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Anaerobic Digestions of By-products from Production of Ethanol

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Introduction

Byproducts from ethanol processing industries such as stillage are expected to be favorable substrates for anaerobic digestion containing abundant organic matter. However the experience of using stillage for biogas production is still limited.

The purpose of the research presented in this paper was to investigate the possibility of anaerobic digestion of byproducts from ethanol processing industries.

Materials and methods

Digested materials

Properties of the raw materials and inoculum used for the continuos digestion tests are shown in Table 1.

The ethanol waste comes from a German plant, using wheat grain as substrate (Novel Ferm Brennerei Dettmannsdorf GmbH)
The inoculum was obtained from a commercial biogas plant which codigested pig manure with co-substrates in a mesophilic condition of 39°C to 40°C.

Table 1. Characteristics of whole stillage and inoculum used in the test.

Biomass	Date	TS (%)	VS (%)	pH	T-N (g/l)	NH4-N (g/l)
Stillage	29-05	8,48	7,94	3,86	5,35	0,11
Stillage	21-06	7,82	7,18		5,19	0,10
Stillage	21-08	7,74	7,18	4,51	6,25	0,29
Stillage	18-09	8,13	7,48	4,64	7,04	0,68
Stillage	16-10	10,16	9,53			0,70
Inoculum	25-5		6,8	8,1	6	4,5

Experimental methods

The experiment was conducted in a pilot digester running at mesophilic temperature (39°C). The pilot digester consisted of a pre-tank with a volume of 120 L and a digester with an active volume of 130 L. Mixing was performed by a central shaft with a propeller at the bottom, rotating at 60 rev min^{-1}. Mixing took place for 1 min every half hour in all digesters. Temperature was controlled by means of heating tubes placed in the bottom of the digester. The gas produced was measured by the volume displacement method.

Furthermore a batch experiment was conducted in 1 litre vessels in 3 replicates for each substrate.

Analytical methods

Standard procedures (DEV, 1979) were used to determine total solids (TS), volatile solids (VS), total Kjeldahl nitrogen (T-N), and ammonia (NH_4-N). Slurry pH was determined with a pH meter (Radiometer A/S, Copenhagen, Denmark). Biogas production was measured by using a large syringe as described by Steed and Hashimoto (Steed and Hashimoto, 1994). The gas samples were analyzed for CO_2 and CH_4 content using gas chromatography.

Both CO_2 and CH_4 were measured on a Perkin Elmer Clarus 500 Gas Chromatograph equipped with an electron capture detector (ECD) and a special Alltech CTR column. The carrier gas was He, and the temperatures of injection port, oven and detector were 110°C, 40°C and 150°C respectively.

Volatile fatty acid (VFA) C_2–C_5 concentrations were determined by means of a gas chromatograph (Hewlett Packard 6850A) with a flame ionization detector (FID). The column was an HP-INOWax, 30 m × 0.25 mm × 0.25 µm. The carrier gas was He. The temperature of the column was gradually increased from 110°C to 220°C at a rate of 10°C min^{-1}. Hydrogen sulfide gas concentrations were measured by an aspirating pump and gas detector tubes (Kitagawa Precision Gas Detector Model APS).

Results and discussion

Batch digestion

From production of ethanol from different bioetanol plants different by-products are produced. The by-products from 3 plants were tested. The whole stillage from corn is from a plant in US, were the raw material is corn and the sample are taken directly after the destilation column. This plant is owned by UWGP (www.uwgp.com). The stillage from wheat is from a plant in France (Chemature) and a German plant (Novel ferm). The French plant is working with a special process (Biostil) were a kind of evaporation is connected to the distillation process and a continuously fermentation. The whole stillage from the German plant uses wheat grain as substrate (Novel Ferm Brennerei Dettmannsdorf GmbH). The characteristics of the by-products are shown in table 2.

Table 2. DM, VS, Nitrogen content and inoculum substrate ratio in the batch digestion.

By product	**DM**	**VS**	**TN**	**NH4+**	**Inoculum:substrat ratio (g VS/g VS)**
	%	% of DM	g/L	g/L	
Stillage (chemature)	26,60	95,93	16,65	0,35	0,4 in first test and 0,8 in second test
Stillage (novelferm)	11,9	94,5	5,5	0,1	2
Whole stillage corn	11,00	91,95	5,22	1,00	0,9

The methane yield in terms of VS is illustrated in figure 1. The yield in the different products differs with the highest yield in the whole stillage from Novelferm. The yield in the stillage from Chemature differs significant between the first and the second batch digestion, because the loading of substrate was twice as high in the first test compared to the second test, leading to an inhibition in the first test. The metane yield in the whole stillage from corn is lower than the wheat based stillage, however because the standard deviation from the test with corn based stillage was very high, the difference was not significant.

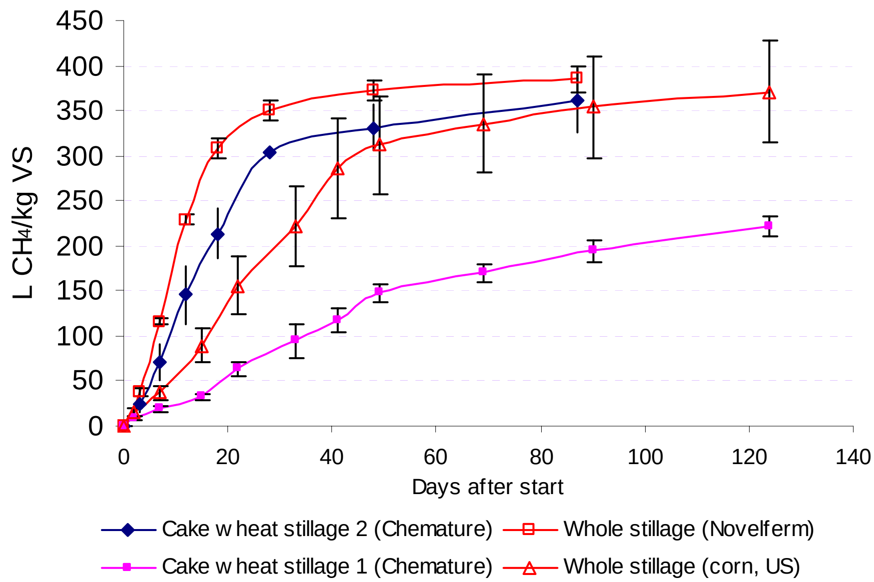

Figure 1. Accumulated ultimate methane yield during batch digestion of by-products from ethanol production.

Continuous experiment

The experiment was started up the 30th of May 2007 and was running to the end of October 2007. During the period the goal was to have one or two daily loadings, but due to some technical problems some of the loadings were not done on a regular basis and the average hydraulic retention time thus was longer than the planned retention time at about 25 days. Furthermore there was an accident the 24th of July where almost all the digested material by accident was pumped to the storage and the digester has to be re-inoculated with digested material. The key parameters for the performance of the digestion process are shown in table 3. It can be seen that the key parameters varies during the test but during the whole period there is a stable gas production. However after the re-inoculation in the end of July it seems that an inhibition develops and the process never fully recovers. In some periods the methane yield exceeds the ultimate yield obtained in batch digestion. The explanation for this is that volatile solids loaded in the preceding period in cases with inhibition first are converted in the following period.

Table 3. Data for performance of the digester during the test

Period		Biogas	Organic load	Biogas	Average hydraulic retention time	Metane yield
		Liter/day	kg VS/m^3 digester/day	Liter/Liter digester/day	days	L CH_4/kg VS
start	*end*					
30-5 07	15-6 07	109,1	2,24	0,84	33	258,3
15-6 07	30-6 07	372,1	3,33	2,86	23	507,4
30-6 07	15-7 07	195,7	2,25	1,51	30	404,3
15-7 07	31-7 07	151,9	1,34	1,17	56	577,0
31-7 07	15-8 07	194,1	2,50	1,49	30	351,1
15-8 07	31-8 07	140,0	2,04	1,08	37	314,4
31-8 07	15-9 07	120,4	2,59	0,93	29	200,8
15-9 07	30-9 07	175,3	2,58	1,35	29	316,5
30-9 07	15-10 07	206,3	4,62	1,59	16	200,7
15-10 07	31-10 07	99,6	1,93	0,77	39	268,7
Average		**176,4**	**2,5**	**1,4**	**32,2**	**339,9**

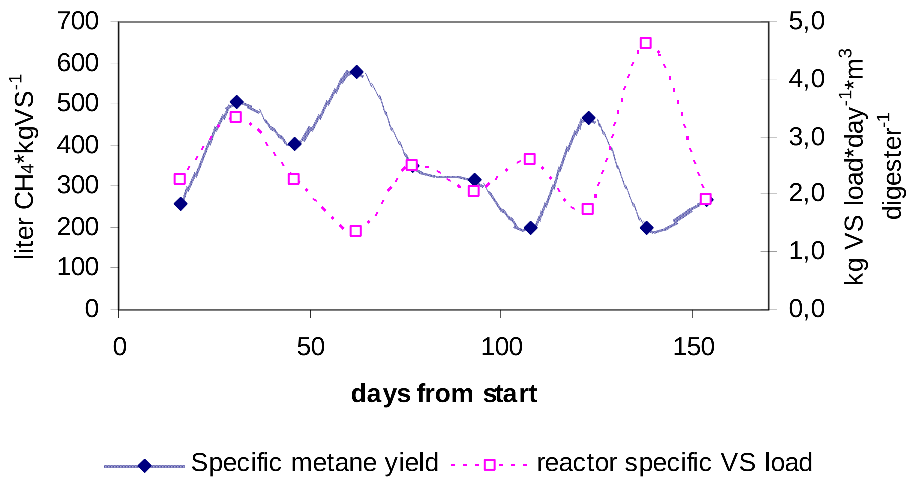

Figure 2. The specific methane yield and the reactor specific daily load of VS, during the test. The shown values are the average of 14 days.

In figure 4 the development of the concentration of volatile fatty acids during the test is illustrated. Until mid July (day 50), the concentations of VFAs are acceptable up to around 8000 mg/L. However after this the content of VFA keeps on increasing until a level above 20.000 mg/L, which usually is associated with a complete process failure. It is especially the propionic acid which increases, while the acetic acid are kept low, indication that the methanogens converting acetetate functions well, while the H_2 converting methanogens probably are inhibited causing high propionate concentrations.

The reason for the observed inhibition is difficult to explain, but since it is initiated after the accident where the process was re-inoculated, the oxygen introduced in the process might be an explanation. Also the NH_4-N content might explain the inhibition, but with a level at around 5 g/L (Figure 4) and mesophilic conditions this should not be considered as a serious inhibitory level.

However in spite of the observed inhibition the gasproduction keeps on being stable (figure 2) and the VS conversion is around 60% during the complete test (figure 3) with some variation, which partly might be explained by sampling error.

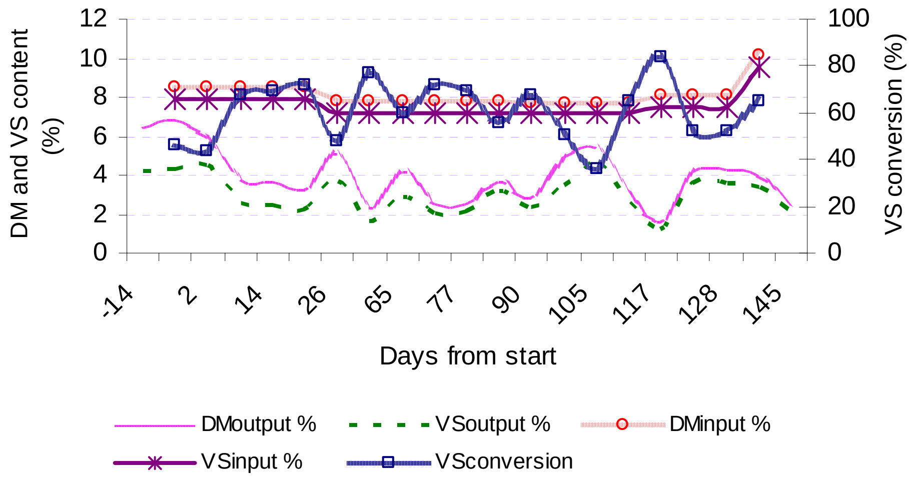

Figure 3. DM, VS concentrations in input and output and the VS conversion during the test

The concentration of methane in the gas fluctuates but it is generally above 50% except for a drop in conjunction with the pumping accident (figure 4).

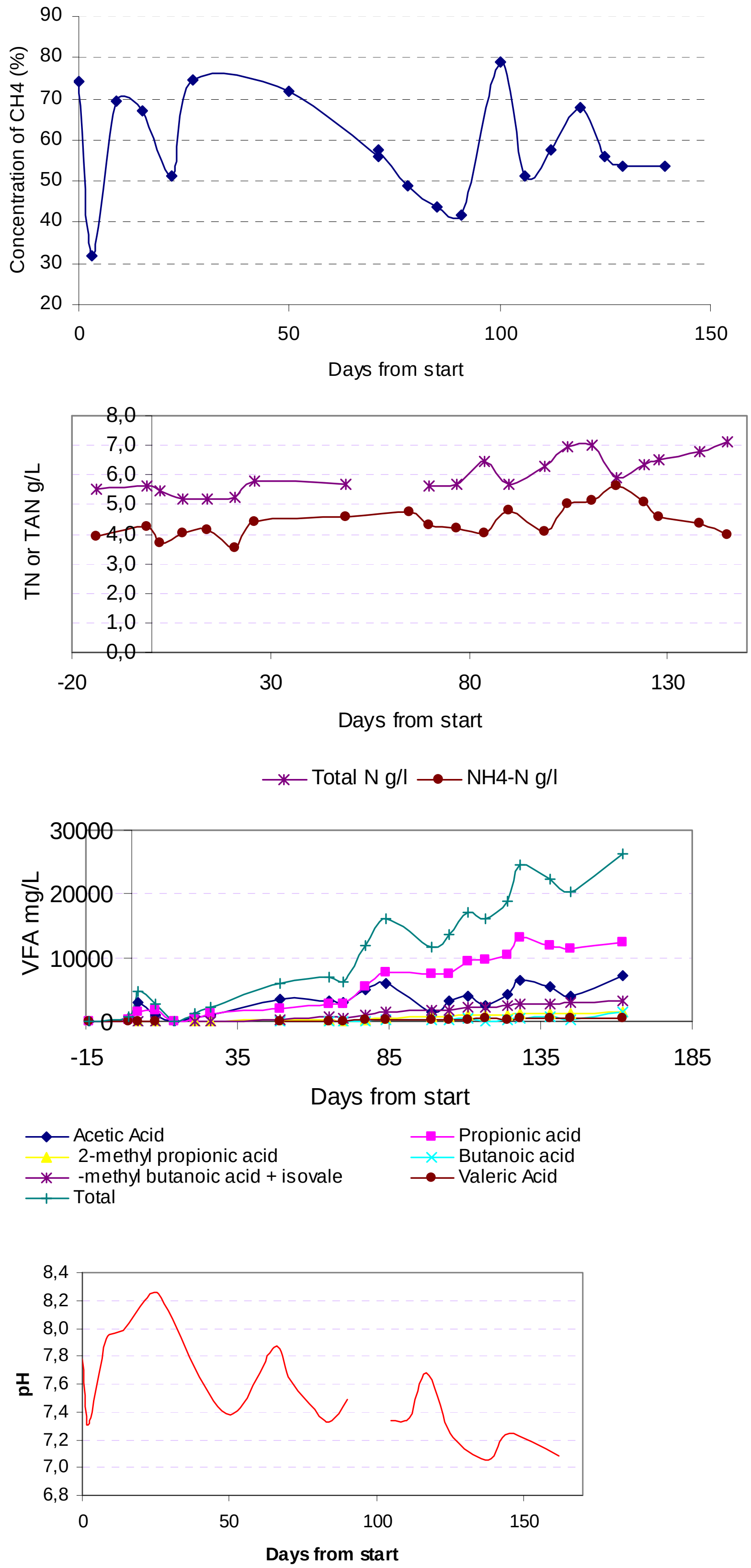

Figure 4. The development of different process state indicators during the process.

Conclusion

In the present study the possibility for digestion of byproducts from ethanol processing industries such as stillage have been tested both in a batch digestion experiment and in a long term mesophilic continuously running experiment. The batch digestion has shown a high and fast digestibility of stillage with a methane yield of more than 350 liter CH_4/kg VS for the stillage with the highest digestibility from Novelferm.

The mesophilic long term digestion lasted more than 5 month and the average hydraulic retention time during the complete period was 39 days. The methane yield was 268 liter CH_4/kg VS in average for the period and the VS conversion was around 60%. In spite of a relatively stable digestion and VS conversion the process showed signs of inhibition and high levels of VFAs indicating that a higher conversion and methane yield could be achieved by prolonging the retention time and/or post digestion. In the first half of the period there was only a slight inhibition, but in the last phase the inhibition was more pronounced, but not at any point leaving to serious drops in gas yield. The inhibition seemed to be initiated by a technical failure were the digester was almost emptied and had to be re-inoculated with the digested material. However some of the inhibition might also be explained by an ammonia level in the upper end of what is normally followed by inhibition. Futhermore the mesophilc temperature at 39^{o}C is in the high range of the mesophilic temperature regime leading to higher sensitivity to ammonia, since a larger part of the ammonia will be in the undissociated form, which is the inhibiting compound. Thus choosing a slightly lower temperature might improve the digestion performance.

Appendix 1

Composition of digested effluent

Date	DM	VS	pH	Total N	NH4-N
	%	%		g/l	g/l
16-05-2007	6,46	4,18	8,02	5,53	3,93
29-05-2007	6,85	4,30	7,83	5,63	4,25
01-06-2007	5,98	4,50	7,31	5,44	3,70
07-06-2007	3,79	2,57	7,92	5,17	4,04
13-06-2007	3,70	2,43	7,98	5,17	4,14
20-06-2007	3,24	2,24	8,20	5,22	3,54
25-06-2007	5,13	3,74	8,25	5,80	4,39
18-07-2007	2,33	1,65	7,39	5,70	4,60
03-08-2007	4,21	2,88	7,86		4,74
08-08-2007	2,57	2,04	7,65	5,64	4,32
15-08-2007	2,51	2,19	7,46	5,70	4,17
22-08-2007	3,74	3,16	7,33	6,46	4,05
28-08-2007	2,85	2,32	7,49	5,70	4,81
06-09-2007	4,91	3,53		6,32	4,10
12-09-2007	5,48	4,58	7,34	6,94	5,01
18-09-2007	3,06	2,54	7,36	7,02	5,11
24-09-2007	1,68	1,19	7,68	5,90	5,62
01-10-2007	4,25	3,58	7,29	6,36	5,10
05-10-2007	4,28	3,56	7,17	6,51	4,56
15-10-2007	4,00	3,34	7,05	6,81	4,37
22-10-2007	2,49	2,04	7,25	7,10	3,99
08-11-2007			7,08		