The Influence of Straw Treatment by Acid Hydrolysis on Methane Production Efficiency of Agricultural Biogas Plant

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Abstract. Straw is largely produce raw material which can have many different uses. One of the most promising applications is the straw usage as substrate for biogas plant feeding. However, it has to be underlined that straw is not easily degradable material because of higher content of lignocellulose compounds. That is why in order to make straw more susceptible for anaerobic digestion process, it has to pass by some pre-treatments (mechanical, thermal, biological etc.). The aim of this study was to estimate the influence of straw treatment by acid hydrolysis (AH) on methane production efficiency in the anaerobic digestion process. In order to increase the digestibility of straw, whole material was also pre-treated by extrusion process. The methane productivity was tested under standard German methodology DIN 38 414/S8 in Ecotechnologies Laboratory (ET) at Institute of Biosystems Engineering. ET, with 250 different fermenters, is the biggest Polish biogas laboratory. The results have shown that acid hydrolysis (happened in pH <4.5 for 48 hours) strongly influenced on methane productivity growth. Extruded straw without acid hydrolysis produced 186.09 m³/Mg of Fresh Mass (224.23 m³/Mg of Volatile Solids) while straw after treatment with acid hydrolysis reached 248.17 Mg of FM (279.43 m³/Mg of VS). Result obtained after acid hydrolysis has showed the growth by 33.4% comparing to treatment without AH. We found also the growth of methane content in produced biogas. The biogas obtained from straw fermented without acid hydrolysis had 49.07% of CH₄ while after AH the CH₄ content reached 52% (almost 6% more). This result shows clearly that application of acid hydrolysis to real scale biogas plant can clearly decrease the annual consumption of straw reaching by app. 1500 Mg for the installation class 500 kW of electric power.

1. Introduction
In the last fifteen years, the agricultural biogas plant sector in Europe has recorded a spectacular increase in the number of installations to over 17,000 in 2017 [1]. Although, as a result of lowering the level of subsidies, the number of biogas plants emerging in Germany has ceased to increase sharply since 2014, other European markets such as Italy, Great Britain, France, and the Czech Republic are still recording strong increases in the number of new biogas plants [2]. It should be expected that as a result of the growing pressure to increase the efficiency of waste treatment and the reduction of greenhouse gases emissions from agriculture, the number of new biogas plants will continue to grow [3, 4]. Agricultural biogas plants should be treated not only as installations for the production of combined electricity and heat, but also (or, above all) as a place for environmentally friendly treatment of bio-waste [5, 6, 7].
1.1. Substrates in biogas plant
In Europe, there are two main scenarios for substrates used in biogas plants. The first of the variants is the use of field crops for biogas plants (e.g., maize silage), additionally the use of livestock faeces, mainly slurry and manure [8, 9, 10]. Such a nutritional scenario occurs primarily in countries with a high degree of co-financing for the prices of electricity produced in biogas plants, i.e., in Germany, Italy, the Czech Republic, Austria, and several others [11, 12]. A completely different scenario is found in Northern European countries (mainly Denmark and Sweden), where various types of bio-waste are used as the main substrates, including municipal waste [13]. Poland is a transitional market in this context. Some biogas plants still use maize silage as the main substrate to feed the fermentation process. However, due to the high cost of this substrate, hence, worse profitability of biogas plant operation, a significant number, and operators of installations are looking for alternative substrates [14]. The effect of this is the increasing use of various types of bio-waste [15]. The Ecotechnologies Laboratory at the Institute of Biosystems Engineering, cooperating with many Polish biogas plants, has so far examined nearly 2,500 samples of various types of organic substrates. This number shows in a very good way how strong is the determination of Polish companies looking for alternative fermentation substrates [16].

1.2. Lignocellulose biomass
Lignocellulosic biomass is produced in European agriculture in a considerable amount, mainly in the form of cereal, maize, rapeseed, lupine, sunflower straw, as well as biomass of energy crops, grasses, etc. [17]. In Poland, among over 30 million tonnes of cereal straw produced annually, almost half (12-15 million tons) could be used as a substrate for biogas plants. Besides, nearly 5 million tons of maize straw, whose fermentation can be extremely effective [18]. Lignocellulosic biomass usually has a high dry matter content and a very high content of organic matter (usually at 92-98%). These parameters mean that as a substrate, this material has a potentially very high methane production rate of 1 ton of fresh mass. Unfortunately, in practice — to achieve high productivity of lignocellulosic biomass, it is necessary to apply pretreatment [19]. There are several types of pretreatment (mechanical, thermal, pressure, ultrasonic, chemical, and biological), which differ in both efficiency and cost [20]. At the end of 2019, Poznan University of Life Sciences built an innovative biogas plant with a capacity of 500 kW, which uses a specialized Biotechnological Accelerator for microbiological pretreatment of substrates through so-called acid hydrolysis. This biogas plant is to be fed by animal manure (manure and liquid manure) and various types of straw. Thus, the aim of this study was to estimate the influence of straw treatment by acid hydrolysis (AH) on methane production efficiency in the anaerobic digestion process. In order to increase the digestibility of straw, whole material was also pre-treated by extrusion process.

2. Methodology
Cereal (wheat) straw collected at the experimental farm of the University of Life Sciences in Lublin (ULSL) was used for the research. The straw was extruded at the Department of Thermal Technology and Food Process Engineering, ULSL, for the initial destruction of lignocellulosic structures. Then the extruded straw samples were transported to Poznan University of Life Sciences (PULS) for biogas testing. The biogas and methane productivity was tested under standard German methodology DIN 38 414/S8 and VDI 4630 in Ecotechnologies Laboratory (ET) at Institute of Biosystems Engineering [21, 22]. ET, with 250 different fermenters, is the biggest Polish biogas laboratory. Straw samples were fermented in two variants:

Variant 1: extruded straw (ES) fermented in traditional technology, without the use of acid hydrolysis (AH);
Variant 2: extruded straw fermented after acid hydrolysis in pH=4.3 (ESaH), which was done for 48 hours before standard fermentation.

Before the fermentation process, straw samples were subjected to a standard procedure of analysis for dry matter content (Total solids – TS) according to the DIN EN 12880 standard and organic dry matter (Volatile Solids – VS) according to DIN EN 12879 standard. The fermentation test was made in the standard 2-litter reactors (Fig. 1).
The straws fermentation was proceed always in 3 repetitions, the samples were mixed with standard inoculum (parameters within DIN 38 414/S8) from agricultural biogas plant. However, the ESaH was mixed initially with inoculum from acid hydrolysis chamber from real-scale biogas plant, then after 48 hours of hydrolysis standard inoculum was added. Whole total volumes of gases produced from typical and acid inoculums (treated as controls) were calculated and reduced from finally obtained production for each material in order to receive “net” production from samples (without inoculum production).

3. Results
The analysis of substrates initial main parameters before the fermentation process are shown in Table. 1.

| Substrate     | Initial substrates parameters |
|---------------|------------------------------|
|               | TS [%]          | VS [%TS]       |
| ES (Variant 1) | 89.97           | 95.88          |
| ESaH (Variant 2) | 92.75       | 95.75          |

Both straws had high dry matter content (TS close to 90-93%) and contained very high percentage of organic matter (over 95%). This high dry mass and organic matter content can suggest potentially increased biogas and methane production. And this supposition was confirmed by the fermentation test results which showed the high dynamic of biogas and methane production in case of both materials (Fig. 2 and Fig. 3).
The results of daily measurements have shown that the most intensive biogas and methane production were notice during the first days of process. After first 3 days, the production decreased continuously in case of both substrates. The fermentation of straw after acid hydrolysis (ESaH) was 3 days longer in comparison to ES process. In order to have better graphical analysis, the figure with cumulative graphical analysis, the figure with cumulative methane production calculated from 1 Mg of organic dry mass (VS) was presented in Fig. 4.
The data showed on Fig. 4 clearly indicate more dynamic growth of CH₄ production in case of extruded straw after acid hydrolysis. It proves that acid hydrolysis pre-treatment can have positive effect on methane productivity. More complete data are presented in the Table. 2.

Table 2. Methane content and cumulated biogas and methane production from fermented substrates.

| Substrate    | Methane content [%] | Cumulated methane [m³/t FM] | Cumulated biogas [m³/t FM] | Cumulated methane [m³/t VS] | Cumulated biogas [m³/t VS] |
|--------------|---------------------|-----------------------------|----------------------------|-----------------------------|-----------------------------|
| ES (Variant 1) | 49.07               | 186.09                      | 379.25                     | 224.23                      | 439.67                      |
| ESaH (Variant 2) | 52.00               | 248.17                      | 477.22                     | 279.43                      | 537.37                      |

The data clearly show the significative methane production growth by 62.08 m³/Mg of fresh matter. This is 32.8% more methane comparing to straw without acid hydrolysis phase. Additionally, methane content in biogas from ESaH (52%) was almost 3 percentage points higher comparing to ES (49.07%). It has to be underlined that in case of both extruded straws the fermentation results (186 and 245 m³ CH₄ / Mg FM) were strongly better in case of the most popular substrate in Europe – maize silage (approx. 105 m³ CH₄ / Mg FM). This is very important information from economic point of view, because both materials (straw and maize silage) have similar price in Poland. So, from biogas plant operator’s point of view, it is more reasonable to use straws because their methane productivities are 1.8-2.4 times higher comparing to typically used maize silage. Based on simple calculation presented by Cieslik et al. [24], it can be assumed that for keeping continuous work (8500 h/a) of 500 kW of electric power, the amount of maize silage should be 10140 Mg, however 5720 Mg of extruded straw and only 4290 Mg of extruded straw after acid hydrolysis. This means financial savings (in the case of corn silage being replaced by straw) at a level 132-175 kEuro yearly.

4. Conclusions

Based on the presented studies, the following conclusions were created:

1. Wheat straw has good parameters for methane fermentation because of very high dry matter and organic matter content.
2. Extruded straw has almost 2-times higher methane productivity comparing to typical European substrate – maize silage.
3. Extruded straw passing by acid hydrolysis phase for 48 hours can increase the methane productivity by 32.8% (62.08 m³/Mg). The content of methane in biogas grows also almost 3 percentage points.
4. The obtained results show that maize silage replacement by extruded straw with addition of separated hydrolysis can give significative financial profits for biogas plant operators.

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**Acknowledgments**

The publication was co-financed within the framework of Ministry of Science and Higher Education programme as “Regional Initiative Excellence” in years 2019-2022, Project No. 005/RID/2018/19.