Biogas production of ozone and/or microwave-pretreated canned maize production sludges

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Abstract

Biogas production from food wastes is of growing importance as concerns its environmental benefits, and renewable energy is produced. The production of canned maize is accompanied by the formation of large volumes of waste water, with high contents of starch, and high chemical and biological oxygen demands. Anaerobic digestion is a sludge treatment process that is used in many wastewater treatment plants. Thermal, chemical, biological and mechanical processes and their different combinations have been studied as possible pretreatment to accelerate sludge hydrolysis.

In our work, the effects of acidic, microwave and ozone pretreatment on the biogas production and biodegradability of canned maize production sludge were examined and the energy balances of the processes were determined when different sludge pretreatments were used. It was found that ozone treatment decreased the chemical oxygen demand, while the biological oxygen demand and the biodegradability increased. The combination of microwave and ozone treatment increased the biodegradability relative to ozone treatment alone. The investigation of biogas production showed that all types of pretreatment enhanced methane production: 30-min ozone treatment and 5-min 250-W microwave treatment resulted in a positive energy balance.

Keywords: ozone, microwave, biogas production, biodegradability, maize

Introduction

Most branches of the food industry, for instance the dairy industry, the meat industry and the cannery industry, have a considerable wastewater output. The problem of pollution is not caused only by the total amount of wastewater production, but also by the high content of organic matter. The sewage sludge is the residue of the primary, secondary or tertiary wastewater technologies. The organic matter content of the sludge is also considerable. Depending on the raw material processed, the sludge may be rich in carbohydrates, lipids or proteins. The production of canned maize produces a high volume of wastewater too, with high chemical (COD) and biological oxygen demands (BOD). After mechanical wastewater treatment, the COD of the sludge may be more than 100 kg m^{-3}, because of the high content of corn starch.

The aim of sewage sludge treatment technologies is to reduce the sludge mass or to modify it so as to make it suitable for further utilization. The methods commonly applied for sludge treatment today include digestion, dewatering, incineration or use in agriculture. Anaerobic digestion is an appropriate technique for the treatment of sludge before its final disposal, and it is used worldwide as the oldest and most important process for sludge stabilization. The mesophilic anaerobic digestion of sludge below a fermentation temperature of 40 °C is more widespread than thermophilic digestion (above 40 °C), because of the lower energy demand, the higher rate of growth of microorganisms and the higher stability. On the other hand, thermophilic anaerobic digestion provides sludge disinfection and an increased extent of methane production, and accordingly is advantageous in municipal sewage sludge treatments [1].

Biogas-producing fermentation involves four major steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. The rate-limiting step of sludge degradation is hydrolysis, during which both solubilization of particulate matter and biological degradation of organic components can occur. Thermal, chemical, biological and mechanical processes and their different combinations have been studied as possible modes of pretreatment accelerating sludge hydrolysis [2, 3]. These pretreatments cause the lysis or degradation of sludge cells, the organic matter therefore becoming more accessible to anaerobic microorganisms. It causes increased methane production and decreases the digestion time. The efficiency of pretreatment is commonly evaluated in terms of biodegradability or biogas production.

Ozonation is regarded as a promising preoxidation process via which to control the levels of organic pollutants in water, because ozone is a strong oxidant and a potent disinfecting agent. Compounds consisting of large molecules may decompose to smaller molecules. In consequence of ozone treatment, organic matter may become more accessible to microorganisms [4]. This may improve the rate of the overall digestion process and the degree of sludge degradation, there by reducing the anaerobic digester retention time and increasing the methane production rates.

The use of microwaves is an alternative treatment procedure for sludge disintegration. This method is very promising, because of the rapid internal heating and selective heating effects: the cell walls of both dead and living microorganisms in sludge are destroyed and the organic substances are digested due to the heat effect. The dissolved organic compounds evolved from the cell fluid improve the efficiency of biological degradation processes. During intensive microwave heating, odorous compounds such as volatile fatty acids present in sludge may be reduced [5].

The aim of our present work was to examine the effects of acidic, microwave and ozone pre-treatment on the biogas production and biodegradability of canned maize production sludge. Because of the high energy demands of the processes, their energy balances were also examined.

Materials and methods

The non-pretreated maize canning sludge originated from the DEKO Food Cannery, Debrecen, Hungary. The chemical oxygen demand (COD) was measured before and after the treatments, by the dichromate standard method, in COD tests with an ET 108 digester Lovibond PC CheckIt photometer. The initial chemical oxygen demand of the sludge was 136 kg m^{-3}.The biochemical oxygen demand measurements were carried out in a respirometric BOD meter (BOI Oxidirect, Lovibond, Germany), at 20 °C. To ensure the consistency of the results, BOD microbe capsules (Cole Parmer, USA) were used in the measurements. The biodegradability during 5 days (BD_5%) was calculated via the expression

$$BD_5\% = (BOD_5/COD_0) \times 100$$

where BOD_5 is the BOD during 5 days.

The ozone treatment was performed in continuously mixed solutions diluted to 6% dry matter content. Ozone was generated from oxygen (Linde 3.0) with a flow-type ozone generator (Ozomatic Modular 4, Wedeco Ltd., Germany) operating via a silent electric discharge, and the ozone-containing gas (flow rate 1.0 dm^3 min^{-1}) was bubbled through 180 cm^3 of solution in a batch reactor through a ceramic diffuser. The ozone concentration in the feed gas was 32 mg dm^{-3}, which was measured at 254 nm with a UV spectrophotometer (WPA Lightwave S2000); the contact time was 30 or 60 min, and the flow rate of the bubbling gas was 1 dm^3 min^{-1}.

The microwave treatment was performed in Labotron 500 professional microwave equipment, at 250 or 500 W microwave power. For the measurements, 200 g of sludge sample was diluted with 200 ml of distilled water in a PTFE vessel, and then irradiated for 5 or 10 min. For acidic and microwave pre-treatment, the pH was adjusted to pH 2 with 1 M HCl. After the treatment, the pH was adjusted to pH 7.2 with 1 M NaOH.

Biogas production tests were performed in batch mode under mesophilic conditions, at 30 °C for 30 days, in an anaerobic digester with a pressure-measuring head (Oxitop Control AN12 measurement system) (WTW Gmbh, Germany). The digester was inoculated with anaerobic sludge from a municipal wastewater treatment plant (Hódmezővásárhely, Hungary). For methane determination, measurements were performed in parallel in two vessels: one of them contained a CO_2 absorber, while the other measured the total gas pressure. The resulting pressure difference was proportional to the CO_2 concentration, and the remaining overpressure was proportional to the methane concentration. The composition of the biogas produced was measured by a gas chromatographic and mass spectrometric method (Agilent 6890N-5976 GC-MS).

The net energy product (NEP) of a process involving with microwave pretreatment can be calculated via the equation:

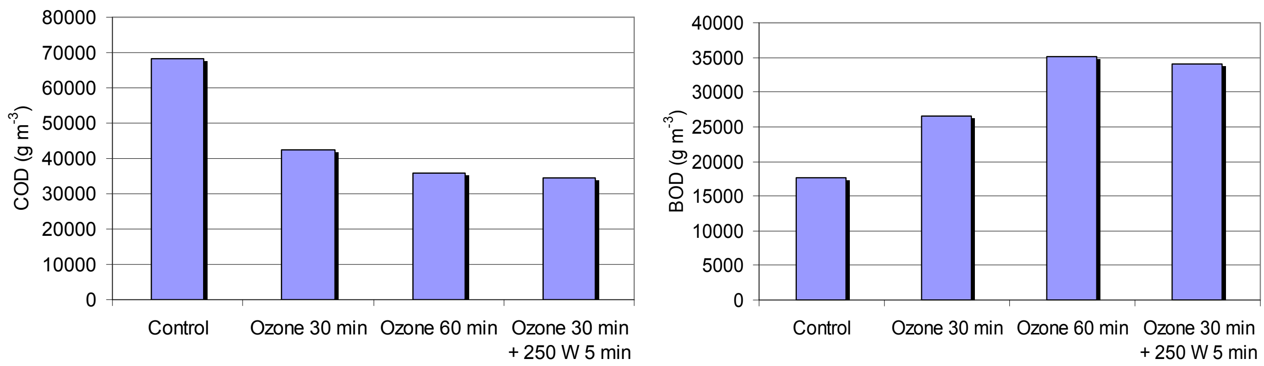
$$NEP = q_{comb} \times m_{methane} - P_m \times \tau$$

where *NEP* is the net energy product [J], q_{comb} is the combustion heat [J kg^{-1}] of methane, $m_{methane}$ is the mass of methane produced [kg], P_m is the power of the microwave magnetron [W], and τ is the duration of treatment [s].

For the examination of preozonation treatment, the same equation was applied except that the magnetron power was replaced by the power of the ozone generator.

Results and discussion

In the first series of measurements the COD and BOD were measured (Fig. 1a, 1b).



(a) (b)

Figure 1. Changes in COD (a) and BOD (b) of diluted sludge solutions due to various treatments

It was found that the ozone treatment and the combined ozone/microwave treatment decreased COD, while BOD increased. After the 30-min ozone pre-treatment, the microwave irradiation caused approximately the same COD decrease as that resulting from the 60-min ozone treatment. At the same time combined treatment was less time-consuming.

The treatments were found to increase the biodegradability.

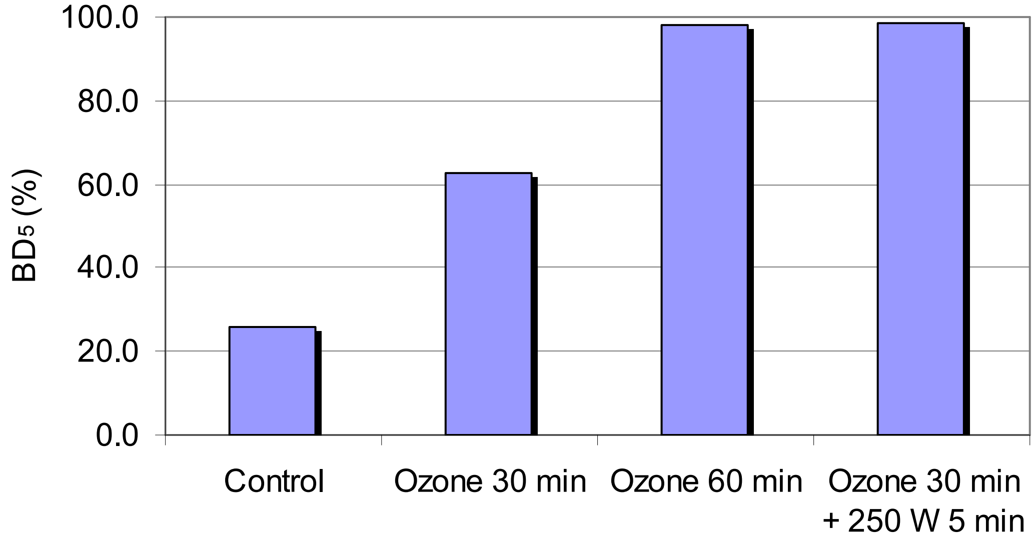


Figure 2. Changes in biodegradability due to ozone treatment and ozone/microwave treatment

The 30-min ozone pretreatment enhanced the biodegradability about to 3-fold, and the 60-min treatment increased it to around 90%. The combination of ozone/microwave treatment increased the biodegradability to close to 100% (Fig. 2).

In the next series of experiments, the biogas production was measured. Gas chromatographic and mass spectrometric measurements showed that after fermentation for 30 days the fermenter contains gaseous CO_2 and CH_4. The non-pretreated sludge was used as control sample. The microwave treatment alone did not have a significant effect on the biogas production, whereas the ozone treatment enhanced it (Fig. 3).

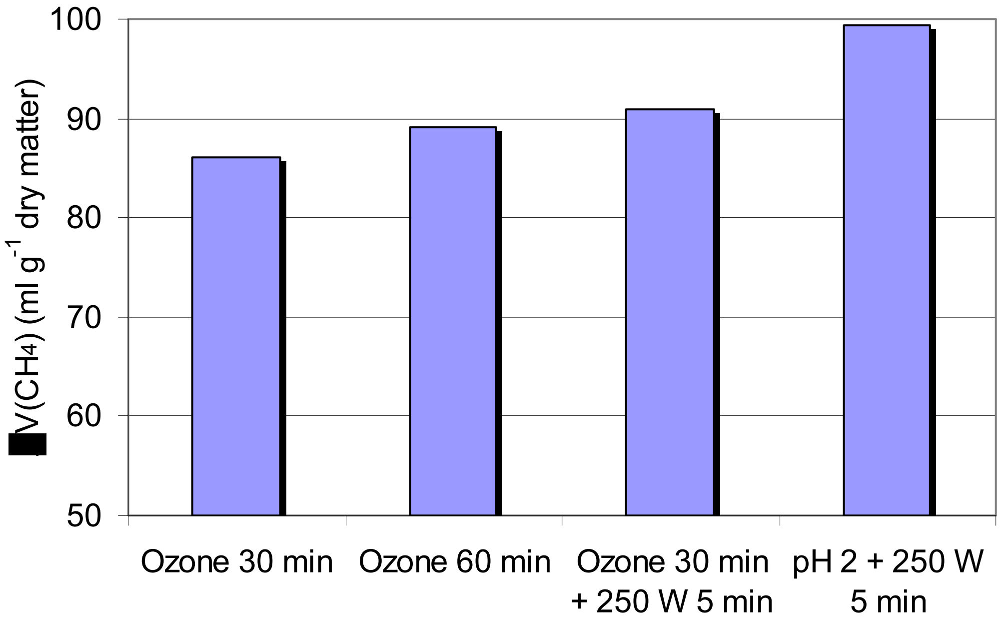


Figure 3. The difference in methane production between the pretreated and control samples

The results revealed, that all types of pretreatment enhanced the methane production relative to the control (18.0 ml g^{-1} dry matter). There was no significant difference between the biogas production of the 60-min ozone and the combined ozone/microwave pretreatments. The microwave treatment at pH 2 resulted in a higher methane production.

The initial specific biogas production rate (dm^3 kg^{-1} day^{-1}) was calculated as the slope of the straight line fitting the amounts of biogas produced during the initial 10 days of the test [6] (Table 1).

Table 1. Parameters of biodegradability after different pretreatments

Pretreatment	Treatment time [min]	BD_5% (BOD_5/COD)×100	Initial biogas production rate [cm^3 $g^{-1}$$day^{-1}$]
Untreated	-	26	1.037
Ozone	30	63	3.77
Ozone	60	94	7.40
Ozone/microwave	30+5	96	9.52
Microwave (pH=2)	5	95	25.75

The results demonstrate that all of the treatments enhanced the initial specific biogas production rate. When combined ozone/microwave treatment was applied, the increase was 10-fold; however, the acidic microwave treatment enhanced the initial biogas product rate about 25-fold.

As concerns the calculated the energy balance of the treatments, the results showed, that the 30-min ozone treatment and the 5-min microwave treatment at pH 2 were associated with an energy increase, while the 60-min ozone treatment and the combined ozone/microwave treatment needed more energy than that obtained from methane production (Fig. 5). Accordingly, differently from the biodegradability and the biogas production, from an energetic aspect the 30-min ozone pretreatment and the microwave pretreatment at pH 2 were more profitable, because of the high energy demand of the long-time treatment.

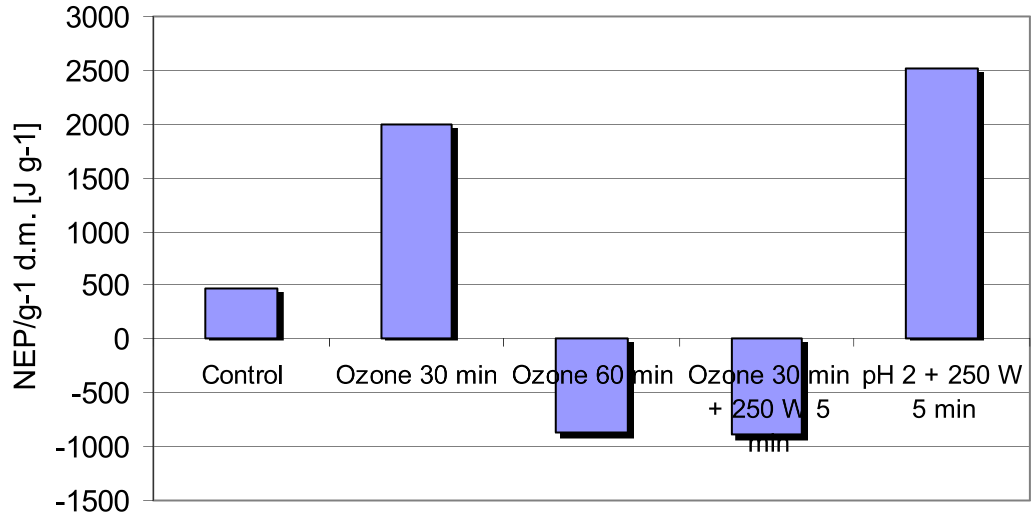


Figure 5. Energy balance of the treatments

Conclusion

The results show that microwave treatment alone has no effect on the biogas production of a maize canning sludge, because it does not change the biodegradability of the starch content of the sludge. The microwave treatment of acidic sludge solution resulted in higher biodegradability and enhanced biogas production. Ozone pretreatment and combined ozone/microwave treatment also increased the biodegradability and the biogas and methane production. However, when the processing time is also taken into consideration, the energetic benefits of the pretreatments are not so unambiguous; only the short-time ozone or microwave treatment resulted in net energy production. These experiments indicate that the ozone pretreatment is appropriate for decreasing the organic content of canning sludge, making the organic content of the sludge more accessible for anaerobic degradation, and thereby increasing biogas production.

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