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Research paper

Anaerobic digestion of corn silage on a commercial scale: Differential utilization of its chemical constituents and characterization of the solid digestate

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ABSTRACT

The utilization of different chemical constituents of corn silage during industrial-scale anaerobic digestion was determined. Corn silage together with the resulting solid digestate generated during biogas production were collected from an industrial plant during a regular operating period. Moisture, water and ethanol extractives, ash, total nitrogen, starch, cellulose, the monomeric composition of hemicellulose, acid soluble and acid insoluble lignin were measured in both corn silage and corn silage solid digestate. The relative consumption of each component of corn silage during its anaerobic digestion was estimated with reference to acid insoluble lignin. It was assumed that lignin was not digested throughout the process. Starch and large fractions of extractives and acid soluble lignin were digested. In contrast, the digestion of cellulose and particularly hemicellulose were limited (40% and 29% respectively). Of the hemicellulose monomers, xylose was the least digested (20%). The present work shows that the digestate produced by commercial corn-silage anaerobic digestion contains a notable quantity of cell wall polymers. These could potentially be used in biorefinery processes, e.g. ethanol and xylo-oligosaccharide production.

1. Introduction

Biogas is an alternative fuel, and its production by the anaerobic fermentation of plant material in farm-based plants in Europe has increased considerably in the last decade. This increase is the result of both favorable tariff systems set up in EU countries together with technical improvements and cost reductions in the production process. Nevertheless, the conversion of the crop biomass to gas is still low, despite the use of carefully selected crops. Hence, biogas production generates a byproduct that is called the solid digestate (SD). The main components of this SD are plant cell wall polymers (cellulose, hemicellulose, and lignin) which are difficult to digest due to the problems of accessibility and depolymerization that also affect the production of second-generation ethanol [1].

The main use of the SD is as soil additive/fertilizer, however, it can also be used as a solid fuel after it has been dried [2,3], as an alternative to straw in the bedding of livestock or as a material for the manufacture of particleboard [4]. Nevertheless, increases in the production of SD brought about by an increase in biogas production still give rise to the problem of its disposal. This is largely because the high nitrogen content of the SD can prohibit its use as a soil additive/fertilizer, and this is due to problems associated with pollution by nitrogenous compounds.

Corn silage (CS) is used all year round as a substrate for biogas production in Europe [5], and there are differences in CS composition (e.g. starch and dry matter content) arising from differences in cob development, climate and soil conditions, time of harvesting and ensiling period [6]. These variations have been the subject of much study in relation to the use of CS as a feed for livestock [7], and might also have relevance for biogas production. However, very little is known about how the different carbohydrates present in CS

Abbreviations: SD, solid digestate; CS, corn silage; CSSD, corn silage solid digestate; AD, anaerobic digestion; NSC, non structural carbohydrates; ASL, acid soluble lignin; AIL, acid insoluble lignin; XOs, xylo-oligosaccharides.

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(i.e. the most abundant non-structural carbohydrates, namely glucose, fructose, sucrose and starch, as well as the most abundant structural carbohydrates, namely cellulose and hemicelluloses) affect its digestion by microbes during biogas production. Although Teater et al. [4] and Pognani et al. [8] determined the composition of dairy manure and a mixture of substrates both before and after anaerobic digestion, only certain components were analyzed. A better understanding of which components of the CS are not digested could be of assistance in the design of a sustainable biorefinery scheme.

The aim of the present study was to estimate the efficiency of an industrial-scale biogas plant. This was done by comparing the composition of the substrate (CS) and of the corn silage solid digestate (CSSD), with particular attention to the amount of carbohydrates still present in CSSD.

2. Materials and methods

2.1. Corn silage and corn silage digestate

CS and CSSD after liquid fraction separation were collected at the "Fattoria Autonoma Tabacchi soc.coop.ar.l." biogas plant (Città di Castello, Perugia, Italy), in July 2013. The CS that was used as the feedstock for biogas production was obtained from plants grown within a radius of 4 km from the anaerobic digester. The corn crops were irrigated during their growth and then harvested between the end of August and the beginning of October 2012, using a Claas Jaguar 960 machine, cut at 0.9 mm. The list of the corn hybrids utilized is shown in Table 1.

Silage was made by piling and pressing green corn chips in a large heap, using a New Holland T8 360 tractor. No microbial starters were added, and each heap was covered by a plastic sheet to reduce the infiltration of atmospheric oxygen. Corn silage remained useable for 7–8 months. The biogas plant consisted of a hydrolyzer and two digesters. In the hydrolyzer the microbial consortia converted carbohydrates, proteins and lipids into short-chained sugars, amino acids, fatty acids and glycerine. Then in the two stainless steel digesters anaerobic wet fermentation took place under mesophilic conditions (42–43 °C). Two fractions were produced by this process. The first was biogas and this was burned locally in a combined heat and power generation engine. The second was a solid–liquid mixture that was termed the digestate. The digestate was mechanically separated into a liquid residue, which was recirculated in the digesters, and a SD which was used as a fertilizer for crops. The plant had a nominal power generating capacity of 1 MW, and used 50 Mg of CS per day. Shortly after their collection, CS and CSSD were freeze-dried until later use.

2.2. Characterization of the substrates

Freeze-dried CS and CSSD samples were milled (MF 10 miller IKA, Staufen, Germany) to pass through a 0.5 mm grid. This ground material was used for all analytical procedures. Ash content was determined by ignition at 575 °C in a furnace (P 300, Nabertherm, Lilienthal/Bremen, Germany) with temperature ramping according to the method NREL/TP-510-42622 [9]. Total nitrogen content was determined using an elemental analyzer (NA1500, Carlo Erba, Milan, Italy), operating a Dumas combustion in helium flow and equipped with oxidation and reduction reactors, followed by a thermal conductivity detector. Nitrogen content was converted to protein-like compounds content using the factor 4.6 as suggested by Hames et al. [10] and Godin et al. [11]. Major non-structural carbohydrates (NSC: glucose, fructose, sucrose, starch), were extracted as in Moscatello et al. [12]. Water and ethanol extractives were collected after two sequential Soxhlet extractions [13]. For the gravimetric determination of the extractives, the water extracts were freeze-dried, while the ethanol extracts were dried using a rotavapor (VV 2000 Heidolph Instruments, Schwabach, Germany). The final extractives-free solid residue was hydrolyzed to determine i) acid-soluble lignin (ASL); ii) acid-insoluble lignin (AIL), after subtraction of the protein-like compounds content; iii) total monosaccharides content according to the method NREL/TP-510-42618 [14]. Starch was hydrolyzed to glucose as in Moscatello et al. [12]. Soluble NSC, glucose resulting from starch hydrolysis, and monomeric sugars resulting from the acid hydrolysis of the extractives-free solid residue were analyzed by high-performance anion exchange chromatography, with pulsed amperometric detection (HPAEC-PAD) (Thermo Scientific™ Dionex™ ICS-5000, Sunnyvale, CA U.S.A.), consisting of an isocratic quaternary pump, a pulsed amperometric detector, an injection valve with a 5 mm^3 injection loop and an analytical CarboPac SA10 column (4 mm × 250 mm) with the guard column. The detection cell contained a gold working electrode (1.0 mm in diameter) and an Ag/AgCl reference electrode. Pulsed amperometric detection was carried out with the following waveform: $E_1 = +0.10$ V ($t_1 = 0.4$ s), $E_2 = -2.00$ V ($t_1 = 0.01$ s), $E_3 = +0.60$ V (t = 0.01 s), E4 = −0.10 V (t = 0.06 s). The electrical signal was integrated in ncoulomb (nC). Runs were carried out at 45 °C. NaOH (1 mmol L^{-1}) was used as mobile phase at a flow rate 1 cm^3 min^{-1} with a post-column addition of concentrated NaOH (300 mmol L^{-1}). Post-column addition was made using a second pump, at a flow rate of 0.5 cm^3 min^{-1}. The carbohydrate standard solutions were prepared using HPLC grade reagents (Sigma, Steinheim, Germany). The instrumentation control, data acquisition, and processing was performed by the software Chromeleon Data System version 6.8 (Thermo Scientific™, Dionex™). Organic acids were analyzed by the ion chromatography system Dionex™ ICS-5000, consisting of an isocratic pump, a conductivity detector, an injection valve with a 25 mm^3 injection loop, an analytical IonPac AS11-HC column (4 mm × 250 mm) with the guard column and a IonPac ATC-1 (Anion Trap Column), coupled with the Anion Self-Regenerating Suppressor (ASRS 300). All components are from Thermo Scientific™, Dionex™, (Sunnyvale, CA U.S.A.). The electrical signal was integrated in μSiemens (μS). Runs were carried out at 30 °C under the following elution conditions: 1 mmol L^{-1} NaOH for 18 min followed by a gradient of NaOH from 15 to 60 mmol L^{-1} in 20 min with a flow rate of 1,5 cm^3 min^{-1}. The eluents and the organic acid standard solutions were prepared using HPLC grade reagents (Sigma, Steinheim, Germany). Samples were filtered through 0.2 μm PPII syringe filters prior to injection. The instrumentation control, data acquisition, and processing was performed by the software Chromeleon Data System version 6.8 (Thermo Scientific™, Dionex™).

Cellulose and hemicellulose contents were calculated from the amounts of monomeric sugars according to Ververis et al. [15]. Following these determinations, the percent depletion of CS

Table 1
Name and cultivation surface of corn hybrids used to feed the plant in the period prior to the sampling.

Seed company	Corn hybrid	Cultivation surface (hm^2)
Pioneer, Johnston, USA	PR31Y43	55.70
	PR31K18	48 50
	PR31A34	39 00
	PR32F73	16 00
	PR33M15	9 00
	P1114	20 50
KWS, Einbeck, Germany	KOBRAS	14 20
DCK, DeKalb, USA	DKC5401	11 00
Maisadour, Haut-Mauco, France	CALCIO	2 60