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Anaerobic biodegradation of sugar beet pulp

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Abstract

Sugar beet pulp is a by-product of sugar production and consists mainly of cellulose, hemicellulose and pectin. Its composition is suitable for biological degradation. A possible alternative for the utilization of this material (besides cattle feeding) can be anaerobic methanogenic degradation. It has an additional advantage – biogas production. Beet pulp was treated by a two-step anaerobic process. The first step consisted of hydrolysis and acidification. The second step was methanogenesis. In this paper, observation of the process of anaerobic degradation and determination of optimal parameters is discussed. A laboratory-scale model for sugar beet pulp anaerobic biodegradation was operated. Results of model performance have shown very good pulp digestion characteristics. In addition, high efficiency removal of organic matter was achieved. Methane yield was over 0.360 m^3 kg^{-1} dried pulp and excess sludge production was 0.094 g per gram COD added.

Introduction

Sugar beet pulp, a by-product of the sugar beet industry, is produced annually in large quantities. In the EU alone, about 10^8 tons of root per year is processed (Spagnuolo et at. 1997). On the one hand, in countries with an intensive cattle-raising industry, pulp is used in feed manufacture. In other countries, it is dumped in landfills (Voragen et al. 1997). On the other hand, however, sugar beet pulp can be an important renewable resource and its bio-conversion appears to be of great biotechnological importance. The processing of 1 ton of beet produces about 250 kg of exhausted pressed pulp, with a water content of approximately 75–80%. This amount can also be converted into 70 kg of exhausted dried pulp, with about 10% water content (Spagnuolo et al. 1997).

The lignocellulosic fraction of dried pulp is composed of 22–30% cellulose, 24–32% of hemicellulose (essentially arabinan), 24–32% of pectins substances and 3–4% of lignin (Spagnuolo et al. 1997). The total hydrolysis of beet pulp yield following monosaccharides: D-glucose, L-arabinose and D-galacturonic acid, are released as components of the main chains of cellulose, hemicellulose, and pectin, respectively. D-galactose, D-xylose, D-manosse, and L-rhamnose are produced in lower amounts (Spagnuolo et al. 1997). Sugar beet pulp is especially rich in pectins (15–30%). It contains high amounts of galacturonic acid and arabinose (each 1/5 to 1/4 of pulp dry weight;). Beet pectins have the common structural features of pectins and are characterized by a backbone of α-(1 $\rightarrow$ 4)-linked galacturonic acid residues, forming long "smooth" regions which may be interrupted by "hairy" regions consisting of galacturonic acid and (1 $\rightarrow$2)-linked rhamnose (Micard et al. 1996). Some rhamnose residues carry side chains consisting mainly of (1 $\rightarrow$ 5)-linked α-arabinans with branches attached to position 3. Other structural features might include (1 $\rightarrow$ 4)-linked β-galactans of low polymerization degree, and highly branched (1 $\rightarrow$ 3,6)-linked galactans (Micard et al. 1996). Beet pectins, however, are different from those of fruit. Several differences have been noted between apple and citrus pectins and beet pectins. Among them is the presence of acetyl groups linked to the α-D-galacturonic acid, the presence of feluric acid, and the content of rhamose. The main

Table 1. Sugar beet composition (dry matter basis) (Micard et al. 1996)

Components	%
Rhamnose	2.4
Fucose	0.2
Arabinose	20.9
Xylose	1.7
Mannose	1.1
Galactose	5.1
Glucose	21.1
Galacturonic acid	21.1
Methanol	1.8
Aceticacid	3.9
Ferulic acid	0.8
Diferulic acid	0.04
Protein	11.3
Ash	3.6

constituents of beet pulp (74% of the dry matter) are shown in Table 1.

Ferulic acid, rhamnose, galacturonic acid, and arabinose may have different commercial uses. Free feluric acid that chemically resembles vanillin, can be bio-transformed by lignolytic microorganisms into an aroma. Rhamnose can be used as a precursor of aroma, such as "furaneol" (applications in caramel, roasted and fruit flavors), by chemical transformation. Galaturonic acid can be transformed by esterification with various fatty acids into tensioactive agents. L-arabinose can be used, for example, for diagnostic purposes in bacteriology. It has been found that it has anti-Parkinson properties (Micard et al. 1996).

In addition, sugar beet pulp can be used not only for the above mentioned pure chemicals, but also for biogas production by an anaerobic treatment (Lane 1984; Weiland 1993). There is only very little information available about beet pulp anaerobic digestion and methane production.

One of the references was found in the paper of Lane (1984). In this work, a 10 liter continuously stirred tank reactor was implemented. For maximum efficiency, the following technological parameters were applied: organic loading rate -4.06 kg m^3 d^{-1} (kg of volatile solids – VS), 95.2% of VS reduction and methane yield of 0.263 m^3 per kg VS added. The pulp was digested at a temperature of 35–37 °C (Lane 1984).

Table 2. Properties of sugar beet pulp used by Weiland (1993)

Parameter	Dimension	Value
Total solids – TS	g kg^{-1}	150–180
Total volatile solids – TVS	% TS	90–95
Total COD – TCOD	g l^{-1}	180–220
Total carbon – TC	%TS	40–41
TKN	% TS	1.0–1.2
C/N	kg kg^{-1}	35–40
pH	–	3.9–4.0

Pilot-scale anaerobic digestion of beet pulp was presented by Weiland (1993). The most important properties of used pulp are shown in Table 2. Sugar beet pulp has a relatively low protein content, which results in a favourable high C:N ratio of 35–40. A completely filled mechanically mixed loop reactor (volume 6 m^3) with a conical bottom and an upper section was used in a one-step operation of methanogenic degradation (Weiland 1993). It was also used in a two-step operation for the liquefaction and acidification of the pulp (volume 2.5 m^3). The volume of the methane reactor in the two-step process was 1.0 m^3. The process was carried out in a semi-liquid phase at 35 °C.

The data in Table 3 demonstrate that one-stage and two-stage processes are similar in efficiency and methane yield. The two-step process results only in a somewhat higher efficiency of COD removal and methane yield. It should be noted that these results were achieved at a longer hydraulic retention (HRT) time than process data for the one-step operation. Effluent quality of both processes differed considerably, because the effluent of the one-stage process contained all undigested suspended solids, whereas in the two-step process, suspended solids were separated by the internal clarifier of the contact process. Hence, the effluent of the one-stage process has shown a high COD load of 10–50 g l^{-1}, whereas the effluent of the two-stage process was polluted with only 1.0–1.4 g COD per liter.

Papers of Lane (1984) and Weiland (1993) along with information about the composition and saccharification (Spagnuolo et al. 1997; Micard et al. 1996) show a realistic possibility of sugar beet pulp anaerobic treatment and its use for biogas production.

The aim of this work was to investigate the processes of sugar beet pulp anaerobic treatment and

Table 3. Characteristic process data for one- and two-stage anaerobic digestion of sugar beet pulp (Weiland 1993)

Parameter	Dimension	One-stage process	Two-stage process	
		Methanogenesis	Hydrolysis	Methanogene
COD-Loading	kg m^{-3} d^{-1}	8	10	6
Hydraulic retention time	d	10	6	7
COD removal efficiency	%	60	–	65
Methane yield	l kg^{-1} COD	210	–	230
Methane content	%	59	–	61

to determine the optimal parameters of an anaerobic process with regard to its realistic utilization.

Materials and methods

Three sets of measurements were carried out:

- determination of characteristics of used sugar beet pulp;
- characterization of the individual phases of anaerobic digestion (tests of hydrolysis, acidogenesis and methanogenesis);
- observation of lab-scale equipment performance for anaerobic treatment of sugar beet pulp.

Standard methods (APHA 1992) were used for the following laboratory analyses: total solids (TS), total suspended solids (TSS), volatile solids (VS), volatile suspended solids (VSS), total Kjeldahl nitrogen (TKN), ammonium nitrogen (NH_4–N), total phosphorus (TP), phosphate phosphorus (PO_4–P), COD and methane content in biogas. The reducing sugars were measured by the dinitrosalicyl acid (DNS) method (Miller 1959). Total carbohydrates in the sample were determined by using phenol-sulfuric reagent (Dubois et al. 1956). The amount of polysaccharides was estimated as the difference between the total sugars and the amount of reducing sugar in the sample. Concentrations of individual volatile fatty acids (VFA) were determined by using the isotachophoretic method (Zábranská 1991).

The laboratory scale model used in this work is described in the following section.

Table 4. Characteristics of used sugar beet pulp

Parameter	Dimension	Average value
TS	%	90
VS	%	90
Specific COD	g g^{-1}	1.295
TKN	mg g^{-1}	110
TP	mg g^{-1}	20

Results and discussion

Characteristics of used sugar beet pulp

Dried sugar beet pulp (90% dry matter) from the sugar beet enterprise JUHOCUKOR, Dunajská Streda, Slovakia, was used in all laboratory experiments. It was cylindrically shaped with 8–9 mm diameter and 10–40 mm length. The size of the pulp was not modified in the dry stage vs. that in a mixture with water. Characteristics of the beet pulp are given in Table 4.

Tests of hydrolysis, acidogenesis and methanogenesis

All tests with beet pulp were conducted in a water mixture. The mixture was formed from 10 g of beet (100% dry matter) filled up with water to 300 ml. Pulp was hydrolyzed and acidified in the water environment. Processes of hydrolysis and acidification were required for the subsequent generation of biogas. The pH reduction in the pulp-water mixture is described in Figure 1. It shows that pH in the mixture declined below 4 during less than 2 days; pH value after five days treatment was 3.2.

Micard et al. (1996), monitored the rate of hydrolysis using several enzymatic complexes. The fastest hydrolysis was observed with enzyme SP 584 (Novo Nordisk, Denmark). For this enzyme, further tests

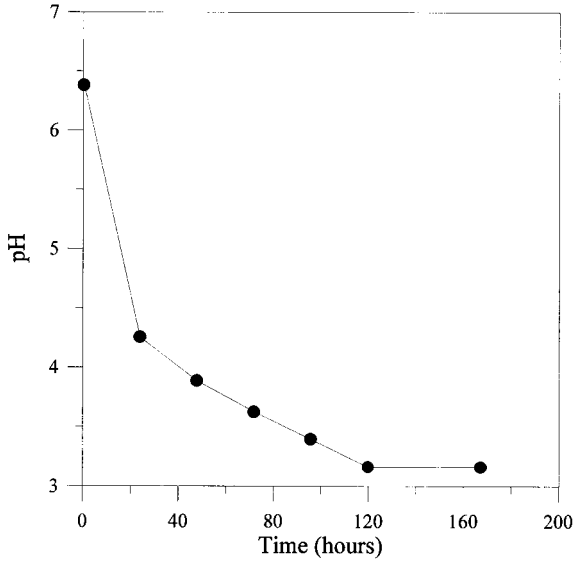

Figure 1. Decrease of pH in pulp-water mixture.

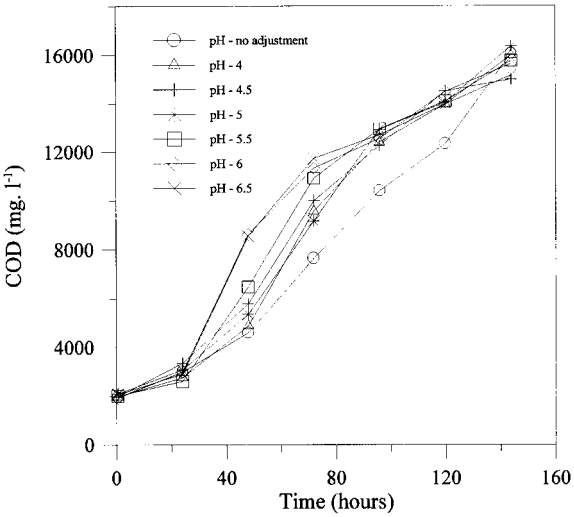

Figure 2. Release of COD into liquid phase in hydrolysis tests.

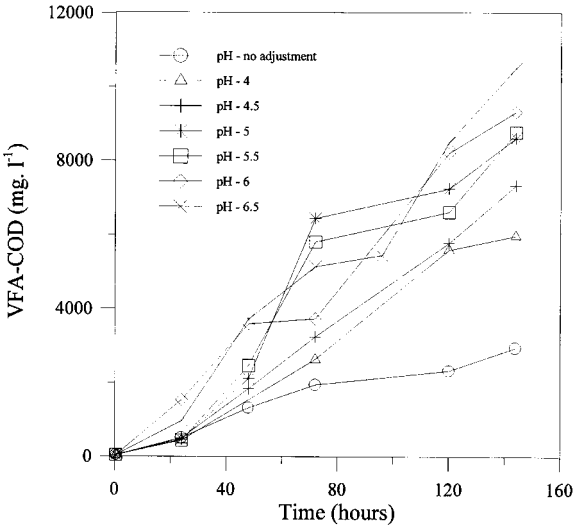

Figure 3. Course of VFA-COD concentration at tests of hydrolysis.

of the rate of hydrolysis depending on pH were carried out (Micard et al. 1996). It was determined that pH 4 was an optimal pH for the hydrolysis. Thus it might be expected that the pH value would also affect anaerobic degradation of the pulp, primarily, in its pre-methanogenesis phase. Therefore, in our work the tests of hydrolysis and acidogenesis were carried out at the pH values of 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, and without pH adjustment. The pH was adjusted only by $NaHCO_3$. Therefore, lower pH values were stabilized after a delay. The course of this stabilization is shown in Figure 1.

Concentrations of filtered COD, total sugars, reducing sugars and individual VFA were monitored in tests of hydrolysis and acidogenesis. For the purpose of comparison, all concentrations were converted to COD units. The results of the tests of hydrolysis and acidogenesis are shown in Figures 2–5. Courses of the COD in solution with the adjusted pH values are very similar (Figure 2). Other monitored components resulted in different patterns. In the case of total sugars, concentration did not increase after 4 days (Figure 4). In the case of reducing sugars at the values of pH 5 or more, concentration decreased after 4 days (Figure 5). Reducing sugars generated during the reaction, were immediately converted to VEA. Figure 3 shows the COD of total VEA. Individual VFAs, formic, L-lactic, acetic, propionic, butyric, and valeric acids were measured by the isotachophoretic method. The results were calculated based upon a specific COD of individual acids. The slowest releases of the COD and the total sugars into a liquid phase and the slowest VFA generation were observed in the tests without pH adjustment. The fastest hydrolysis processes occurred in pH of 6 and 6.5. The differences in the rates of hydrolysis and acidogenesis of the individual tests with adjusted pH differed less than in those tests without pH adjustment. The tests implied that it is efficient to adjust the system pH, which results in an optimal hydrolysis. Thus the optimal pH was 4.0–4.5, taking into consideration a high consumption of a buffer medium.

The tests of methanogenesis were carried out with the pulp samples after hydrolysis and acidogenesis in

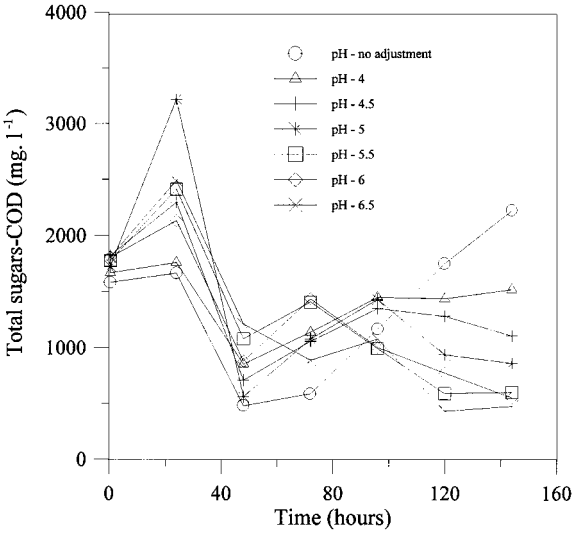

Figure 4. Concentration of total sugar-COD in hydrolysis tests.

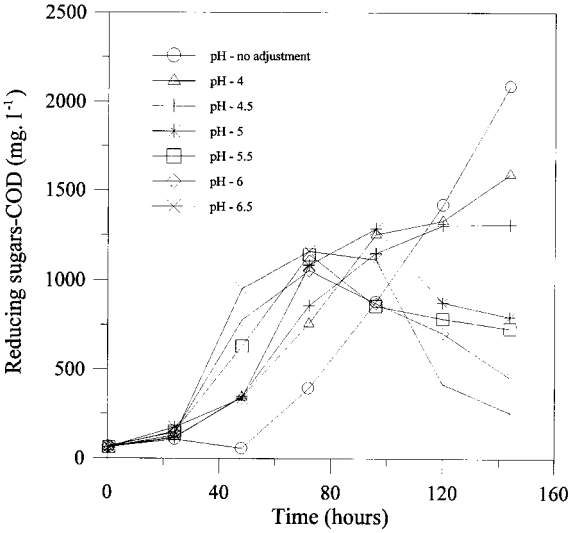

Figure 5. Concentration of reducing sugars-COD in hydrolysis tests.

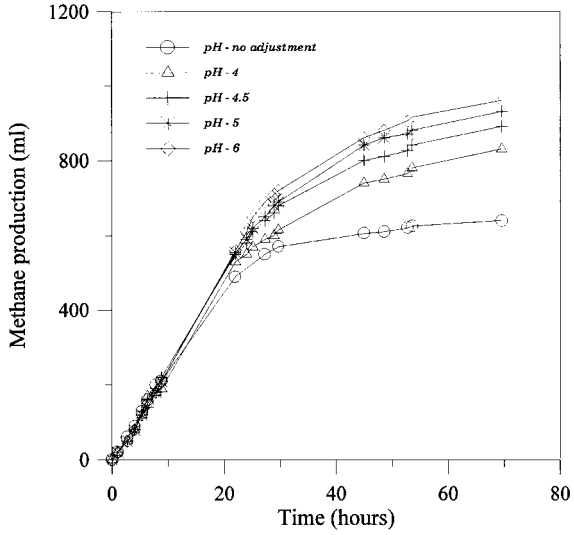

Figure 6. Methane production in methanogenic tests at HRT = 6 d.

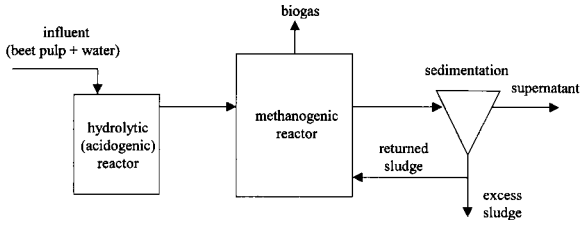

Figure 7. Laboratory semi-continuous model of two-step anaerobic treatment of sugar beet pulp.

semi-continuous reactors. The acidogenic reactors (at pH 4, 4.5, 5, 6, and without pH adjustment) were operated at hydraulic retention times 2, 3, 4, 5, and 6 days, respectively. Total number of reactors used was 25. The dose for each reactor was 5 g of dry sugar beet pulp filled up with water to 150 ml. We assumed that reactors were in steady state condition after a period that was 5 times higher as hydraulic retention time (equal to acidific sludge age). Anaerobic stabilized sludge (Central WWTP Bratislava–Vrakuna) was used for methanogenic tests. The tests were conducted as follows: 100 ml of the acidified pulp was gradually removed from each reactor and was mixed with anaerobic sludge in a 1 l tank to a concentration of 5–8 g l^{-1} of digested sludge VSS. The average values of maximum specific methanogenic activities (expressed in mg of methane COD per gram of VSS of anaerobic sludge per day) for the individual hydraulic retention periods are shown in Table 5. The results of methanogenic tests show that four days of retention time are sufficient for the hydrolysis and acidogenesis. A course of methanogenic tests for thc individual pH and for the 4-day hydraulic retention time is shown in Figure 6. It is evident that an optimal pH for hydrolysis and acidogenesis is 4–4.5. A similar course was observed for each hydraulic retention time. Lowest methane generation was measured in experiments without pH adjustment.

Operation of the lab-scale model

Based on the results of the tests of hydrolysis, acidogenesis and methanogenesis, a two-step laboratory semi-continuous model was designed and operated. A

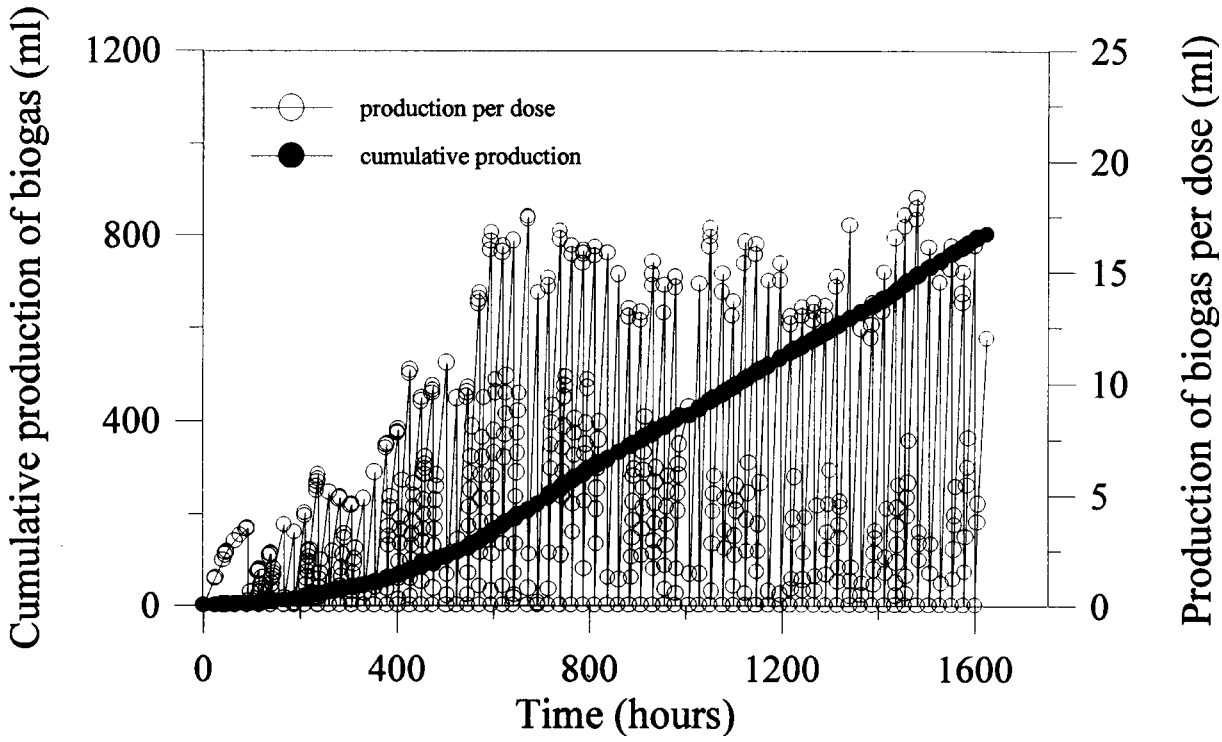

Figure 8. Biogas production per dose of the beet pulp and cumulative values.

Table 5. Average values of maximum specific methanogenic activity (mg of methane COD per g VSS per day) in methanogenic tests

Hydraulic retention time d	Methanogenic activity mg g^{-1} d^{-1}
2	163.3
3	208.0
4	253.6
5	266.5
6	267.5

schematic view of this model is shown in Figure 7. The first step consisted of hydrolysis and acidogenesis. Volume used was designed to meet organic loading of an acidogenenic and methanogenic reactor. The reactor was not stirred. The second stage consisted of an unstirred methanogenic reactor with 4 liters constant volume. Both reactors were operated at a temperature of 35 °C. The acidogenic reactor operated at pH of 4.0–4.5 and a hydraulic retention time (HRT) of 4 days. pH was maintained by $NaHCO_3$ dosage of 0.02 g per g of the dry pulp. The sludge from the UASB reactor of the sugar enterprise in Trencianska Teplá was used for the seeding of the methanogenic reactor in such amounts that an initial concentration of sludge was 15.1 g l^{-1} (VSS 9.5 g l^{-1}). The parameters of the operation are listed in Table 6.

The model equipment was fed once a day. After 30 minutes sedimentation, 300 and 450 ml of sludge water, respectively, was daily removed from the methanogenic reactor (Table 6). The same amount of the beet pulp from the acidogenesis reactor was added to the methanogenic reactor. Subsequently, a dose of fresh beet pulp and water was put into the acidogenesis reactor. Exact amounts can be found in Table 6. It was not necessary to adjust the pH value in the methanogenic reactor. pH was naturally sustained at 6.7–7.2.

The following parameters were monitored in the methanogenic reactor:

- characteristics of sludge water – filtered COD, non-filtered COD (after a half hour sedimentation), NH_4–N, PO_4–P, SS;
- characteristics of sludge – SS, VSS;
- characteristics of biogas – amount of biogas generated, concentration of methane in biogas.

Figure 8 shows biogas production per beet pulp dose and cumulative values from the beginning of the

Table 6. Average parameters of acidification and methanogenic reactor

Dose of dried pulp g	Volume of dose ml	Volume of acidification ml	Acidification		Methanogenesis		Day of performance
			Organic load kg m^{-3} d^{-1}	HRT d	Organic load kg m^{-3} d^{-1}	HRT d	
10	300	1200	10.8	4	3.24	13.3	1–12
20	300	1200	21.6	4	6.48	13.3	13–22
30	450	1800	21.6	4	9.71	8.9	23–67

operation. For each increase in the organic load (see Table 6) production of biogas increased proportionally. An average specific production of biogas was calculated based on the total amount of the processed pulp during the operational period (1.65 kg). The total amount of produced biogas was 801.59 1. It amounted to 485.8 ml per gram of dry beet pulp. The average content of methane in the biogas was 71.9%. An average specific production of biogas involved a start-up of a model and a transitive reduced specific production at a step increase of an organic load. 504.1 1 of biogas per gram of dry beet pulp was determined when a calculation of the specific production involved only the values of the steady state (approximately 10 days after the start-up and 4–5 days after the each step increase of the organic load, respectively). Important parameters of the process are listed in Table 7. As one can see from Table 7, a high efficiency of COD removal was obtained. Production of dry sludge per gram of COD removed (Table 7) responded to values that are commonly reported for readily biodegradable dissolved substrates. This suggests that decomposition of suspended solids of the dry beet is high.

A course of concentrations of the monitored substances in the methanogenic reactor is in Figure 9 and 10, respectively. Figure 9 compares the difference between filtered and non-filtered COD. It is evident that this difference increased during the operation in the methanogenic reactor. It is a result of sludge water cloudiness and badly settled insoluble material. This caused an increased concentration of suspended solids in the reactor effluent.

Figure 10 shows concentrations of NH_4–N, PO_4–P in sludge water and concentration of suspended solids in a methanogenic reactor. An average concentration of NH_4–N in sludge water during the operation of the methanogenic reactor was 115.5 mg/l and, of PO_4–P was 1.94 mg/l. The concentration of sludge in the reactor increased from 15.7 g/l to 58.5 g/l. Excess sludge was removed beginning on the 33rd day of the opera-

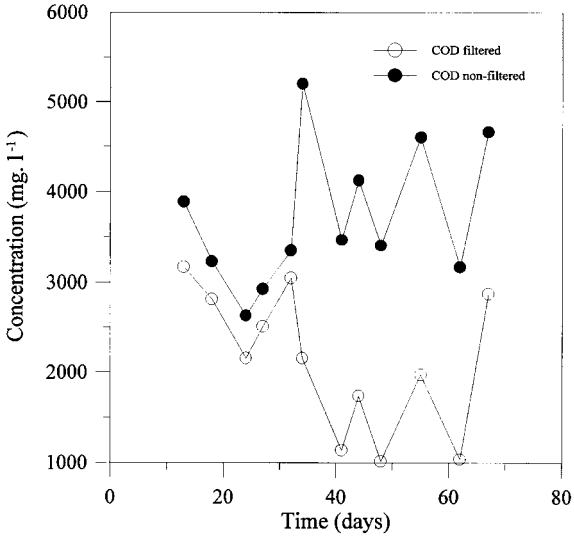

Figure 9. Filtered and non-filtered COD concentration in sludge water from the methanogenic reactor.

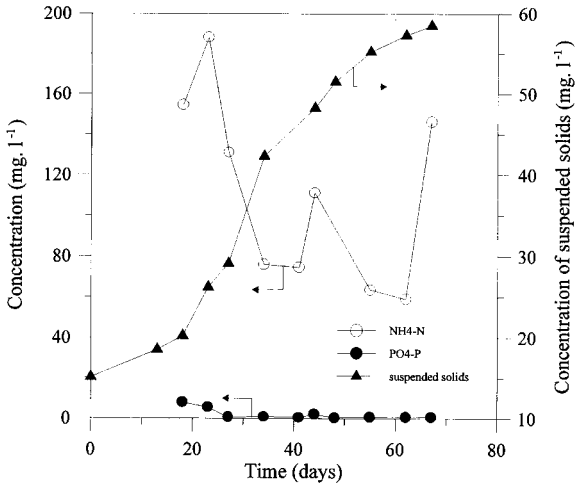

Figure 10. Concentration of NH_4–N and PO_4–P in sludge water and concentration of suspended solids in effluent from the methanogenic reactor.

Table 7. Parameters of the anaerobic treatment of sugar beet pulp

Parameter	Dimension	Average value
Efficiency of COD removal	%	96
Specific production of biogas	ml g^{-1} VS	504.1
Specific production of methane	ml g^{-1} VS	363
Specific production of methane	ml g^{-1} COD	280
Methane content	%	71.9
Production of excess sludge	g g^{-1} VS	0.125
Production of excess sludge	g g^{-1} COD	0.094

tion. It was noticed that it was not possible to separate the sludge water in the volume being daily removed from the methanogenic reactor (above mentioned 300, and 450 ml, respectively). Once a week, 450 ml of the sludge mixture was taken from the anaerobic reactor. This represents a sludge age of about 65 days. The average concentration of the VSS in the sludge was 68%.

The characteristics of sludge activity in the methanogenic reactor were interesting. A maximum specific methanogenic sludge activity was calculated from a course of biogas production per one dose in a semi-continuous cycle. This was expressed in mg of COD of methane per g of VSS per day. Development of activity changes is shown in Figure 11. The achieved methanogenic activity was approximately 1000 mg g^{-1} d^{-1}. Such a high value refers to anaerobic granulated biomass more than suspended biomass.

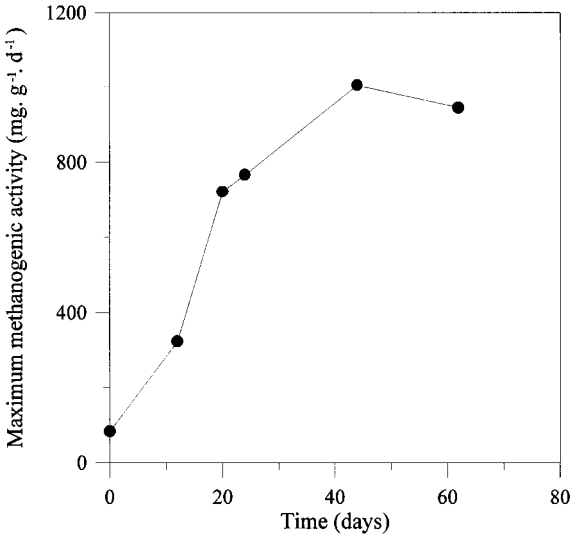

Figure 11. Development of methanogenic activity (mg of methane COD per g VSS per day) during of methanogenic reactor performance.

Conclusion

Laboratory investigation of anaerobic treatment options of sugar beet pulp indicated that this pulp is a very suitable substrate. In comparison with other studies (Lane 1984; Weiland 1993) related to anaerobic decomposition, this study resulted in a higher organic load, lower retention time and a higher specific production of biogas and methane. Higher treatment efficiency (96% of COD removal efficiency) in comparison with work of Weiland (1993) was achieved by processing of homogenized content of an acidogenic reactor in a methanogenic reactor. In the work of Weiland (1993) only a liquid fraction from an acidogenic reactor was added to a methanogenic reactor (60–65% of COD removal efficiency).

The energy content of methane is approximately 35 MJ m^{-3} (natural gas 38 MJ m^{-3}). Thus, the produced biogas might be a significant alternative source of energy in sugar companies.

To transfer an investigated process to full-scale conditions, it is necessary to take into an account the following issues. The experiment was carried out in unstirred reactors. Proper stirring might impact on the performance of the processes. This is mainly due to a high concentration of suspended solids in the acidogenic reactor. The concentration of 6–7% of suspended solids was realized as a limit value. A non-continual operation was another disadvantage of the lab-scale equipment, mainly for the methanogenic reactor. The acidified beet pulp was dosed into this reactor once a day. That meant that anaerobic sludge was highly loaded at the beginning of a semicontinuous cycle and biogas production rate was several times higher than at the end of the cycle. A full-scale operation would allow the use of pumps with a continual dosage and balanced processes. Pilot-scale operations are underway.

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