

ANAEROBIC DIGESTION OF CORN-DDGS: EFFECT OF PH-CONTROL, AGITATION AND BATCH REPETITION

László GYENGE¹, Silvia CROGNALE², Szabolcs LÁNYI³, Beáta ÁBRAHÁM⁴,
Botond RÁDULY⁵

This work investigates the effect of technical parameters on the anaerobic digestion of the corn-DDGS in laboratory-scale bioreactors under mesophilic conditions. The experimental results show that both pH-control and stirring have a significant influence on the methane production. With respect to the conditions without stirring and without pH-control 41% higher methane production has been observed when applying agitation; a further increase of 24% was observed when applying also pH-control. The results of the fed-batch experiment with partial evacuation of the biomass indicate a clear improvement of the digestion performance parameters, attributable to the acclimation of the anaerobic biomass to the substrate.

Keywords: anaerobic digestion, corn-DDGS, repeated batch, pH, stirring

1. Introduction

One of today's most popular processes in the renewable liquid fuels industry is certainly the corn-based ethanol production. Much of the US bioethanol production, which itself accounts for more than 60% of the global bioethanol production, uses corn as feedstock [1]. One of the main problems of the corn bioethanol industry is the large amount of by-product generated in the distillation operation. This by-product is referred to as distillery wastewater or whole stillage, and it is basically the fermentation residue, i.e. it contains the whole amount of the fermentation mass except the ethanol. Because the whole stillage volumes exceed 10-20 times the volume of the produced ethanol, and

¹ PhD student, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania, gyengelaszlo@sapientia.siculorum.ro

² PhD, Department for Innovation in Biological, Agro-food and Forest systems (DIBAF), University of Tuscia, Viterbo, Italy⁵

³ Prof., Department of Bioengineering, Sapientia Hungarian University of Transylvania, Miercurea Ciuc, Romania

⁴ Associate Prof. Department of Bioengineering, Sapientia Hungarian University of Transylvania, Miercurea Ciuc, Romania

⁵ PhD, Department of Bioengineering, Sapientia Hungarian University of Transylvania, Miercurea Ciuc, Romania

because of the explosive growth of corn bioethanol production, the fate of this by-product is a matter of concern [2].

Most frequently the whole stillage is dried to water content less than 5% to prevent early deterioration, and it is commercialized as animal feedstock under the name of DDGS (distiller's dried grains with solubles). This stillage processing method, however, not only makes the profitability of the bioethanol production liable to the request of the animal feed markets, but it is also very energy-intensive. Indeed, stillage drying can make up almost half of the total energy consumption of a bioethanol plant, and rises the bioethanol production costs [3,4].

Anaerobic digestion (AD) is seen as a promising by-product processing method, which could eliminate the above problematic aspects of the traditional stillage handling. The AD process (also called biomethanation in the industry) is a complex chain of biochemical transformations (hydrolysis, acidogenesis, acetogenesis and methanogenesis) carried out by unique groups of anaerobic microorganisms that degrade and transform organic matter into biogas [5]. In the bioethanol production facilities AD could replace stillage drying, and could convert the organic matter content of the whole stillage into biogas. Biogas can be used on-site for cogeneration of heat and electricity, thus AD has the potential of significantly improve the energy balance of ethanol production [6]. The AD by-product – the digestate – is harmless to the environment and can be used for soil amendment, biochar production or in fungiculture [7,8].

Whole stillage is reported to be digestible without any co-substrate. In biochemical methane potential (BMP) assays it gives a specific methane yield of about 400-500 mL CH₄ for each g of volatile solids (VS) added [4,9]. Since the AD process is known to be significantly influenced by a series of factors (such as temperature, pH, stirring, etc.), the efficiency of methane production from corn whole stillage could be improved by process optimization. Previous studies investigate the effect of inoculum type, inoculum-to-substrate ratio, and temperature on the digestion of corn whole stillage [4,9,10], however the pH and stirring effect on this substrate is still remained unexplored.

The aim of this work is the investigation of the effect of pH-control, of agitation and of batch repetition on the mesophilic AD of corn whole stillage. The pH has an important effect on the biogas production, as the methanogenic activity will slow down considerably with pH less than 6.3 and higher than 7.8. Below 6.3 it is inhibited by the accumulated volatile fatty acids, while above 7.8 by the ammonia [11]. Agitation and batch repetition are also known to improve the biogas yields, due to the better homogenization of the biomass/substrate mixture and due to the acclimation of microorganisms to the substrate [12,13]. However, the degree of the impact of these factors on the biomethane production from a specific substrate cannot be predicted, but it has to be determined experimentally.

The results of such an investigation could provide helpful references for biogas engineering design.

2. Materials and methods

2.1. Substrate and inoculum characterization

Rehydrated corn distiller's dried grains with solubles (DDGS) was used as substrate in the anaerobic digestion experiments. The DDGS was obtained from a dry-grind corn ethanol plant (SC Bio Fuel Energy SRL) situated in Zimnicea (Romania) and it was stored in cool and dry place until use. Before using the DDGS in the experiments, it has been rehydrated with distilled water to a total solids (TS) content of 8.5%, in order to arrive to a TS content of whole stillage (precursor of DDGS) still stirrable by means of magnetic stirrers.

As inoculum a granular type anaerobic sludge has been used, obtained from the mesophilic up-flow anaerobic sludge blanket (UASB) reactor treating the wastewater of a local brewery (Miercurea Ciuc, Romania). This anaerobic sludge gave very good results in previous digestion experiments of corn-bioethanol by-products [9]. Prior to the experiments the inoculum was incubated at 37°C for two weeks to minimize the potential endogenous activity.

Table 1
Characteristics of the rehydrated DDGS and of the inoculum used

Parameter	Rehydrated DDGS	Granular inoculum
pH	3.73	7.04
ρ [kg/m ³]	996.00	1009.00
TS [%], w/w]	8.50	8.50
VS [%], w/w]	8.14	4.09
VS/TS [%]	95.76	48.12
COD [mg/L]	142810.93	75167.69
SCOD [mg/L]	34282.60	n/a

Total solids (TS), volatile solids (VS), and chemical oxygen demand (COD) determinations for the substrate and inoculum were carried out according to Standard Methods [14]. Soluble chemical oxygen demand (SCOD) determinations were performed on the filtrate passing the 0.45 μ m glass-fiber filter. A summary of the characteristics of the mesophilic inoculum and the rehydrated DDGS are presented in Table 1.

2.2. Experimental set-up

The anaerobic digestion experiments were carried out in reactors of 1.125 L volume, equipped with stirrers (120 rpm) and placed in warm water bath (37°C) in order to ensure mesophilic conditions. Each reactor has been filled up to 734

mL with a mixture of substrate and inoculum, so that the ISR in each reactor was 3:1 on dry weight basis (meaning 552 mL of inoculum and 182 mL of pH-neutralized rehydrated DDGS), having an initial pH of 7. Before closing the reactors, the remaining headspace has been flushed with nitrogen gas. The pH has been monitored using temperature-compensated pH sensors while pH-control has been accomplished manually, injecting the necessary quantity of 1M NaOH solution in the reactor for adjusting the pH to 7.2 when it dropped to 7.

Three repeated batch digestion sessions have been performed, removing a volume of 182 mL of digested sludge and feeding the same amount of fresh substrate every 5th day. All other aspects of the repeated batch experiment (temperature, initial substrate and inoculum quantities, initial pH, etc.) were as described above.

2.3. Biogas determination

The volume of the produced biogas has been measured by a bubble counting flow meter [15]. The biogas volumes were all temperature-corrected, and the values reported in this work refer to normal conditions (273 K, 101325 Pa).

The methane content of the produced biogas was determined using a gas chromatograph (HP 5890 Series II) equipped with a Thermal Conductivity Detector (TCD) and a Mol Sieve 5A PLOT Capillary GC Column (Supelco). Nitrogen has been used as carrier gas with a back pressure of 34.47 kPa. During the measuring the oven was maintained at a constant temperature of 80°C for 180 s. Both the injector and the detector temperatures were 120°C. The system was calibrated with analytical grade methane (Merck). Biogas sampling has been performed every 2nd day using a Hamilton GasTight 250 µL syringe. For the initial 5 days of the experiment the CH₄ concentrations revealed on the 6th day have been considered, because of the dilution of biogas before completely replacing the nitrogen from the headspace.

3. Results and discussion

For the evaluation of the effect of pH-control and agitation on the AD of the corn-DDGS, different operating conditions have been set in three reactors: R1 – stirred, with pH-control; R2 – stirred, without pH control; R3 – no stirring, no pH control. The cumulative biogas production curves of the three reactors are shown on Fig. 1a. As can be seen the highest total biogas production (6614 mL) was observed in the case of R1. The curves of R1 and R2 start to show a visibly different behaviour after 2-3 days of fermentation. After this point the reactor without pH-control produced significantly less biogas. The dynamics of the curves match well the period the reactors spent in different pH-range: addition of NaOH in R1 was necessary only in the first days of the experiment to keep the pH

above neutral. Hence the weaker biogas production of R2 reflects a drop of pH in R2, due to the accumulation of organic acids (intermediate metabolites), which exert a methanation inhibition. This is in concordance with the environmental preferences of methanogens reported in the literature, namely that methanogenic activity is inhibited by low pH values [11]. The fact that after the 3rd day no further decrease of the pH was observed in R1, indicates the end of the accumulation of volatile fatty acids (VFAs) partly because of substrate depletion and partly because the consumption of VFAs by the methanogenic biomass (increased in the meantime).

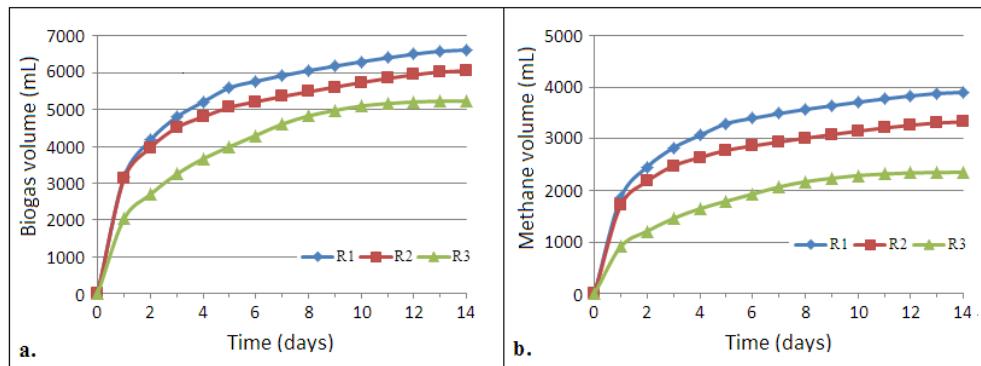


Fig.1. Cumulative biogas (a) and methane production (b) of three bioreactors: R1-with pH-control and stirring; R2 - stirring only; R3 - without pH-control and stirring

The cumulative biogas production of R3 is distinctly lower when comparing it to the production curves of R1 and R2. The difference is significant from the beginning of the experiment, indeed, after two days of biodigestion the biogas production in R3 was about 35% lower than in the other two reactors. At the final time of the experiment the total biogas production of R3 was with 22% lower than that of R1. The weak biogas production in R3 is mainly due to the lack of stirring. Larger difference in biogas production was revealed in the first – more dynamic – days of the experiment, when the lack of pH correction does not significantly penalize the gas production (see the curves for R1 and R2). Therefore the weak biogas production experienced in this period can be entirely attributed to the insufficient dispersion of the substrate in the liquid suspension and reduced bioavailability of the substrate in the anaerobic process. This is important for higher-scale (typically fed-batch) operating conditions, and indicates that high biogas production rates in corn-DDGS digestion can be achieved only by applying agitation. This observation is in agreement with the findings of Rojas et al. [16], namely that the availability of bacteria in the reactor does not assure that the substrate will be totally digested, if mass transfer between

the bacteria and the substrate is not efficient. Optimization of agitation speed would very likely further increase the methane production, as it has been demonstrated on the AD of other substrates [12].

Important to mention, that not only the volumes but also the observed methane concentrations of the biogas produced in the three reactors were different. The final CH_4 concentrations revealed were 59%, 55% and 45% in R1, R2 and R3, respectively. As the lowest biogas production is paired with the lowest methane concentration, the specific methane production curves markedly differ from each other (Fig. 1b). The cumulative methane productions at the final time of the experiment were 3902, 3328 and 2355 mL CH_4 for reactors R1, R2 and R3, respectively. In other words, the agitation alone brought a 41% benefit in terms of methane production when compared to the situation with no agitation and no pH control, while the application of pH-control caused a further increase of 24% in the methane production. These results show again, that the lack of stirring has a very significant negative effect on the methane production, since the toxic metabolites are not efficiently eliminated and inhibit the methanogenic activity. The fact that biogas production is less affected by the lack of stirring than methane production, can be attributed to the higher sensitivity of the methanogens to the effect of inhibiting compounds (such as for example VFAs) with respect to hydrolytic and acidolytic microorganisms.

As R1 proved to be the more efficient in terms of methane production among the three reactors, the same stirring and pH-control have been applied under repeated batch conditions, in order to evaluate the feasibility of semi-continuous digestion. For this reason the same reactor set-up and initial conditions have been used as in case of R1, but digested sludge has been removed from and fresh substrate has been added to the reactor on days 5 and 10. For the ease of results interpretation, the removed and added volumes were identical with the initial substrate amount (182 mL). This feeding rate is equivalent to a daily organic loading rate (OLR) of $4.0 \text{ g VS L}^{-1} \text{ d}^{-1}$ (daily VS quantity added relative to 1 L of reactor volume), which is comparable to OLRs practiced at full scale suspended media anaerobic digesters [17].

The cumulative methane production of the repeated batch experiment is presented in Fig. 2. Note that the produced methane volumes became higher and higher in each consequent batch, the production in the 3rd batch being 4693 mL CH_4 . The specific methane production relative to the unit mass of added VS increased from the initial 233 in batch#1 to 316 mL $\text{CH}_4 \text{ g}^{-1} \text{ VS}$ in batch#3.

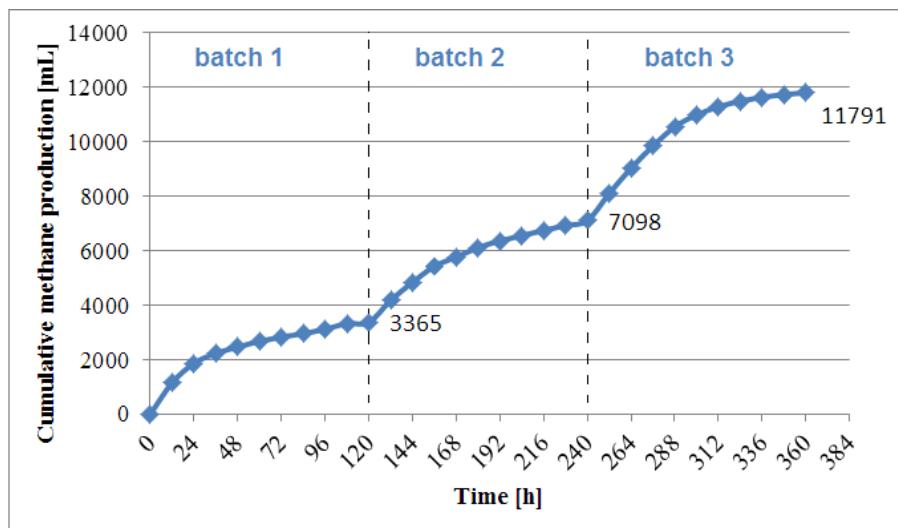


Fig. 2. Typical time course of methane production in the repeated batch experiment. Substrate has been added on days 5 and 10.

This is somewhat lower than the specific methane yields obtained in previous BMP assays using corn-DDGS [18], but it has to be considered that the methane production of the named BMP assays refers to a 30-day period, while the repeated batches of this experiment were of only 5 days each. Hence, the observed specific methane production rates (with a maximum of $39.1 \text{ mL g}^{-1} \text{ VS h}^{-1}$ in the 3rd batch) are several times higher than those experienced in the case of BMP assays. Throughout the 3 repeated batches the methane production rates showed a 40% increase; this is suggested also by the increasing slope of the methane production curves of the three consecutive batches. The increasing trend of the process performance indicators can be explained by the growth of the anaerobic biomass acclimated to the substrate. The final volumetric methane yield relative to 1 L of reactor volume was $1278.8 \text{ mL L}^{-1} \text{ d}^{-1}$. A summary of the process performance indicators is shown in Table 2.

Table 2

Process performance indicators of the repeated batches; V_{CH_4} - methane volume, Y_{CH_4} - specific methane yield, $Y_{\text{CH}_4}^*$ - volumetric methane yield, r_{CH_4} - specific methane production rate

	V_{CH_4} [mL]	Y_{CH_4} [mL g ⁻¹ VS]	$Y_{\text{CH}_4}^*$ [mL L ⁻¹ d ⁻¹]	r_{CH_4} [mL g ⁻¹ VS h ⁻¹]
batch#1	3365	228.1	916.9	1.90
batch#2	3733	253.0	1017.2	2.11
batch#3	4693	318.1	1278.8	2.65

Although the specific methane yields obtained in this experiment are not very high, they showed an increasing tendency. Very likely further significant improvement of the specific yields could be obtained by further process optimization (optimized stirring, better acclimation of microorganisms, increased feeding frequency, addition of trace minerals and vitamins for the methanogens).

4. Conclusions

The results indicate that both the pH-control and the agitation influence significantly the efficiency of mesophilic biomethanation of the corn-DDGS. Agitation caused a 41% improvement, while pH-control brought a further 24% improvement of the methane production (as compared to the case without agitation and pH-control). The repeated batch digestion tests also gave positive results: the digestion performance indicators showed a significant improvement after only three batch repetitions, most probably due to the acclimation of the anaerobic inoculum to this specific substrate. Although the methane yields obtained in this study are not very high, significant increase of the yields is expected from further optimization of feeding and of the digestion conditions, subject of future research work.

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