Anaerobic Treatment of Wheat Stillage

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Wheat stillage was treated in anaerobic one- and two-stage laboratory model. Work presented has showed very good anaerobic biodegradability of this material. From a developed laboratory model it was concluded that a two-stage anaerobic technology with previous acidification is not necessary in anaerobic treatment of wheat stillage. However, it could be stated that acidification may help to stability at the start-up of the process. Various parameters were measured in the laboratory model. Organic loading rate was 11.6 kg m^{-3} d^{-1}, hydraulic retention time was 9.25 d, COD efficiency removal was more than 90 %, excess sludge production – was 0.07 – 0.09 kg per kg loaded COD, and methane yield was 0.225 m^3 per kg loaded COD. Because sludge water at the amount similar than volume of the treated stillage is a potential pollutant, both from point of view of organic pollution and content of nitrogen and phosphorus, it needs to be taken into account in proposing technology for anaerobic treatment of wheat stillage.

Keywords:
Anaerobic treatment, biogas, wheat stillage

Introduction

Ethanol can be produced from different agricultural materials, containing both, higher and lower carbohydrates via fermentation and followed by distillation. Examples of these carbohydrates may be sugar (sugar cane, sugar beet, molasses, etc.), starch (corn, grain, rise, etc.), milk products (whey), cellulose materials (rests of vegetables, vegetables with high energy content, bagasse, wood waste, organic fraction of municipal waste). Stillage is a liquid by-product of ethanol distillation, and it may be potentially highly polluting matter. For example, one litre of ethanol produced may result in twenty litres of stillage, depending on the used fermentation material. Potential pollution may reach 100 g L^{-1} COD.

Stillage production and characteristics vary by amount and quality, and mostly depend on a used material and ethanol production process. Table 1 shows average characteristics of stillage produced from different materials.[1] There is only a little information available on grain stillage content in journals. Table 2 shows data published by Japanese authors[2,3] (production of alcohol containing "shochu" drink).

The higher the sugar content of a carbohydrate source, the lower the residual organic matter, and the lower the stillage amount after distillation. For example, work of *Wilkie* et al.[1] showed that the lowest content of organic materials given as BOD_5 and a COD was in stillage from cane syrup (Table 1). Because, sugar concentration in molasses is significantly lower after sugar production process, portion of an organic matter that does not undergo further fermentation is higher and it results in higher stillage amount than stillage from the sugar cane. Relatively high content of nitrogen in barley stillage

Table 1 – *Selected average parameters of stillage from different materials*[1]

Material quantity	Molasses (sugar beet)	Cane syrup	Molasses (sugar cane)	Cellulose materials
stillage yield, L per L ethanol	11.6	16.3	14.0	11.1
γ_{BOD5}, g L^{-1}	44.9	16.7	39.0	27.6
γ_{COD}, g L^{-1}	91.1	30.4	84.9	61.3
$\zeta_{COD:BOD5}$	1.95	1.96	2.49	2.49
γ_{Ntotal}, g L^{-1}	3.57	0.63	1.23	2.79
γ_{Ptotal}, g L^{-1}	0.16	0.130	0.19	0.03
γ_K, g L^{-1}	10.0	19.5	5.1	0.039
γ_{Stot} (as SO_4^{2-}), g L^{-1}	3.72	1.36	3.48	0.65
pH	5.35	4.04	4.46	5.35

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Table 2 – *Selected parameters of grain stillage*

Parameter	barley stillage[2]	wheat stillage[3]
stillage yield (L per L ethanol)	1,5	–
γ_{BOD5}, g L^{-1}	83	25.9
γ_{COD}, g L^{-1}	97	50.1
$\zeta_{COD:BOD5}$	1.17	1.93
γ_{Ntotal}, g L^{-1}	6.0	1.5
γ_{Ptotal}, g L^{-1}	–	0.17
γ_K, g L^{-1}	–	–
γ_{Stot} (as SO_4^{2-}), g L^{-1}	–	–
pH	3.7–4.1	4.6

(Table 2) relates to higher amount of proteins in crops compared to other materials used for ethanol production. This amount of nitrogen is high enough to create inhibitive concentration of ammonia ions, or ammonia in the output flow from barley processing distilleries. For a better comparison $\zeta_{COD:N}$ ratio for stillage in Table 1 and 2 are given in Table 3.

Table 3 – *Mass ratio $\zeta_{COD:N}$ for different types of stillage*

Substrate	Molasses (sugar beet)	Cane syrup	Molasses (sugar cane)	Cellulose materials	Barley stillage	Wheat stillage
$\zeta_{COD:N}$ ratio	25.5	48.4	69.1	23.0	13.8	17.3

It is obvious from Table 3 that $\zeta_{COD:N}$ is significantly lower for grain stillage vs. that of sugar beet and sugar cane products. This difference is even more obvious for stillage from other ethanol production materials, as demonstrated in Table 4.

Higher concentration of sulphates in molasses liquids (for data see Table 1) relates rather to sugar production process rather than to the composition of sugar cane and sugar beet itself. Similarly, significant sulphate concentration may also be expected in grain stillage (though this data is not shown) due to acidic hydrolysis of grain with sulphuric acid. Higher sulphate mass concentration may negatively affect anaerobic treatment of stillage (see below), thus it is important to minimize its content in the feed-stock materials. *Wilkie* et al.[1] also summarises organic composition of stillage. The essential low molecular mass constituents of sugar cane stillage are lactic acid, glycerol, ethanol, and acetic acid. In addition to these components, stillage from whey, also contains lactose, glucose, arabinitol and ribitol. Traces of amino acids are contained in all types of stillage. However, corn stillage contains high level of alanine and proline.

Differences in composition were found when comparing barley and wheat stillage. Barley stillage contain more fibres and less proteins than wheat stillage. Concentration of most amino acids is also higher in barley stillage.[11]

Anaerobic treatment of stillage

There is a wide range of stillage treatment and/or its use. Stillage may be thickened and landfilled, added to road construction materials,

Table 4 – *Characteristics of stillage from other traditional materials*

Material parameter	Apples/pears	Cherries	Pears/cherries	Corn	Grapes (wine)	Grapes (brandy)	Potatoes
γ_{BOD5}, g L^{-1}	22.0	–	–	43.1	–	–	–
γ_{COD}, g L^{-1}	48.9	80.0	109	59.4	30.0	26.0	39.0
COD/BOD_5	2.22	–	–	1.38	–	–	–
γ_{Ntotal}, g L^{-1}	0.38	–	0.73	0.55	0.45	–	1.0
$\gamma_{COD:N}$	128.7	–	149.3	108.0	66.7	–	39.0
γ_{Ptotal}, g L^{-1}	0.062	–	0.040	0.228	0.065	–	0.430
γ_K, g L^{-1}	–	–	–	–	–	0.8	4.0
γ_{Stot} (as SO_4^{2-}) g L^{-1}	–	0.034	–	0.299	0.250	–	–
pH	3.4	3.5–4.0	3.9	–	3.5–4.0	3.0–3.2	–
Reference N°	4	5	6	7	8	9	10

used for fertilization and production of biogas and chemicals, or anaerobically treated.[1]

Anaerobic treatment of stillage is often referred to as an efficient usage option. However, some authors though oversee the options of anaerobic treatment of stillage and deal only with its aerobic treatment. High COD concentration means high aeration requirements, with almost half of COD concentration converted to sludge that needs further treatment. Anaerobic treatment turns more than half of stillage COD concentration to biogas, and further utilisation of the latter may significantly improve energy balance of a distillery.[1]

Most authors describe anaerobic treatment of stillage produced from a common materials such as molasses (sugar beet, sugar cane). COD of this material ranges in mass concentrations even higher than 100 g L^{-1}, which may result in unstable anaerobic process. Therefore, stillage is diluted with other waste flows in a distillery. The most common problems of anaerobic treatment are high content of potassium, metals, sulphates and phenol compounds. *Wilkie* et al.[1] compared mesophilic anaerobic treatment of molasses stillage and showed an average organic loading rate 9 – 12 kg m^{-3} d^{-1} with average COD removal efficiency higher than 70 %. Methane yielded about 0.25 m^3 per kg added COD. Average hydraulic retention time was ranging between 6 – 7 days. The most commonly used reactors were a UASB reactor, an anaerobic filter, and a mixed reactor. Because temperature of stillage from distillation often exceeds 90 °C, it needs to be cooled. Required temperature of stillage is 35–42 °C for mesophilic processes, for thermophilic processes stillage temperature may be 60 °C. Anaerobic treatment efficiency of molasses stillage in thermophilic conditions is comparable with that of mesophilic treatment, though with doubled organic loading rate reached. Since effluents from termophilic processes have higher COD concentration (it is the reason for their lower efficiency), methane yields to added COD is slightly lower in thermophilic processes. This is consistent with work of *Wilkie* et al.[1] that shows methane yields of 0.28–0.37 m^3 per unit mass (kg) added COD, with 80–98 %. COD removal efficiency for mesophilic anaerobic treatment of other substrates, such as barley and sweet potatoes, cherries, corn, grape (brandy), grape (wine), wheat and sweet potatoes, whey.

Grain stillage differ significantly in the content and other characteristics from other common stillages treated anaerobically (from molasses, rice, fruits, potatoes etc.). Some differences may be expected in their anaerobic treatment arising from higher content of proteins and higher saccharides of lower biodegradability. There is only a little information on this issue in the literature. One example is work of *Akunna* and *Clark*[12] that deals with a stillage treatment from Scotch whisky. Stillage COD was ranging between 16.6–58 g L^{-1}, suspended solids were 0.232–7.81 g L^{-1}, TKN was 500–1200 mg L^{-1}, γ_{Ptotal} 150–600 mg L^{-1} and pH 3.8. Stillage was treated in granular-bed anaerobic baffled reactor of total volume 35 L at 37 °C. Stillage was diluted to COD 9500 mg L^{-1} before loading to the reactor. Maximum organic loading rate was 4.53 kg m^{-3} d^{-1} with hydraulic retention time 2 days and 80 % COD removal efficiency. Biogas production at this load was 22 L with 60–70 % of methane. This equals 0.146 m^3 of biogas yields per kg of added COD. *Weiland* and *Thomsen*[13] used decanted wheat stillage as one of the substrates, which were anaerobically treated after acidification in full-scale fixed bed reactor. Maximum organic loading rate for this material was 4 kg m^{-3} d^{-1} with 90 % COD removal efficiency. Specific production of biogas was not presented.

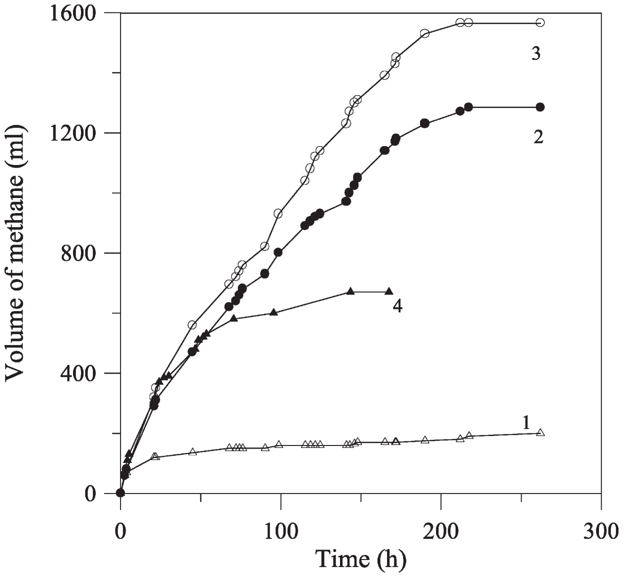
Presented work investigates possibilities of anaerobic treatment of wheat stillage in order to obtain technological parameters for optimal design of this process. Important is also information about sludge water quality with regard to concentration of COD and $\zeta_{NH4\text{-}N}$ and its next treating. There are several distilleries in the Slovak Republic interested to improve their energy balance by anaerobic treatment of grain stillage.

Experimental

Biochemical methane potential (BMP) of the used wheat stillage was measured before long-term monitoring of stillage anaerobic treatment laboratory model. Stillage from two separate distilleries was used in experiments. Their characteristics are shown in Table 5.

Table 5 – *Selected quantities of used stillage*

Quantity	Stillage 1	Stillage 2
γ_{COD}, g L^{-1}	90.75	107.0
γ_{TS}, g L^{-1}	38.6	70.34
w_{TVS}, %	93.4	91.3
γ_{DS}, g L^{-1}	18.3	20.38
w_{VDS}, %	86.6	91.1
γ_{TKN}, g L^{-1}	4.09	8.80
γ_{Ptotal}, g L^{-1}	0.403	0.218
pH	3.35	3.7



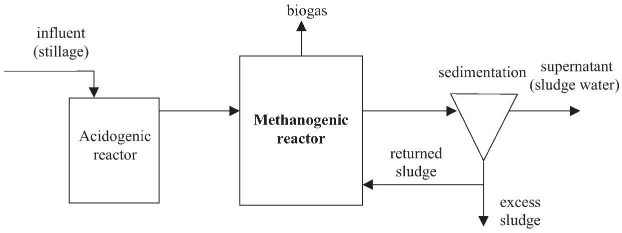
F i g . 1 – *Anaerobic biodegradability tests*
1 – methane production by anaerobically stabilised sludge (blind test); 2 – methane production from 100 ml stillage feed; 3 – biogas production from 100 ml stillage feed; 4 – methane production from 25 ml stillage feed

Measurements of BMP were performed at 48 °C. $NaHCO_3$ was used to adjust stillage pH value to 7. Figure 1 shows results of BMP measurements.

100 ml of stillage was tested in the first test. 0.5 L of anaerobically stabilised sludge from municipal wastewater treatment plant was used. Net methane production (less production from the sludge) was 1085 mL. Theoretical methane production from 100 mL of stillage was 3585 ml. Measured anaerobic biodegradability was 30.3 %. Testing period was 262 h.

25 ml of stillage was treated in the second test. 1.0 l of anaerobically stabilised sludge was used. Net methane production (less production from the sludge) was 270 mL. Theoretical methane production from 25 mL of stillage was 896.2 mL. Measured anaerobic biodegradability was 30.1 %. Testing period was 168 h. Biogas composition had 82 % of methane. Biogas composition was measured by approximation method measuring biogas production difference in two parallel tests; in one of the tests biogas flew through NaOH solution where CO_2 was caught.

Stillage was treated in mixed semi-continuous laboratory model, at 43 – 45 °C. In a period from 50th to 81st day the model was operated as a two-stage model. First stage was acidification in a mixed reactor with 4 days hydraulic retention time. Second stage was methanogenic reactor with a volume 3.7 L. A schematic view of this model is shown in Figure 2. Besides the period mentioned above, lab-scale model was operated as one-stage process,



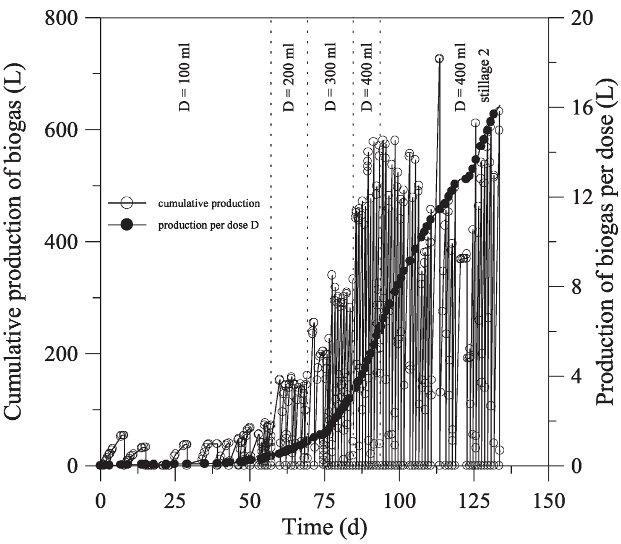
F i g . 2 – *Laboratory semi-continuous model of two-stage anaerobic treatment of grain stillage*

without the acidogenesis. The methanogenic reactor was filled with anaerobically stabilised sludge from municipal wastewater treatment plant. This sludge was used also for anaerobic biodegradability tests. Its total amount in reactor was 75.54 g (VSS 43.5 g – 57.6 %) at the beginning. Semi-continuous cycle was 24 hours, which means that stillage was fed once a day. At the end of the semi-continuous cycle, content of the reactor was decanted. Clarified sludge water of the same volume as volume of fed stillage was pumped out from the upper part of the reactor, and stillage (acidificated or without acidification) was added to the reactor.

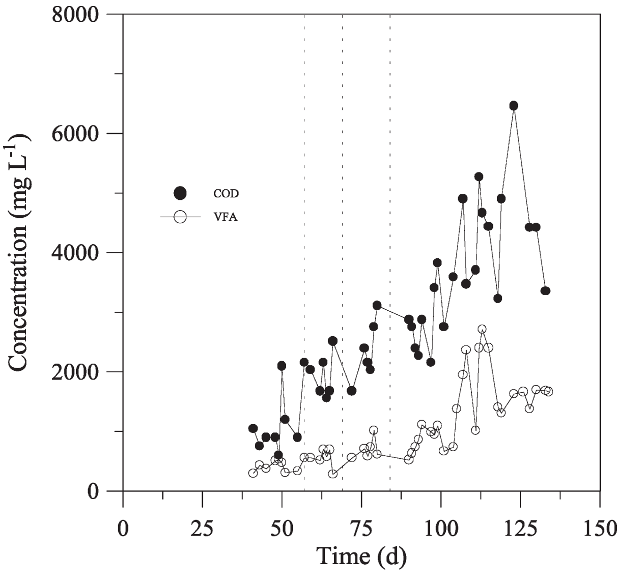
Results and discussion

Kinetic tests showed relatively low level of direct anaerobic biodegradation of the used stillage. Measured specific production of methane was 10.84 m^3 per m^3 of stillage, (13.22 m^3 of biogas) i.e. 0.12 m^3 per kg COD of added stillage (0.146 m^3 of biogas). Anaerobic biodegradability may be expected to increase after biomass adaptation to stillage, or after their previous acidification.

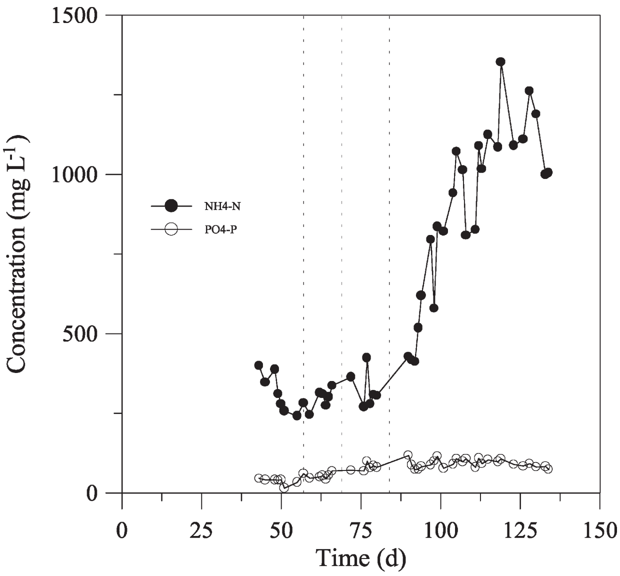
Figure 3 shows biogas production per stillage dose, and cumulative production of biogas in



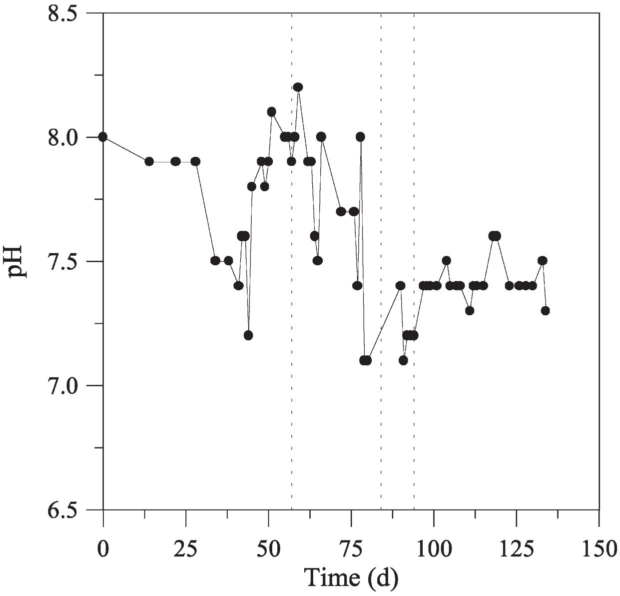
F i g . 3 – *Biogas production during methanogenic reactor operation* methanogenic reactor. Reactor operation may be split to five phases. In phase I, 100 mL of stillage was dosed. This amount lasted approximately till 57th day of reactor operation. In the phase II, 200 ml stillage was used (till 69th day of operation), in the phase III about 300 ml was dosed (till 83rd day), in the phase IV 400 ml of stillage was dosed, (till 92nd day), and lastly 400 ml of new stillage was dosed in phase V. New stillage was added from 93rd day (stillage 2, Table 5). Production of biogas as well as the following quantities of sludge water were measured during the reactor operation; COD mass concentration (filtered), VFA, pH, γ_{NH4-N} and ζ_{PO4-P}. Measured values are shown in Figures 4–6.



F i g . 4 – *COD and VFA concentration in sludge water from methanogenic reactor*



F i g . 5 – *NH_4-N and PO_4-P concentration in sludge water from methanogenic reactor*



F i g . 6 – *pH of sludge water during methanogenic reactor operation*

As shown in Figure 3, biodegradation of stillage was very slow at the beginning of reactor operation. For example 0.08 L of biogas were produced in one day after the first dose of 100 ml stillage was added. About 1.36 L was produced in one week after the second dose of 100 ml. Degradation of 100 mL stillage dose lasted ~3 days even after 50 days of operation. It was determined that slow hydrolysis and acidification in methanogenic reactor was the reason for a slow degradation. This was proved also by preliminary kinetic tests of anaerobic biodegradability. Therefore, hydrolysis and acidification reactor was installed before methanogenic reactor in this period. Retention time in acidification was set up to 4 days. This time was chosen based on some previous experience with other substrates.[14] As expected, anaerobic degradation of stillage improved significantly after inclusion of acidification stage. Biogas production per stillage dose increased slightly. 1 day was sufficient time for degradation in methanogenic reactor (see Figure 3 for more details).

Two additional acidification tests were performed. In the first test, sodium bicarbonate was used to adjust pH value of stillage to 6.5, because original pH value of 3.35 could inhibit acidification. Table 6 shows the results of this acidification tests. Because, this acidification test should lead to hydrolysis of high molecular organic matters to low molecular matters, and creation of volatile fatty acids (VFA), concentration of dissolved COD and VFA were measured, along with concentration of dissolved ammonia nitrogen and phosphate phosphorus. Surprisingly, concentration of VFA, ammonia, and phosphate, did not change significantly (Table 6),

Table 6 – *Results of hydrolysis and acidification tests*

Test day	pH	γ_{COD} mg L^{-1}	γ_{NH4-N} mg L^{-1}	γ_{PO4-P} mg L^{-1}	γ_{VFA} mg L^{-1}
1st test					
0	6.5	19500	120	140	3600
1	6.9	20020	130	145	4020
2	7.2	19700	139	147	4130
3	6.8	20220	137	148	4640
6	6.3	20600	165	156	6220
7	6.2	18500	201	150	6490
2nd test					
0	5.5	19400	120	148	3630
1	5.4	19300	121	129	3650
5	5.4	19100	130	130	3760
6	5.4	19440	141	127	3890
7	5.3	20320	148	137	4140
8	5.2	21520	148	141	3250
9	5.4	19700	143	131	3130
12	5.8	23010	161	143	3850
13	5.9	23600	159	140	3990
14	6.3	20920	114	115	3960
15	6.3	20620	143	115	3830

and therefore pH was adjusted to only to 5.5 in the second test.

In the first test, VFA mass concentration increase was 2890 mg L^{-1} (as acetic acid) which corresponds to COD of approximately 3090 mg L^{-1}. This value is negligible at total stillage COD 90750 mg L^{-1}. Moreover, VFA value showed no increase with increased dissolved COD. Similar results were obtained in the second test, thus it could be concluded, that neither acidification tests showed significant effect on dissolved COD and VFA concentration increase. Despite these measurements, sensory evaluation of acidified stillage showed change in quality. Odour of both acidified stillages grew, they color turned dark and it was also visible, that a structure of suspended solid particles changed. Their edges were less clear and sharp than before acidification.

As mentioned above, acidification effect was shown in improved anaerobic biodegradability of stillage in a methanogenic reactor. Stillages were fed to the reactor after acidification (retention time 4 days) approximately till 81st day. During this period, methanogenic reactor operation was stabilised, thus it was decided to try dosing of a stillage without its previous acidification. As shown in Figures 3–6, no negative effects on this reactor were observed. This observation could be explained in two ways:

1. stillage was sufficiently acidified during its long-term storage in refrigerator (almost three months at 5 °C)

2. anaerobic biomass is sufficiently adapted to this substrate

Addition of fresh stillage (stillage 2, Table 5) on 93rd day of reactor operation without its previous acidification, followed by a successful treatment, proved that biomass was sufficiently adapted to this substrate and that acidification of the substrate was not necessary.

Table 7 shows several selected technological parameters during individual phases.

Table 7 – *Selected technological quantities of semi-continuous methanogenic reactor*

Quantity	Phase I.	II.	III.	IV.	V.
Stillage dose, ml	100	200	300	400	400
Number of doses	14	7	12	8	33
Organic loading rate, kg m^{-3} d^{-1}	2.45	4.9	7.35	9.8	11.6
Hydraulic retention time, d	37	18.5	12.3	9.25	9.25
Max. volume production of biogas, L	1.92	4.03	8.5	14.45	18.18
Production of biogas per kg added COD, m^3 kg^{-1}	0.212	0.222	0.312	0.398	0.425

Values of specific biogas production were about 0.4 m^3 per added COD (or 39.55 m^3 per m^3 of stillage). Such values were measured for substrates with very good anaerobic biodegradability.[1] Organic loading rate exceeding 10 kg m^{-3} d^{-1} also range within upper values of this quantity for similar substrates. It is also important to mention that specific biogas production was measured at 35 °C (reactor temperature was higher than measuring and catching temperature of biogas). For the sake of data comparison, data biogas production needs to be adjusted for the same temperature. The most common conditions at which biogas production is measured are called "normal" (m^3 – Nm^3) and referring to standard conditions at 0 °C and pressure 1 bar.

No anaerobic sludge waste was taken from the reactor by end of the second phase. This was decided upon the fact that sludge and sludge water were clearly separated (clear margin between sludge and sludge water) and sludge water could be pumped-out without a sludge in the amount equal to a volume of added stillage. Concentration of SS in sludge water after sedimentation was ranging from 500 to 1500 mg L^{-1}. This had changed immediately after addition of 400 ml of stillage. Produced amount of biogas reached values at which sludge and sludge water were not separated during the whole semi-continuous cycle. Excess sludge was not pump out regularly, only minimum required amount was taken out, in order to allow feeding of stillage for anaerobic treatment. It is also important to mention that the individual amounts pumped out were not quantified, but collected separately for further anaerobic sludge balance and specific sludge production. Total sludge amount increased in the reactor from 75.54 g (VSS 43.5 g – 57.6 %) to 154.2 g (VSS 127.36 g – 82.6 %). Amount of collected excess sludge was 64.9 g (VSS 50.7 g – 78.2 %). Increased value of total sludge amount reached 143.5 g. Total added COD during reactor operation was 1977.5 g. Production of excess sludge was 0.073 kg per kg added COD, i.e. 6.3 kg per m^3 of stillage. Concentration of SS in sludge water after sedimentation was not measured regularly. Taking into account also maximum value of this quantity 1.5 g L^{-1}, amount of SS in effluent was 34.2 g at total volume of produced sludge water 22.8 L (relevant to the amount of stillage treated). If this amount was added to the total sludge growth, specific production of excess sludge was 0.09 kg per kg added COD, or 7.8 kg per m^3 of stillage.

Table 8 shows average concentration of filtered sludge water quantities in the reactor. The most significant changes were recorded in the fifth phase as obvious from this table, when new stillage started to be fed to the reactor. This is also obvious from Figures 4 – 6. Although comparison of composition of stillage used (Table 5) showed that the largest difference between them was in TKN concentration, new stillage feed was also reflected in sludge water by increased concentration of ammonia nitrogen, COD and VFA. Despite quite high value of VFA (1530 mg L^{-1}) there were no problems in the process of the methanisation. During this phase, also pH reached the most stable values (Figure 6). As mentioned above dosing of $NaHCO_3$ in first phase and at the beginning of phase II (till 63rd day) also affected pH. Addition of $NaHCO_3$ at 0.4 g per 100 ml of stillage was sufficient to maintain pH at 7. When stillage was pre-acidified, commenced $NaHCO_3$ was added in amount to maintain pH in acidification above 5.5. Because this pH value of acidified stillage didn't cause any problems in methanisation, dosing of $NaHCO_3$ was stopped on 64th day of reactor operation. Figure 6 shows that pH in the reactor gradually slightly increased to 7.4. Such stability at high measured $\gamma_{NH4\text{-}N}$ and $\gamma_{PO4\text{-}P}$ concentrations may be explained by the presence of NH_3/NH_4^+ buffer and $H_2PO_4^-/HPO_4^{2-}$ systems.

Table 8 – *Average values of quantities in sludge water measured in individual phases and during the whole period of reactor operation*

Quantity	Ist phase	IInd phase	IIIrd phase	IVth phase	Vth phase
γ_{COD}, mg L^{-1}	1046	1964	2351	2570	3990
γ_{VFA}, mg L^{-1}	405	552	702	690	1530
$\gamma_{NH4\text{-}N}$, mg L^{-1}	317	295	325	444	982
$\gamma_{PO4\text{-}P}$, mg L^{-1}	36.4	53.7	80.3	88.0	92.9
pH	7.77	7.87	7.5	7.23	7.4

COD removal efficiency of stillage exceeded 90% during the whole test. This value was also reached in the another, extremely unfavourable sample of non-filtered settled COD in sludge water – 10 000 mg L^{-1}, however this value was measured only once. Quality of sludge water after anaerobic treatment of stillage shows that it is significant source of pollution. If wheat stillage anaerobic treatment becomes a practically usable technology, then post treatment of the sludge water have to become its important part. The volume of sludge water treated will be approximately the same as the volume of treated stillage.

Biogas composition was measured twice during the reactor operation. 1st measurement was made on 82nd day of operation (approximately at the end of phase III), 2nd measurement on 133rd day of operation. Both measurements were made with stillage dose of 400 ml, one with "old" stillage (stillage 1, Table 5) and the second one with "new" stillage (stillage 2, Table 5). Results are given in Table 9.

Content of the methane in biogas is typical for carbohydrate substrates, or those containing VFA, aldehydes, ketones etc. Pure carbohydrate substrates show lower content of methane, at about 50%. Almost no hydrogen sulphide was traced in biogas in the first measurement, though its presence

Table 9 – *Biogas composition*

Component	I^{st} measurement	II^{nd} measurement
w_{CH4}, %	64.5	62.2
w_{CO2}, %	32.5	33.7
w_{O2}, %	1.9	1.9
γ_{H2}, mg m^{-3}	150	155
γ_{H2S}, mg m^{-3}	< 1.5	> 280

was expected due to utilisation of sulphuric acid in the process of wheat fermentation. It can be explained by the fact that used biogas was caught after gas meter in the first measurement. Calcium dichromate solution was used as medium in the wet gas meter. It caused oxidation of hydrogen sulphide, thus it was not detected. In the second measurement, biogas was caught without measuring its amount in wet gas meter, and measured amount of hydrogen sulphide exceeded detection limit of the used measuring device – 280 mg m^{-3} of hydrogen sulphide.

Specific biogas production of 0.4 m^3 per added COD at 35 °C (39.55 m^3 per m^3 of stillage) equalled to biogas production 0.355 Nm^3. This represents 0.254 m^3 of methane at 35 °C (0.225 Nm^3 of methane) at average methane content 63.4 %. Energetic content of methane is 39.3 MJ m^{-3}. Thus energy content of biogas from one kg COD of stillage was 8.84 MJ, or 874 MJ from one m^3 of stillage.

Conclusions

The results of laboratory modelling of anaerobic biodegradability of wheat stillage may be summarised as follows:

– very good anaerobic biodegradability of wheat stillage was proved despite worse results of specific methanogenic activity kinetic tests.

– two-stage anaerobic technology with previous acidification is not necessary in anaerobic treatment of wheat stillage. It could be stated that it may help to stability at the start-up of the process.

– Methane yield 0.225 Nm^3 per kg of added COD compare wheat stillage to other substrates with very good yields. Comparable and better results were reached as those given for similar substrates in the literature.[1,12]

– Amount of sludge water is comparable with the volume of wheat stillage. It is a significant pollution source and its treatment needs to be taken into account in proposing technology for anaerobic treatment of wheat stillage.

– Wheat stillage was fed to reactor in one dose per day for technical reasons, which needs to be taken into account in assessing the results of laboratory modelling. Continuous feeding may improve the process qualitatively and quantitatively, mainly from the point of view of quality of biogas, sludge water etc., and also from point of view of possible higher organic loading rates or lower hydraulic retention times.

– Quantities, which were reached in the laboratory model operation will be used in design of anaerobic wheat treatment technology.

– As stated above in experimental part, the reactor was operated at 43–45 °C, which is higher than those usually experienced in mesophilic conditions. Although this process cannot be called a “thermophilic”. Higher temperature couldn’t be realistically expected, despite the fact that wheat stillage temperature after distillation is exceeding 90 °C. Hot wheat stillage probably couldn’t stand higher temperature with real hydraulic retention time 3 days and more days in methanogenic reactor.

Abbreviations and symbols

BMP – biochemical methane potential
BOD_5 – Biochemical Oxygen Demand
COD – Chemical Oxygen Demand
DS – Dissolved Solids
NH_4-N – ammonia nitrogen
N_{total} – Total Nitrogen
PO_4-P – Phosphate Phosphorus
P_{total} – Total Phosphorus
SS – suspended solids
TKN – Total Kjeldahl Nitrogen
TS – Total Solids
TVS – Total Volatile Solids
VDS – Dissolved Volatile Solids
VFA – Volatile Fatty Acids
VSS – Volatile Suspended Solids
γ – mass concentration, g L^{-1}
Y – yield
$\zeta_{COD:B}$ – mass ratio, m_{COD}/m_B
w – mass fraction, %

References

1. *Wilkie, A. C., Riedesel, K. J., Owens J. M.* Biomass and Bioenergy **19** (2000) 63.
2. *Kitamura, Y., Maekawa, T., Tagawa, A., Hayashi, H., Farrell-Poe, K. L.* App. Eng. Agric. **12** (1996) 709.
3. *Nagano, A., Arikawa, E., Kobayashi, H.* Water Sci. Technol. **26** (1992) 887.

4. *Robertiello. A.* Agric. Wastes **4** (1982) 387.
5. *Stadlbauer, E. A., Stadlbauer, E .A., Achenbach, R., Doll, D., Jehle, B., Kufne, B., Oey, E.*: Wat. Sci. Technol. **25** (1992) 351.
6. *Hutnan, M., Drtil, M., Bilanin, M.* Anaerobic treatment of distillery slops in WWTP Partizánske. Research report ZoD 4/96, Faculty of Chem. Technol. Bratislava, Slovakia 1996 (in Slovak).
7. *Dahab, M. F., Young, J. C.* Biotechnol. Bioeng. Symp. **11** (1981) 381.
8. *Driessen, W. J. B. M., Tielbaard M. H., Vereijken T. L. F. M.*: Wat. Sci. Technol. **30** (1994) 193.
9. *Henry, M., Michelot, E., Jover, J. P.*: Anaerobic treatment of molasses sugar cane stillage with high minerals, in Scholze Jr, R. J., Smith, E. D., Bandy, J. T., Wu, Y. C., Basilico, J. V.(Ed.), Biotechnology for degradation of toxic chemicals in hazardous wastes. Park Ridge, NJ, Noyes Data Corporation, 1998, 443.
10. *Wulfert, K., Weiland, P.*: Two-phase digestion of distillery slops using a fixed bed reactor for biomethanation, in Palz, W., Coombs, J., Hall, D. O. (Ed.), Energy from biomass. 3rd E. C. Conference, London, Elsevier, 1985, pp. 562.
11. *Mustafa, A. F., McKinnon, J. J., Christensen, D. A.* Anim. Feed Sci. Technol. **80** (1999) 247.
12. *Akunna, J. C., Clark, M.* Biores. Technol. **74** (2000) 257.
13. *Weiland, P., Thomsen H.* Wat. Sci. Tech. **22**, (1990) 385.
14. *Hutnan, M., Drtil, M., Mrafková, L.*: Biodegradation **11** (2000) 203.