
<th>Poultry [t.y⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bratislava</td>
<td>16 756</td>
<td>25 890</td>
<td>487 259</td>
</tr>
<tr>
<td></td>
<td>303 283</td>
<td>40 906</td>
<td>29 235</td>
</tr>
<tr>
<td>Trnava</td>
<td>87 240</td>
<td>278 275</td>
<td>2 101 932</td>
</tr>
<tr>
<td></td>
<td>1 579 044</td>
<td>439 675</td>
<td>126 115</td>
</tr>
<tr>
<td>Trenčín</td>
<td>53 285</td>
<td>190 876</td>
<td>2 332 641</td>
</tr>
<tr>
<td></td>
<td>964 458</td>
<td>139 958</td>
<td></td>
</tr>
<tr>
<td>Nitra</td>
<td>83 539</td>
<td>501 602</td>
<td>74 579</td>
</tr>
<tr>
<td></td>
<td>1 512 056</td>
<td>224 327</td>
<td></td>
</tr>
<tr>
<td>Žilina</td>
<td>72 516</td>
<td>57 986</td>
<td>74 579</td>
</tr>
<tr>
<td></td>
<td>1 312 540</td>
<td>224 327</td>
<td></td>
</tr>
<tr>
<td>Banská Bystrica</td>
<td>81 510</td>
<td>1 475 351</td>
<td>1 451 716</td>
</tr>
<tr>
<td></td>
<td>1 475 351</td>
<td>1 451 716</td>
<td>87 102</td>
</tr>
<tr>
<td>Prešov</td>
<td>81 139</td>
<td>132 283</td>
<td>70 983</td>
</tr>
<tr>
<td></td>
<td>1 469 616</td>
<td>1 183 055</td>
<td></td>
</tr>
<tr>
<td>Košice</td>
<td>51 904</td>
<td>167 936</td>
<td>92 741</td>
</tr>
<tr>
<td></td>
<td>939 462</td>
<td>154 589</td>
<td></td>
</tr>
<tr>
<td>Slovensko</td>
<td>527 889</td>
<td>1 108 265</td>
<td>845 040</td>
</tr>
<tr>
<td></td>
<td>9 555 790</td>
<td>1 751 056</td>
<td></td>
</tr>
</tbody>
</table>

2. Experimental

2.1 Overview

Aim of all research is monitoring of biogas production and its composition from agro-food wastes. The first of all, anaerobic digestion of hen’s manure and wasted kitchen oil is investigated. Organic fraction ratio of hen’s manure and wasted oil in this presented work is 9:1. Temperature value of this anaerobic process is maintaining in mesophilic scale i.e. 37°C. As an anaerobic laboratory apparatus, semicontinuous reactor is used. Substrates feeding and excess sludge removal is every day. Every week biogas composition by the mobile IR spectrophotometer is measured. As an anaerobic stabilized inoculum waste water sludge is used. Average input substrate’s parameters, resp. inoculum like COD, ammonia concentration, pH and organic fraction (OF) is in table 3.

Tab.3 Average input parameters of substrates and inocculum

<table>
<thead>
<tr>
<th>Hen’s manure</th>
<th>Wasted kitchen oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD [mgO₂/l]</td>
<td>Organic fraction [%]</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>2 340 000</td>
<td>99.98</td>
</tr>
</tbody>
</table>
Hen’s manure is sampled from poultry farm, resp. waste oil from university canteen. In this work, organic fraction (OF) ratio of waste kitchen oil and hen’s manure is still 1/9. Aim of all this research for different OF ratios using substrates (1/9-9/1), co-digestion process to study (biogas production, methane content). Reactor’s volume loading according anaerobic parameters (pH, VFA – volatile fat acids, NH$_4^+$) is changed.

2.2 Laboratory-scale reactor

![Image](image1.png)

Picture 1. Anaerobic semicontinuous laboratory-scale reactor
Total reactor volume is cca 17 l, where anaerobic mixture occupies 15 l. Therefore, remaining space cca 2 l as an improvised gasholder is servient. From there, excess gas through the bubbler to flow-meter is led away. Mixing of anaerobic mixture by propeller blender is secured. Process temperature is measured by thermometer, which the mixture’s heating is regulating.

3. Results and discussions
Because co-digestion of hen’s manure and waste kitchen oil is still not ended, results are published only for the first 45 days. Complete experimental datas on poster at SSCHE conference 2009 in Tatranské Matliare will be given.

![COD and NH₄⁺ concentration during anaerobic semicontinuous co-digestion](image1)

High COD and ammonia value in last 15 co-fermentation days by the change of the reactor’s loading can be caused. At 24th day, value of reactor’s loading from 0.5 to 0.7 kg OF/m²/d was changed. More or less, to 35th day anaerobic system was stabilized, after this day, system has started to oscillate, what it can be expressed as an instability system sign.

![pH development during anaerobic semicontinuous co-digestion](image2)

In the initial co-fermentation’s days, pH value was decreased. It is typical for the first (hydrolysis) and second (acidogenesis) phase, when fat acids from polymer substances (polysaccharides, lipids, proteins) are generated. However, optimal pH value for anaerobic digestion is in scale 6.2-7.8, high protein’s content in hen’s manure (high NH₄⁺ concentration) moved pH forward to higher value.
As it can be seemed, last and the slowest co-fermentation’s phase (methanogenesis) after 25th day was occured. Then pH value is stabilized but only to 35th day, when pH value is decreased, due to new reactor’s loading (0.5-0.7 kg OF/m^3/d).

At 20th day of anaerobic process, system to acetogenic phase was come in, high VFA (volatile fatty acids) concentration was rapidly decreased, VFA to H_2, CO_2 and CH_3COOH had been catabolized. Later, after 35th co-digestion’s day, VFA concentration was again increased, what can be caused by stabilization of anaerobic system after reactor’s loading changing (35th day).

Manure’s change at 24th and 36th and reactor’s loading change at 13th and 24th was occured. These changes has propably caused short-time decline in biogas production (Fig.4). Last days biogas generation is again increased, that means anaerobic system is to new conditions adapted. Next days will show if anaerobic process is stabilized or not (reactor’s volume loading rate 0.7 kg OF/m^3/d).
As it can be seemed (Tab.6), methane content in biogas still declines against other gas components like CO₂, H₂S. Increasing ash content in hen manure (Tab.4) is the most probably reason of this, when competitive inhibition to anaerobic process by the operation of sulfate- and nitrate-reducing community is occured. In this case, production toxic compounds than H₂S and NH₃ (Fig.1) is increasing and carbon substrates for NO₃⁻, resp. SO₄²⁻ reduction is consumed. This means that methanogenesis finally is reduced.

<table>
<thead>
<tr>
<th></th>
<th>10.th day of co-digestion</th>
<th>18.th day of co-digestion</th>
<th>30.th day of co-digestion</th>
<th>40.th day of co-digestion</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ [%]</td>
<td>60.4</td>
<td>56.6</td>
<td>53.9</td>
<td>45.2</td>
</tr>
<tr>
<td>CO₂ [%]</td>
<td>33.3</td>
<td>36.8</td>
<td>40.1</td>
<td>48.7</td>
</tr>
<tr>
<td>O₂ [%]</td>
<td>1.1</td>
<td>1.4</td>
<td>1.3</td>
<td>1.6</td>
</tr>
<tr>
<td>H₂S [ppm]</td>
<td>104</td>
<td>137</td>
<td>740</td>
<td>1210</td>
</tr>
<tr>
<td>H₂ [ppm]</td>
<td>165</td>
<td>42</td>
<td>55</td>
<td>51</td>
</tr>
</tbody>
</table>

### 4. Conclusions

In spite of that anaerobic co-digestion of hen’s manure – waste kitchen oil mixture is still running, it can be said, that ash content in hen’s manure and reactor’s loading have a big influence for methanogenesis. High ash proportion in poultry excrement leads to increased H₂S and NH₃ production (competitive inhibition) and concurrently to decrease of methane content in biogas. Likewise, changes in the reactor’s loading cause short-time changes in the anaerobic process (decrease of biogas production and VFA increase).

### 5. References

2. Schulz H., Eder B.: Bioplyn v praxi, HEL, Ostrava-Plesná, 28, 2004

### 6. Acknowledgements

The presented contribution was created as a part of project SK00023 financed by Norwegian Financial Mechanism, Financial Mechanism of EEA and the State Budget of the Slovak Republic.