INVESTIGATION OF BIOGAS PRODUCTION OF CHEESE WHEY IN PROCESSING WITH OZONE BEFORE ANAEROBIC DIGESTION

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Abstract. The investigations were aimed to evaluate biogas yield from cheese whey, if cheese whey is processed with ozone. This method is proposed for increasing hydrolysis. In preliminary investigations acceptable concentration of ozone – 0.005 $g_{O3} \cdot g_{Tswhey}^{-1}$ was found. Anaerobic digestion took place in laboratory batch digesters. Results 732 $l \cdot kg_{dom}^{-1}$ from control digester and 696.6 $l \cdot kg_{dom}^{-1}$ from digester with ozone prove that such method is not accepted.

Keywords: biogas, anaerobic digestion, ozone, methane yield.

Introduction

Dairy industry in Latvia is well developed and efficient management of dairy waste is an urgent issue. Usage of waste to partially retrieve energy spent in the production process is desirable. Methane production from dairy waste in anaerobic fermentation process is one of the options to achieve this goal.

Cheese whey is a left over in production of cheese, curd and casein. Denaturation of milk proteins can be done using several techniques, usage of organic or inorganic acid as well as addition of enzyme are widespread. Several parameters of different whey are compared in Table 1.

Table 1

Comparison of different whey [1]

Parameter	Denaturating agent used			Nanofiltered whey
	Enzyme	Organic acid	Inorganic acid	
pH	6.1	6.6-4.5	4.7-4.4	-
TS, %	6.0	6.4-5.7	6.2- 6.1	-
Fat Mass, %	<0.8	trace	<0.01	-
Protein Mass, %	<0.9	<0.9	0.50	-
Lactose Mass, %	4.5	5.0-3.8	4.6-4.7	4.00-4.48
Ash Mass, %	0.5-0.7	0.7-0.8	0.90	-

Usage of organic acid to denaturise milk protein is a widespread technology among small size dairy enterprises. In the current study cheese whey was obtained from the micro scale cheese maker using technology with organic acid denaturation.

To increase effectiveness of anaerobic fermentation different substrate pre-treatment methods are being studied. Pre-treatment with ozone is one of the chemical pre-treatment methods. Ozone is frequently used in processing of tap water where ozonation is used to disinfect water. Ozonation is also used in wastewater treatment with the concentration of ozone from 1 to 16 $g_{O3} \cdot g_{VOS}^{-1}$ [1; 4], depending on the biochemical composition of waste water and technology used. Treatment with ozone increases the degradation level of organic substances [1]. Pre-treatment of waste water sludge with ozone can increase the methane yield by 40-85 % [1]. Methane yields from whey 0.31-0.424 $m^3_{CH4} \cdot kg_{COD}^{-1}$ and 23.4 $l_{CH4} \cdot l_{whey}^{-1}$ have been reported [2; 3].

The goal of this study was to determine the effect of cheese whey ozone pre-treatment on biogas production in anaerobic fermentation. The aim of the pre-treatment is to hydrolyze complex organic molecules to increase the speed of their biodegradation. Two experiments were carried out in this study.

Methods and materials

Experiment 1

The characteristics of cheese whey used in Experiment 1 are summarized in Table 2. Ozone pre-treatment was carried out according to the scheme in Figure 1. The ozone generator ENALY OZX03K

was used with nominal ozone generation power of 3 $g_{O3} \cdot h^{-1}$ with oxygen flow 2 $lmin^{-1}$. The diffuser from porous ceramic material was used to diffuse ozone in whey.

Table 2

Characteristics of cheese whey used in Experiment 1

Parameter	Value	Unit
Total solids (TS)	4.49	%
Volatile solids (VS)	3.98	%
COD	79 500±8 290	$mg \cdot l^{-1}$
pH	5.7±0.1	-

3 kg of whey were treated with ozone for 30 min with oxygen flow 1.5 $l \cdot min^{-1}$, temperature +18 ºC, atmospheric pressure. During pre-treatment the ozone generator produced 1.125 g_{O3}, attributing to the amount of the sample - 0.005 $g_{O3} \cdot g_{TS}^{-1}$.

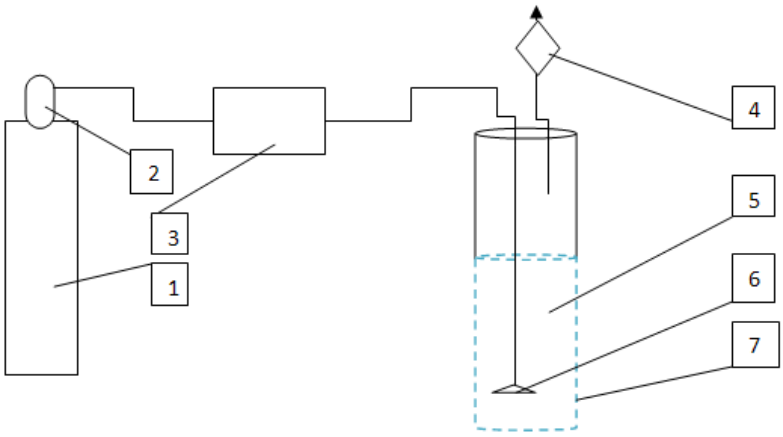

Fig. 1. **Scheme of ozonation equipment:** 1 – oxygen cylinder; 2 – pressure regulator; 3 – ozone generator; 4 – ozone destructor; 5 – cheese whey; 6 – diffuser; 7 – glass cylinder

To remove excess ozone from the treated whey, de-ozonation was performed. The treated whey was stirred for 60 min at temperature +40 ºC with the mixer Zanussi 700 W.

The mixture of components for batch bioreactors in Experiment 1 is described in Table 5. The seed material was obtained from anaerobic batch reactors used for seed material cultivation in own laboratory. Diluted cow manure was used as initial substrate. Fresh inoculum from the batch reactor, which produced biogas with average methane content of 60 % was used for the startup procedure.

Figure 2 is a picture of bioreactors used in the study. The total volume of the reactors is 5 l. Cultivation was carried out at temperature +37.5±0.5 ºC. The amount of biogas, pH and composition of biogas were measured daily.

Fig. 2. **Laboratory equipment B4**

During the first 20 days of the experiment pH in the reactors was corrected when necessary with solution of $NaHCO_3$ to the value of 6.5. Duration of the experiment was 163 days. At the end of the experiment the total amount of biogas, average methane content and methane yield were calculated.

Experiment 2

The aim of Experiment 2 was to investigate the dynamic of biogas production from ozonated and untreated whey during the first seven days. The parameters of whey used in Experiment 2 are summarized in Table 3.

Table 3

Characteristics of cheese whey used in Experiment 2

Parameter	Value	Unit
Total solids (TS)	6.69	%
Volatile solids (VS)	6.04	%
pH	5.1±0.1	-

Pre-treatment with ozone was done according to the scheme described earlier. 600 g of whey were treated with ozone for 30 min with oxygen flow 3.5 $l \cdot min^{-1}$, temperature +7 ºC, atmospheric pressure. The dose of ozone during pre-treatment was 0.037 $g_{O3} \cdot g_{TS}^{-1}$.

To remove excess ozone from the treated whey, de-ozonation was performed as follows: the treated whey was kept in a hallow glass vessel for 120 min at temperature +40 ºC, afterwards whey was stirred for 45 min at temperature +40 ºC under vacuum.

Anaerobic fermentation was performed in batch bioreactors with the volume 0.5 l under temperature of +37.5 ±0.5 ºC. Duration of the experiment was seven days. During the experiment the amount of biogas was determined every 12 hours. The mixture of substrate components is described in Table 4.

Table 4

Substrate mixture in Experiment 2

Reactor Nr.	Cheese whey, g	Seed material, g	Total mass, g	Pre-treatment of whey
0;1	0	500	500	-
2;3;4	50	450	500	ozone
5;6;7	50	450	500	-

Analytical methods

Total solids were determined by moisture balance (MOC-120H, Shimadzu). Volatile solids were determined by keeping dried samples in a laboratory furnace (L3/11/B170, Nabertherm) at constant temperature of 550±5 ºC during the period of 0.5 hours. Gas composition was determined by a gas analyzer (GA2000, Geotech). For substrate preparation laboratory scales KERN (5 kg±2 g) were used.

Results and discussion

Results of Experiment 1 are summarized in Table 5. The process of fermentation in the reactors B1 and B2 can be assessed as slow. According to the results achieved, no positive effect of ozone pre-treatment on biogas yield or methane yield was discovered.

The results of Experiment 2 are depicted in Figure 3. During the experiment no significant difference in the biogas amount produced from pre-treated or untreated whey was discovered. After 170 hours 1419±33 ml of biogas were produced from pre-treated whey and 1479±12 ml from untreated whey (in average per one reactor). The average biogas yield for pre-treated and untreated whey is 240 $l \cdot kg_{vsd}^{-1}$.

During Experiment 2 no methane content in biogas was analyzed due to the small amount of gas produced that was insufficient for the gas analyzer.

Table 5

Results of Experiment 1

Parameter	Unit	B1 with ozone	B2
Substrate composition	%	14 in, 65 who, 21 w	14 in, 65 wh, 21 w
Total substrate weight	g	4633	4632
Total solids after digestion	% g	2.56 96.44	2.33 83.88
Organic solids after digestion	% g	30.23 29.15	20.62 17.29
Biogas yield	$l \cdot kg_{vsd}^{-1}$	696.1	732.1
Average methane content	%	62.3	61.4
Methane yield	$l \cdot kg_{vsd}^{-1}$	433.6	449.5
Conversion rate	%	75.55	85.51

Remarks: in – inoculum, wh – cheese whey, who – cheese whey after processing with ozone, w – water, vsd – volatile solids destroyed.

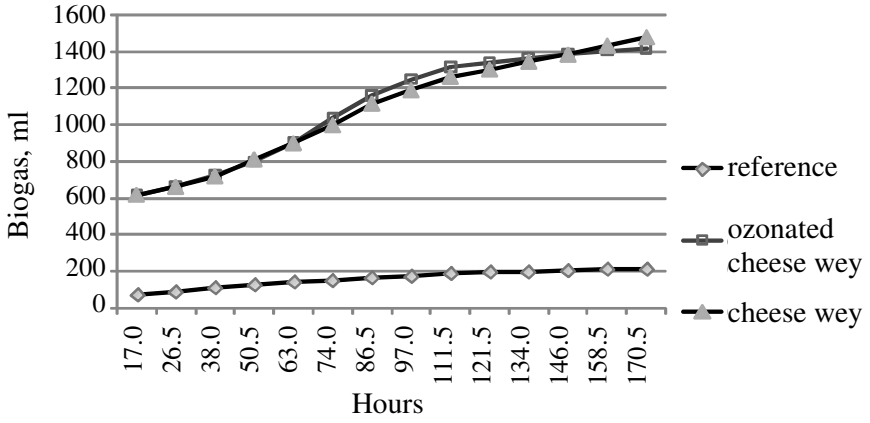

Fig. 3. **Cumulative amount of biogas in Experiment 2**

Cheese whey is characterized by fast hydrolysis and short HRT (3-5 days) in continuous stage fermentation [5]. Ozonation of cheese whey should increase the amount of small organic molecules shortening the time for bacterial hydrolysis even more. The acidogenic phase, acetogenic and methanogenic phases should start faster in pre-treated whey. According to Figure 3 there is almost no *lag* phase when bacteria are growing and substrate is being hydrolyzed, but the biogas amount produced and dynamic of production is almost identical for treated and untreated whey.

Taking into account reports from other scientists [6] about positive effect of substrate ozone pre-treatment on biogas yields, technology and experiment protocols are being revised. As only few parameters were controlled during the experiments no well-grounded conclusions can be drawn.

Determination of volatile organic acids would characterize differences in the start and dynamic of the acidogenic phase between pre-treated and untreated whey. The difference in chemical oxygen demand before and after fermentation and determination of organic solids should be used to take into account the mass balance of also volatile acids and alcohols. The concentration of acetic acid/acetate should be controlled to determine the start of the acetogenic phase. Biogas and methane production should be controlled more often than once in 12 hours to detect the start and dynamics of methane production.

Conclusions

During the study no positive effect of ozone pre-treatment of cheese whey on biogas or methane production was discovered under the described technological conditions. The experiments are going to be continued after improvement of the ozonation and de-ozonation techniques. Vacuum evaporation had good results on dissolved ozone elimination from liquid. To enhance technological capability,

laboratory Continuous Quench Flow System (CQFS) with pH and temperature control functions is going to be developed. In further study more process parameters including volatile organic acids and chemical oxygen demand (COD) are going to be controlled before and after ozonation.

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