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# Anaerobic co-fermentation of molasses and oil with straw pellets

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**Abstract.** The average grain and straw production in Latvia is increasing in last decade. Straw is not always managed properly and its utilisation in biogas plants can be considered as an alternative. Straw is not the best feedstock for methane production, because it has high C/N ratio. Co-fermentation with other biomass with higher N content can improve the methane production. Purpose of investigation is to evaluate the wheat straw pellets biomass suitability for production of the methane and effect of its co-fermentation with molasses, fried sunflower oil and catalyst Metaferm. The anaerobic digestion process for biogas production was investigated in 0.75 L digesters, operated in batch mode at temperature 38 ± 1.0 °C. The average biogas yield per unit of dry organic matter added from digestion of wheat straw pellets was 0.540 L $g^{-1}_{DOM}$ and methane yield was 0.285 L $g^{-1}_{DOM}$. Average biogas yield from co-fermentation of wheat straw pellets and molasses was 0.777 L $g^{-1}_{DOM}$ and methane yield was 0.408 L $g^{-1}_{DOM}$. Average biogas yield from fermentation of wheat straw pellets with 1ml Metaferm was 0.692 L $g^{-1}_{DOM}$ and methane yield was 0.349 L $g^{-1}_{DOM}$. Average biogas yield from co-fermentation of wheat straw pellets and sunflowers oil was 1.041 L $g^{-1}_{DOM}$ and methane yield was 0.639 L $g^{-1}_{DOM}$. All investigated biomasses can be used for methane production.

**Key words:** anaerobic digestion, biogas, methane, molasses, sunflower oil, wheat straw pellets.

## INTRODUCTION

Agricultural production generates a lot of waste and residue, which would be a substantial biomass resource for biogas production. 59 biogas plants are running in Latvia, and different raw materials are utilised for methane production. One of the biomass most widely used by dairy farmers owing biogas plants is the maize silage, due to high biogas and methane volumes obtainable per unit of area (Dubrovskis & Adamovics, 2012). However, some farmers' organizations have recently been influenced by the Ministry of Agriculture in agreeing in repealing an excise tax relief on diesel sold for farmers for corn production. This government decision was based on the need to use the arable land for food production. The production of corn silage is an expensive technology and in situation, when excise tax relief is not more available for corn production, energy corn growing for biogas production turns unprofitable. Therefore, it is essential for biogas producers to find inexpensive raw biomasses capable to substitute corn in feedstock for biogas plants. A more cost effective raw material could be the straw, especially the cereals straw. Straw in Latvia is not used properly and part of straw is wasted in harvesting process or in biodegradation process during storage. Also, emissions of greenhouse gases ($CO_2$, $N_2O$, and others) ongoing from straw biomass left on the ground surface or during storage in heaps or bales should be considered. Especially high dry mass losses are observed from straw biomass if uncovered straw biomass is exposed to weather conditions. Low natural density of straw or straw bales increase the transport expenses so limiting, to a certain extent, the straw usage for biogas production.

There can be different ways in straw usage for the biogas production. Usually, straw is used in livestock barns and poultry houses as the litter, so forming the mixture with manure utilisable as cheap raw material in biogas plants. According to the literature, many researchers have obtained biogas from different straw materials (Table 1).

There are only a few studies in Latvia about the potential of biogas from different straw and grasslands. From the crushed and pre-soaked barley straw, a relatively good (0.296 L $g^{-1}_{DOM}$) methane yield was obtained, mainly due to the positive effect of pre–treatment (Dubrovskis & Adamovics, 2012). Also good (0.280 L $g^{-1}_{DOM}$) average specific methane yield was obtained from chopped barley (Dubrovskis et al., 2012).

**Table 1.** Biogas (methane) production from different straw biomass

| Raw material | Methane, $m^3$ $kg^{-1}_{DOM}$ | Methane content, % | Biogas, $m^3$ $kg^{-1}_{DOM}$ | Literature source |
|---|---|---|---|---|
| Wheat straw | | 58.0 | 0.342 | Angelidaki et al., 2009 |
| Flax straw | | 59.0 | 0.359 | Angelidaki et al., 2009 |
| Rice straw | 0.161 | 57.4 | | Leyrica et al., 1984 |
| Wheat straw 30 mm | | 50.0 | 0.306 | Baader et al., 1978 |
| Wheat straw 2 mm | | 51.0 | 0.343 | Baader et al., 1978 |
| Wheat straw | 0.189 | 51.0 | 0.370 | Becker et al., 2007 |
| Straw | | 52.0 | 0.388 | Cenian et al., 2012 |

In other countries straw is also used for biogas production. The relatively low yield of biogas (methane) from roughly chopped wheat straw substrate was 188.4

L·$kg^{-1}_{DOM}$ (78.4 L $kg^{-1}_{DOM}$). If the same wheat straw was pre-treated with NaOH, then better biogas (methane) yield of 353.2 L $kg^{-1}_{DOM}$ (165.90 L $kg_{DOM}^{-1}$) was observed. Hydrothermal treatment of the same straw resulted into specific biogas (methane) production yield 205.7 L $kg^{-1}_{DOM}$ (94.1 L $kg^{-1}_{DOM}$). Compared to untreated wheat straw, methane yield increases by 111.6% from straw treated with NaOH and by 20% from hydrothermally pre-treated straw (Chandr et al., 2012).

In Germany, FNR shows, that a specific biogas yield of 370 L $kg^{-1}_{DOM}$ is obtainable from wheat straw with methane content 51% in biogas (Becker et al., 2007).

In Denmark, at University of Arhus extensive studies were carried out on the use of the straw briquettes for biogas production. Laboratory studies show, that 250 $m^3$ of methane was obtained per ton of straw briquettes (Moller & Hansen, 2014). Studies show, that methane yield from the briquettes was higher by 19% compared to that from the roughly chopped straw.

Straw was also studied in Sweden for the production of biogas. Studies at the Biogas Research Centre in Wadsworth show that the use of straw in combination with manure is effective (Duong, 2014).

In Denmark, the co-fermentation of straw briquettes with bovine and porcine manure is foreseen as the main raw material for biogas production. According to the program, at least 50% of all manure is expected to utilise for biogas in 2020. The great advantage of briquetting technology is the reduced straw transport costs, especially in transporting over long distances. Due to increased briquettes density the transport costs decreases drastically, as the truckload capacity increases from 12 to 33 tonnes with the straw briquettes compared to capacity with the straw bales (www.kineticbiofuel.com).

Use of the straw pellets for biogas production is investigated in Denmark also. It is supposed that 10% of the pellets by the weight are acceptable percentage for its co–fermentation with the manure. Company Xergi was built a biogas plant using the manure and the straw pellets for production of 8 million $m^3$ biogas per year (Walsh, 2015).

Purpose of investigation is evaluation the biogas and methane output from the wheat straw pellets co-fermentation with molasses and sunflower oil, and effect of added catalyst Metaferm.

## MATERIALS AND METHODS

Biomass never fully degrades in practice therefore the studies are needed to assess the potential of methane for each particular biomass. Several methods can be used for this purpose. In our research, we used the methodology approved by the German scientists (Kaltschmitt, 2010).

The research was provided on wheat straw pellets in diameter of 6.0 mm (Fig. 1), marketed commercially and used as bedding material for animal premises usually.

According to observations, when the straw pellets are added in the water, the pellets do not form a floating layer (Fig. 2). The straw pellets have ability to absorb the large volume of liquids and tend to disintegrate in the substrate.

**Figure 1.** Straw pellets.

**Figure 2.** Straw pellets in water (not floating).

Average sample of straw pellets was taken and chemical composition was determined in the LUA laboratory according to standardized methodology ISO 6496:1999. Total dry organic matter, dry matter, ashes content, and content of basic elements was determined for average sample of each group of the raw materials. Each group of raw materials and inoculums was weighed carefully. Each bioreactor (R1-R16) in volume of 0.75 L was filled with the same inoculum (almost finished cows manure digestate taken from a continuously operating bioreactor in volume of 120 L). Bioreactors R1 and R16 with inoculum only were used as control to obtain the values, e.g. volume of biogas and methane produced from pure inoculums needed for correction of biogas and methane volumes obtained from bioreactors R2–R15 with added biomass (straw pellets, molasses, sunflower oil, catalyst Metaferm).

Wheat straw pellets 20 g were added in each reactor R2–R15. Molasses 4.6 g (or 23% of pellets weight) was added in bioreactors R5–R8. Metaferm 1 mL (or 5% of pellets weight) was added in bioreactors R9–R11 and sunflower fried oil 3.8 g (or 19% of pellets weight) was added in bioreactors R12–R15. Molasses is the by-product from sugar beets processing at sugar factories, and were purchased from Belorussia as a feedstock for biogas plant. Actual sample of molasses was obtained at local biogas plant and quality of molasses was impaired.

Fried sunflower oil is the by-product obtained after cooking (frying) process of vegetables (was poured out of the pan).

Metaferm (made in Latvia) is the bio-stimulator for promoting of bacteria activity in anaerobic fermentation process. Catalyst Metaferm contains vitamins, micronutrients and biologically active substances however the precise composition of Metaferm is unknown, due to producer proprietary rights on this product.

Accuracy of raw material sample and additives weight measurement was ± 0.001 g, and accuracy of inoculums weight measurement was ± 0.2 g respectively. Each bioreactor was filled in with planned mixture and sealed carefully. Every bioreactor was connected with gas storage bag fitted with check valve in the input and manually operated tap in the output for gases measurement. All the bioreactors were placed in the thermostat operating at pre-set working temperature 38 ± 0.5 °C. The volume and composition of the produced biogas was measured once a day. The bioreactors were also shaken regularly to reduce the floating layer. Anaerobic fermentation was provided in a single filling (batch) mode and lasted until the biogas production ceases.

After the fermentation process was finished, every digestate from bioreactors was weighed and dry matter, ashes and dry organic matter (DOM) content was measured. The dry matter content was determined in the special unit, model Shimazu, at a temperature of 105°C, and the organic matter content was determined in the oven, model Nabertherm, by burning of the samples at 550 °C according to the special program.

The gas composition (methane, carbon dioxide, oxygen and hydrogen sulphide) was measured with the gas analyser, model GA 2000. Biogas and methane yield from the added biomass (straw pellets, molasses, sunflower oil, catalyst Metaferm) in inoculums was calculated as the biogas (methane) volume from each reactor (R2 to R15) minus the average biogas (methane) volume obtained from the control bioreactors (R1, R16).

The accuracy of the measurements was ± 0.02 for pH, ± 0.025 L for gas volume and ± 0.1 °C for temperature. Methane $CH_4$, carbon dioxide $CO_2$ and oxygen $O_2$ content in biogas was measured periodically with the accuracy ± 2.0%.

Oxygen measurements were provided for control of tightness of gas collection system only. The unit Kern FKB 16KO2 with accuracy ± 0.2 g was used for measurement of total weight of substrates, and the unit Shimazu with accuracy ± 0.001 g was used for weighting of biomass samples to obtain total solids and dry organic matter content. Substrates pH value was measured with pH meter, model PP-50.

Biogas and methane yield from the added biomass (straw pellets, molasses, sunflower oil, catalyst Metaferm) in inoculums was calculated as the biogas (methane) volume from each reactor (R2 to R15) minus the average biogas (methane) volume obtained from the control bioreactors (R1, R16).

## RESULTS AND DISCUSSION

Investigation of biogas and methane output from wheat straw pellets and from its co-fermentation with molasses, sunflower oil and catalyst Metaferm was provided according to experimental plan. Results of raw material analysis are shown in Table 2.

**Table 2.** Results of analysis of raw materials

| Bioreactor | Raw material | Weight g | pH | TS % | TS g | ASH % | DOM % | DOM g |
|---|---|---|---|---|---|---|---|---|
| R1, R16 | IN | 500 | 7.53 | 2.21 | 11.050 | 25.25 | 74.75 | 8.260 |
| R2–R4 | SP | 20 | | 89.37 | 17.874 | 9.99 | 90.01 | 16.088 |
| R2–R4 | IN+SP | 520 | 7.35 | 5.56 | 28.924 | 15.82 | 84.18 | 24.348 |
| R5–R8 | MO | 4.597 | | 89.98 | 4.136 | 23.25 | 76.75 | 3.174 |
| R5–R8 | IN+SP+MO | 524.6 | 7.36 | 6.31 | 33.06 | 16.75 | 83.25 | 27.522 |
| R9–R11 | IN+SP+MF | 521 | | 5.55 | 28.932 | 15.82 | 84.18 | 24.356 |
| R12–R15 | SO | 3.829 | | 99.95 | 3.829 | 0.30 | 99.70 | 3.815 |
| R12–R15 | IN+SP+SO | 523.8 | 7.34 | 6.25 | 32.753 | 14.01 | 85.99 | 28.163 |

Abbreviations: TS – total solids; ASH – ashes; DOM – dry organic matter; IN – inoculums; SP – straw pellets; MO – molasses; MF – Metaferm; SO – sunflower oil.

As can be seen from the table, the straw pellets have a high dry matter and organic matter content, and are suitable for biogas production. Straw pellets absorbs moisture and disintegrates in substrate quickly without forming a floating layer, and behave different compared to non-chopped straw forming the floating layer in substrates usually.

The outputs (yields) of biogas and methane from the wheat straw pellets without and with additives are shown in Table 3.

**Table 3.** Biogas and methane yields from experimental bioreactors

| Reactor | Raw material | Biogas, L | Biogas, L $g^{-1}_{DOM}$ | Methane aver. % | Methane, L | Methane, L $g^{-1}_{DOM}$ |
|---|---|---|---|---|---|---|
| R1 | IN500 | 0.00 | | | 0.00 | |
| R16 | IN500 | 0.00 | | | 0.00 | |
| R2 | IN500+SP20 | 8.60 | 0.534 | 52.06 | 4.472 | 0.278 |
| R3 | IN500+SP20 | 8.60 | 0.538 | 52.97 | 4.585 | 0.285 |
| R4 | IN500+SP20 | 8.80 | 0.550 | 53.09 | 4.698 | 0.292 |
| | **Aver. R2–R4** | **8.667** | **0.54** | **52.78** | **4.585** | **0.285** |
| | **± st.dev.** | **± 0.12** | **± 0.01** | **± 0.56** | **± 0.11** | **± 0.01** |
| R5 | IN500+SP20+MO5 | 15.90 | 0.825 | 52.29 | 8.314 | 0.432 |
| R6 | IN500+SP20+MO5 | 16.60 | 0.862 | 50.65 | 8.408 | 0.437 |
| R7 | IN500+SP20+MO5 | 15.30 | 0.794 | 55.93 | 8.252 | 0.428 |
| R8 | IN500+SP20+MO5 | 12.10 | 0.628 | 53.22 | 6.44 | 0.334 |
| | **Aver. R5–R8** | **14.975** | **0.777** | **53.02** | **7.854** | **0.408** |
| | **± st.dev.** | **± 1.19** | **± 0.01** | **± 2.21** | **± 0.94** | **± 0.05** |

*Table 3 (continued)*

| | | | | | | |
|---|---|---|---|---|---|---|
| R9 | IN500+SP20+ MF1 | 10.00 | 0.621 | 51.46 | 5.146 | 0.320 |
| R10 | IN500+SP20+ MF1 | 11.50 | 0.715 | 48.81 | 5.613 | 0.349 |
| R11 | IN500+SP20+ MF1 | 11.90 | 0.740 | 50.93 | 6.061 | 0.377 |
| | **Aver. R9–R11** | **11.133** | **10.692** | **50.40** | **5.607** | **0.349** |
| | **± st.dev.** | **± 1.00** | **± 0.06** | **± 1.40** | **± 0.46** | **± 0.03** |
| R12 | IN500+SP20+SO4 | 20.90 | 1.050 | 70.22 | 14.677 | 0.737 |
| R13 | IN500+SP20+SO4 | 22.20 | 1.115 | 57.46 | 12.757 | 0.641 |
| R14 | IN500+SP20+SO4 | 20.90 | 1.050 | 58.57 | 12.241 | 0.615 |
| R15 | IN500+SP20+SO4 | 18.90 | 0.950 | 59.22 | 11.192 | 0.562 |
| | **Aver. R12–R15** | **20.725** | **1.041** | **61.38** | **12.717** | **0.639** |
| | **± st.dev.** | **±1.36** | **± 0.07** | **± 5.95** | **± 1.46** | **± 0.07** |

Oxygen content in biogas was very low, that confirms that tightness of gas collection system was not impaired. Biogas or methane values in Table 3 and in Fig. 3 are presented with subtracted average biogas or methane volumes obtained from the control bioreactors (R1, R16). Specific biogas and methane yield from every bioreactor with wheat straw pellets or wheat straw pellets with additives is shown in Fig. 3.

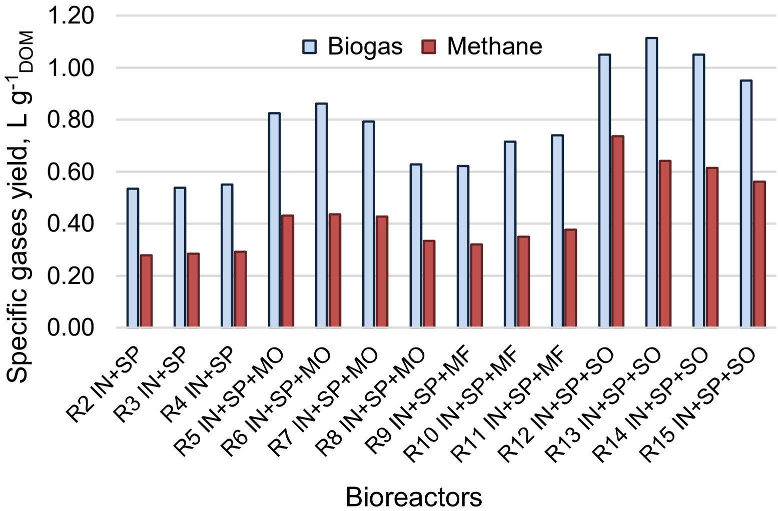


**Figure 3.** Specific biogas and methane yield from bioreactors with wheat straw pellets or its co-fermentation with molasses, sunflower oil and catalyst Metaferm.

Pre-grinding of wheat straw before pelletizing also may increase methane yield significantly. This could be explained by the fact that the raw materials were well distributed within substrate and microbial access to the raw material was improved. Average specific methane yield and methane percentage in biogas from every group of similar bioreactors is shown in Fig. 4.

As can be seen from the Table 3 and Fig. 4, the co-fermentation results of wheat straw pellets with sunflower oil or with molasses, results increase of average methane production by 124.1% or 43.1% respectively. The addition of catalyst Metaferm 1 mL (5% of pellets weight) in straw pellets substrate increases methane yield by 22.3%. Content of methane in biogas from wheat pellets decreases by 2.3% after addition of the catalyst Metaferm. Methane content increases by 0.3% or 8.7% after addition of the molasses or sunflower oil respectively. Increase of methane content in biogas with sunflower oil can be explained with high content of the fatty acids in additive. Metaferm containing vitamins and micronutrients have the positive effect on anaerobic fermentation of wheat straw pellets.

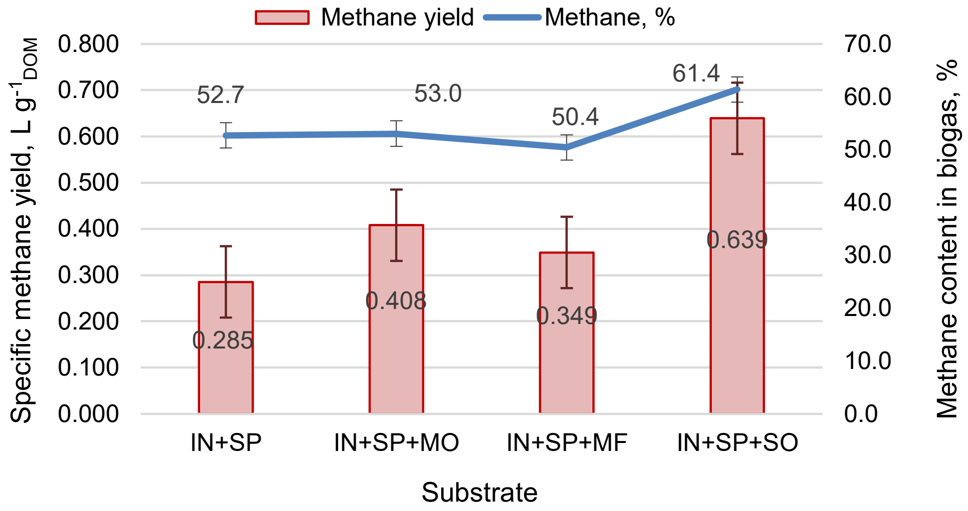


**Figure 4.** Average specific methane yield and average methane content in biogas from different straw pellets co-fermentation substrates.

Further investigations are needed to explore the biogas and methane potential from different local straw type, straw pellets and briquettes, and from its co-fermentation with different nutrients, micronutrients and biologically active substances.

## CONCLUSIONS

Wheat straw pellets sinking in the liquid without forming a floating layer can be regarded as an advantage compared to anaerobic fermentation of roughly chopped straw.

The average specific biogas or methane yield from wheat straw pellets without additives was 0.540 L $g^{-1}_{DOM}$ or 0.285 L $g^{-1}_{DOM}$ respectively.

The average methane content in biogas from wheat straw pellets in biogas was 52.7%. The results of the study show that wheat straw pellets are a good raw material for methane production.

Co-fermentation of wheat straw pellets with fried sunflower oil (23% of straw pellets weight) produces the specific methane yield 0.639 L $g^{-1}_{DOM}$ that was higher by 124% compared to wheat straw pellets without additives.

Specific methane yield obtained from co-fermentation of straw pellets with addition of molasses (19% of pellets weight) was 0.408 L $g^{-1}_{DOM}$ that was higher by 43.1% compared to wheat straw pellets without additives.

Addition of 1 mL (5% of pellets weight) catalyst Metaferm in straw pellets substrate increase the specific methane yield by 22.3% compared to wheat straw pellets without additive. Catalyst Metaferm can be recommended as an effective additive to improve the fermentation process and to increase the methane yield from wheat straw pellets.

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