BIOGAS POTENTIAL FROM BIODIESEL PRODUCTION RESIDUES

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Abstract. Biogas production is developing rapidly all over the world. In some countries as Germany and Sweden, its supply after purification in naturaL·gas networks has already started. Biogas production is one of the most promising and environmentally friendly alternative energy technologies, so its development will continue. Also in Latvia, the profitability of biogas production will continue to increase, especially from the point of view of environmental protection. Biogas is now more advantageously used for cleaning and feeding into gas networks for electricity and heat production, but in the future it could also be used as a fuel in city buses, as it is already done today in Linköping and Stockholm. This would further reduce GHG emissions. It is also important to use various organic residues from different productions. In order to find out what is the potential of biogas from the raw materials of production residues of the biodiesel production plant, a study was conducted using laboratory equipment. In 16 bioreactors, filled with raw materials taken from the residues of the biodiesel production, anaerobic fermentation took place at 38°C. After 30 days fermentation produced 0.888 $L\cdot g^{-1}$DOM of biogas (0.497 $L\cdot g^{-1}$DOM of methane) from rapeseed meal, and 1.371 $L\cdot g^{-1}$DOM of biogas (0.814 $L\cdot g^{-1}$DOM of methane) from rapeseed oil refining by-product, as well as 0.765 $L\cdot g^{-1}$DOM of biogas (0.414 $L\cdot g^{-1}$DOM methane) from the glycerol distillation residue. 1.265 $L\cdot g^{-1}$DOM biogas (0.252 $L\cdot g^{-1}$DOM methane) was obtained from biodiesel production wastewater. The study shows that it is possible to obtain an unusually high amount of methane per unit of dry organic matter from biodiesel production residues, but with a high content of hydrogen sulfide from rapeseed meal and glycerin distillation residues. The use of these residues in the production of biogas could be very useful.

Keywords: biogas, methane, biomass, anaerobic fermentation, digestate.

Introduction

Biodiesel and biogas both are two very important sources of renewable energy, particularly in the EU countries. While biogas is produced mostly from waste materials (landfills, manure, sludge from wastewater treatment, agricultural waste), biodiesel in the EU is mostly produced from rapeseed or other oil crops that are used as food, which raises the ‘food or fuel’ concerns. Such biodiesel production also generates a lot of organic waste that can be used for biogas production. Then this waste would be put to good use [1].

Biodiesel and biogas represent crucial renewable energy sources, especially within the EU. Biogas predominantly originates from various waste materials such as landfills, manure, wastewater treatment sludge, and agricultural waste. Conversely, biodiesel production in the EU primarily relies on oil crops like rapeseed, often prompting concerns regarding the competition between food and fuel resources. Notably, the biodiesel manufacturing process yields significant organic waste, which can be repurposed for biogas production, thus ensuring a beneficial utilization of resources [2].

Biodiesel production generates various residues, including glycerol, fatty acids, soap stocks, and excess methanol. The composition of these residues depends on the feedstock and production process employed. Glycerol, a major byproduct of biodiesel production, is particularly suitable for anaerobic digestion due to its high organic content. Biodiesel residues typically contain high levels of organic matter, primarily in the form of lipids, proteins, and carbohydrates. These organic compounds serve as substrates for microbial activity during anaerobic digestion, leading to biogas production. However, the presence of inhibitory compounds such as free fatty acids and methanol can impede the digestion process and affect the biogas yield [3].

Co-digestion of biodiesel residues with complementary feedstocks can improve the process stability, nutrient balance, and biogas yield. However, careful selection of co-substrates is essential to avoid inhibitory effects and maintain optimal process conditions. Co-digestion offers potential synergies for waste valorization and renewable energy generation in integrated biorefinery systems [4].

The possibilities of using biodiesel production residue and waste in biogas production have been studied in several countries. The results of German researchers are presented in the Biogas handbook [5]. 420 $L\cdot kg^{-1}$DOM was obtained from rapeseed meal, 500 $L\cdot kg^{-1}$DOM from glycerin, and 500 $L\cdot kg^{-1}$DOM from oil residues. Data of others researchers are also presented in Faustzahlen Biogas [6]. It is shown there that 425 $L\cdot kg^{-1}$DOM was obtained from glycerin, and 408 $L\cdot kg^{-1}$DOM from rapeseed meal. Austrian researchers show that glycerin and rapeseed poultices can be used well together with traditional raw materials [7; 8]. The work carried out by Takeda et al. (2022) aimed to produce biogas using landfill leachate and crude glycerol as the raw materials. The authors analyzed the following parameters: removal of organic matter, time, glycerol content, and substrate/inoculum ratio. From the optimization of the mentioned parameters it was possible to maximize the efficiency of organic matter removal (90.15%) and specific production of biogas (403.15 $mL \cdot g^{-1}$ SSV) under the conditions of 33.2 days, glycerol content of 1.71%, and substrate/inoculum ratio of 0.37 g $COD \cdot g^{-1}$ VSS. The authors concluded that the average specific production of biogas was 20.3 times higher than that obtained by monodigestion of landfill leachate [9].

Materials, methods and description of work

Raw materials brought from the biodiesel plant were used in the research: the plant rapeseed pulp and impurities RSS, rapeseed oil purification by-product GUMS, glycerin distillation residue DRS, as well as biodiesel production wastewater FLOKAS. The research used a methodology similar to that used earlier and abroad [10; 11]. An average sample was taken, and its chemical composition determined in the LBTU laboratory according to standardized methodologies ISO 6496:1999. Total dry matter, organic dry matter, ash and major element content were determined for each group of raw materials for the average sample and inoculum. Analyses were performed according to standard methods. The raw materials of each group were carefully weighed, the inoculum was also weighed and thoroughly mixed. One inoculum - digestate from a continuous bioreactor was used for all samples. 10 g, 20 g or 100 g of raw material and 0.5 kg of inoculum were filled into 0.75 l bioreactors (its weight was recorded to the nearest 0.2 g). All data were recorded in an experiment logbook and computer. In bioreactors R1 and R16, 500 g of inoculum was filled in each. Bioreactors R2-R5 were filled with 500 g of inoculum and 10 ± 0.01 g of rape seed pulp and impurities from the production plant. Bioreactors R6-R9 were filled with 500 g of inoculum and 20 ± 0.01 g of rapeseed oil purification by-products GUMS. Into bioreactors R10 - R12, 500 g of inoculum and 20 ± 0.01 g of glycerol distillation residues DRS were filled. In bioreactors R13 - R15, 500 g of inoculum and 100 ± 0.05 g of biodiesel production wastewater FLOKAS were filled. All bioreactors were connected to Tedlar gas storage bags and taps, placed in a drying oven and set to a working temperature of 38 ± 0.5 ºC. The amount and composition of the released gas was measured every day when necessary. Fermentation took place in single filling mode and lasted until biogas was no longer released (25 days). The measurement accuracy was ± 0.02 for pH, ± 0.025 l for gas volume and ± 0.1 ˚C for temperature. The composition of the produced biogas was periodically measured - the content of CH_4, carbonic acid gas CO_2, oxygen O_2 and hydrogen sulfide H_2S was determined. The amount of biogas production was studied using laboratory equipment consisting of 16 bioreactors with a volume of 0.75 l. Standard containers were converted into bioreactors. A constant working temperature was ensured by a drying oven SNOL. The total dry matter was determined with a Shimazu dry balance at a temperature of 120 ºC, the composition of organic matter with the help of a Nabertherm drying oven drying the samples according to a special program at 550 ºC. The gas composition was measured with a gas analyzer GA 2000. The content of methane, oxygen, carbonic acid gas and hydrogen sulphide in the biogas was measured, as well as the pressure and the normal volume of the gas were calculated. Scales (Kern FKB 16KO2) were used for weighing, pH meter with accessories (PP-50) stationary was used for pH measurement.

Results and Discussion

When calculating the amounts of biogas and methane obtained, the amount of biogas and methane obtained from all 16 bioreactors was evaluated. Mean results were calculated. The results were tabulated and presented in figures. The results of raw material analyses are shown in Table 1.

As it can be seen from the table, the raw material - rape seed pulp and impurities of the production plant had a high content of dry matter and organic dry matter. The residue of distillation of glycerin, the other raw material, also contains a lot of dry matter, and is also well suited for biogas production. The third raw material is a by-product of rapeseed oil refining, although it looks liquid, it also contains a lot of dry matter. The fourth raw material – production wastewater (flotation sludge) is very liquid, therefore, in order to obtain even a little gas, 100 g were filled into the bioreactors. The results of biogas and methane extraction from each bioreactor are shown in Table 2.

Table 1

Raw material analysis results

Feedstock/bioreactor	pH	DM, %	DM, g	Ash, %	DOM, %	DOM, g	Weight, g
R1, R16 inoculum(In)	8.23	2.00	10.000	39.74	60.26	6.026	500
R2-R5 + 10g RSS	-	91.82	9.182	14.76	85.24	7.827	10
R2-R5 + 500gIn + 10g RSS	8.12	3.76	19.182	27.78	72.22	13.853	510
R6 –R9 + 20g GUMS	-	31.38	6.276	15.44	84.56	5.307	20
R6-R9 + 500gIn + 20g GUMS	7.71	3.13	16.276	30.37	69.63	11.333	520
R10-R12 20g DRS	-	54.90	16.980	17.10	82.90	9.102	20
R10-R12 + 500gIn + 20g DRS	7.80	4.030	20.980	27.89	72.11	15.128	520
R13 – R15 100g FLOKAS	7.24	1.05	1.050	76.71	23.29	0.245	100
R13 – R15 + 500gIn + 100g FLOKAS	7.52	1.84	11.050	43.25	56.75	6.271	600

Designations: DM-full dry matter; DOM- dry organic matter; RSS – rapeseed seeds and impurities of the production plant; GUMS - rapeseed oil refining by-product; DRS - glycerin distillation residue; FLOKAS – wastewater from biodiesel production; In- inoculum.

Table 2

Biogas and methane production

Bioreactor, raw material	Biogas, l	Biogas, $L \cdot g^{-1}$DOM	Methane average, %	Methane, l	Methane, $L \cdot g^{-1}$DOM
R1 inoculum	0.2	0.033	7.8	0.016	0.003
R16 inoculum	0.2	0.033	8.0	0.016	0.003
R1, R16 average	0.2	0.033	7.9	0.016	0.003
R2 RSS 10g + In 500g	7.0	0.894	57.67	4.037	0.515
R3 RSS 10g + In 500g	6.9	0.881	56.24	3.881	0.495
R4 RSS 10g + In 500g	7.1	0.907	54.82	3.892	0.497
R5RSS 10g + In 500g	6.8	0.907	55.28	3.759	0.480
Average R2-R5	6.95 ± 0.1	0.888 ± 0.01	56.00 ± 0.953	3.892 ± 0.072	0.497 ± 0.009
R6 500gIn + 20g GUMS	8.0	1.507	61.16	4.892	0.922
R7 500gIn + 20g GUMS	7.1	1.338	58.61	4.161	0.784
R8 500gIn + 20g GUMS	7.0	1.319	58.42	4.089	0.770
R9 500gIn + 20g GUMS	7.0	1.319	59.12	4.138	0.780
Average R6-R9	7.275 ± 0.525	1.371 ± 0.068	59.33 ± 0.916	4.320 ± 0.286	0.814 ± 0.054
R10 500gIn + 20g DRS	7.9	0.868	54.14	4.277	0.470
R11500gIn + 20g DRS	6.9	0.758	52.83	3.645	0.400
R12 500gIn + 20g DRS	6.1	0.670	55.72	3.399	0.373
Average R10-R12	6.967 ± 0.622	0.765 ± 0.068	54.23 ± 0.993	3.778 ± 0.336	0.415 ± 0.037
R13 500gIn + 20g FLOKAS	0.32	1.306	21.82	0.070	0.285
R14 500gIn + 20g FLOKAS	0.3	1.224	22.73	0.068	0.278
R15 500gIn + 20g FLOKAS	0.31	1.265	15.22	0.047	0.192
Average R13-R15	0.31 ± 0.007	1.265 ± 0.027	19.92 ± 3.136	0.062 ± 0.009	0.252 ± 0.040

Designations: $L \cdot g^{-1}$DOM - liters applied to the initial amount of dry organic matter of the raw material.

The yield of methane from the rape seed pulp of the production plant can be assessed as very good. As a drawback, it should be mentioned that a lot of H_2S was released during the anaerobic fermentation process, the exact amount of which could not be recorded, because it quickly exceeded the capabilities of the gas analyzer (over 550 ppm). Biogas and methane were best produced from glycerin distillation residues. Here, not so much hydrogen sulphide was formed in the process either. The by-product of rapeseed oil refining also produced a lot of biogas and methane, but it also produced a lot of H_2S. Theoretically, more gas should have been obtained from the sewage, but this did not happen, because there were very little organic solids (DOM) in it, but the bacteria used it well. The large amount of biogas from wastewater is not correct and can be explained by the large proportion of air in the gas. The relatively good methane content in the average gas can be explained by the fact that the raw materials contain a lot of oil impurities, which bacteria use well. The very large amount of biogas from glycerin distillation residues is a surprise, and until now such a large amount had only been experienced in the laboratory by fermenting very fatty products. The relatively high yield of methane from the dry organic matter decomposed in the glycerol distillation residues could also be explained by the relatively higher content of oil and glycerol. The yield of biogas and methane from all four feedstocks from each bioreactor is shown in Fig. 1.

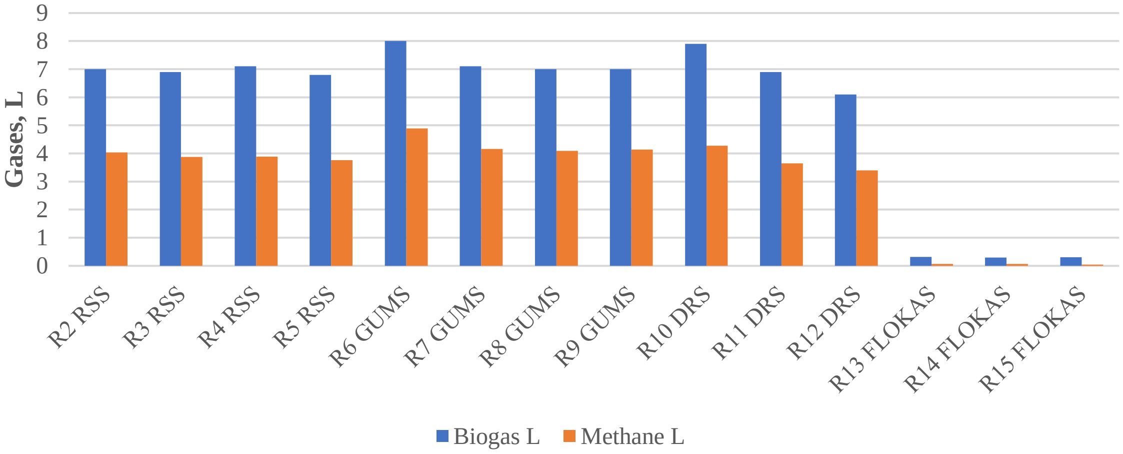

Fig. 1. **Biogas and methane yield from the production plant raw materials from each bioreactor**

The average specific yields of biogas and methane from each raw material and bioreactor, applied to the raw material initial amount of dry organic matter in grams, are shown in Fig. 2.

Comparing the obtained results with those presented in the literature, it can be seen that they are better for RSS and GUMS, but worse for DRS. However, such a comparison is not correct because the concentration of the active substance in each mixture and the fermentation conditions are not known. If our results turned out to be better, it means that in our mixtures RSS and GUMS bacteria used these substances better, and DRS worse.

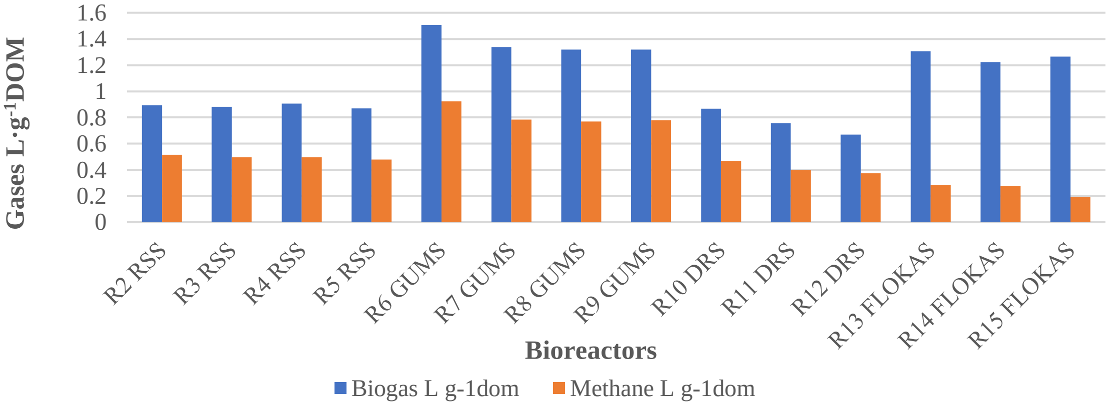

Fig. 2. **Biogas and methane yield in $L \cdot g^{-1}$DOM from the plant for raw materials from each bioreactor**

The average yields of biogas and methane from each raw material, applied to the raw material initial amount of dry organic matter in grams, are shown in Fig. 3.

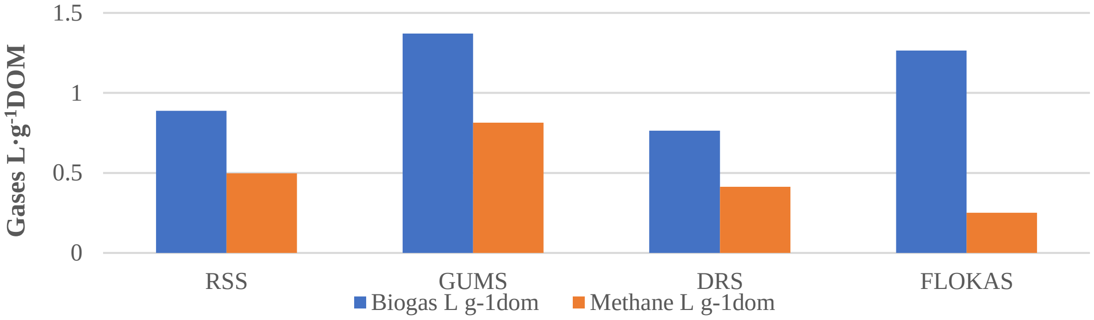

Fig. 3. **Average yields of biogas and methane from each raw material**

Fig. 4 shows the average content of methane from each bioreactor. It is good from the three raw materials, but very low from the wastewater.

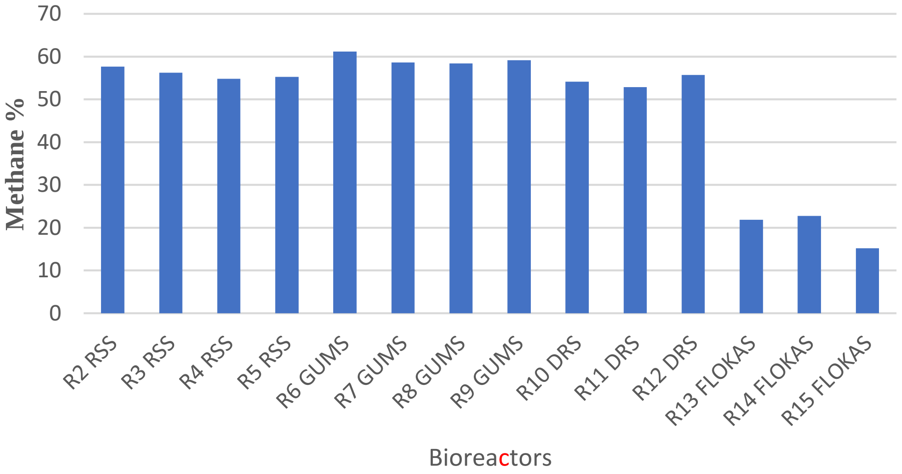

Fig. 4. **Average content of methane in% from each bioreactor**

Conclusions and proposals

1. Methane obtained from rapeseed pulp on average 0.497 L·g^{-1}DOM.
2. Methane obtained from glycerol distillation residues on average 0.814 L·g^{-1}DOM.
3. Methane obtained from rapeseed oil refining by-products on average 0.414 L·g^{-1}DOM.
4. Methane obtained from biodiesel production wastewater on average 0.252 L·g^{-1}DOM.
5. Results show that all tested biomasses are acceptable as raw materials for methane production.
6. Using biodiesel production residues, measures should be taken to reduce the H_2S content.
7. Biogas production from biodiesel residues offers a sustainable solution for waste management, renewable energy generation, and greenhouse gas mitigation. Anaerobic digestion of biodiesel residues provides a cost-effective pathway for valorizing organic waste streams and producing biogas as a clean energy source. However, technical, economic, and regulatory challenges must be addressed to realize the full potential of biogas production from biodiesel residues. Future research and innovation efforts are essential for advancing biogas technologies, optimizing process performance, and scaling up deployment to accelerate the transition towards a low-carbon, circular economy.

Author contributions

Conceptualization, V.D., methodology, P.I. and V.D; software, V.D., validation, P. I. and V.D; formal analysis, V.D., investigation, V.D., P.I., data curation, V.D., writing – original draft preparation, V.D., writing – review and editing, V.D., visualization, V.D., project administration, V.D., funding acquisition, P.I. All authors have read and agreed to the published version of the manuscript.

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