METHANE PRODUCTION FROM STILLAGE

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Abstract. By-products from production of alcohol distilling dregs (stillage) contain much organic matter, therefore could be useful for the production of biogas. The purpose of the study is assessment of the methane volume obtainable from stillage in the anaerobic fermentation process. Investigation was provided in 16 bioreactors operated in batch mode at 38 ºC. Stillage was filled into 14 bioreactors and only inoculum was filled into two bioreactors for control. The yield of biogas was 0.616 $l \cdot g^{-1}_{DOM}$ and methane 0.360 $l \cdot g^{-1}_{DOM}$ after 37 days of anaerobic digestion. The investigated average methane content in biogas from stillage was 58.5 %. The study demonstrates that stillage is a good raw material for the production of methane.

Key words: methane; stillage, anaerobic digestion.

Introduction

The alcoholic beverage plants are characterized by relatively large quantities of liquid organic by-products. Recycling or further use of such by-products is not fully solved in Latvia. The biogas production from distilling dregs residue can be considered as the most suitable technology for alternative energy production due to large amount of organic solids. However, balanced composition of active substances in substrate should be provided to ensure activity of the bacteria for successful biomethane production.

Biodegviela Ltd. is one of three distilleries in Latvia located in Kalsnava. The factory has been expanding production by building the fuel alcohol plant. Production of biogas is provided both from distilling stillage residue 450 $t \cdot d^{-1}$ and cattle manure 60 $t \cdot d^{-1}$, and total cogeneration electrical capacity is 2 MW el. Heat produced is used for technological purposes.

The distilling stillage residue utilization for production of feed additives is ongoing in Iecava alchocol plant, and the by-products utilization is provided only partially in Jaunpagasts alcoholic beverages plant. Suitability of distilling stillage residue for biogas production can be judged from raw material analysis (Table 1) [3].

Table 1

Analysis of distillery stillage from Kalsnava alcohol factory

Parameter	Amount
pH	~3
Humidity W %	92
Dry matter, DM, $g \cdot l^{-1}$	90
Ashes, A, $mg \cdot l^{-1}$	3.3 at 850 ºC (Dry mass of the residue)
Phosphorus, P, % by weight	0.7
Nitrogen, N, % by weight	4.57
Carbon (C, % by weight	42.13
Hydrogen, H, % by weight	6.05

Distilling stillage is a residual product of the ethanol production process and it is good raw biomass for production of biogas. The potential of biogas from stillage was investigated by many researchers in different countries [1-11].

In recent years, many of industrial distilleries, particularly those using cellulose containing raw biomass, have started the usage of distillery stillage also for biogas production in order to improve energy and economic effectiveness. Three main types of raw materials – wheat, triticale and cellulose containing the raw materials – were used for ethanol production worldwide. The wheat and triticale grains are used almost exclusively in distilleries in Latvia, even though the price on grain is relatively high, but there are lower transport expenses on locally produced grain suitable for high quality ethanol production.

Researchers at the Swedish University of Agricultural Sciences (SLU) have estimated the biogas potential from wheat stillage using five laboratory bioreactors during 640 days at temperature

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38 ºC. Stability problems arise after 120 days of the anaerobic fermentation process, while stillage was used as the only biomass medium in the digester. The anaerobic digestion process was stabilized after cattle manure was added into bioreactors, so providing the organic load (OLR) of 2.8 g^{-1}_{VS}. The investigated methane yield per unit of volatile solids (VS) was 310 $ml \cdot g^{-1}_{VS}$ for pulp (85 %) and manure mixture (15 %), and the hydraulic retention time (HRT) was 45 days [10].

Researchers at the University of Florida investigated stillage produced from grain and raw materials with a high cellulose content treatment in the anaerobic digestion process. Investigations showed that quite similar biogas quantity is obtainable from raw materials in mesophilic or in thermophilic treatment mode, but the thermophilic process can be provided almost twice as fast, so the digester can to work with double organic load (OLR) [8] in thermophilic treatment.

The theoretical biogas potential investigated at the Swedish University of Boras was 0.473 $m^3 \cdot kg^{-1}_{VS}$ or 0.407 $m^3 \cdot kg^{-1}_{VS}$ from wheat stillage or cellulose stillage respectively. The average methane yield was 0.288 $m^3 \cdot kg^{-1}_{VS}$ or 0.218 $m^3 \cdot kg^{-1}_{VS}$ from wheat or cellulose stillage respectively [9].

The highest potential of 691-788 $ml \cdot g^{-1}_{VS}$ biogas and 401-458 $ml \cdot g^{-1}_{VS}$ methane was obtained from maize stillage. The rate of organic matter decomposition was 76-94 % [14].

The German researchers also collected information [6], but with less data on stillage anaerobic fermentation.

The outcome of biogas from stillage is not investigated in Latvia before. The hydrogen sulphide content usually increases in stillage substrate during anaerobic fermentation, so additional measures should be provided to reduce this harmful substance.

The purpose of the study is evaluation the biogas and methane production from stillage in the anaerobic fermentation process.

Materials and methods

The raw biomass material (stillage) samples were analysed to clear up the general elements before fermentation. The data were used for calculation of organic loading rates.

16 bioreactors were filled with substrate and placed in the heated container-thermostat Memmert, and gas released from each bioreactor was collected into separate flexible storage bags located outside the thermostat. The widely applied methods were used for preparation of raw biomass substrate, investigation of the fermentation process and analysing of the results [12; 13].

Dry organic matter (DOM) content was determined by investigation of raw weight, dry weight and ashes weight of substrate components and mixtures before and after the anaerobic fermentation process using a moisture-balance measuring unit (model MOC-120H) at 105 ºC temperature and the oven (model Nabertherm) at 550 ºC. All mixtures were prepared, carefully mixed and all bioreactors were placed into the container-thermostat at the same time before starting of the anaerobic digestion process. Gases volumes were measured using the flow meter (Ritter drum-type gas meter). The composition of gases, e.g., oxygen, carbon dioxide, methane, and hydrogen sulphide, was measured using the gas analyser (model GA 2000). The substrates pH values were measured before and after finishing of the anaerobic digestion using the pH meter (model PP-50). Total weight of substrates before and after the anaerobic fermentation process was measured with the scales (model KFB 16KO2).

2 bioreactors were filled with 500.0 ± 0.2 g inoculums only (for control) and 14 bioreactors (all having volume of 0.75 l) were filled with mixtures of inoculums (500 g) and added stillage (20 ± 0.005 g). Almost completely fermented cattle manure from 120 l bioreactor working in continuous mode was used as the inoculums. Batch mode anaerobic digestion process was provided at thermostat temperature 38 ± 0.5 ºC. Biogas released from each bioreactor was collected into a gas bag both for the gas volume and content measurements at regular time intervals. The anaerobic fermentation process was provided until biogas release ceases within 37 days.

Results and discussion

Amount of raw material was prepared, mixed and preciously distributed between reactors (R2-R15), and accuracy of substrate dose in every reactor equals to measurement accuracy of the scales used. The results of investigation of raw biomass substrates, including inoculums and stillage components, are shown in Table 2.

Table 2

Results of analyses of raw material samples before anaerobic digestion

Bio-reactor	Raw material	pH	TS, %	TS, g	ASH, %	DOM, %	DOM, g	Weight, g
R1; R16	IN	7.44	0.36	1.800±0.005	49.25	50.75	0.914±0.005	500±0.2
	S	4.29	11.18	2.236±0.005	6.18	93.82	2.098±0.005	20±0.005
R2-R15	IN+S	7.28	0.78	4.036±0.005	26.37	74.63	3.012±0.005	520±0.21

Abbreviations: IN – inoculum; S – stillage; ASH – ashes; TS – total solids; DOM – dry organic matter (on raw substrate basis); R1-R16 – bioreactors.

As it can be seen from the raw materials analyses in Table 1 stillage contains higher dry matter (11.18 %) and organic dry matter (6-8 %) content compared to that from other distilleries.

The results of analysis of finished digestate from every bioreactor after the anaerobic fermentation process are shown in Table 3.

Table 3

Results of analyses of finished digestate

Reactor	Substrate	pH	TS %	TS g	ASH %	DOM %	DOM, g	Weight, g
R1	500g IN	7.58	0.35	1.743	49.10	50.90	0.887	498.2
R16	500g IN	7.60	0.35	1.743	49.94	50.06	0.872	498.0
R2	500g IN+20gS	7.48	0.52	2.612	76.84	23.16	0.605	502.4
R3	500g IN+20gS	7.6	0.34	1.725	36.51	63.49	1.095	507.4
R4	500g IN+20gS	7.52	0.38	1.930	42.18	57.82	1.116	508.0
R5	500g IN+20gS	7.48	0.28	1.420	70.96	29.04	0.585	507.0
R6	500g IN+20gS	7.42	0.38	1.931	43.11	56.89	1.099	508.2
R7	500g IN+20gS	7.46	0.37	1.880	40.23	59.77	1.123	508.0
R8	500g IN+20gS	7.51	0.39	1.980	39.34	60.66	1.201	507.8
R9	500g IN+20gS	7.50	0.38	1.929	38.25	61.75	1.191	507.6
R10	500g IN+20gS	7.55	0.40	2.031	39.51	60.49	1.229	507.8
R11	500g IN+20gS	7.54	0.39	1.980	39.58	60.42	1.196	507.7
R12	500g IN+20gS	7.55	0.39	1.981	41.88	58.12	1.151	508.0
R13	500g IN+20gS	7.44	0.38	1.930	41.51	58.49	1.129	507.8
R14	500g IN+20gS	7.49	0.39	1.979	40.38	59.62	1.180	507.6
R15	500g IN+20gS	7.52	0.40	2.032	42.18	57.82	1.175	508.0
R2-R15	Average	7.50	0.385	1.953	45.16	54.84	1.076	507.4

The production of biogas and methane from stillage and from control reactors is presented in Table 4.

The inoculums continue to degrade slightly in average by 0.034 g DOM or by 3.77 % in the control bioreactors R1 and R16, see Table 3. The remaining average total dry organic matter of substrates with stillage and inoculums (R2-R15) was 1.076 g, and the calculated total biodegradation rate was 64.28 %. The calculated remaining average dry organic matter of the stillage component in finished substrate (R2-R15) was (0.196 g), and average biodegradation rate of stillage was 90.66 %. Even in theoretically the worst case, if the inoculums can be degraded by 100 %, stillage should still degrade by 0.197 g or by 9.37 % to match the experimental results. In fact, the calculated biodegradation rate of inoculum was negligible, and the volume of biogas in the control reactors R1 and R16 with inoculums was so small that it was not possible to distinguish any gases volume using the above mentioned measurement techniques, see Table 4. It confirms that stillage has lot of easy degradable substances facilitating the anaerobic fermentation process.

Table 4

Production of biogas and methane

Bioreactor/Raw material	Biogas, l	Biogas, $l \cdot g^{-1}_{DOM}$	Methane, aver. %	Methane, l	Methane, $l \cdot g^{-1}_{DOM}$
R1 500g IN	0	0	0	0	0
R16 500g IN	0	0	0	0	0
R2 500g IN+20gS	1.2	0.572	61.3	0.736	0.351
R3 500g IN+20gS	1.4	0.667	56.11	0.786	0.374
R4 500g IN+20gS	1.5	0.715	57.42	0.861	0.411
R5 500g IN+20gS	1.2	0.572	58.83	0.706	0.337
R6 500g IN+20gS	1.3	0.620	58.42	0.759	0.362
R7 500g IN+20gS	1.2	0.572	59.14	0.710	0.338
R8 500g IN+20gS	1.2	0.572	58.18	0.698	0.333
R9 500g IN+20gS	1.3	0.620	57.83	0.751	0.358
R10 500g IN+20gS	1.3	0.620	58.28	0.758	0.361
R11 500g IN+20gS	1.2	0.572	59.23	0.711	0.339
R12 500g IN+20gS	1.4	0.667	56.83	0.796	0.379
R13 500g IN+20gS	1.4	0.667	57.13	0.800	0.381
R14 500g IN+20gS	1.2	0.572	60.12	0.721	0.344
R15 500g IN+20gS	1.3	0.620	60.18	0.782	0.373
Average, 500g IN+20gS	1.3 ± 0.15	0.616 ± 0.072	58.5 ± 2.3	0.755 ± 0.082	0.360 ± 0.039

Note: $l \cdot g^{-1}_{DOM}$ – litres per 1 g dry organic matter added (added fresh biomass into inoculums).

The average methane content in biogas from stillage is shown in Fig. 1.

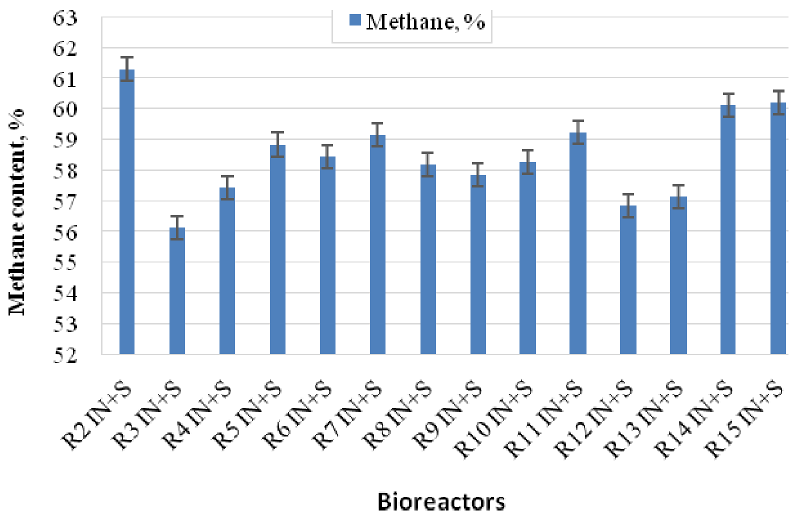

Fig. 1. **Average methane content in biogas produced from stillage**

The relatively high methane content in biogas from stillage can be explained by the fact that stillage contains a lot of raw sugars. There was a high hydrogen sulphide content observed in biogas, even 2-3 times higher compared to the permissible level (150 ppm), especially at the beginning of the anaerobic fermentation process. To prevent damage to the equipment, while working with stillage, it is required to reduce the formation of hydrogen sulphide or to provide the treatment of biogas before its utilisation in cogeneration engines.

The specific average biogas and methane production volumes ($l \cdot g^{-1}_{DOM}$) calculated for bioreactors with added stillage biomass are shown in Fig. 2. The specific biogas and methane yields (Table 4 and

Fig. 2) are representing the average data calculated for the whole period of the stillage anaerobic digestion process.

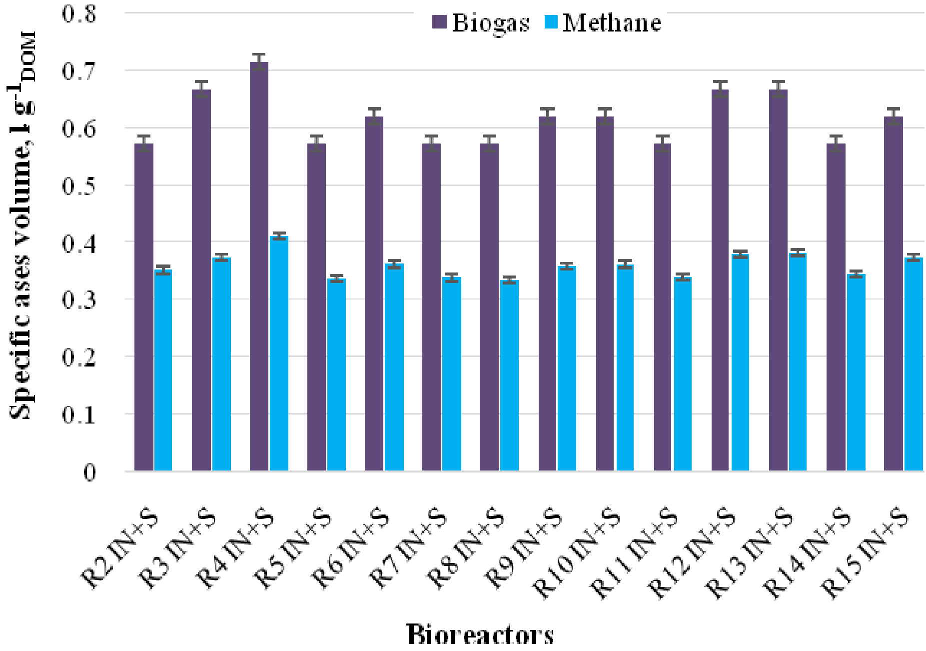

Fig. 2. **Average specific biogas and methane yields from stillage**

The good results obtained are similar to the literature data reported from other studies [8; 10; 13;]. It could be explained by the fact that the stillage biomass chemical composition is consisting of substances easily degradable by micro-organisms (having much sugars and juice easily accessible by bacteria).

Conclusions

1. The investigated average specific biogas yield was 0.616 ± 0.072 $l \cdot g^{-1}_{DOM}$ of raw stillage organic matter.
2. Relatively high average specific methane yield was obtained from stillage (mean value 0.360 ± 0.039 $l \cdot g^{-1}_{DOM}$ download).
3. The investigated relatively high methane content in biogas of 58.5 % confirms that stillage from ethanol plants is a good resource for biomethane production.
4. Relatively high content of hydrogen sulphide in biogas was observed during the stillage anaerobic fermentation process, therefore biogas purifying should be provided before its usage in cogeneration engines.

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