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A study of the energy potential of vinasse

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The by-product remaining after distillation during the production of wine brandies is called vinasse. It is characterized mainly by a high content of organic matter (proteins, VFA, amino acids) and its typically balanced composition. The aim of this study is to determine the energy potential of organic waste from the production of wine brandy, i.e. vinasse, and to optimize the process of vinasse biomethanation. Process thermal stability was also investigated.

The main characteristics of vinasse as a substrate for biomethanation (pH 3,17, 6,34 g l^{-1} protein, 296 gO_2 l^{-1} COD, etc.) were determined. A high specific yield of methane was reached by appropriate adapted methanogenic consortium. Biochemical methane potential (BMP) of vinasse was determined at a value of 0,36 lCH_4 $gCOD^{-1}$. A BMP assay provides a measure of the anaerobic digestibility of a given substrate. The BMP test was carried out in batch mode at mesophilic temperature (35°C). The information provided by BMPs is valuable when evaluating potential anaerobic substrates and for optimizing the design and operation of an anaerobic digester. Biomethanation process was optimized by adding appropriate microelements in the medium as the production of methane increased significantly. In a study of thermal stability of the process it was found that biomethanation takes place also under psychrophilic conditions (20 °C), but the period for methane production is extended.

The results showed that the vinasse is a valuable substrate for biomethanation and the process is successfully optimized by adding appropriate microelements in the medium.

Keywords: biochemical methane potential, vinasse, biomethane, methanogenic consortium

INTRODUCTION

In recent years the use of the anaerobic digestion as process to treat organic solid wastes became more frequent. The reason of this new tendency in treatments of solid wastes can be explained considering mainly three factors: 1) the need to apply a process to dispose of organic solid wastes more environmental friendly than landfills as requested by the latest rules concerning the environmental protection in many countries in the world; 2) the opportunity to obtain from this process a renewable fuel called biogas alternative to fossil ones; 3) the advantage of relatively low costs in starting up and managing this process. Biomethanation is the formation of methane by microbes, known as methanogens, in the decomposition of biomass to a final energetically worthwhile gaseous product, called biogas. Biogas production is an efficient method of reducing greenhouse gas emissions (GHG) [1].

The biochemical methane potential (BMP) assay is best suited when used to elucidate what types of substrates, from an array of potential substrates, have the highest biomethane potential. In addition, BMP assays can be used to estimate the optimum ratios between co-substrates when co-digestion is intended. Lastly, BMP assay results can be used to determine the extent of anaerobic biodegradability of substrates, and thus, relative residence times required for complete digestion. The determination of the BMP of an organic residue can help in the design and economic evaluation of a biogas plant [2]. In this analysis by stoichiometric conversion production of methane is associated directly with the degree of degradation of the organic mass. BMP - test requires a minimum of equipment and tools for organizing and monitoring compared to similar more extensive research and provides more accurate information regarding the specific organic waste that available in the literature. The BMP tests are conducted in batch conditions and in bench scale, measuring the maximum amount of biogas or bio-methane produced per gram of biodegradable biomass contained in the organics used as substrates in the biomethanation process. In literature there are different attempts to define a standard protocol in order to gain comparable results but so far such standardization has not been reached.

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waste from the production of wine brandy, i.e. vinasse, and to optimize the process of vinasse biomethanation.

MATERIALS AND METHODS

Vinasse

The model vinasse substrate used in the study was laboratory prepared by distilling red wine. The distillate was then concentrated. It has the same properties as industrial. The substrate was stored in the refrigerator at 4 °C.

Methanogenic consortia

Methanogens were obtained as activated sludge from a factory producing bioethanol "Almagest", Ihtiman, Bulgaria.

Analytical methods

The chemical oxygen demand (COD), total suspended solids, volatile suspended solids (VSS) and volatile fatty acids (VFA) were determined according to APHA (1992) [3]. The protein content was determined according to the method of Lowry et al. (1951) [4]. Gas production rate measurements were performed using a manual constant pressure liquid displacement system. The biogas composition was estimated using the absorptive method as was described previously by Lalov et al. [5].

Procedure for BMP test

There is no detailed standard procedure for conducting BMP – test, but most studies used very similar procedures. In our BMP – test was used a batch process of biomethanation of vinasse at 35 °C. Test bottles (500 ml) were filled with 300 ml activated sludge mixed methanogenic consortium and 10 ml neutralized vinasse (pH 7). Test bottles were flushed out with nitrogen for 15 minutes and then placed in a thermostat at 35 °C. Scheme of laboratory biomethanation system used in BMP test experiments is shown on Fig. 1

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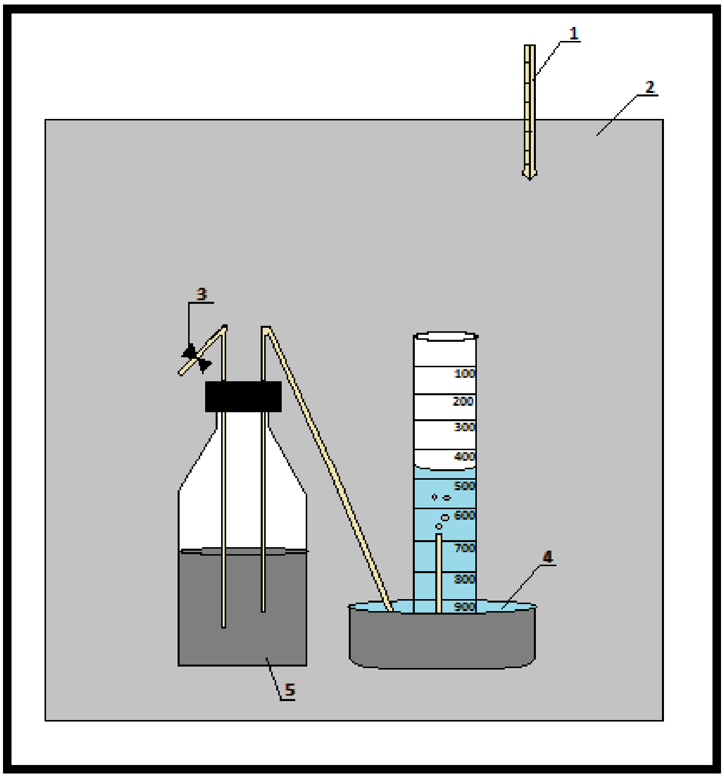

Fig. 1. Installation scheme of biomethanation; Legend: 1 – thermometer, 2 – thermostat, 3 – closing clip, 4 – gas holder, 5 – bioreactor

RESULTS AND DISCUSSION

Characteristics of vinasse

Vinasse is a residual liquid remaining from the fermentation and distillation of alcoholic liquors. It has low total solids content and total solids ranging from 5-10 %. Vinasse has high levels of potassium, calcium and organic matter in its chemical composition as well as moderate amounts of nitrogen and phosphorus and could represent an alternative to supply such nutrients in crop production. It is characterized mainly by a high content of organic matter (proteins, VFA, amino acids) and its typically balanced composition. With aim to characterize this industrial waste as a potential substrate for methanation many analyses were conducted and the results of which are summarized in Table 1.

Table 1. Characteristics of vinasse

Parameter	Value
pH	3.17
COD, gO_2 l^{-1}	270
Protein content, g l^{-1}	6.34
Volatile fatty acids, mg l^{-1}	8.45

As can be seen from the results presented in the table 1 vinasse is characterized by a high organic load. Therefore its anaerobic treatment to generate energy in the form of biogas would be efficient.

Characteristics of activated sludge

Mixed methanogenic consortium isolated from industrial wastewater treatment plant was used as standard inoculum in our experiments. The initial characterization of the mixed anaerobic culture included a study of its structure (morphological analysis) as well as determination of its microbial content.

The type of methanogenic culture is demonstrated in Fig. 2. As it can be seen culture is granulated in the form of spherical flocs (soft pellets). The particles have diameters varying in the range of 2-3 mm. The pellets displayed good mechanical stability, maintaining its intact structure at low stirring speeds, especially if no direct mechanical impact was applied. Thus structured consortium has a number of advantages such as rapid sedimentation ability to be retained in the reactor volume at relatively high flow rates, increased resistance to toxic shock, etc. which makes it suitable for use in numerous reaction systems.

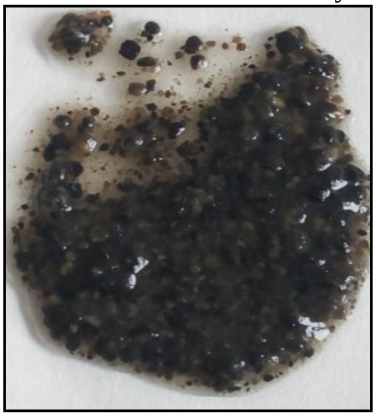

Fig. 2. Photo of activated sludge

An analysis to determine the organic content of the sludge (as VS) showed that the granules contain about 87% organic matter and 13% mineral mass. This feature further confirmed the good qualities of the consortium selected item as it is evident mainly the presence of biomass and EPS as opposed to sludge from a natural source, wherein the mineral component reaches 70%. Dry weight (D/W) was 4.06 %.

Optimization of the BMP test procedure

In order to determine the real (maximum) achievable BMP of vinasse preliminary experiments for optimization of the process have been conducted. The volume of the biogas (methane) produced per unit of converted organic matter was used as optimization criterion. Two parameters were subjected to optimization: the composition of the medium and process temperature.

The lack of appropriate amounts of trace elements in the medium could be a significant barrier in determining the real BMP of the substrate. On the other hand BMP tests have to be carried out keeping the pH around the neutral point (values ranging between 7,0 to 7,8). Drop of the pH value below 6,0-6,5 will inhibit the methane bacteria activity. To avoid drops in pH chemicals are added to the organic substrate to supply a buffer capacity. Sodium bicarbonate, sodium hydroxide, sodium carbonate and sodium sulphide are the most used chemicals [6].

To evaluate the effect of the presence of appropriate micronutrients in the biomethanation medium two different batch processes were carried out simultaneously. Processes of biomethanization of 10 ml vinasse in presence and absence of micronutrients, respectively, were repeated three times. Composition of mineral contents is presented in the Table. 2. A comparison of the kinetics of biogas production during the two biomethanation processes is shown in Fig. 3.

Table2. Concentrations of nutrients in the middle.

Displacement		500 ml
Activated sludge		300 ml
Minerals	NH_4Cl	107.73 mg
	KCl	351.14 mg
	$(NH_4)_2HPO_4$	21.62 mg
	$CaCl_2$. $2H_2O$	67.64 mg
	$MgCl_2.6H_2O$	486.00 mg
	$MnSO_4.H_2O$	5.39 mg
	H_3BO_3	1.54 mg
	$ZnCl_2$	0.57 mg
	$CuCl_2.2H_2O$	0.73 mg
	$NaMo_4.2H_2O$	0.69 mg
	$CoCl_2.6H_2O$	8.10 mg

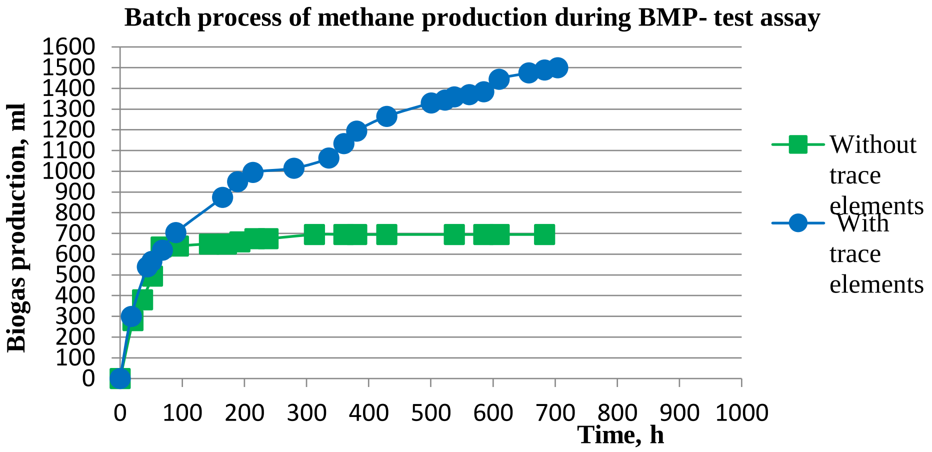

Fig. 3. Batch process of biogas production during BMP-test assay with and without trace elements

As can be seen from the graphs the process of biogas generation strongly depends on the presence of a suitable mineral composition. Obviously, the addition of trace elements resulted in a twofold increase in the yield of biomethane.

Temperature also affects the biomethanation rate and usually higher temperatures imply greater methane yields in a shorter digestion time. Nevertheless sharp increases of temperature should be avoided because they can cause a decrease in biomethane production due to the death of specific bacteria strains, particularly sensitive to temperature changes [7]. To keep constant the temperature during BMP tests it is needed to submerge the reactors in a water bath kept at the selected temperature [8] or to incubate them in a thermostatically controlled room [9]. Anaerobic digestion of biomass can be performed in three different ranges: psychrophilic (10-20 °C), mesophilic (20-45 °C) and thermophilic (45-68 °C). Most often, the temperature range used in the anaerobic reactor is mesophilic (with optimum at 35 °C) [10].

The study of the temperature optimum of the process was related to the establishment of boundaries of temperature stability of methanogenic consortium. During the experiment temperature was increased with stepwise increments of 5 °C in the range 20-60 °C. After each establishment of the new temperature value a batch methanation of 10 ml vinasse containing trace elements has been carried out for a week (Fig. 4).

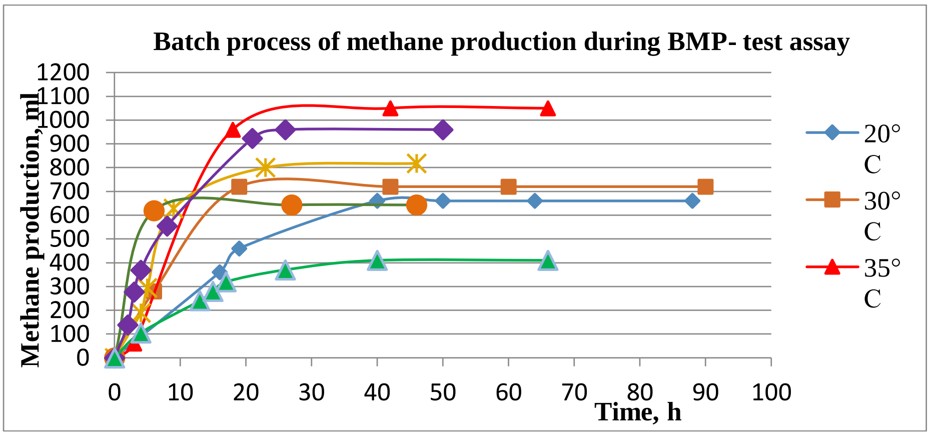

Fig. 4. Batch process of methane production during BMP-test assay at different temperatures

As a result of carried out studies it was found that the optimum temperature of the process is 35 °C. Paradoxically to some extent, additional temperature optimum was observed when temperature was increased to 50 °C. The occurrence of this lower additional optimum could be attributed to the probable processes of temperature adaptation of the methanogenic consortium as a result of gradual increase of the reactor temperature. Additional proof of the presumed successful adaptation was the fact that the consortium demonstrated metaboli cactivity even at a subsequent rise in temperature to 60 °C.

Calculation of BMP of vinasse

After the above described optimization of the BMP test procedure, the process was repeated four times at optimal conditions. The obtained results were used in the final determination of the real energy potential of vinasse.BMP was determined according to the following Eq.(1).

$$BMP = \frac{V_{biogas} . C_{methane}}{V_{sub} . COD_{sub}} \qquad (1)$$

where:

- BMP – biochemical methane potential, lCH_4 $gCOD^{-1}$;
- V_{biogas} – volume of produced biogas, l;
- $C_{methane}$ – methane concentration, %;
- V_{sub} – volume of the substrate used in the BMP-test, l;
- COD_{sub} – chemical oxygen demand of the substrate, gO_2 l^{-1}.

To determine the BMP a batch process of biomethanation at 35°C was repeated four times. BMP of vinasse is 0,36 l CH_4 $gCOD^{-1}$.

CONCLUSION

The test methanogenic consortium keeps good metabolic activity in psychrophilic conditions at 20 °C. During the optimization of the BMP test procedure it was found that the yield of methane can be doubled by the adding of appropriate trace elements in the medium. The process of biomethanation of vinasse occurs most optimally in the presence of suitable microelements in the medium at mesophilic conditions (35 °C).

Determined under the above described conditions BMP of vinasse reached 0,36 lCH_4 $gCOD^{-1}$. Theo ccurrence of the second temperature optimumat 50 °C lead us to hypothesis that even higher value could be reached in the case of thermophilic methanogenic consortium.

As a result of this study it can be concluded that the vinasse has high bioenergy potential and it is a valuable substrate for biomethanation.

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ИЗСЛЕДВАНЕ ЕНЕРГИЙНИЯ ПОТЕНЦИАЛ НА ВИНАСА

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(Резюме)

Вторичният продукт, оставащ след дестилацията при производството на винено бренди, се нарича винаса. Тя се характеризира главно с високо съдържание на органични вещества (протеини, летливи мастни киселини, аминокиселини) и със своя балансиран състав. Целта на това изследване е да се определи енергийният потенциал на течния органичен отпадък от производството на винено бренди, т.е. винасата, и да се оптимизира процесът на неговата биометанизация. Изследвана е и термалната стабилност на процеса.

Определени са основни характеристики на винасата като субстрат за биометанизация (pH 3,17, белтък 6,34 г $л^{-1}$, 296 $гO_2$ $л^{-1}$ ХПК и др.). Постигнат е висок специфичен добив на метан посредством използването на подходящо адаптиран метаногенен консорциум. Определен е биохимичният метанов потенциал (БМП) на винасата - 0,36 $лCH_4$ $гХПК^{-1}$. Анализът на БМП представлява мярка за анаеробната разградимост на даден субстрат. Тестът за БМП се провежда в периодичен режим при мезофилна температура (35 °C). Информацията, предоставена от БМП, е ценна при оценката на потенциални анаеробни субстрати и за оптимизиране дизайна и работата на анаеробния биореактор. Процесът на биометанизация е оптимизиран чрез добавяне на подходящи микроелементи в средата като производството на метан се увеличи значително. При изследване на термичната стабилност на процеса е установено, че биометанизация се извършва и при психрофилни условия (20 °C), но периодът на производство на метан се удължава.

Резултатите показват, че винасата е ценен субстрат за биометанизация и процесът е оптимизиран успешно чрез добавяне на подходящи микроелементи в средата.