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Predicting anaerobic biogasification potential of ingestates and digestates of a full-scale biogas plant using chemical and biological parameters

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ABSTRACT

The aim of this work was to develop simple and fast tests to predict anaerobic biogasification potential (ABP) of ingestates and digestates from a biogas plant. Forty-six samples of both ingestates and digestates were collected within an eight-month observation period and were analyzed in terms of biological and chemical parameters, namely, ABP test, oxygen demand in a 20-h respirometric test (OD20), total solids (TS), volatile solids (VS), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), ammonia, cell solubles (CS), acid detergent fibers (ADF), lignin (ADL), cellulose, and hemicellulose. Considering both quantitative (VS and TOC) and qualitative aspects (OD20 and CS) of organic matter (OM), four models (linear regressions; $0.80 < R^2 < 0.913$; 16% < standard errors < 23%) were proposed to predict ABP. The models were chosen according to the needed accuracy of the evaluation in terms of time schedule and the availability of the required laboratory analyses.

1. Introduction

Anaerobic digestion (AD) for biogas production could substitute for fossil fuel-derived energy and reduce environmental impacts by providing a clean fuel from renewable feedstock, such as energy crops, organic fractions of municipal solid wastes, and agro-industrial wastes (Chynoweth et al., 2001). Today, in northern Italy, because many biogas plants need to very quickly vary their feeding, depending on the availability of feedstock on the market, it would become necessary to predict the quality of a new ingestate mixture in just a few days. At the same time, ready responses on digestate slurries would give an evaluation of degradation yields achieved by the AD process.

Chemical characterization of both ingestates and digestates is still the most widely used method to evaluate process trends (Holm-Nielsen et al., 2006). While only a few parameters are determined by online monitoring (temperature, pH and biogas composition), fermentation process control is mostly achieved through manual sample extraction and time-consuming laboratory analyses (Sanderson et al., 1996; Wilman et al., 2000), such as total solids (TS), volatile solids (VS), total Kjeldahl nitrogen (TKN), ammonia, total organic carbon (TOC; Holm-Nielsen et al., 2006), total phosphorus (P_2O_5), acid detergent fibers (ADF), acid detergent lignin (ADL), cellulose, hemicellulose, and cell solubles (CS; Gunaseelan, 1997; Zhang et al., 2007).

Anaerobic biogasification potential (ABP) assay, also known as biochemical methane potential (BMP), can be used in evaluating biogas potential of both organic matrices composing an ingestate mixture and residual biogas in digestates. Moreover, such information allows a direct assessment of biogas production yields achieved by the AD process. On the other hand, such an assay lasts for at least 60 d (Adani et al., 2001; Hansen et al., 2004), requiring considerable laboratory work.

In the literature, some efforts have been done in studying the relationships between ABP, digestibility, and chemical parameters of both fresh matrices and digested bioslurries (Bjorndal and Moore, 1985; Chandler et al., 1979; Gunaseelan, 2007; Han et al., 1975; Habig, 1985; Tong et al., 1990). Some interesting regression models predicting ABP through chemical composition can be found in Gunaseelan's recent work (Gunaseelan, 2007). Focusing only on some fresh lignocellulosic feedstock such as sorghum, napier grass and fruit, and vegetable solid wastes, some regressions were found between ABP and single chemical parameters.

Near-infrared spectroscopy (NIR) has been frequently reported as an easy and low-cost analysis, which could substitute for many laboratory analyses. Some authors focused on its possible use as an online technology for monitoring bioslurry compositions in biogas plants (Holm-Nielsen et al., 2006). Others reported regression models between NIR responses and chemical composition of biomass feedstock, mostly focusing on silages and crops for animal feed (Nousiainen et al., 2004; Sanderson et al., 1996; Wilman et al., 2000). On the other hand, to our knowledge, NIR has never been correlated to ABP.

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Biological analyses can also be used to predict ABP. Muller et al. (1998) indicated respirometric activity of municipal solid waste to be significantly correlated with anaerobic processes, i.e., biogas production from the same matrices.

The aim of this study was to determine regression models between ABP and some chemical and biological parameters of both ingestate mixtures and digested slurries of the observed biogas plant. This could enable a quick prediction of ABP and readily give information for future monitoring and operating of the AD process of the biogas plant.

2. Methods

2.1. Feedstock sample collection

In 2006, Di.Pro.Ve. – University of Milan – Italy was involved in monitoring a full-scale biogas plant in northern Italy, consulting its operators regarding process start-up and optimization. A series of 46 samples was collected during an eight-mo plant-monitoring period (February–September 2006), with the aim of applying any positive result on operational management. The plant produced 2 MW of electrical power by codigesting, in four continuously stirred tank thermophilic reactors (CSTR) plus a post digester, a mixture of energetic crops, pig manure slurry, agro-industrial waste, and organic fraction of municipal solid waste (OFMSW).

Samples were divided into two groups. The first 12 samples were feed-in mixtures (ingestates) of the biogas plant. Due to practical requirements of the full-scale process, the composition of these mixtures significantly varied during the observation period. The second group included 34 samples representing the outputs of the five digesters after approximately 40 or 50 d of AD.

All the samples were dried for 24 h at 105 °C (APHA, 1992) and were shredded in a blender to pass through a 2-mm mesh. Both biological and chemical analyses in this study were performed using the same dried and shredded samples.

2.2. Analytical methods

Representative samples were used to carry out all the analytical tests. TS, VS, and TOC were determined according to standard procedures (APHA, 1998). Ammonia and TKN (detected on fresh material) were determined according to the analytical method for wastewater sludges (IRSA CNR, 1994). Total phosphorus (P_2O_5) content was determined using the standard methods for the exam-

Table 1
Chemical characterization of the analyzed samples

Date	RT[a] (Days)	TS (%FM)	VS (%TS)	TOC (%TS)	Ammonia (%TS)	TKN (%TS)	P_2O_5 (%TS)	TOC/TKN	Ammonia/TKN
1/2/2006	0	13.80 ± 0.20	92.40 ± 0.20	40.80 ± 0.10	0.47	2.75 ± 0.04	0.45 ± 0.01	14.84	0.17
9/2/2006	0	12.70 ± 0.50	91.80 ± 0.50	44.50 ± 0.30	0.75	3.32 ± 0.05	0.65 ± 0.09	13.40	0.23
15/02/06	0	11.92 ± 0.40	90.90 ± 0.30	47.20 ± 0.20	0.81	3.51 ± 0.05	0.59 ± 0.00	13.45	0.23
23/02/06	0	11.98 ± 0.70	92.10 ± 0.60	43.00 ± 1.00	0.63	3.09 ± 0.10	0.65 ± 0.01	13.92	0.20
2/3/2006	0	14.70 ± 1.00	91.80 ± 1.10	44.50 ± 0.70	0.49	2.98 ± 0.03	0.83 ± 0.11	14.93	0.16
8/3/2006	0	12.24 ± 0.80	92.00 ± 0.30	42.30 ± 0.70	0.64	3.05 ± 0.10	0.81 ± 0.13	13.87	0.21
22/03/06	0	13.51 ± 1.10	92.40 ± 0.80	44.10 ± 0.50	0.67	3.53 ± 0.04	0.86 ± 0.03	12.49	0.19
27/03/06	0	11.08 ± 0.60	89.00 ± 1.50	43.00 ± 0.40	0.64	3.73 ± 0.00	0.95 ± 0.08	11.53	0.17
3/5/2006	0	12.29 ± 0.20	93.00 ± 1.00	45.60 ± 0.00	1.00	3.67 ± 0.05	0.54 ± 0.11	12.43	0.27
31/05/06	0	15.03 ± 0.50	81.00 ± 0.80	43.80 ± 0.30	1.39	5.15 ± 0.08	1.77 ± 0.07	8.50	0.27
1/8/2006	0	19.56 ± 1.10	93.10 ± 0.10	51.50 ± 0.70	1.05	1.96 ± 0.01	0.48 ± 0.01	14.88	0.30
22/08/06	0	14.03 ± 0.30	89.60 ± 0.50	42.70 ± 0.20	0.06	3.18 ± 0.01	0.62 ± 0.07	13.43	0.33
1/2/2006	40	9.58 ± 0.80	77.40 ± 0.60	35.80 ± 0.90	1.80	4.94 ± 0.05	1.90 ± 0.31	7.25	0.36
1/2/2006	40	8.92 ± 1.50	72.20 ± 0.80	30.10 ± 1.00	2.37	5.58 ± 0.04	3.37 ± 0.25	5.39	0.42
9/2/2006	40	9.08 ± 1.00	72.30 ± 1.00	37.90 ± 1.20	1.74	5.26 ± 0.02	1.67 ± 0.20	7.21	0.33
9/2/2006	40	5.46 ± 0.80	67.20 ± 0.20	33.60 ± 1.70	3.32	6.82 ± 0.09	1.87 ± 0.21	4.93	0.49
15/02/06	40	3.62 ± 0.10	73.30 ± 0.10	31.90 ± 0.80	2.40	5.97 ± 0.13	1.50 ± 0.09	5.34	0.40
23/02/06	40	8.26 ± 0.50	79.30 ± 0.50	43.00 ± 0.80	1.88	4.43 ± 0.15	2.61 ± 0.36	9.71	0.42
23/02/06	40	8.21 ± 0.60	68.60 ± 1.10	37.80 ± 0.00	2.23	5.26 ± 0.03	3.29 ± 0.05	7.19	0.42
2/3/2006	40	8.47 ± 0.80	75.70 ± 0.20	39.20 ± 0.20	1.78	5.26 ± 0.37	2.14 ± 0.20	7.45	0.34
2/3/2006	40	8.10 ± 1.00	77.40 ± 0.50	33.80 ± 0.10	1.96	4.56 ± 0.02	2.75 ± 0.38	7.41	0.43
8/3/2006	40	8.39 ± 0.20	81.90 ± 0.80	39.50 ± 0.90	2.16	5.39 ± 0.19	2.45 ± 0.02	7.33	0.40
8/3/2006	40	7.09 ± 0.10	78.60 ± 1.50	36.90 ± 0.70	2.92	6.37 ± 0.01	2.28 ± 0.05	5.79	0.46
27/03/06	40	5.16 ± 0.50	75.40 ± 0.60	37.50 ± 1.10	4.26	7.39 ± 0.13	2.38 ± 0.12	5.07	0.58
27/03/06	40	5.28 ± 1.10	75.70 ± 2.00	40.20 ± 2.00	4.34	7.66 ± 0.02	2.09 ± 0.00	5.25	0.57
3/5/2006	40	6.45 ± 0.20	75.70 ± 1.50	38.50 ± 0.40	3.90	6.58 ± 0.03	2.02 ± 0.12	5.85	0.59
31/05/06	40	8.57 ± 0.50	71.70 ± 0.60	37.00 ± 0.70	3.25	6.61 ± 0.15	2.88 ± 0.26	5.60	0.49
31/05/06	40	9.16 ± 0.80	70.40 ± 0.20	35.30 ± 0.40	3.07	7.05 ± 0.12	2.58 ± 0.04	5.01	0.44
31/05/06	40	12.92 ± 1.50	76.10 ± 0.40	40.90 ± 0.80	2.05	4.96 ± 0.10	2.84 ± 0.28	8.25	0.41
11/7/2006	40	2.00 ± 0.60	70.50 ± 1.10	36.40 ± 0.20	4.02	8.48 ± 0.07	2.46 ± 0.04	4.29	0.47
22/08/06	40	6.39 ± 2.00	74.80 ± 0.60	41.60 ± 0.20	2.67	5.42 ± 0.09	2.18 ± 0.00	7.68	0.49
22/08/06	40	4.09 ± 1.50	73.60 ± 0.20	36.60 ± 0.20	6.15	9.12 ± 0.05	2.41 ± 0.16	4.01	0.67
22/08/06	40	7.26 ± 0.60	77.00 ± 0.70	42.90 ± 1.80	2.33	5.03 ± 0.12	1.79 ± 0.09	8.53	0.46
6/9/2006	40	3.28 ± 0.20	90.90 ± 0.20	33.40 ± 0.50	6.79	10.82 ± 0.07	2.25 ± 0.01	3.09	0.63
6/9/2006	40	5.04 ± 0.40	71.00 ± 1.00	37.80 ± 0.00	5.79	8.71 ± 0.02	2.00 ± 0.11	4.34	0.66
6/9/2006	40	4.62 ± 1.10	68.70 ± 1.10	36.70 ± 1.80	6.43	9.52 ± 0.17	2.50 ± 0.00	3.86	0.68
8/9/2006	40	7.01 ± 0.60	79.40 ± 0.20	38.80 ± 0.40	3.87	6.05 ± 0.02	2.66 ± 0.18	6.41	0.64
8/9/2006	40	5.40 ± 0.20	76.00 ± 0.50	39.40 ± 2.10	4.80	7.52 ± 0.03	2.11 ± 0.03	5.24	0.64
13/09/06	40	3.72 ± 0.70	69.90 ± 0.20	37.10 ± 0.80	6.71	10.52 ± 0.06	2.21 ± 0.14	3.53	0.64
13/09/06	40	5.26 ± 0.20	73.30 ± 0.50	37.80 ± 1.00	4.82	7.71 ± 0.01	2.78 ± 0.13	4.90	0.63
15/09/06	40	4.61 ± 1.00	72.90 ± 0.40	39.40 ± 0.00	5.47	8.56 ± 0.02	2.11 ± 0.07	4.60	0.64
15/09/06	40	5.27 ± 1.10	71.70 ± 0.70	37.60 ± 0.10	4.88	7.67 ± 0.02	2.62 ± 0.10	4.90	0.64
11/7/2006	50	3.50 ± 0.20	70.20 ± 1.00	39.00 ± 1.20	6.60	10.20 ± 0.01	2.87 ± 0.04	3.82	0.65
22/08/06	50	3.00 ± 0.50	68.40 ± 0.80	37.75 ± 0.20	8.19	11.00 ± 0.03	3.01 ± 0.21	3.43	0.74
13/09/06	50	4.40 ± 0.20	71.30 ± 1.10	36.40 ± 0.20	5.66	8.90 ± 0.01	2.23 ± 0.01	4.09	0.64
15/09/06	50	3.48 ± 0.50	71.20 ± 0.60	36.10 ± 0.10	6.63	10.60 ± 0.04	2.32 ± 0.03	3.41	0.63

[a] Retention time into the anaerobic digesters.

ination of water and wastewater (APHA, 1998). Fiber analyses were performed for neutral detergent fiber (NDF), neutral detergent acid detergent fibers (NDADF), and acid detergent lignin (ADL), following Van Soest's method (Van Soest et al., 1991). Cell solubles (CS), lignin plus unhydrolyzable lipid (ADL), cellulose (NDADF–ADL), and hemicellulose (NDF–NDADF) were calculated according to Van Soest et al. (1991). All analyses were performed in duplicates.

2.3. Anaerobic biogasification potential (ABP) assay

2.3.1. Seed inoculum preparation

Inoculum in stable methanogenic activity (CH_4 > 60% in biogas, v/v) was obtained using the output digestate of the post digester of the plant. The pH was around 7.8; TS and VS contents were about 3–4% on wet weight basis (w/w) and 70–80% on TS basis, respectively. Digestate was incubated at 37 ± 1 °C for 15 d before use.

2.3.2. ABP assay

The ABP of all samples was determined using the method of Adani et al. (2001) with a few modifications developed, according to Hansen et al. (2004). In 100-ml serum bottles, 0.62 g of dried sample was added to 37.5 ml of inoculum and 22 ml of deionized water. The batch tests were carried out with 60-ml samples (about 3.5% TS) and 40 ml of headspace. The fresh feedstock and inoculum percentages of TS were 35% and 65%, respectively. Control blanks were prepared using 60 ml of inoculum.

All batches were sealed with teflon hermetic caps, flushed with a N_2 atmosphere, and incubated at 37 ± 1 °C, until no further biogas production was detected (normally around 60 d). Assay bottles were periodically analyzed for both quantitative and qualitative determination of biogas production. Quantitative biogas production was estimated by withdrawing extra-pressure gas with a 60-ml syringe. Biogas production of blank control batches was subtracted from biogas production of every sample. Qualitative characterization of biogas was performed by a gas chromatograph (Carlo Erba Megaseries 5300, capillary column 25-m × 0.32-mm diameter and flame ionization detector (FID)) to determine CH_4–CO_2 ratio in the biogas. The carrier gas was nitrogen at 20 kPa pressure and temperatures of injector and FID were 130 and 150 °C, respectively. Comparison of obtained peak areas was carried out with a standard gas mixture of 30:70 CH_4:CO_2. All tests were run in duplicates.

Table 2
Fibers content and results of biological tests (ABP and OD20) on dry matter

Date	RT[a] (Days)	ADF (%TS)	ADL (%TS)	Hemicellulose (%TS)	Cellulose (%TS)	CS (%TS)	OD 20 (mg O_2 g^{-1} TS)	ABP (Nml g^{-1} TS)
1/2/2006	0	7.6 ± 0.3	3.1 ± 0.1	2.8 ± 0.1	4.5 ± 0.2	89.7 ± 3.1	164 ± 5.7	608 ± 6
9/2/2006	0	12.9 ± 0.8	6.7 ± 0.4	3.2 ± 0.2	6.2 ± 0.4	83.9 ± 5.3	143 ± 9.1	636 ± 2
15/02/06	0	13.3 ± 1.1	8.0 ± 0.7	4.1 ± 0.3	5.3 ± 0.4	82.7 ± 6.8	160 ± 13.2	627 ± 6
23/02/06	0	8.9 ± 0.5	4.0 ± 0.2	2.9 ± 0.2	4.9 ± 0.3	88.2 ± 4.8	218 ± 11.9	498 ± 26
2/3/2006	0	9.9 ± 0.1	4.6 ± 0.1	3.8 ± 0.1	5.2 ± 0.1	86.4 ± 1.3	175 ± 2.5	692 ± 11
8/3/2006	0	7.1 ± 0.2	3.2 ± 0.1	3.9 ± 0.1	4.0 ± 0.1	89.0 ± 3.1	166 ± 5.7	720 ± 23
22/03/06	0	9.2 ± 0.6	4.6 ± 0.3	4.2 ± 0.3	4.6 ± 0.3	86.5 ± 5.5	275 ± 17.4	715 ± 7
27/03/06	0	8.8 ± 0.7	4.6 ± 0.4	3.4 ± 0.3	5.2 ± 0.4	86.8 ± 7.2	305 ± 25.1	700 ± 19
3/5/2006	0	25.3 ± 1.4	4.0 ± 0.2	5.4 ± 0.3	4.8 ± 0.3	85.8 ± 4.7	279 ± 15.2	772 ± 34
31/05/06	0	18.9 ± 0.3	15.0 ± 0.2	3.9 ± 0.1	10.4 ± 0.2	70.7 ± 1.0	310 ± 4.5	588 ± 6
1/8/2006	0	16.6 ± 2.2	23.7 ± 3.2	0.0 ± 0.0	9.0 ± 1.2	67.3 ± 9.1	200 ± 26.9	619 ± 11
22/08/06	0	17.8 ± 0.6	9.8 ± 0.3	2.9 ± 0.1	9.7 ± 0.3	77.6 ± 2.7	235 ± 8.1	582 ± 14
1/2/2006	40	43.9 ± 2.8	24.8 ± 1.6	11.7 ± 0.7	19.1 ± 1.2	44.4 ± 2.8	68.2 ± 4.3	194 ± 4
1/2/2006	40	34.9 ± 2.9	22.5 ± 1.9	9.9 ± 0.8	12.4 ± 1.0	55.2 ± 4.6	62.5 ± 5.2	115 ± 1
9/2/2006	40	20.5 ± 1.1	12.6 ± 0.7	10.5 ± 0.6	7.9 ± 0.4	69.1 ± 3.8	85.7 ± 4.7	213 ± 1
9/2/2006	40	13.4 ± 0.2	10.7 ± 0.2	13.0 ± 0.2	2.7 ± 0.0	73.6 ± 1.1	84.3 ± 1.2	153 ± 6
15/02/06	40	14.2 ± 0.5	12.4 ± 0.4	13.2 ± 0.5	1.8 ± 0.1	72.6 ± 2.5	95.7 ± 3.3	215 ± 6
23/02/06	40	21.9 ± 1.4	13.0 ± 0.8	9.8 ± 0.6	8.9 ± 0.6	68.3 ± 4.3	90.5 ± 5.7	380 ± 10
23/02/06	40	22.8 ± 1.9	14.4 ± 1.2	13.9 ± 1.1	8.4 ± 0.7	63.3 ± 5.2	122 ± 10.1	235 ± 4
2/3/2006	40	16.8 ± 0.9	11.5 ± 0.6	9.4 ± 0.5	5.3 ± 0.3	73.8 ± 4.0	81.2 ± 4.4	405 ± 26
2/3/2006	40	35.9 ± 0.5	17.3 ± 0.3	8.8 ± 0.1	18.6 ± 0.3	55.4 ± 0.8	64.3 ± 0.9	240 ± 9
8/3/2006	40	21.2 ± 2.9	12.5 ± 1.7	9.5 ± 1.3	8.7 ± 1.2	69.3 ± 9.3	143 ± 19.3	369 ± 14
8/3/2006	40	21.2 ± 0.7	14.2 ± 0.5	11.8 ± 0.4	7.0 ± 0.2	67.0 ± 2.3	91.9 ± 3.2	245 ± 21
27/03/06	40	32.5 ± 2.1	21.3 ± 1.4	7.2 ± 0.5	11.2 ± 0.7	60.4 ± 3.8	116 ± 7.4	333 ± 13
27/03/06	40	31.0 ± 2.6	21.3 ± 1.8	7.4 ± 0.6	9.7 ± 0.8	61.6 ± 5.1	113 ± 9.3	283 ± 12
3/5/2006	40	45.1 ± 2.5	32.9 ± 1.8	11.3 ± 0.6	12.2 ± 0.7	43.6 ± 2.4	98.8 ± 5.4	224 ± 3
31/05/06	40	23.1 ± 0.3	15.6 ± 0.2	8.5 ± 0.1	7.5 ± 0.1	68.3 ± 1.0	98.5 ± 1.4	319 ± 23
31/05/06	40	24.1 ± 3.2	17.6 ± 2.4	7.8 ± 1.0	6.5 ± 0.9	68.1 ± 9.2	135 ± 18.2	252 ± 9
31/05/06	40	27.2 ± 0.9	19.2 ± 0.7	7.7 ± 0.3	8.0 ± 0.3	65.1 ± 2.2	128 ± 4.4	416 ± 3
11/7/2006	40	26.5 ± 1.7	20.8 ± 1.3	4.5 ± 0.3	5.7 ± 0.4	69.0 ± 4.4	64.8 ± 4.1	286 ± 11
22/08/06	40	27.7 ± 2.3	19.2 ± 1.6	2.6 ± 0.2	8.5 ± 0.7	69.8 ± 5.8	102 ± 8.4	412 ± 5
22/08/06	40	29.8 ± 1.6	21.8 ± 1.2	1.4 ± 0.1	8.0 ± 0.4	68.8 ± 3.7	71.2 ± 3.9	312 ± 0
22/08/06	40	41.3 ± 0.6	29.3 ± 0.4	0.0 ± 0.0	12.0 ± 0.2	60.2 ± 0.9	101 ± 1.5	437 ± 37
6/9/2006	40	29.1 ± 6.8	21.5 ± 5.0	0.8 ± 0.2	7.6 ± 1.8	70.1 ± 16.4	79.3 ± 18.6	265 ± 6
6/9/2006	40	41.0 ± 1.4	30.7 ± 1.1	0.0 ± 0.0	10.3 ± 0.4	60.0 ± 2.1	58.2 ± 2.0	232 ± 10
6/9/2006	40	36.7 ± 2.3	26.4 ± 1.7	1.5 ± 0.1	10.3 ± 0.7	61.8 ± 3.9	91.1 ± 5.8	188 ± 6
8/9/2006	40	39.8 ± 3.3	27.5 ± 2.3	0.0 ± 0.0	12.3 ± 1.0	58.1 ± 4.8	99 ± 8.2	242 ± 3
8/9/2006	40	34.1 ± 1.9	24.7 ± 1.3	4.6 ± 0.3	9.4 ± 0.5	61.4 ± 3.3	79.2 ± 4.3	279 ± 3
13/09/06	40	30.4 ± 0.4	22.2 ± 0.3	0.0 ± 0.0	8.2 ± 0.1	72.2 ± 1.0	129 ± 1.9	244 ± 8
13/09/06	40	33.0 ± 4.4	23.5 ± 3.2	4.4 ± 0.6	9.5 ± 1.3	62.6 ± 8.4	104 ± 14.0	244 ± 6
15/09/06	40	31.3 ± 1.1	21.5 ± 0.7	8.6 ± 0.3	9.8 ± 0.3	60.1 ± 2.1	88 ± 3.0	268 ± 4
15/09/06	40	30.9 ± 2.0	21.3 ± 1.4	0.5 ± 0.0	9.6 ± 0.6	68.7 ± 4.4	93 ± 5.9	274 ± 13
11/7/2006	50	36.5 ± 3.0	27.1 ± 2.2	5.3 ± 0.4	9.4 ± 0.8	58.0 ± 4.8	13.6 ± 1.1	66 ± 1
22/08/06	50	27.9 ± 1.5	22.1 ± 1.2	11.6 ± 0.6	5.8 ± 0.3	60.5 ± 3.3	29.9 ± 1.6	77 ± 8
13/09/06	50	34.0 ± 0.5	24.4 ± 0.4	5.0 ± 0.1	9.6 ± 0.1	61.0 ± 0.9	77.2 ± 1.1	235 ± 6
15/09/06	50	27.8 ± 6.5	19.7 ± 4.6	0.7 ± 0.2	8.1 ± 1.9	71.5 ± 16.8	128 ± 30.0	245 ± 12

[a] Retention time into the anaerobic digesters.

Table 3
ANOVA applied on the two groups of samples (ingestates and digestates)

Parameter	Groups	Mean [a]	Minimum	Maximum
TS (%FM)	Ingestates	13.6 ± 2.2 b	11.1	19.6
	Digestates	6.2 ± 2.4 a	2.0	12.9
VS (%TS)	Ingestates	90.8 ± 3.3 b	81.0	93.1
	Digestates	73.8 ± 3.8 a	67.2	81.9
TOC (%TS)	Ingestates	44.4 ± 2.8 b	40.8	51.5
	Digestates	37.5 ± 2.8 a	30.1	43.0
TKN (%TS)	Ingestates	3.45 ± 0.61 a	2.75	5.15
	Digestates	7.23 ± 2.00 b	4.43	11.00
Ammonia (%TS)	Ingestates	0.72 ± 0.33 a	0.06	1.39
	Digestates	4.04 ± 1.86 b	1.74	8.19
P_2O_5 (%TS)	Ingestates	0.77 ± 0.35 a	0.45	1.77
	Digestates	2.39 ± 0.44 b	1.50	3.37
TOC/TKN	Ingestates	13.1 ± 1.8 b	8.5	14.9
	Digestates	5.6 ± 1.7 a	3.1	9.7
ADL (%TS)	Ingestates	6.1 ± 2.6 a	3.1	11.0
	Digestates	20.5 ± 5.7 b	10.7	32.9
Hemicell (%TS)	Ingestates	3.4 ± 1.3 a	0.9	5.4
	Digestates	6.6 ± 4.5 b	0.0	13.9
Cellulose (%TS)	Ingestates	6.6 ± 2.6 a	4.0	11.9
	Digestates	9.1 ± 3.4 b	1.8	19.1
CS (%TS)	Ingestates	83.6 ± 5.5 b	70.7	89.7
	Digestates	63.9 ± 7.3 a	43.6	73.8
ADF (%TS)	Ingestates	12.7 ± 4.9 a	7.1	21.4
	Digestates	29.6 ± 8.1 b	13.4	45.1
OD20 (mg O_2 g^{-1} TS)	Ingestates	219.1 ± 60.3 b	143.2	310.0
	Digestates	90.8 ± 28.1 a	13.6	143.2
ABP (Nml g^{-1} TS)	Ingestates	646.4 ± 75.8 b	498.0	772.0
	Digestates	261.7 ± 89.1 a	66.0	437.0

[a] Means followed in the same column by the same letter are not statistically different ($p < 0.05$) according to Tukey's test.

2.4. Specific oxygen uptake rate assay

The specific oxygen uptake rate (SOUR) test is a biological aerobic assay. It is a measure of the oxygen uptake rate in a water solution during microbial respiration in degrading a suspended solid matrix. The microbial respiration works out in standardized moisture conditions and in maximized conditions of both oxygenation and bacteria–substrate interaction, amplifying the differences among different samples.

Dried and mechanically shredded samples (Ø < 1 mm) underwent the SOUR test, which was performed following the method reported by Lasaridi and Stentiford (1998). Briefly, 0.2 g of dry matter was set in a flask to which the following were added: 500 ml of deionized water, 12 ml of phosphate buffer solution (KH_2PO_4 0.062 mol l^{-1}, K_2HPO_4 0.125 mol l^{-1}, $Na_2HPO_4 \cdot 7H_2O$ 0.125 mol l^{-1}; pH 7.2), and 5 ml of nutritive solution ($CaCl_2$ 0.25 mol l^{-1}, $FeCl_3$ 0.9 mmol l^{-1} and $MgSO_4$ 0.09 mol l^{-1}) made up according to the standard BOD test procedures (APHA, 1992). No nitrogen was added. During the test, standard conditions were maintained to ensure optimum microbial activity and reaction rates. To allow oxygen diffusion, the slurry was kept under agitation by using a magnetic stirrer and by performing intermittent aeration every 15 min. Potential oxygen uptake was reported as cumulative oxygen demand during the 20-h test (OD20, mg O_2 g TS^{-1} h^{-1}).

2.5. Statistical approach

All statistical analyses were preceded by the determination of the normal distribution of the data set, as the successive linear regression and step wise regression analyses were based on the assumption of normality among distributions. Normal distributions were accomplished using the Shaphiro–Wilk test (ISO, 1994). Parameters that were not following normal distributions were normalized using the Box–Cox method (Box and Cox, 1964; Klemm et al., 2002). All statistical analyses were performed using the SPSS 13.0 package (SPSS International, Chicago, IL). Regression standard errors (SE) were reported as percentage of the mean (M) of the observed data set (SEM = SE/M × 100) and were used as a qualitative indicator of the obtained linear regressions.

3. Results and discussion

3.1. Chemical and biological parameters

The results of all chemical analyses plus the OD20 respirometric test are reported in Tables 1 and 2. All parameters were observed to be influenced by the degradation degree of organic matter (OM), which is directly related to retention time (RT) in the digesters of the biogas plant. All ingestates resulted in TS contents within the range of 11–20% w/w, whereas those of digestates were found in the lower range (3–12% w/w). Characterization of total TS and biological parameters also showed differences in ingestates and digestates. ANOVA was performed to assess the significance of the RT as a factor influencing all parameters (Table 3).

As expected, RT was found to significantly ($P < 0.001$) influence most of the parameters, while for hemicellulose and cellulose, the significance was lower ($P < 0.05$). TS, VS, TOC, CS, OD20, ABP, and TOC/TKN showed lower means in the digestates, as a consequence of OM degradation. On the other hand, TKN, ammonia, ammonia/TKN, ADF, ADL, cellulose, hemicellulose, and P_2O_5 were higher in the digestates, probably due to the concentration effect during digestion.

3.2. Simple linear regressions of ABP versus chemical and biological parameters

Only some of the parameters, such as OD20, cellulose, TKN, and TOC/TKN, needed to be normalized for the statistical approach, while the others showed normal distributions.

Assuming that ABP was a dependent variable, significant ($P < 0.001$) positive regressions were found for VS, TOC/TKN, OD20, TOC, TS, and CS (Fig. 1). Negative significant regressions were shown by ammonia, TKN, ammonia/TKN, P_2O_5, ADF, and ADL (Fig. 1). Very poor regression and lower significance levels ($P > 0.05$) were found for cellulose and hemicellulose contents (data not shown). The best regression was obtained for ABP vs. VS (model 1, Table 4), with a regression coefficient of 0.806. The calculated SEM was around 23–24% (Table 4).

This result was unexpected as the literature suggests that ABP depends not only on VS content (quantitative aspect of the OM) but also on OM composition (e.g., content of carbohydrates, proteins, lipids, etc.) and OM quality (degradation efficiency; Chandler et al., 1979; Hashimoto, 1986; Robbins et al., 1979). In this work, as the considered set of samples included ingestates and the corresponding digestates, the main factor affecting ABP was the degree of OM degradation, which depends on the occurring processes (Table 3). Since the total OM content (approximately equal to VS content) was also affected by degradation, ABP showed good correlation with VS.

Volatile solid tests are very simple and less time-consuming analyses (within 24 h) and they could be directly performed in the biogas plant itself. Plant operators could easily obtain a quick assessment of the ABP of both ingestate mixtures and digestate slurries. This could help them monitor the AD process by estimating degradation and biogas yields.

This method is particularly suitable as an "*on-the-field method*", but it does not consider parameters describing OM quality. On the other hand, correlations obtained (Fig. 1) suggested that, OD20, CS, ADL, and ADF, all describing OM quality, influence ABP. Habig (1985) reported regression models between ABP and readily degradable fractions such as carbohydrate content ($R^2 = 0.83$) and carbohydrate plus protein content ($R^2 = 0.92$). Gunaseelan (2007)

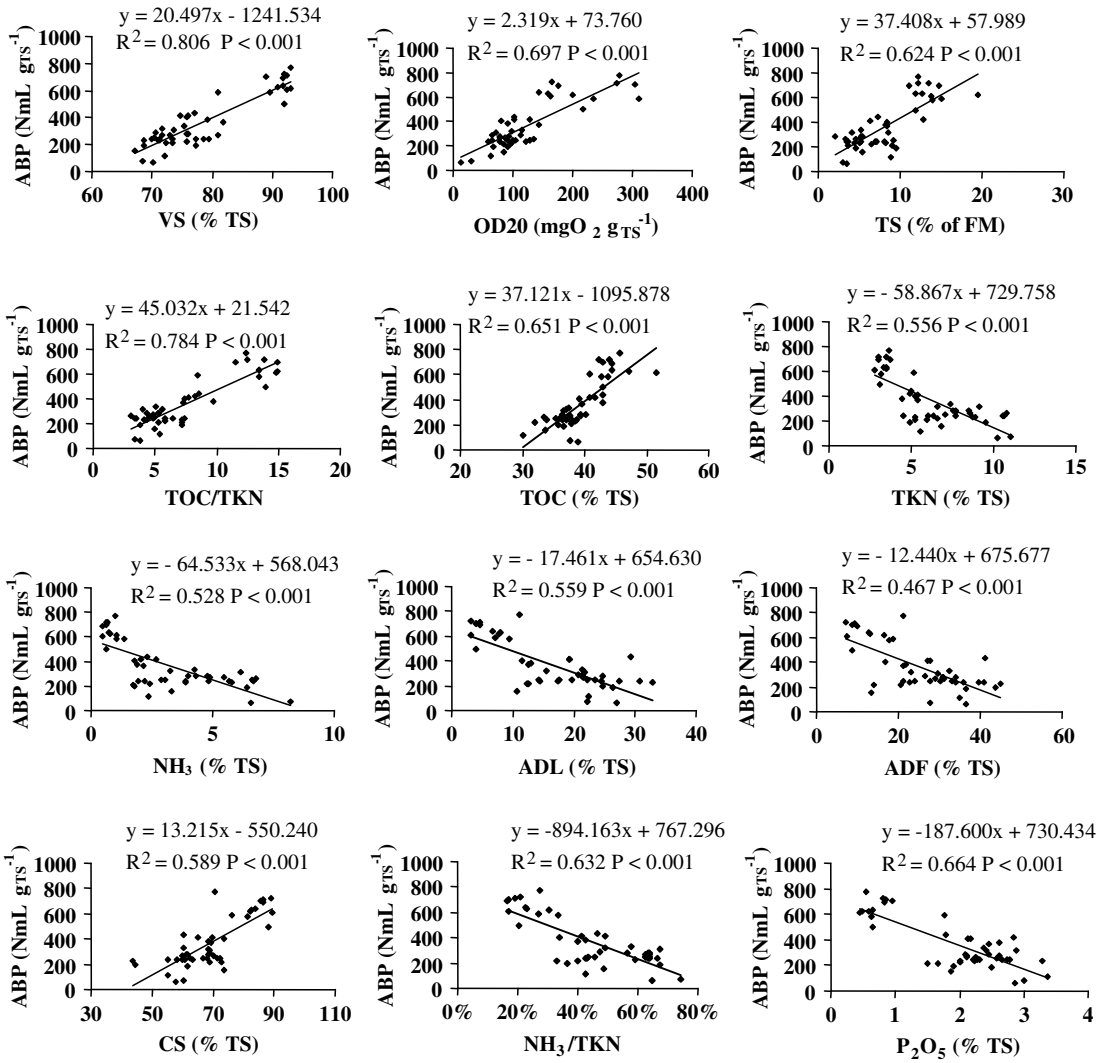

Fig. 1. Linear regressions between ABP and chemical and biochemical parameters, performed on the 46 samples studied.

Table 4
Multiple stepwise linear regression for predicting ABP

Model	Equation	Variables involved	R^2	Intercept	Slope	P	SEM (%)
1	ABP = 20.497∗VS−1241.534	VS	0.806	−1241.534	20.497	<0.001	23.5
2	ABP = 13.782∗VS + 26.161∗$OD20^{1/2}$−997.890	VS	0.880	−997.890	13.782	<0.001	18.7
		$OD20^{1/2}$			26.161		
3	ABP = 10.480∗VS + 23.178∗$OD20^{1/2}$ + 10.979∗TOC−1038.667	VS	0.904	−1038.667	10.480	<0.001	16.9
		$OD20^{1/2}$			23.178		
		TOC			10.979		
4	ABP = 8.445∗VS + 19.173∗$OD20^{1/2}$ + 10.942∗TOC + 2.913∗CS−1067.198	VS	0.918	−1067.198	8.445	<0.001	15.8
		$OD20^{1/2}$			19.173		
		TOC			10.942		
		CS			2.913		

confirmed this result by studying a series of vegetable waste and crops. The same author also showed how methane potential was correlated not only to VS and ash content but also to ADF content, cellulose, ADL, and TKN. Moreover, the literature confirms that the increase in ADL content increases the resistance of lignocellulosic material to anaerobic biodegradation (Chandler et al., 1979; Hashimoto and Chen, 1979; Robbins et al., 1979).

Therefore, more than just one parameter should be used to predict ABP. Gunaseelan (2007), for example, predicted ABP through multiple linear regression using carbohydrates, VS, ADF, ADL, and TKN (R^2 = 0.90).

3.3. Multiple stepwise linear regression

To consider both quantitative and qualitative aspects of the OM and to obtain a more reliable model to predict ABP, a multiple stepwise linear regression was performed, maintaining ABP as the dependent variable. Independent variables (all parameters studied) were introduced step by step, excluding nonsignificant ones. The results were three additional linear models, reported in Table 4. As expected, their R^2 coefficients increased at each step, while the SEM decreased.

Using VS and $OD20^{1/2}$ together as independent variables, a significant increase of the R^2 was obtained (0.880) and the SEM

decreased to 18.7% (model 2). When TOC (normalized to natural logarithm; model 3) and CS (model 4) were also considered, relatively weak increases of the R^2 value were obtained (respectively, 0.904 and 0.918) and the SEM dropped to 16.9% and 15.8%.

Model 2 may represent the best solution because it ensures a relatively high SEM decrease and it contains information about both total OM quantity (VS) and its degradability (OD20; D'Imporzano and Adani, 2007). At the same time, it requires reasonable laboratory work and only 24 h to conduct both analyses.

Models 3 and 4 are finer models predicting ABP as they consider with more depth both the quantitative (VS and TOC) and qualitative (OD20 and CS) characteristics of the OM. On the other hand, they would require much laboratory work without a satisfactory increase in estimation accuracy (SEM).

4. Conclusions

A statistical model for predicting ABP using quicker laboratory analysis was studied. An increasing number of the four most significant variables (VS, OD20, TOC, and CS) were used, representing both OM content and OM quality of the matrices. Four linear models were proposed, with R^2 coefficients ranging between 0.844 and 0.913 and the SEM between 16% and 23%.

To predict biogas potentials and assess degradation yields of the observed biogas plant, the linear regressions obtained can be used, depending on the needed accuracy and the number of laboratory analyses to be performed on the ingestates and digestates. As the number of analyses would be reduced, the most convenient solution could be achieved using only OD20 and VS (model 2); moreover, with an SEM around 19%, results could be relatively satisfactory in evaluating AD process performance, within operational time schedules.

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