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Evaluation of the biogas productivity potential of some Italian Agro-industrial biomasses

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Abstract

Batch trials were carried out to asses the biogas productivity potential of rice and barley straw, grape stalks, grape marcs, maize drying up residues, tomato skins and seeds, and whey.

Trials were carried out in 2-l glass digesters kept in a thermostate controlled room at 40°C for 40 days. The most productive biomasses, in terms of specific methane yield, were the whey and the maize drying up residues. Their specific methane yields were 501 and 317 l_N CH_4*kgSV^{-1}, respectively. Barley and rice straw gave a specific methane yield of 229 and 195 l_N *kgVS^{-1}. Similar result was also obtained from tomato skins and seeds. Grape stalks and grape marcs produced lowest amounts of specific methane, respectively, 98 and 116 l_N CH_4*kgSV^{-1}. According to trial results and considering the availability of examined biomasses in Italy, it is possible to estimate their total energetic potential close to a value of 21900 TJ*year^{-1}. This energetic potential value is equal to that obtainable from the anaerobic digestion of about 6.5 million tons of maize silage.

Keywords: Anaerobic Digestion, Biogas, By-products.

1. Introduction

Many agricultural biogas plants for the production and transformation of biogas into electric and thermal energy in Italy, as well as in other European Countries, were recently built, due to the strong public support for renewable energies. These biogas plants are mainly fed with animal manure and agricultural products, in particular, cereals silage and maize. Cereals are the most important source of food in the world, both for human nutrition and livestock feed. According to FAO (2009), food demand is expected to increase in the future. A shift from fossil energy towards energy from food crops could lead to increasing food prices and additional pressures on agricultural biodiversity as well as on soil, water, and air resources (EEA, 2007; Gerbens-Leenes et al., 2009). This has caused a wide spread debate about necessity and convenience of using large amount of food products for energy production. At present, large quantities of agro-industrial by-products have no market and are destined to landfill or, as in the case of cereals straw, remain in the fields after harvesting operations (ITABIA, 2003). Such biomasses are suitable to be used in anaerobic digestion plants (Schievano et al., 2009) and could be used to replace food crops for energy production. However, little research has been conducted to investigate the potential of using such biomasses to produce biogas. In this context, the EU-Agro Biogas project (Balsari et al., 2009; Amon et al., 2009) was initiated which had the objective of evaluating biogas yield of some agro-industrial by-products and creating a European database. This paper describes the results of batch trials on the following biomasses: rice straw, barley straw, grape stalks, grape marcs, maize drying up residues (pith, seeds and stalk), tomato skins and seeds, and whey. Tomato skins and seeds were obtained by juices and peeled tomatoes industries. Whey was obtained by production of fresh cheese.

2. Materials and methods

Trials were carried out according to Stardard Procedure VDI 4630 (2006). In detail, 2 litres glass digesters, glass gas tap with an "L" exit tube, and manually closed valve were used. Each digester was joined to a Tedlar bag for biogas collection. Trials were carried out under mesophilic conditions (40°C ± 2°C) within a temperature-controlled chamber, for a period of 40 days. Each trial was performed in triplicate and was composed of a mixture of biomass and inoculum with 1:2 ratio on volatile solids content. The inoculum consisted of digested slurry, collected from a co-digestion plant. The blank trial (inoculum only) was also carried out in triplicate. Before starting the experiments, rice and barley straws were chopped into pieces of 50-100 mm. To prevent the formation of dry and inactive floating layer, all batch digesters were manually stirred twice a day. At the beginning of the trials, each substrate was analysed for pH, total solids (TS), volatile solids (VS), total Nitrogen (TN), neutral detergent fibre (NDF), acid detergent fibre (ADF), acid detergent lignin (ADL), hemicelluloses (HC), and celluloses (CE) (Table 1). The pH was measured by a portable pH meter (Hanna Instruments HI 9026) using a glass electrode combined with a thermal automatic compensation system. Total solids were determined after 24 hours at 105°C. Volatile solids were determined after 4 hours at 550°C in a muffle furnace (AOAC, 2000). Total nitrogen was determined by Kjeldahl instrument after total mineralization. NDF, ADF and ADL were determined by Van Soest methods (Van Soest et al., 1991). Hemicelluloses and celluloses were calculated as the difference between NDF and ADF, and ADF and ADL, respectively. The biogas and methane yield was monitored daily during the whole period of the experiment. Biogas volume was determined connecting the Tedlar bags to a Ritter drum-type gas meter type TG05/5 instrument, while the biogas composition was analysed by a Draeger Multiwarn II, SD instrument with infrared sensors. The daily data of the biogas volume were normalized to normal litres (l_N) (dry gas, T= 0 °C, P= 1013 hPa) according to the following equation (VDI 4630, 2006):

$$V_0^{tr} = V \frac{(p - p_w) T_0}{p_0 T} \qquad (1)$$

where V_0^{tr} = volume of the dry biogas in the normal state (l_N), V = recorded volume of the biogas (l), p= pressure of the biogas phase at the time of reading (hPa), p_w = vapour pressure as a function of temperature of the ambient space (hPa), T_0 = normal temperature (T_0 = 0 °C), p_0 = normal pressure (p_0 =1013 hPa), T = temperature of the ambient space (°C).

Methane concentration of recorded biogas was calculated as follow (VDI 4630, 2006):

$$C_{CH4}^{tr} = C_{CH4}^{f} \frac{p}{(p - p_w)} \qquad (2)$$

where C_{CH4}^{tr} = methane concentration in the dry biogas (% by volume), C_{CH4}^{f} = methane concentration in the moist biogas (% by volume), p= pressure of the biogas phase at the time of reading (hPa), p_w = vapour pressure as a function of temperature of the ambient space (hPa). Net biogas and methane yield of the tested biomasses were obtained by subtracting the biogas and methane volume of the blank. Data were analysed by analysis of variance procedure (ANOVA) followed by Tukey's means grouping tests. Pearson correlation coefficients "r" were determined to evaluate the relationships between biogas yield and the main chemical parameters of the tested biomasses.

3. Results and Discussion

Daily biogas yield shown a similar trend for each tested sample (Fig. 1); this trend was characterised at the beginning (days 3-10), by a peak and later, by a progressive and regular biogas yield decrease, which dropped to zero after about 40 days from the trial start. In all trials, the percentage of methane in biogas gradually increased up to the greatest value during the first week, then it stabilized between 50 and 60%. The higher concentrations of methane in biogas were 56.0 and 76.3%, respectively, for rice straw and whey. Fig.s 2 and 3 show the whole specific biogas and methane yield from the tested biomasses. The whey gave the greatest specific yields (due to its high content of proteins and fermentable sugars - Frigon et al., 2009), respectively, 953 l_N biogas*kg^{-1}VS and 501 l_N CH_4*kg^{-1}VS put into the batch digesters. Interesting results were obtained also from maize drying up residues, tomato skins and seeds, barley straw, and rice straw samples. On average rice straw produced 416 l_N biogas*kgVS^{-1} (Fig. 2) whereas, He et al. (2009) reported lower biogas yield (360 l_N*kgVS^{-1}) for untreated rice straw due to the lower hemicelluloses and celluloses content. The main components of rice straw samples used in this experiment were hemicelluloses and celluloses (Table 1), which provided the main carbon source for anaerobic microorganisms. The whole methane yield obtained from barley straw was about 15% higher than the rice straw (Fig. 3), but this difference was not statistically significative ($p > 0.05$). Low specific biogas yields were obtained from grape stalks (225 l_N biogas*kgVS^{-1}) and from grape marcs (250 l_N biogas*kgVS^{-1}), due to their high lignine content (Table 1), that, as reported by other authors (e.g. Angelidaki et al., 2000; Ward et al., 2008), could not be degraded during the anaerobic digestion. On average grape marcs produced 116 l_N CH_4*kgVS^{-1}. This value agrees with the 90-125 l_N CH_4*kgVS^{-1}, reported by Araldi et al. (2009). As shown in Fig. 4, the biomass that produced the higher biogas and methane yield, expressed as m^3_N per ton of fresh biomass (m^3_N*t^{-1}fm) put into the digester, was the maize drying up residues, due to the high TS and VS contents (Table 1) and its easily fermentable organic component. Barley and rice straws, produced approximately 350 m^3_Nbiogas*t^{-1}fm put into the digester. Whey gave the lowest yield per ton of fresh matter put into digester (Fig. 4) due to its low total and volatile solids contents (Table 1). The correlation between biogas and methane yields and the main chemical biomasses (Table 2) confirmed that chemical composition of fibre fractions of biomass is essential to estimate the biogas potential, as reported by other authors (e.g. Angelidaki et al., 1999). The Pearson coefficient was found to correlate significantly and positively with hemicelluloses content. A negative and statistically significant correlation was obtained between biogas yield and ADF parameter and especially between biogas yield and fibre lignification grade (ADL/NDF). The absence of correlation between biogas yield and cellulose biomass content can be partially explained by the different chemical characteristics of the tested biomasses. Indeed authors (e.g. Jimenez et al., 1990) highlighted that, although the cellulose is usually degradable by microorganisms which operate in anaerobic environment, could become refractory if it is bound to lignine. According to results obtained in this study and considering the availability of examined biomasses in Italy (ISTAT, 2008) it is possible to estimate their total energetic potential close to a value of 2450 GWhel*year^{-1} (Table 3). This value represents about 0.6% of the electric energy demand in Italy (*TERNA*, 2006). This energetic potential value is equal to that obtainable from the anaerobic digestion of about 6.5 million tons of maize silage that require a land surface of over one million hectares (about 7.8% of the Italian agricultural lands).

4. Conclusions

Trial results highlighted the energetic potential of the tested by-products. Their utilisation to produce biogas could contribute to reduce the dependence from fossil fuels, follow and fulfil the Kyoto Protocol requirements, and diversify and widen the potential energetic sources. Consequently, it could permit to reduce the pressure on the availability and on the prices of agricultural food used to produce renewable energy (e.g. cereals silage). Due to their high national availability, barley and rice straws and whey could respectively contribute 50 and 30% to the estimated total Italian energetic production (Table 3).

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Figure legends

Fig. 1. Specific biogas yield and methane concentration in the biogas. Error bars indicate standard error (N = 3).

Fig. 2. Biomass specific biogas yield. Error bars indicate standard error (N = 3).

Fig. 3. Biomass specific methane yield. Error bars indicate standard error (N = 3).

Fig. 4. Biogas yield per ton of biomass.

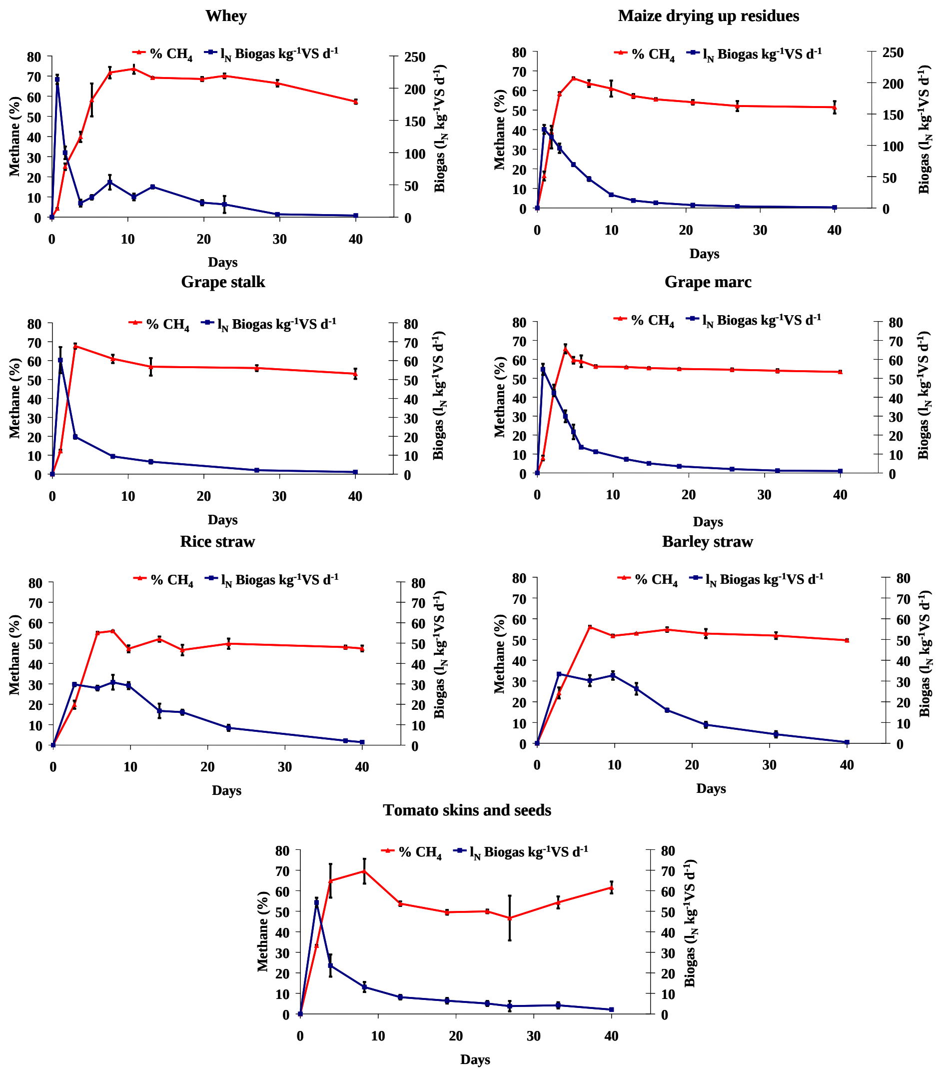
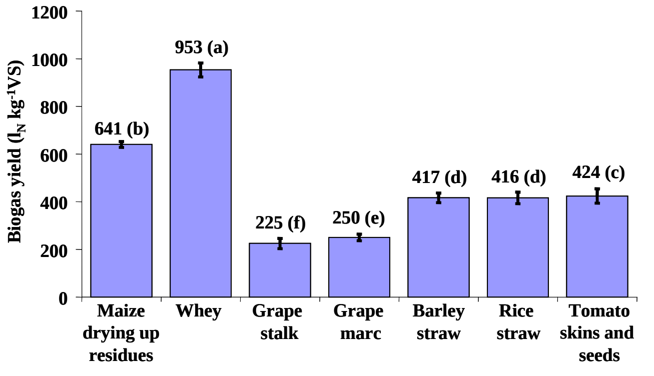
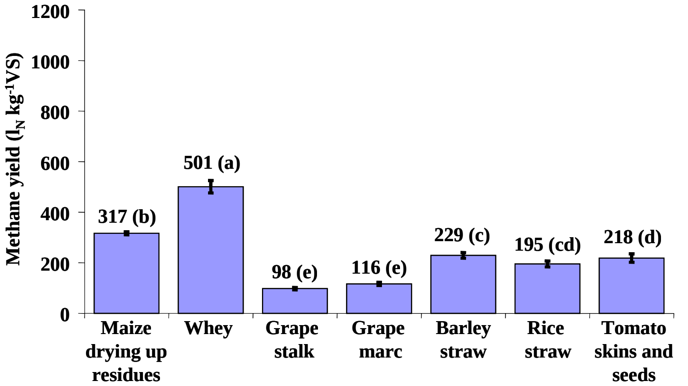


Fig. 1.



Means followed by the same letter are not statistically different using Tukey's test at 5% level

Fig. 2.



Means followed by the same letter are not statistically different using Tukey's test at 5% level

Fig. 3.

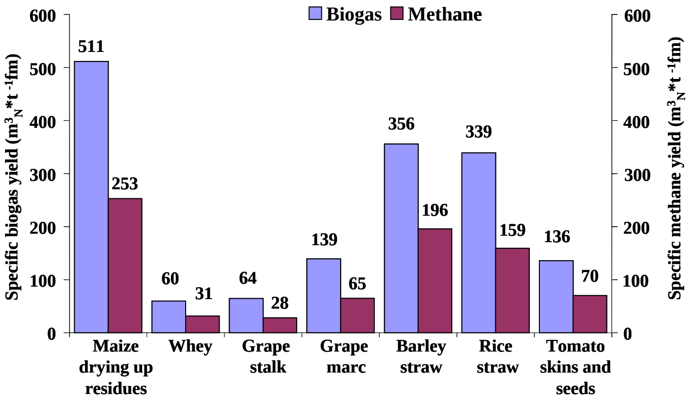


Fig. 4.

Table legends

Table 1. Chemical and physical characteristics of the biomasses used in the trials.

Table 2. Pearson correlation coefficients between specific biogas and methane yield and main chemical biomasses parameters.

Table 3. Energetic potential of analyzed biomasses.

Biomass	pH	TS (%)	VS (% TS)	TN (% TS)	NDF (% TS)	ADF (% TS)	ADL (% TS)	HC (% TS)	CE (% TS)
Tomato skins and seeds	4.7	32.	97.8	3.34	45.3	36.6	3.56	8.70	34.0
Barley straw	7.87	90.5	94.3	0.99	86.4	56.4	9.60	30.0	46.8
Rice straw	8.14	88.7	91.9	0.88	78.4	28.0	8.33	50.4	19.6
Grape stalks	4.40	31.1	91.9	1.99	62.6	46.7	23.3	15.9	23.5
Maize drying up residues	5.05	81.8	97.5	1.29	44.9	14.7	2.33	30.2	12.4
Whey	5.20	6.86	91.1	1.83	-	-	-	-	-
Grape marcs	3.58	61.4	90.7	2.30	60.4	39.4	23.9	21.0	15.5
Inoculum	8.00	7.62	70.0	5.93	-	-	-	-	-

Table 1.

Chemical biomasses parameters	Biogas (l_N *$kgVS^{-1}$)	Methane (l_N *$kgVS^{-1}$)
TS	-0.183	-0.204
VS	0.080	0.089
TN	-0.282	-0.213
NDF	-0.119	-0.209
ADF	-0.626(**)	-0.631(**)
ADL	-0.824(**)	-0.839(**)
HC	0.451	0.356
CE	-0.080	-0.072
ADF/NDF	-0.711(**)	-0.654(**)
ADL/NDF	-0.836(**)	-0.836(**)
HC/NDF	0.711(**)	0.654(**)
CE/NDF	-0.094	-0.035

** The correlation is significative at value 0.01.

Table 2.

Biomass	Biomass availability in Italy (tfm*year^{-1})[a]	Energetic equivalent		
		(TJ*year^{-1})	(GWhel*year^{-1})[b]	(TES*year^{-1})[c]
Tomato skins and seeds	97000	215	24	63960
Barley straw	996500	6169	686	1838920
Rice straw	1112000	5602	623	1669950
Grape stalks	181100	160	18	47620
Maize drying up residue	141910	1135	126	338320
Whey	6513340	6452	717	1923200
Grape marcs	1054240	2159	240	643430
Total		21892	2433	6525400

[a] Source: ISTAT (2008).
[b] Values obtained assuming the use of biogas to feed a combined heat and power unit (CHP) and considering an electric yield of 40% of input energy.
[c] Tons Equivalent of maize silage. **1 TES= 3.371 GJ;** it represents the quantity of potential energy that can be obtained from combustion of the biogas produced from anaerobic digestion of 1 ton of maize silage (VS=30% of fresh weight).

Table 3.