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Ph.D. in Agricultural Ecology XXVII Cycle

Study of the problems of energy production from anaerobic fermentation in agriculture

"Weaknesses and unresolved issues"

Ph.D. Thesis

Marco Negri N° R09762

Supervisor	**Academic Year**	*Coordinator*
Prof. Marco Acutis	**2013-2014**	**Prof. Graziano Zocchi**

……… To my mother and my father.

Ph. D. Thesis

Department of Agricultural and Environmental Science

Production, Landscape, Agroenergy

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And my family for everything

Introduction.

During the last two decades there has been a growing interest on both, energy savings and renewable energy. This is primarily related to the issues of energy supply, climate change, *but also to such environmental concerns as air pollution, acid precipitation, ozone depletion, forest destruction, and emission of radioactive substances. Energy is the convertible currency of technology* (Ibrahim Dincer, 1999).The higher costs of renewable energy respect traditional ones, (e.g. fossil fuels and nuclear power) require both a strong public resource and a strong implementation of knowledge and development of related technology. *The concept that consumers share responsibility for pollution and its cost has been increasingly accepted. In some jurisdictions, the prices of many energy resources have increased over the last one to two decades, in part to account for environmental costs* (Ibrahim Dincer, 1999). In 1997, the Kyoto Protocol found global guidelines for energy management in order to promote renewable energy use with minimal environmental impacts. In this frame, over the last years, EU took a propelling role in supporting the actions undertaken by the single Member States for the achievement of these objectives, by issuing several supporting regulations. Since 1997, with the White Paper on Renewable Energies (COM(97) 599), a series of measures were promoted so that the percentage of energy from renewable sources could double, compared to 1997 levels, and reach 12% in end-use by 2010. This paper was the starting point for issuing in 2001 the Directive 2001/77/CE that fixed tentative national objectives, compatible with the global objective of 12% of Gross domestic energy consumption by 2010 by renewable sources, and in particular a tentative percentage of 22.1% of electricity produced by renewable energy sources on EU total power consumption by 2010. Italy was given a 25% objective. The need to comply with the objectives set by the Kyoto Protocol, pushed several countries to support and increase energy production from renewable sources, through new incentive programs, which guarantee a compensation for the producer of each electric kW, bought at a price higher than current market price. In this context, the EU has taken a leading role in years, issuing a set of measures to strengthen the actions of the various member countries to achieve those objectives, since 1997 when, with the White Paper of renewables (COM (97) 599), were shown a series of measures to ensure that the percentage of energy from renewable sources doubled compared to 1997 levels, and will arrive by 2010 to 12% renewable energy in final use. This document was the basis for the enactment in 2001 of the Dir. 2001/77 / EC which put the national indicative targets consistent with the overall objective of 12% of gross domestic energy consumption by 2010 and in particular with indicative share 22.1% of electricity produced from renewable energy sources in total electricity consumption in the Community by 2010. To Italy was given a target of 25%.

The need to adapt to the objectives of the Kyoto Protocol, has pushed countries to support increasing energy production from renewable sources, through new incentive programs, which guarantee payment of the purchase of electric kW-highest market price.

Biogas - The Italian situation

In 1991 the Prices Interministry Commetee (Comitato Interministeriale Prezzi - CIP) approved a written incentivisation to production of energy from renewable sources named CIP 6, that would be implemented into Law n. 9 the same year.

The law says that those subjects producing energy from renewable sources or assimilates acquires the right to sell it to the Energy Services Managing Company (Gestore dei Servizi Energetici - GSE) at a price greater than that of the market.

The law find the financial budgeting through a 6 - 7% extra charge for the final consumer.

In Italy starting from 2007 with the Budget Law for year 2008, have been introduced incentivisation rules to the energy production, with different combinations depending on the plant production capacity, source (wind, sun, thermochemical from biomasses, anaerobic digestion of biomasses, sea-motion or oceanic and geothermal) that, in case of DA, for plant production capacity below 1 MW from biomasses with a short supply chain (lower than 70 Km of distance), allowed after December 31st, 2007, considers an all-encompassing payment of 180 Euro/MW electrical power, for a 15 years duration, with further incentivisation for using the resulting heat.

With the Law 99, July 23rd, 2009 the concept of biomasses supply chain is cancelled and the all-encompassing payment, for the anaerobic digestion of biomasses plants with production dimension of 998 KW electrical power, rises to 280 Euro/MW electrical power, granted for 15 years.

Starting from January 1st, 2'13 the incentivisation system further changes, for the new realized plants, making more favourable those with production size of 100 - 300 KW electrical power and the use of no-food cultivations biomasses, by-product from cultivations and agricultural industry, the generation of high performance energy production and the pulling down of nitrogen in ....

With Decree-Law n.28, in year 2011 are fixed the characteristics of purity, pressure and smell of methane from biomasses (bio-methane). The following Minister for Economic Development Decree of December 5th, 2013 defines the modality to incentivise the intake in the net of bio-methane.

The Decree considers as net the public and private methane pipelines, the tank-trucks (trucks with pressurized tanks) and the fuel pumps, public and private, on the roads, also those for agricultural use only.

The Decree defines a row of incentives that sum up to two times of average price of standard cubic meter (scm) methane in year 2012, minus the current average monthly price. It also introduces some conditions for the usage of by-products and discards from agricultural activities and agricultural industry. This last Decree concerns both the new generation plants as well as the existing ones giving the possibility to diversify the productions, producing at the same time electricity, heat and bio-methane.

The spread of bio-methane production plants is restrained, not impeded, due to normative constrains related to security of the plants and warehousing of gases and by technologies for purification of biogases fully mature.

The biogas - Italian productive reality

The strong profitability mostly granted by the all-encompassing fee of 280 Euro/MW electrical power and by its duration (15 years) for the production established by the production capacity of the plants have given a strong impulse to the sector, quickly moving up to 400 the number of plants in the sole Lombardy.

Thus new production realities born:

- cereal-zoo-technical agricultural companies, that introduced among their activities the energy production, making worth of the zoo-technical effluents alone, or in co-management with dedicated biomass cultures,
- cereal-zoo-technical agricultural companies have abandoned the zoo-technical activity replacing it with the energy production, making value of the DA replacing the production of meat or milk,
- cereal agricultural companies or industrial cultures that make value from their cultural production with energy production,
- agricultural companies among farmers and energy production companies,

- investors more or less specialized in energy production that effectively conduce a production activity similar to breeding without fields, doing only transformation totally buying from the market
- The relevant demand of biomasses deriving from the growth of energy production has de facto created a market, previously not existing, of silge from summer herbal productions (corn in particular, but also sorghum and sunflowers) and of autumn cereal (triticale, barley, wheat, rye and ryegrass).

General objectives

Electricity production from anaerobic digestion of dedicated energy crops has become a profitable economic solution inside the traditional livestock production system and it is an alternative way to use these feedstock: energy generation instead of milk and meat production.

The general aim of this study is to evaluate for the bioenergy system based on the anaerobic digestion of cereal silages elect in order to identify the main weaknesses and unresolved issues for what concern the choice of different cropping systems as well as the different energy crops.

The most widespread cropping systems in northern Italy have been studied considering:

1) The biomass production for the main cereals used as energy crops: to this purpose the biomass yield for the main cereal crops has been studied by means of experimental field tests;

2) The chemical-physical characteristics and the specific methane production of these cereal silages, with regards to the measurement of methane production a laboratory device has been specifically developed and used;

3) Their influence on the performances of the AD plant, to this aim several AD plants have been daily monitored in order to evaluate biogas plant efficiency;

Chapter I

Biomethane production from different crop systems of cereals in Northern Italy

Biomass Bioenergy

Biomethane production from different crop systems of cereals in Northern Italy

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Abstract

Global warming is linked to the reduction of green house gas emissions (GHG). The anaerobic digestion of animal

manure and energy crops is a promising way of reducing GHG emissions.
The increasing number of biogas plants involves a high consumption of energy crops and the needed of big agricultural area. In Italy, cereals silages are the main feedstock for biogas production and are commonly grown under two different crop systems: single crop (only maize) and double crops (maize later winter cereals).
In this paper we present the results of experimental field tests carried out by monitoring the anaerobic biomethane potential (ABP) of different cereals silages commonly grown in the Padanian Plan.
A laboratory device has been developed to measure the specific biomethane production of the different cereal silages. The different energy crops have been evaluated, in single and double crop systems, expressing the biomethane production per hectare.
The maize hybrids show higher specific biomethane potentials respect to winter cereals. Maize FAO Class 700

achieves the highest production per hectare as single crop. Nevertheless, the highest biomethane productions per hectare are reached with double crop system in particular when maize FAO Class 500 follows triticale (+ 12% respect the best single crop system).

Keywords

Biogas, Anaerobic Digestion, Energy crops, Anaerobic Biomethane Potential, Italy

1.1 Introduction

Renewable energy generation is increasing thanks ambitious energy policies such as the EU target of 20% renewable energy by 2020 come into effect. Agricultural biogas is one such source. Biogas has proved to be interesting for energy generation to rural areas when used locally [1]. Nevertheless, energy production from biogas must occur in a sustainable framework. Concerning this over the years several studies have been carried out and different methodologies have been developed [2-4].

Agricultural biogas plants can be fed with energy crops (mainly cereals) but also with agricultural by-products (animal sewage) and residues from agro-industry [5-7].

The use of animal sewage as raw material for biogas production had been strongly encouraged in the last years by the guidelines for energy, environmental and agricultural policies set out in all the norms whose final objectives were: (i) decreasing air and soil pollution linked to sewage disposal [8]; (ii) producing good quality amendment from by-products; (iii) increasing the amount of energy deriving from renewable sources by using the simple technology already existing on site. This led to a global reconsideration of all animal dejections which, from refuse, became a resource both from the environmental and the economic point of view [9-11]. As consequence of this, and thanks to the strong contribution of small agricultural biogas units which started taking advance of the co-digestion of dedicated energy crops, in 2011, biogas produced 35.922 TWh of electricity in Europe [8]. Manure is an easily available resource on farms, but the limited production rate, the low biogas yield and high investment cost do not make the production of biogas from manure economically feasible without adequate support [12]: as a matter of fact, if we consider that the anaerobic digestion of the sole animal dejections hardly ever allows farmers to reach 150–200 kW of installed power, it is clear how the improvement of co-digestion of animal manures with energy-rich co-substrates such as energy crops or, rather, with agroindustrial by-products and other biodegradable wastes has an increasing attractiveness [13, 14] effectively enhanced by the incentives provided [15].

With reference to Italy, it is doubtless that the history of livestock breeding goes together with the history of livestock breeding in the Po Valley and, in particular, with that of the Lombardy Region which is the undisputed leader in this sector [11] with many big intensive livestock farms spread on the territory. Also for the Regional policies, Lombardy is actually the Region with the highest number of biogas plants in Italy with about 370 fully working units (with an average electric power of 714 kW) and where energy crop production is still nowadays based on traditional cropping systems for fodder production and silage conservation, whose technologies are already available in farms. Overall in Italy there are 994 anaerobic digestion plants for a global power of 757 MW. In the 2011, Italy, with 3.405 TWh of electricity produced from biogas, was the third European producer after Germany (19.426 TWh) and United Kingdom (5.735 TWh) and ahead of France (1.196 TWh) and Netherdland (1.027 TWh) [8].

Currently, biogas production is mainly based on the anaerobic digestion of cereals silages (maize, wheat, triticale and sorghum), grass silages, grain crops and agroindustrial waste. Energy crops are the most commonly used substrates and have already been studied for their use in biogas processes [7,16-20] or in the framework of different energetic approaches [5, 21]. In Lombardy, 600 – 700 FAO Class maize hybrids are the most used crops for energy production as single culture system, while 300 - 400 - 500 FAO Class maize hybrids, after the harvesting of winter crops like wheat or triticale, can be suitable if the double culture system is chosen.

Over the years, the spread of biogas plants, often concentrated in specific areas (such as the provinces of Cremona, Lodi and Mantua), resulted in the growth of concerns about the fact that more and more agricultural land is tilled for feeding the digesters. In 2013 growing seasons, about 10% of the overall Italian maize area (approximately 10.000 km^2) [22] is earmarked to biogas production. This issue have been reported in all the other European countries where agricultural biogas production is widespread. In Germany, in 2011 about 650.000 hectares were specifically grown for biogas production

[19]. The reduction of agricultural land used to feed the digester can be achieved mainly by increasing biogas production per hectare.

In this paper we present the results of experimental field tests carried out by monitoring the anaerobic biomethane potential (BMP) of ensiled crops commonly grown in the Padanian Plan evaluating them both as single and double culture systems and with reference both to their specific BMP and to the average biogas yield achievable per hectare of surface. The aim of the study is to evaluate the most productive crop systems for biogas production as well as to provide useful information about the most important cereals used to feed the digesters. The achieved results can be useful not only for northern Italy but also for all the areas characterized by temperate climate in which biogas plant are fed with cereals silages.

1.2 Methods

1.2.1. Crops

All the farms where field tests were carried out are placed in Lombardy Region (Italy), located in the Po valley (45° 60′ – 44° 77′ lat. N, 7° 65′ – 12°22′ long. E). This plan can actually be described as a large basin surrounded by high mountains (Alps and Apennines) and opened only toward East which causes it to be exposed to winter cold outbreaks of polar continental air (mainly coming from Siberia) while Alps and Apennines protect the area from the influence of Mediterranean and Central Europe Climate. As consequence of this, the climate of the Po Valley is a climate of transition between the Mediterranean climate, dominated by anticyclonic patterns and the Central European climate (Koeppen's Cfb), dominated by the oceanic influence of westerlies. Confirm of this transitional climatic character lies in the precipitation regime that, with two minima (in summer and winter) and two maxima (in spring and fall) is partially opposite in phase with respect to the evapotranspirational request of the atmosphere which has its maximum in summer.

Wheat (*Triticum aestivum* L.), Triticale (× *Triticosecale*) and Maize (*Zea mays* L.) plants were grown (both as single and double crop) in the following farms all placed in Lombardy:

- *"Muraro"* farm (district of Lodi)
- *"Dotti"* experimental farm (district of Lodi)
- "*Eurosia*" farm (district of Cremona).

Both *"Muraro"* and *"Dotti"* farms have medium loam soils while *"Eurosia"* farm soil is sandy loam: at the moment of the experiment all of them had been regularly fertilized and amended for long time with zootechnical sludge.

Table 1 and Table 2 report the main technical information about the energy crops cultivated.

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OPERATION	NN.	MONTH	TRACTOR	OPERATIVE MACHINE			NOTE
			Mass Power	Type Size	Mass (kg)	Working Time ($h \cdot ha^{-1}$)	
Pre-seeding organic fertilization	1	May	5050 kg 90 kW	Manure spreader 20 m^3	2000	3.33	85 $t.ha^{-1}$ Digestate[a]
Ploughing	1	May	10500 kg 190 kW	Plough	2000	1.11	-
Harrowing	1	May	7300 kg 130 kW	Rotary Harrow 4.0 m	1800	1.20	-
Sowing	1	May	5050 kg 90 kW	Pneumatic seeder 4 lines	900	1.00	20 $kg{\cdot}ha^{-1}$
Chemical Weeding	3	May Jun Jun	4450 kg 80 kW	Sprayer 15 m	600	0.33	4 $kg{\cdot}ha^{-1}$ lumax 1 $kg{\cdot}ha^{-1}$ dual 1 $kg{\cdot}ha^{-1}$ dual
Irrigation	5	Jun Jul Aug	4450 kg 80 kW	Pump 950 m^3 h^{-1}	550	1.20	4400 $m^3{\cdot}ha^{-1}$
Mechanical Weeding	1	Jun	5050 kg 90 kW	Weeder 2.8 m	550	0.33	-
Top fertilization	1	Jun	6850 kg 120 kW	Fertilizer spreader 2500 dm^3	500	0.13	60 $kg{\cdot}ha^{-1}$ urea
Harvesting	1	Sep	-	Forage harvester 335 kW	13000	1.00	
Transport	1	Sep	5050 kg 90 kW	3 Farm trailers 30 m^3	5500	3.03	-
Ensilage	1	Set	5050 kg 90 kW	2 Frontal loader 2 m^3	450	3.03	

[a] Mass Fraction of dry matter: N = 0.40%; P_2O_5 = 0.08%; K_2O = 0.31%

Table 1 - Field and ensilage operations for Single Crop system (SC) (maize 600 and 700)

	OPERATIO N	NN.	MONTH	TRACTOR	OPERATIVE MACHINE			NOTE
				Mass, Power	Type, Size	Mass (kg)	Workin g Time (h · ha^{-1})	
WHEAT OR TRITICALE	Pre-seeding organic fertilization	1	Sep	5050 kg 90 kW	Manure spreader 20 m^3	2000	3.33	40 t·ha^{-1} Digestate[a]
	Ploughing	1	Sep	10500 kg 190 kW	Plough 3-shovel	2000	1.11	
	Harrowing	1	Sep	7300 kg 130 kW	Rotary harrow 4.0 m	1800	1.20	
	Seeding	1	Oct	5050 kg 90 kW	Seeder	900	1.00	200 kg·ha^{-1}
	Mechanial Weeding	1	Oct	4450 kg 80 kW	Spraying 15 m	600	0.33	Terbutilazin a + Alachlor 5 kg·ha^{-1}
	Top fertilization	2	Nov Feb	6850 kg 120 kW	Fertilizer spreader 2500 dm^3	500	0.13	60 kg·ha^{-1} ammonium nitrate 60 kg·ha^{-1} urea
	Harvesting	1	May	-	Forage harvester 335 kW	13000	1.00	
	Trasport	1	May	5050 kg 90 kW	2 Farm trailers 30 m^3	5500	2.00	
	Ensilage	1	May	5050 kg 90 kW	2 Frontal loader 2 m^3	450	2.00	
MAIZE 5CLASSES 300-400-500	Pre-seeding organic fertilization	1	May	5050 kg 90 kW	Manure spreader 20 m^3	2000	3.33	45 t·ha^{-1} Digestate
	Ploughing	1	May	10500 kg 190 kW	Plough 3-shovel	2000	1.11	-
	Post-seeding mineral fertilization	1	May	6850 kg 120 kW	Fertilizer spreader 2500 dm^3	500	0.13	100 kg·ha^{-1} P_2O_5 and K_2O
	Harrowing	1	May	7300 kg 130 kW	Rotary harrow 4.0 m	1800	1.20	-
	Seeding	1	May	5050 kg 90 kW	Pneumatic seeder 4 lines	900	1.00	19 kg·ha^{-1}
	Chemical Weeding	3	May Jun Jun	4450 kg 80 kW	Sprayer 15 m	600	0.33	1 kg·ha^{-1} dual 4 kg·ha^{-1} lumax
	Irrigation	4	Jun, 2 Jul, Aug	4450 kg 80 kW	Pump 950 m^3 h^{-1}	550	1.20	3600 m^3·ha^{-1}
	Weeding	1	Jun	5050 kg 90 kW	Weeder 2.8 m	550	0.33	
	Top fertilization	1	Jun	6850 kg 120 kW	Fertilizer spreader 2500 dm^3	500	0.13	60 kg·ha^{-1} urea
	Harvesting	1	Sep	-	Forage Harvester 335 kW	13000	1.00	
	Transport	1	Sep	5050 kg 90 kW	3 Farm trailers 30 m^3	5500	3.03	
	Ensilage	1	May	5050 kg 90 kW	2 Frontal loader 2 m^3	450	3.03	

[a] **Mass Fraction of dry matter: N = 0.40%; P_2O_5 = 0.08%; K_2O = 0.31%**

Table 2 - Field and ensilage operations for Double Crop System (DC) (winter cereals + maize)

Maize hybrids were sown between April and May with the plant density of 6 · m^{-2} in 1 ha experimental fields taking care of harvesting them as soon as they reached the waxy ripeness stage according to their FAO Class.

Fertilization had been carried out according to good agricultural practices by spreading the liquid phase of anaerobic digestate before sowing and prilled urea (granular formulate treated against caking) after plant emergence. Weed control was carried out by means of Terbuthylazine and Alachlor. Crops were irrigated four times: the first one was carried out by means of a travelling sprinkler to help seed germination while the remaining three were carried out by surface irrigation.

Wheat and Triticale crops were sown in October and harvested in June in all the chosen sites.

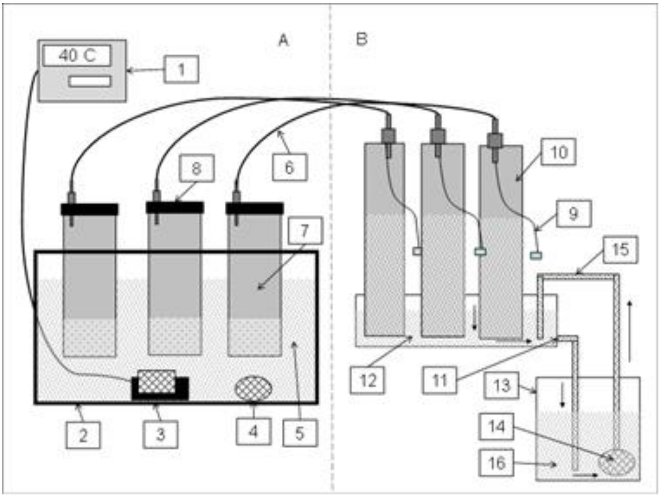
The double culture technique consists in sowing, in autumn, any winter crop (wheat, barley, triticale or rye) which the following year is subsequently harvested in late spring as chopped forage for silage or in early summer for grain. Immediately after the harvest of the winter grain crop the same field is sown with any summer maize hybrid (FAO class 300, 400 or 500) which will be harvested in autumn to produce corn silage.

1.2.2 Silage analysis

After the storage the silos were opened. For each silos 3 samples were analyzed. Dry matter (DM), organic dry matter (ODM), raw protein, ether extract (EE), neutral detergent fiber (NDF), acid detergent fiber (ADF), ammonia, glucose, fructose mannitole, ethanol, lactic acid, acetic acid, propionic acid, butyric acid and starch were measured according to [23] Martillotti et al..

The remaining silages were stored at -20°C before to be analyzed for the Anaerobic Biomethane Potential. Silages were prepared in triplicate for each lab scale silo.

Lab-scale unstirred fermenters (Figure 1) were placed in thermostatic baths (2) at 40°C (1) filled of warm water (5) and equipped with a submerged heater (3) and a mixing pump (4).



A	FERMENTATION EQUIPMENT	B	MEASUREMENT SYSTEM
1	Temperature set	9	Pipe equipped with valve for biogas sampling and gasometer recharge
2	Plastic bin	10	Gasometer
3	Submerged heater	11	Carbonated solution interception device
4	Water mixing pump	12	Carbonated solution bin for gasometer allocation
5	Warm water	13	Carbonated solution tank
6	Flexible hose for biogas	14	Recirculating pump
7	Fermenter	15	Recirculating Hose
8	Fermenter metallic cover	16	Carbonated solution

Figure 1: lab scale fermenter equipment

The fermenters (7) were made of a hermetically sealed glass jar with one metallic cover holding (8) the valve through which the biogas produced by the tested samples reached the corresponding gasometer by flowing into one flexible nylon hose (6). Gasometers (10) are made by methacrylate Torricelli pipes with 3.5 litres volume. Each gasometer has, on top, two hoses: one carrying the biogas from the fermenter and one, made of PVC, equipped with a valve for gasometer recharge (9). At the beginning of the measurement the gasometers are filled with aqueous solution saturated with $CaCO_3$ (12 and 16) in order to prevent CO_2 solubilisation into water.

When the biogas flows from the fermenter into the gasometer, the aqueous solution is moved in a vessel equipped with one overflow device (11) which allows to the aqueous solution to be collected in a tank (13). From this tank, by means of a pump (14), the aqueous solution can be pumped back in the vessel (15) when the gasometers must be recharged. For the gasometer recharge a compressor is used to suck in, through the specific valve placed on the gasometer top, the biogas, and, thereby, refill the pipe with the aqueous solution. During this operation the valve placed on the metallic cover of the fermenter is closed to preserve the anaerobic conditions in the whole system.

Samples of fermenting biomass from different full scale anaerobic digesters were collected to be used as inoculum. Before the set-up of the fermenters the inoculum was filtered with 2 mm sieves and placed at 40°C for 48 hours in order to stabilize microbial population and to minimize the amount of fermentable carbon, since a high content of fermentable carbon of the inoculum could influence biogas production.

In each fermenter the inoculum/substrate ratio was kept at 2:1 on volatile solids basis [24]: on average, each fermenter contained 2 kg of inoculum (Total Solids 3% ± 0.2 of raw material) and 30g of dried biomass. Before digestion all substrates were ground sing a professional grinder.

During the experiment the temperature in each fermenter was kept at 40°C by putting all of them in a warm bath. To keep the biomass conditions as homogeneous as possible and facilitate biogas collection fermenters were daily shaked. Fermenters were kept in these conditions as long as substrate's biogas production was significantly different from the inoculum one. Biogas volumes where daily recorded: the centimetres ran by the carbonated solution in the gasometers were read and the equivalent volume in virtue of gasometer diameter was calculated.

Biogas composition in terms of methane, oxygen and carbon dioxide percentages were monitored by means of one "Binder Combigas GA-m^3" (from Binder, D) portable gas analyser equipped with one electrochemical cell for oxygen measurement and one infrared dispersion cell for methane and carbon dioxide percentage determination.

All statistical analysis was carried out using SPSS 13.0 for Windows (SPSS, Inc.).

1.3 Results and discussion

1.3.1 Yields

The results of average biomass production of the evaluated energy crops are shown in Table 3.

Crop	FAO Class	No.	Average Yield ($t \cdot ha^{-1}$)
Maize	300	3	14.96 ± 0.4 (a)
	400	3	17.50 ± 0.4 (b)
	500	3	18.89 ± 0.7 (b)
	600	3	23.89 ± 1.3 (c)
	700	3	26.12 ± 1.1 (d)
Triticale	-	3	14.58 ± 0.8 (b)
Wheat	-	3	12.30 ± 0.4 (a)

Table 3: Dry matter yield for the different crops.

Among the biomass productions of the maize hybrids, the ANOVA analysis ($\alpha = 0.05$) shows that the dry matter production increases with the lengthening of the crop cycle, with the exception of maize 400 and 500 that have similar yields. Also between the winter cereals there are significant differences (α = 0.05); triticale has higher production than wheat.

Regarding the water content can be stated that all the crops present a dry matter content that allows a correct biomass ensilage. Among the maize hybrids can be underlined that, probably due to the late harvest time, the maize class 500 shows the higher dry matter content.

1.3.2 Biomass characterization and biogas specific production

Table 4 reports the characterization of the different silage biomasses, the specific biogas productions and the biomethane content.

	Crop						
	Maize					Wheat	Triticale
FAO Class	**300**	**400**	**500**	**600**	**700**	**-**	**-**
Number of measurements	9	9	9	9	9	9	9
Water fraction (%)	66 ± 2.6	48 ± 4.4	55 ± 8.1	71 ± 0.3	71 ± 1.0	68 ± 0.6	65 ± 1.6
pH	3.91 ± 0.07	3.89 ± 0.03	4.00 ± 0.12	3.97 ± 0.05	3.94 ± 0.05	4.02 ± 0.16	3.91 ± 0.01
CEN (%)	4.71 ± 0.42	3.88 ± 0.16	4.54 ± 0.7	4.70 ± 0.10	4.86 ± 0.26	9.28 ± 2.08	9.74 ± 0.43
Raw Protein (%)	7.43 ± 0.59	7.63 ± 0.30	7.43 ± 0.05	7.69 ± 0.26	7.69 ± 0.34	10.44 ± 1.79	10.11 ± 1.81
EE (%)	-	-	-	-	-	1.93 ± 0.10	1.76 ± 0.35
NDF (%)	49.24 ± 2.12	43.86 ± 0.56	48.08 ± 4.38	44.45 ± 1.54	44.16 ± 2.12	58.57 ± 2.04	59.01 ± 2.22
ADF (%)	26.23 ± 1.22	24.28 ± 0.06	25.88 ± 2.04	24.23 ± 0.88	24.50 ± 1.46	35.25 ± 2.08	36.48 ± 1.60
Ammonia Nitrogen (%)	7.16 ± 1.14	5.62 ± 0.59	7.76 ± 2.68	5.00 ± 0.29	5.22 ± 0.71	8.10 ± 1.82	8.09 ± 0.71
Glucose (%)	0.41 ± 0.08	0.38 ± 0.03	0.42 ± 0.03	0.48 ± 0.06	0.47 ± 0.04	0.72 ± 0.51	0.56 ± 0.07
Fructose (%)	0.23 ± 0.09	0.34 ± 0.07	0.19 ± 0.20	0.42 ± 0.08	0.39 ± 0.04	1.92 ± 1.15	2.25 ± 0.37
Mannitol (%)	0.32 ± 0.15	0.47 ± 0.16	0.21 ± 0.21	0.44 ± 0.24	0.28 ± 0.09	2.22 ± 0.97	2.46 ± 0.41
Ethanol (%)	0.03 ± 0.02	0.11 ± 0.08	0.07 ± 0.08	0.36 ± 0.18	0.41 ± 0.19	0.65 ± 0.35	0.92 ± 0.45
Lactic Acid (%)	3.05 ± 0.51	3.13 ± 0.01	2.31 ± 0.77	2.43 ± 0.24	2.84 ± 0.68	5.30 ± 1.34	6.29 ± 0.48
Acetic Acid (%)	1.91 ± 0.96	0.69 ± 0.1	2.34 ± 2.13	0.57 ± 0.25	0.46 ± 0.52	2.37 ± 0.61	2.05 ± 0.25
Propionic Acid (%)	0.75 ± 0-33	0.11 ± 0.05	0.70 ± 0.73	0.32 ± 0.08	0.25 ± 0.15	0.23 ± 0.02	0.25 ± 0.06
Butyric Acid (%)	0.04 ± 0.02	0.04 ± 002	0.05 ± 0.01	0.03 ± 0.004	0.03 ± 0.01	0.06 ± 0.07	0.03 ± 0.03
Starch (%)	27.83 ± 1.59	31.63 ± 0.21	29.03 ± 2.98	30.55 ± 1.12	30.56 ± 2.52	-	-
Anaerobic Biogas Potential[a] ($m^3 \cdot t^{-1}$)	521 ± 67.7	555.5 ± 49.0	497.7 ± 57.3	589.6 ± 65.4	579.7 ± 62.0	455.5 ± 83.9	487.01 ± 132.2
Methane volume fraction (%)	54.82 ± 1.79	54.79 ± 2.06	56.09 ± 1.23	56.03 ± 0.98	55.50 ± 1.74	53.83 ± 1.32	54.50 ± 1.18

Table 4: Results of the laboratory analysis (mean ± standard deviation expressed on dry matter basis) for the different crop

Regarding the specific biogas production the maize hybrids show higher production compared to the winter cereals. Among the maize classes there is high variation. The class 600 has higher specific biogas production; it produces 13% more biogas than class 300, 6% more than class 400 and 18% more than class 500. Between the maize classes for single crop system the specific biogas production is similar (+ 2% for class 600 respect to class 700). The maize class 500 shows the lower specific biogas production probably due to the late harvest time and the consequently high content of recalcitrant compounds (lignin, cellulose, etc.). Between the winter cereals, the specific biogas production of triticale is about 7% higher than for wheat.

The methane content in the biogas ranges from 54.82% to 56.03%; on average maize silages produce a biogas with a slightly higher CH_4 percentage respect to the one produced by the two winter crops.

1.3.3 Biogas production per hectare

Biogas production per hectare ($m^3 \cdot ha^{-1}$) can be linked to diverse biomass yields and/or different specific biogas productions (Table 5).

CROP	BIOGAS[a]
	$m^3 \cdot ha^{-1}$
Maize FAO Class 300	7513.2 ± 844.5
Maize FAO Class 400	8863.3 ± 867.9
Maize FAO Class 500	9613.3 ± 632.1
Maize FAO Class 600	13256.9 ± 1445.6
Maize FAO Class 700	14804.7 ± 1291.3
Triticale	7245.8 ± 271.0
Wheat	5561.5 ± 754.6

[a] 20°C and 1 bar

Table 5: Biogas production for hectare (mean and standard deviation).

Regarding the biogas production per hectare, there are significant differences among the energy crops. Only maize class 300 and triticale show similar biogas production. Maize hybrids, with the exception of class 300, have higher biogas production than the two winter cereals. Maize class 700, although has not the higher specific biogas production (about - 2% respect to class 600), shows the highest biogas production per hectare (+11% respect class 600). Between the winter cereals wheat achieves lower biogas productions than triticale (-30%). Similar conclusions can be drawn taking into account the biomethane production per hectare.

The results of comparison between single crop system and double crop system are reported in Table 6 and Figure 2 in term of biomethane production. Maize class 700 (the single crop with higher production) has been assume as reference. The comparison considers that, in DC systems, the maize classes 300-400-500 are cultivated after winter cereals in the same fields while, in SC systems, the maize classes with long crop cycle (600 and 700) don't allow the cultivation of other crops in the same field.

SYSTEM	CROPS		METHANE[a]	
	1st harvest	2nd harvest	$m^3 \cdot ha^{-1}$	%
DC	Triticale	Maize FAO Class 300	8018.4	-2.41%
	Wheat		7149.8	-12.98%
	Triticale	Maize FAO Class 400	8755.9	+6.56%
	Wheat		7887.2	- 4.01%
	Triticale	Maize FAO Class 500	9291.7	+13.09
	Wheat		8423.1	+2.51%
SC	Maize FAO Class 600	-	7427.9	-9.60%
	Maize FAO Class 700	-	8216.6	-

[a] 20°C and 1 bar

Table 6: Biomethane production of the different crop systems (mean and standard deviation).

The higher biomethane productions are achieved in DC systems with the maize class 500 after winter cereals or when the maize class 400 follows triticale. The DC with triticale and maize class 500 achieve about 13% more biomethane than maize class 700. DC carried out with triticale and maize class 300 or with wheat and maize class 400 shows a biomethane production slightly lower lower than maize class 700.

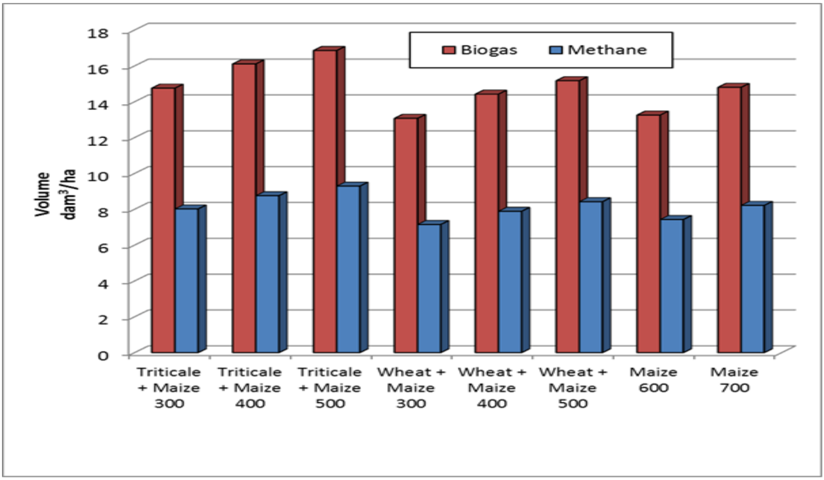


Figure 2: production of biogas and methane

1.4 Discussion

Cereals silages are important feedstock for energy production as well as for breeding activities. In Northern Italy, the cereals are by far the most important annual crops and Padanian valley is one of the most suitable areas for their cultivation.

The biomass yields achieved in the experimental trials carried out are similar to the ones recorded in related studies [25, 26]. For triticale and wheat grown in Padanian Valley, analogous dry matter productions are recorded by Bortolazzo et al. [27], (14.80 t $\cdot$ ha^{-1} for triticale) González et al. [28] (14.20 t $\cdot$ ha^{-1} for triticale and 12.01 t $\cdot$ ha^{-1} for wheat) and Bacenetti et al. [29] (12.27 t $\cdot$ ha^{-1} for wheat). Faccini and Cattivelli [30] observed biomass yields slightly higher: 17.7 t $\cdot$ ha^{-1} and 12.30 t $\cdot$ ha^{-1}, respectively for triticale and wheat.

Also for maize class 600 and 700 the dry matter production is comparable to previously reported data, in particular our results are very similar to the average yields recorded in Northern Italy during the years 2010 (24.29 t ·ha^{-1}), 2011 (25.84 t ·ha^{-1}) and 2012 (23.71 t ·ha^{-1}) [31]. D'Imporzano et al. [32] report considerably higher yield for triticale (16.50 t ·ha^{-1}) but lower productions for maize class 600 and 700.

For the different maize classes and the two winter cereals evaluated specific biogas production and methane content are in accordance with other studies carried out in Italy [16,29, 33] and in other European countries [18, 34-36]. The values reported in Table 4 are referred to the ensiled biomass and not to the fresh material. This explains the differences among the lower values reported by Herrmann et al. [37], Amon et al. [19] and Bauer et al. [21] that are referred to the fresh biomass of different maize classes. Herrmann et al. [38] highlighted that for maize, triticale, wheat and sorghum the specific biogas productions of the fresh biomass are lower (11-13%) than the ones of the ensiled biomass. However, when ensilage losses are taken into account the specific biogas productions are similar.

Considering the biomethane production per hectare, the maize classes 600 and 700 show better performances compared with the maize classes suitable for the DC (Classes 300, 400 and 500); among these the class 500 shows clearly the best results. Between the winter cereals, the triticale is the most suitable energy crop; compared with wheat, triticale shows higher yield and has bigger specific biogas production with upper methane content: consequently, it produces more biogas for hectare (+12%).

1.5 **Conclusions**

Biogas from biomass is a promising renewable energy source and its importance is increasing increased in European countries. In this study several energy crops have been evaluated in term of biogas and methane production considering the possibility to carry out two different crop systems: single crop and double crop.

However, the biomethane product per hectare is a product of specific biomethane production and biomass yield. Therefore, a higher biomass yield is also of prime importance in evaluating utility for biogas production. In the present study, the specific biomethane production from maize hybrid class 600 was higher than class 700 but, owing to its lower biomass yield, the net gain in biomethane production per ha was lower.

The comparison between single and double crop system is drafted in term of biogas and biomethane production per hectare. Double crop system carried out with triticale and maize class 500 achieved that highest biogas and biomethane productions per hectare. Nevertheless the results of comparison between single crop and double crop system are variable and not unambiguous. The choice between the two crop systems must be carefully evaluated.

The above results don't refer to small and experimental plots but they concern 3 real farms with a total surface of the experimental fields of 6.3 hectares. Further improvements of the research will take into account to collect experimental data also regarding other energy crops (i.e. sorghum) suitable for biogas production in this climatic area and, in addition, to compare the same crop systems in other areas.

1.6 Acknowledgments

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Chapter 2

Evaluation of methane production from maize silage by harvest of different plant portions.

Biomass and Bioenergy

Evaluation of methane production from maize silage by harvest of different plant portions

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Abstract.

Biogas production is mainly based on the anaerobic digestion of cereals silages and maize silage is the most utilized. Regarding biogas production, the most important portion of the plant is the ear. The corn ear, due to high starch content, is characterized by a higher biogas production compared to the silage of the whole plant.

In this paper we present the results of experimental field tests carried out in Northern Italy to evaluate the anaerobic methane potential (BMP) of different portions of ensiled maize hybrids. The BMP production is evaluated considering the possibility of harvesting and ensiling: the whole plant; the plant cut at 0.75 m of height; only the ear; the plant without the ear. For the different solutions the results are reported as specific BMP and as average biogas production achievable per hectare. The methane production by harvesting and ensiling the whole plant (10212 and 10605 $m^3 \cdot ha^1$, for maize class 600 and 700 respectively) is higher than the ones achievable by the other plant portions (7961 and 7707 $m^3 \cdot ha^{-1}$, from the ear; 9523 and 9784 $m^3 \cdot ha^{-1}$, from the plant cut at 0.75 m; 3328 and 3554 $m^3 \cdot ha^{-1}$, from the plant without the ear, for maize class 600 and 700 respectively). The harvest of the whole plant, although it is the most productive solution, couldn’t be the best solution under an economic and environmental point of view. Harvesting only the ear can be very interesting when the biomass has to be transported over long distances.

Keywords.

Anaerobic Digestion, Biomethane Potential, Maize, Plant Portions, Corn Ear Silage

2.1 Introduction.

The agricultural contribution to greenhouse gases (GHG) emissions is undeniable [1]. Agricultural activities play a significant role in increasing the concentration of GHG in the atmosphere and, hence, agriculture contributes to global warming and climate change [2]. The two most important GHG emitted by primary sector are methane from livestock and nitrous dioxide from fertilizer use [3]. In Europe, agricultural activities are responsible for 10% of the total GHG emissions (about 405 Mt CO_2 eq. per year). Nitrous oxide emissions (from fertilizer application as well as from manure management) represent approximately 210 MtCO2eq, while methane emissions (from enteric fermentation, manure management, and rice cultivation) account for about 195 $MtCO_2eq$. [4].

The reduction of fossil fuel consumptions and the mitigation of greenhouse gases (GHG) emissions are both key issues for a sustainable development. In this context, the renewable energy generation can help to meet both these ambitious targets. In Europe, the generation of energy from renewable sources is increasing thanks to energy policies (i.e. EU target of 20% renewable energy by 2020) [5-6].

The EU objectives can be met by the development of all the different renewable energy sources [6-7]. Among these, the biogas has proved to be interesting for energy generation in rural areas in particular, when the generated energy is used locally [7-10].

In Italy, during the past 15 years, biogas production from anaerobic digestion of agricultural biomasses was considerably increased. Nowadays, more than 1000 agricultural biogas plants are running mainly in northern regions [11]. In 2011, 3405 GWh of electricity were generated from biogas [12] with an increase of 65% in respect to 2010. At the end of 2012, the installed electrical power was 756 MW and 1.65% of the Italian electric consumption was produced from agricultural biogas plants. Most of agricultural biogas plants operate in codigestion and, consequently, are fed with energy crops (mainly cereal silage), agricultural by-products (animal sewage) and residues from agro-industry [3; 11; 13-15].

Strong public incentives were granted for electricity produced from biogas, for the AD plants put into operation before 31 December 2012 and with electrical power lower than 1 MW. 280 €/MWhe were fixed for the electricity fed into the grid without any consideration regarding by-product utilization for feeding and heat valorisation. The public incentives framework for electricity production from biogas has been updated with the D.M. of 6 July 2012 [11]. In general, the incentives (€/kWh) have been strongly reduced (15-35%) and more importance has been paid, by means of the introduction of bonus, to the heat valorisation and by-products utilization. From the 1 January 2013, the higher incentives are granted to small plants (electrical power < 300 kW) mainly fed with by-products (minimum 70% of the biomass introduced into the digesters).

As consequence of the new incentive framework, the ratio between the mass of by-products and silages must be carefully evaluated. In Northern Italy, the most widespread agricultural by-products are pig and cow slurries [9; 11-12; 14-15], that are characterized by low specific biogas productions [16-18] (approximately 6-25 times smaller than maize silage) [19- 20]. The feeding of the AD plant only with these slurries allows to get the higher subsidy but, on the other hand, it requires to build big digesters with higher cost and it can involve long transport distances for the feedstock. When the biogas plants are built for the valorisation of animal slurry available on the farm, the codigestion with feedstock characterized by high energy density (e.g example cereal silage) allows to maximize the electrical CHP power and to achieve the highest incentive

On the other hand, it must be considered that, over the years, the spread of biogas plants, often concentrated in specific areas, resulted in the growth of the biomass transport distances and feedstock prices.

Currently, biogas production is mainly based on the anaerobic digestion of cereals silages [3; 21-23]; among these the maize silage is the most utilized [24]. Maize hybrids are the most used crops for energy production [13; 25-26]; they can be grown as single crop system or, after the harvesting of winter crops like wheat or triticale, as double crop system. Regarding the biogas production the most important portion of the plant is the ear. The corn ear represents a very good feedstock for biogas production because, due to high starch content, is characterized by a higher biogas production compared to the silage of the whole plant. However, detailed information about the biogas production of the different plant portions is lacking both regarding specific production (m^3/kg) and global production (m^3/ha).

In this paper we present the results of experimental field tests carried out in the Po Valley (Northern Italy) to evaluate the anaerobic methane potential (BMP) of different plant portions of ensiled maize hybrids. The BMP production is evaluated considering the possibility to harvest and silage: (1) the whole plant; (2) the plant cut at 0.75 m of height; (3) only the ear; (4) the plant without the ear. For the different solutions the results are referred both to their specific BMP and to the average biogas yield achievable per hectare.

2. 2 Methods.

2.2.1 Experimental field.

The experimental field tests were carried out on a farm sited in Lombardy, a region located in the middle of the Po valley. This valley is surrounded by high mountains (Alps and Apennines) and it is characterized by good water availability. Although the precipitation regime has two minima in summer and winter the irrigation systems (lakes, rivers, canals, ditches) guarantee a good water supply also in summer.

The maize hybrids (1 FAO Class 600 and 1 FAO Class 700) were grown in single crop system so no winter cereals are sown after the harvest. The experimental field test has a rectangular shape (126m x 60 m) and covers a global area of 0.60 ha. The field, long the longer size, was subdivided in 3 sections each one with 30 rows for maize class 600 and 30 rows for maize class 700 (Figure 1):

i) 0.2 ha for the harvest of the Whole Plant (WP) with a cut height of 0.10 meters,;

ii) 0.2 ha in which the harvest was carried out with a higher cut height (HC) than in the section 1. In more details the plant were cut at 0.75 m of height;

iii) 0.2 ha in which the corn ear (OE) was harvested separately from the rest of the plant constituted

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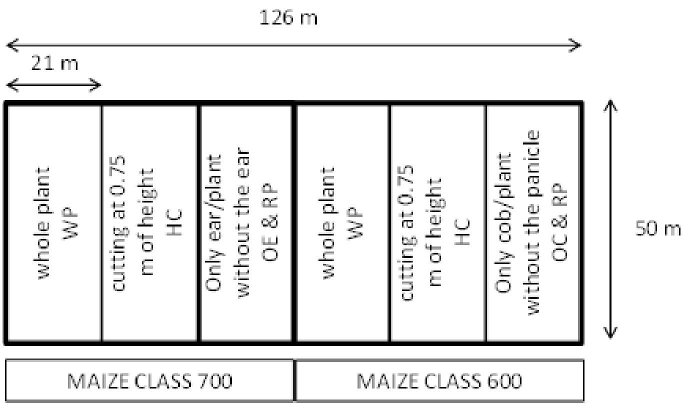

stover and leaves (RP).

Figure 1– Subdivision of the experimental field

The crop cultivation is schematized in Figure 2.

The field operations carried out during the crop growth can be subdivided in 4 sections:

i) Tillage operation, organic fertilization with digestate (85 t $\cdot$ ha^{-1}) was carried out before a 35 cm depth ploughing and two interventions with rotary harrow;

ii) Sowing, maize hybrids were sown using a pneumatic precision drill seeders in April with the density of 60000 plants $\cdot$ ha^{-1} (20 kg $\cdot$ ha^{-1} of seed);

iii) Crop management, top fertilization was carried out according to good agricultural practices [27] by spreading, using a fertilizer spreader, prilled urea after plant emergence (60 kg $\cdot$ ha^{-1} of seed). Chemical weed control was carried out by means of two treatments (the first with Terbuthylazine, a systemic herbicide absorbed by roots, and, the second with Alaclor, an herbicide for control the growth of broad-leafed weeds and grasses). The crops were irrigated 5 times for a global irrigation volume of 3800 $m^3 \cdot ha^{-1}$.The first irrigation was carried out, after sowing, by means of a travelling sprinkler to help seed germination (600 $m^3 \cdot ha^{-1}$) while the remaining three were carried out by surface irrigation (800 $m^3 \cdot ha^{-1}$).

iv) The harvest was carried out by hand at the same time.

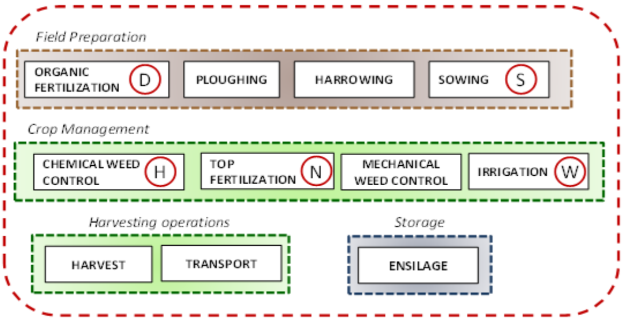

Figure 2– Schematization of the crop cultivation practice

Ensilage of the different portion of the plant was performed by pressing about 30 kg of freshly harvested and chopped biomass in to a plastic bag. The plastic bag was sealed realizing anaerobic condition into the plastic bag. The lab scale silos were stored for 90 days. Considering the subdivision of the experimental field, 4 types of silages were produced: from the whole plant (WP), from the plant cut at 0.75 m (HC), from the ear (OE) and from only the plant without the ear (RP).

2.2.2 Silage analysis.

After the storage 3 samples for each plant portion were analyzed. Dry matter (DM), organic dry matter (ODM), raw protein, ether extract (EE), neutral detergent fiber (NDF), acid detergent fiber (ADF), ammonia, glucose, fructose mannitole, ethanol, lactic acid, acetic acid, propionic acid, butyric acid and starch were measured according to Martillotti et al. [28].

The remaining silages were analyzed for the Anaerobic Methane Potential. Silages were prepared in triplicate for each plant portion. The analysis were carried out in lab-scale unstirred fermenters were placed in thermostatic baths at 40°C[24].

Samples of fermenting biomass from different full scale anaerobic digesters were collected to be used as inoculum. In each fermenter the inoculum/substrate ratio was kept at 2:1 on volatile solids basis [29]: on average, each fermenter contained 2 kg of inoculum (Total Solids 3% ± 0.2 of raw material) and 30g of dried biomass. Before digestion all substrates were ground sing a professional grinder.

During the experiment the temperature in each fermenter was kept at 40°C by putting all of them in a warm bath. Fermenters were kept in these conditions as long as substrate's biogas production was significantly different from the inoculum one. Biogas volumes where daily recorded.

Biogas composition in terms of methane, oxygen and carbon dioxide percentages were monitored by means of one “Binder Combigas GA-m^3” (from Binder, D) portable gas analyser equipped with one electrochemical cell for oxygen measurement and one infrared dispersion cell for methane and carbon dioxide percentage determination.

2.3. Results and discussion.

2.3.1 Biomass Yields.

The results of biomass production before silage operations are shown in Table 1.

The different plant portions are characterized by different dry matter content. In more details, the ear presents the highest values (double than the whole plant) while the plant without the ear the lower. The biomass from the harvest of the plant cut at 0.75 m shows a dry matter content higher (about + 10%) than that of the whole plant.

Regarding the production of dry matter it can be stated that:

Plant portion	FAO Class	Yield	Dry matter fraction	Dry matter yield
		t · ha^{-1}	%	t · ha^{-1}
Whole plant (WP)	600	80.54	37.00%	29.80
	700	83.98	35.90%	30.15
Only plant without the ear (RP)	600	48.66	31.75%	15.45
	700	58.18	30.25%	17.60
Only ear (OE)	600	22.48	61.40%	13.80
	700	20.33	61.25%	12.45
Plant cut at 0.75 m (HC)	600	45.60	47.15%	21.50
	700	60.99	45.25%	23.60

Table 1 – Biomass production for the different plant portions

i) As expected, the harvest of the whole plant shows the highest productions and it represents the maximum production. The maize hybrid Class 700 has a slightly higher biomass production (+2%) compared to the maize hybrid Class 600;

ii) When the plant is cut at 0.75 m the production is about 72-78% of the maximum production, respectively for maize class 600 and 700;

iii) When only the ear is collected the production is about the 46-41% compared to the maximum, respectively for maize class 600 and 700. This plant portion is the only one for which the production of maize Class 600 is higher than for maize Class 700 (+11%);

iv) The harvest of plants without the ear produces about half of the maximum (52-58%, respectively for maize class 600 and 700).

v) The sum of the ear (OE) and the plant without the ear (RP) is very similar to the maximum productions (98.2-99.7%, respectively for maize class 600 and 700).

2. 3.2 Biomass characterization and methane specific production.

Table 2 reports the characterization of the different plant portions, the specific biogas production, the methane content and, consequently, the specific methane production.

The dry matter content of the whole silage (35.05% and 37.60%, respectively for maize 700 and maize 600) indicates that, for both the maize classes, the harvesting operations have been carried out at the appropriate time. As expected the HC silage shows a higher dry matter content; by increasing the proportion of the corn ear the dry matter content increase.

In fact, the corn ear show a high dry matter content (60.18% and 59.53%, respectively for maize 700 and maize 600) while the silage produced by the rest of the plant (RP) show lower dry matter content (26.83% and 29.96%, respectively for maize 700 and maize 600). Regarding the silages composition, it is interesting to note that the starch, that is the most easily degradable compounds, shows similar values between the two maize classes. Nevertheless, compared to the WP, in the HC the starch content is higher (about + 6% for maize class 700 and +17% for maize class 600) while in the OE silage is double.

FAO Class	-	700				600			
Plant Portions	-	WP	OE	HC	RP	WP	OE	HC	RP
Dry Matter	$\%_{WB}$	35.05	60.18	37.80	26.83	37.60	59.53	42.50	29.96
pH	-	3.90	4.12	3.90	3.84	4.05	4.06	3.91	3.91
Ash	$\%_{DM}$	4.69	1.28	4.24	5.92	4.37	1.30	3.76	5.51
Raw Protein	$\%_{DM}$	7.31	8.38	7.20	6.85	7.08	8.53	7.04	6.36
Ether Extract	$\%_{DM}$	0.00	2.74	0.00	0.00	0.00	2.68	0.00	0.00
Neutral Detergent Fibre	$\%_{DM}$	43.25	16.48	41.91	59.40	43.52	17.51	38.88	60.06
Acid Detergent Fibre	$\%_{DM}$	24.28	0.00	23.21	36.89	24.20	0.00	21.78	37.61
Ammonia Nitrogen	$\%_{DM}$	3.53	2.52	3.63	2.43	2.91	2.50	4.19	2.50
Glucose	$\%_{DM}$	0.37	0.93	0.33	0.57	0.30	0.64	0.34	0.40
Fructose	$\%_{DM}$	0.44	0.46	0.37	0.57	0.34	0.42	0.36	0.38
Mannitol	$\%_{DM}$	0.61	0.42	0.52	1.19	0.49	0.43	0.51	0.64
Ethanol	$\%_{DM}$	0.69	0.26	0.29	0.92	0.44	0.37	0.52	0.66
Lactic Acid	$\%_{DM}$	3.35	3.52	2.74	3.26	1.73	3.83	2.77	2.41
Acetic Acid	$\%_{DM}$	0.11	0.22	0.04	0.31	0.00	0.30	0.20	0.00
Propionic Acid	$\%_{DM}$	0.03	0.35	0.01	0.22	0.00	0.38	0.04	0.11
Butyric Acid	$\%_{DM}$	0.03	0.03	0.03	0.04	0.03	0.02	0.03	0.03
Strarch	$\%_{DM}$	31.63	64.43	33.52	12.14	31.69	63.26	37.22	14.51
Anaerobic Biogas Potential[a]	$m^3 \cdot t^{-1}$	651.35	997.90	739.40	420.25	658.25	977.30	804.85	430.70
Metane Volume Fraction	%	54.00	62.03	56.07	48.05	52.06	59.03	55.03	50.01
Anaerobic Methane Production[a]	$m^3 \cdot t^{-1}$	351.73	619.00	414.58	201.93	342.68	576.90	442.91	215.39

Table 2 – Results of the laboratory analysis for the different plant portions

Regarding the specific biogas production the different plant portions show a high variation; also for the methane volume fraction is quite variable. Consequently, high variations are recorded for methane specific production; in particular:

i) The whole plant (WP) shows a production in midway between PA and RP;

ii) The ear (OE) shows, as expected, the higher values (+68% and +76%, respectively for maize class 600 and 700); ear silage generates more than two times methane than the rest of the plant (RP);

iii) RP produces the lowest volumes (-37% and -43%, respectively for maize class 600 and 700);

iv) The plant cut at 0.75 meters (HC) produces more than WP (+29% and +18%, respectively for maize class 600 and 700) but less than OE (-23%

and -33%, respectively for maize class 600 and 700).

It is interesting to note that HC as well as for RP Class 600 shows higher values in respect to Class 700; this is due to higher dry matter content in the biomas.

2.3.3 Methane production per hectare

Table 3 and Figure 3 shows the methane production per hectare ($m^3 \cdot ha^{-1}$). The big differences among the methane production achievable by the different plant portions depend on variations in biomass yields and specific methane productions

Although characterized by lower specific production, WP achieves the highest methane production per hectare. Compared to the solution that entails the ensiling of the whole plant, the other plant portions produce less methane per hectare:

Plant portion	FAO Class	Methane[a] m^3 · ha^{-1}
Whole plant (WP)	600	10212
	700	10605
Only plant without cob (RP)	600	3328
	700	3554
Only ear (OE)	600	7961
	700	7707
Plant cut at 0.75 m (HC)	600	9523
	700	9784

[a] 20 °C and 1 bar

Table 3– Methane production per hectare.

i) OE - 22% and - 27%, respectively for maize class 600 and 700;

ii) HC - 7% and - 8%, respectively for maize class 600 and 700;

iii) RP - 37% and - 43%, respectively for maize class 600 and 700.

Among the different plant portions, the comparison between maize hybrids class 600 and class 700 shows that, except for OE, the maize class 700 reaches higher methane productions. Regarding the OE the higher production for maize Class 600 is due to the higher dry matter production

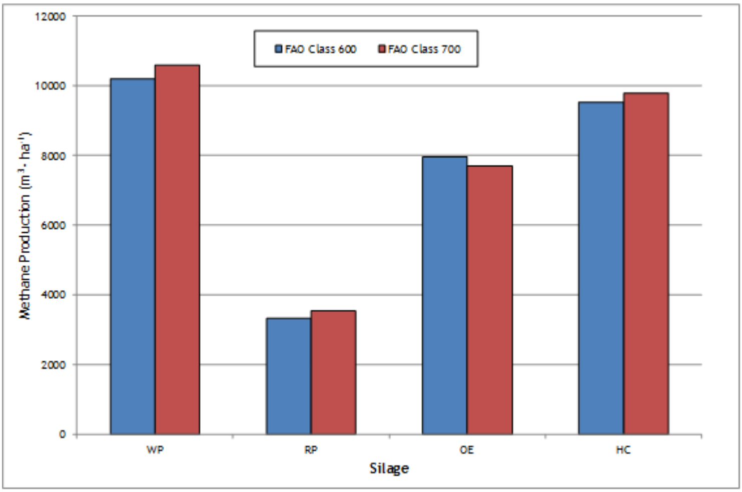

Figure 3 – Methane production per hectare for the different plant portions

2.4 Discussion.

Cereals silages are important feedstock for energy production as well as for breeding activities; Northern Italy is one of the most suitable areas for their cultivation. Over the years, the use of cereal silages in to fed the digesters for biogas production has greatly increased causing logistic and environmental issues. In particular, the transport over long distance of feedstock as well as digestate is not sustainable under an economic and environmental point of view.

Over the years, several studies have paid a strong attention to the use of cereal silage for energy purpose [30-34]. Nevertheless, these studies are focused mainly to:

i) To evaluate the biomass yield of energy crops. In this regard, considering the harvest of the whole plant, the biomass yields achieved in the experimental trials are similar to the ones recorded in northern Italy [35-37]. In particular, similar dry matter yields were recorded in Northern Italy during the years 2010 (24.29 t · ha^{-1}), 2011 (25.84 t · ha^{-1}) and 2012 (23.71 t · ha^{-1}) by Soldano [38]. D'Imporzano et al. [36] report lower productions for maize class 600 and 700.

ii) To measure the methane specific production of the different energy crops; regarding the specific methane production of different maize classes the achieved results are in accordance with other studies carried out in Italy [20-21; 24; 39] and in other European countries [13; 16; 23; 25; 40-46].

iii) To assess different cropping systems; Negri et al. [24] evaluate different cropping systems of cereals and highlight that the double crop achieves higher methane productions (+12%) compared to single crop of maize, similar results were obtained by Bacenetti et al. [22]

that evaluate the environmental impact of single and double crop in term of methane production. Other studies, conducted by Grab et al. [45], and Gan et al. [47] assessed the biomass production of cropping systems characterized by legumes. The introduction of sorghum instead of maize, in areas with low water availability, have been studied by Borghi et al. [48] and Mahamod [49]. In particular Mahamud reports for maize a methane production of 7120 $m^3 \cdot ha^{-1}$ higher than for 12 varieties of sorghum (from 3924 to 6554 $m^3 \cdot ha^{-1}$).

However, few researches have been carried out to evaluate the methane production achievable for the utilization of the different maize plant portions. Some studies [50-51] regard the corn stover utilization for biogas production but are referred to the by-product of corn productions (characterized by high dry matter and very high C/N ratio because harvested later than the waxy ripeness). Cuetos et al. [52] measure in bacth assays at laboratory scale the methane production of maize leaves and reports a specific methane production (157 $m^3 \cdot t^{-1}$ of volatile solid) considerably lower than the ones recorded in this study for RC (plant without the ear). Fabbri et al. [53-54] report specific methane production for the corn cob in Italian conditions (143 $m^3 \cdot t^{-1}$ for the biomass after the harvest and 170 $m^3 \cdot t^{-1}$ for the silage).

2.5. Conclusions.

Several energy crops have been evaluated in term of biogas and methane production considering the possibility to carry out two different crop systems but there are no studies that assess the possibility to harvest, separately, the different plant portions.

Regarding the methane production from maize silage the results of our tests are in agreement with other related studies carried out previously; the methane production by harvesting and ensiling the whole plant of maize is higher than the ones achievable by the other plant portions. Nevertheless, it must be underlined that the harvest of the whole plant, although it is the most productive solution, couldn't be the best solution under an economic and environmental point of view.

The harvest of only the ear can be very interesting because it is characterized by considerably high specific production. Therefore, this solution can be better than the WP when the biomass must be transported for long distances. On the other hand, in light of the recent revision of the Italian subsidy framework, in which only the 30% of the mass introduced into the digester can be specifically produced to this aim, the ear can be interesting to maximize the power of biogas plants mainly fed with animal slurry.

Finally, the achieved results regarding the RP are interesting considering the future possibility to use the byproduct of corn production (stover) for energy purpose. In more details, if by means of breeding, maize hybrids characterized by a strong "stay green" are developed, this solution will be very useful by allowing producing both corn grain and biomass for energy purposes.

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Chapter 3

Study for the anaerobic degradation of triticale silage, wheat silage, maize silage and ear maize silage by using Nylon bags and estimation of the produced digestate mass

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Study for the anaerobic degradation of triticale silage, wheat silage, maize silage and ear maize silage by using Nylon bags and estimation of the produced digestate mass

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3.1 Introduction

The EU objectives can be met by the development of all the different renewable energy sources [1, 2]. Among these, the biogas has proved to be interesting for energy generation in rural areas in particular, when the generated energy is locally used [3-6]. Moreover, the

Anaerobic Digestion (AD) can significantly contribute to minimize dissipation of fossil energy resources and greenhouse gas (GHG) emissions [7].
The AD has been used already some tens years ago to convert organic matter to energy (biogas) and fertilizer (digestate). With the shortage of fossil fuels and the perception that GHG from combustion of fossil fuels is a major factor of the global climate change scenario, AD is gaining more and more attraction worldwide, in particular if renewable (organic) energy carriers are converted [8].

Biogas production from agricultural biomass is of growing importance as it offers considerable environmental benefits [9; 12].

Currently, biogas production is mainly based on the anaerobic digestion of cereals silages (maize, wheat, triticale and sorghum), grass silages, grain crops and agro-industrial waste. Energy crops are the most commonly used substrates and have already been studied for their use in biogas processes [10 - 11].

In Italy, during the past 15 years, biogas production from anaerobic digestion of agricultural biomasses has considerably increased. Nowadays, more than 1100 agricultural biogas plants are running, mainly in the northern regions [12].

The aim of this study is to evaluate the anaerobic degradation of maize silages. To this purpose, laboratory experimental tests carried were carried out considering the silages from the energy crops commonly grown in the Po Valley. During the tests, the dry matter anaerobic degradation was monitored for 4 different cereal silage: maize silage from the whole plants, maize silage from the ear, triticale silage and wheat silage. Beside the degradation of the dry matter the production of digestate was evaluated too.

Keywords: Biogas, anaerobic fermentation, nylon bags, in sacco, digestate, maize silage, ear maize silage, triticale silage, wheat silage.

3.2 Methods

3.2.1 Crop and silage

The ensiled biomasses under evaluation are the most common silage crops cultivated in Lombardy Region, in Northern Italy [13]. Maize silage from the whole plant was produced by cultivating of 4 commercial forage hybrids class FAO 700 (Identification of samples- Id: Am, Bm, Cm, Dm). For ear maize silage, 4 commercial grain hybrids class (FAO 600) were grown (Identification of samples- Id: Ae, Be, Ce, De). Triticale (Id samples: At, Bt, Ct, Dt) and wheat silages (Id samples: Aw, Bw, Cw,Dw) were produced growing 4 commercial forage cultivars each.

Triticale silage, wheat silage and maize silage consist of the whole plant completely harvested, chopped and ensiled. On the opposite, ear maize silage is only made of the grain, cob and bracts, which are harvested, chopped and ensiled.

With regard to the crop cultivations, the common cropping systems performed in Northern Italy was considered: single crop system for maize hybrids 600 and 700 and double crop system for triticale and wheat. To produce silage from the whole plant triticale, wheat and maize were harvested with a plant dry matter content ranging between 30-35%, whereas, to produce ear silage the maize was harvested with a ear dry matter content equal to 60%.

Crops ensilage was performed by pressing about 30 kg of freshly harvested and chopped biomass into a plastic bag. The plastic bag was sealed realizing anaerobic conditions. The lab-scale silos were stored for days [13].

3.2.2 Silage analysis

After the storage silos were opened. For each of them 3 samples were analyzed. Dry matter (DM), organic dry matter (ODM), raw protein, ether extract (EE), neutral detergent fiber (NDF), acid detergent fiber (ADF), ammonia, glucose, fructose, mannitol, ethanol, lactic acid, acetic acid, propionic acid, butyric acid and starch were measured according to Martinotti [14].

3.2.3 Nylon bags incubation

To determinate and quantify the dry matter loss of the different silage during AD nylon bags were used.

Biomass was included in bags made of permeable Nylon tissue. Nylon bags have pores with a diameter of 41 μm (FISHER SCIENTIFIC – cod 11745488) and were sewed with nylon fishing line. The pores are permeable to bacterial and enzymes but are not permeable to biomass particles. During the incubation in the batch lab-scale fermenters, bacteria and enzymes can cross the nylon bag tissue and, therefore, degrade the dry matter of silage but the degraded biomass cannot be scattered in the digester fluid. As a consequence it was possible to quantify the not degraded biomass by weighing the bag.

The degradation test was made by modifying the evaluative technique of in vivo rumen degradation for feed [15,16,17,18,19, 20]. The modification consisted in putting a 50 g silage sample in a nylon bag, formerly sealed with plastic pincers.

Nylon bags were put in a batch fermenter of 3000 mL volume with 2500 mL volume of inoculum, in accordance to Negri et al. [14]. The fermenter was hermetically sealed. The fermenter cover had an opening from which the biogas could spill out. No air could enter due the presence of a syphon that made possible the exit of biogas but not the entrance of air; therefore, anaerobic conditions were ensured.

Nylon bags are 5 x 20 cm. Incubation was performed at 40° C for 75 days long. The incubation time was chosen as an average suggested value of the hydraulic retention time in real scale plants.

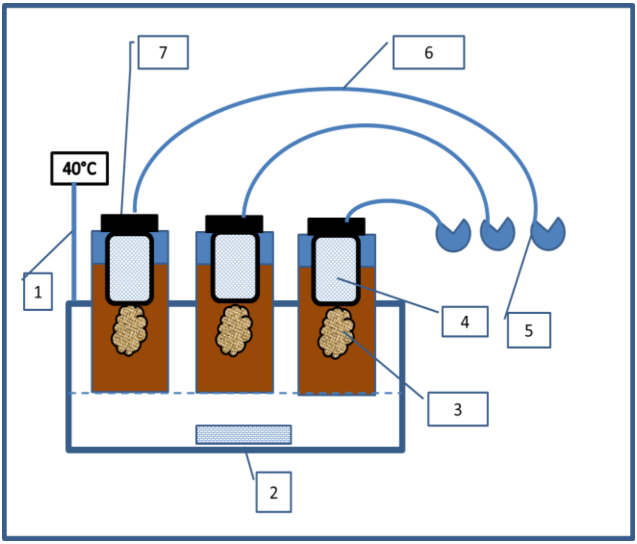
After 3, 7, 25, 35, 50, 75 days from the beginning of the test two nylon bags per type of biomass were taken. The collected nylon bags were washed in running washing water till it got clear. The following step was the drying in a ventilated oven at 105°C till the reach of constant weight. Dried bags were weighted and the net weight of the biomass inside was calculated.

Weight loss of dry matter was calculated at $t_{=i}$:

$DM_{Loss} = weight_{DM}\ t_0 - weight_{DM}\ t_{=i}$

3.2.4 Calculation of digestate mass at t=i

% mass of digestate in respect to the mass of biomass = (% water content) + (% $_{(t=i)}$ DM residue).



	Equipement
1	Temperature set
2	thermostatic bath
3	Nylon bag
4	Presser to keep the nylon bags immersed
5	Siphon
6	Flexible hose for biogas
7	Batch lab scale Fermenter

Figure 1- incubation apparatus

3.3 Results

3.3.1 Analysis of biomasses

The results of the ensiled biomasses analyses are shown in Table 1 and 2.

Each of the silage samples has qualitative values included in the normality. This means that the ensiling process was performed correctly. pH is around 4, lactic acid content ranges between 4-6% on DM content, acetic acid content is around 2% DM and propionic acid, butyric acid and NNH_3 content is low.

With regard to ash content:

i) Silage of winter cereals (triticale and wheat) show the higher values (for triticale it ranges between 9.12% and 10.27% DM while, for wheat, between 7.00 and 9.50% DM);
ii) Maize silage from the whole plant shows values ranging between 4.75% and 4.95% DM;

iii) Ear maize silage samples have lower ashes content (between 1.24% and 1.31% DM).

Triticale and wheat silage samples do not show starch content at all. Maize silage's starch content ranges between 30.15% and 31.80% DM. Ear maize silage samples show starch contents ranging between 62.62% and 65.54% DM.

Neutral Detergent Fiber NDF/DM is higher in winter cereals silages rather than maize silages (whole plant and only ear); NDF/DM:

i) For triticale silage ranges between 55.81% and 61.66% (average 59.17%.);

ii) For wheat silage is between 55.34% and 60.49% (average 58.87%);

iii) For maize silage from the whole plant vary between 43.27% and 44.04% (average 43.74%);

iv) For ear maize silage samples is between 15.44% and 18.41%, (average 16.99%).

For what concerns Acid Detergent Fiber ADF/DM the highest values measured in the samples are also shown in winter cereals silages; in more details, ADF/DM content ranges between:

i) 34.05% and 38.17% (average 36.57%) for triticale silage;
ii) 33.19% and 39.37%, on average 35.54%, for wheat silage;
iii) 23.4% and 24.38% (average 24.25%) for maize silage from the whole plant;

Biomass		Wheat				Triticale			
ID Sample		Aw	Bw	Cw	Dw	At	Bt	Ct	Dt
Dry matter	%	31,81±1,2	32,32±1,1	31,40±2,0	32,92±1,8	34,11±2,1	37,31±3,2	34,22±2,8	33,92±0,8
pH		4,15±0,07	4,28±0,3	3,88±0,1	3,88±0,05	3,9±0,2	3,91±0,06	3,93±0,04	3,89±0,03
Ashes	%	7,43±0,2	9,37±0,3	7,98±0,1	9,27±0,3	9,84±0,5	9,75±04	10,27±0,3	9,12±0,2
Raw protein	%	8,4±0,3	11,69±0,4	8,15±0,2	10,76±1,0	10,27±0,8	7,97±1,2	9,47±0,7	12,75±0,8
Ether extract	%	1,89±0.1	1,97±0.11	2,03±0,2	1,74±0,8	1,64±0,7	1,5±0,9	1,57±0,6	2,34±0,8
NDF_SS	%	59,17±1,8	61,66±8,3	55,81±1,8	58,84±1,2	60,07±0,3	60,15±0,1	60,49±0,6	55,34±0,5
ADF_SS	%	34,45±1,5	39,37±1,5	33,18±1,1	35,19±1,5	36,4±0,8	38,17±0,9	37,28±0,9	34,05±0,8
N_NH3_SS	%	6,7±0,5	8,94±0,5	5,39±0,3	8,42±0,3	7,76±0,4	9,2±0,6	8,0±10,5	7,37±0,3
Gluocose	%	1,27±0.2	0,5±0,8	1,45±1,6	0,56±0,8	0,59±0,6	0,52±0,8	0,47±0,9	0,64±0,8
Fructose	%	2,09±1,01	1,2±0,8	3,79±0,7	1,94±0,6	1,77±0,9	2,55±0,12	2,62±0,8	2,07±0,7
Mannitol	%	2,42±0,8	0,63±1,4	3,59±0,8	2,64±0,6	2,61±1,1	2,6±1,3	2,79±0,9	1,79±0,8
Ethanol	%	0,31±0,2	0,28±0,1	1,19±0,1	0,85±0,4	0,63±0,3	1,29±0,5	1,38±0,6	0,38±1,1
Lactic acid	%	3,58±1,1	3,89±1,5	4,66±0,7	4,57±0,6	6,13±0,3	5,89±0,5	6,06±0,2	7,07±0,2
Acetica acid	%	2±0,4	3,65±0,2	1,99±0,4	2,1±1,0	1,97±0,2	2,46±0,4	1,97±0,6	1,81±1,1
Propionic acid	%	0,2±0,3	0,24±0,1	0,21±0,3	0,24±0,4	0,23±0,5	0,32±0,3	0,27±0,8	0,17±0,5
Butirryc acid	%	0,17±0,4	0,1±0,4	0,13±0,3	0,2±0,4	0,4±0,6	0,05±0,2	0,06±0,2	0,6±0,3

Table 1- Analysis results of triticale and wheat silages.

Biomass		Ear maize silage				Whole maize silage			
ID sample		Ae	Be	Ce	De	Am	Bm	Cm	Dm
Dry matter	%	65,62±1,2	63,50±1,1	62,51±1,6	64,92±1,3	35,0±0,8	35,67±0,7	34,4±1,0	35,7±0,9
pH		4,23±0,07	4,02±0,06	4,11±0,02	4,02±0,02	3,91± 0,05	3,87±0,2	3,87±0,03	3,96±0,04
Ashes	%	1,32±0,2	1,24±0,4	1,29±0,6	1,31±0,4	4,86±0,3	4,71±0,4	4,97±0,6	4,75±0,5
Raw protein	%	8,6±0,2	8,15±0,3	8,30±0,6	8,77±0,7	7,29±0,5	7,17±0,7	7,48±0,8	8,08±0,9
Ether extract	%	2,5±0,5	2,99±0,4	2,64±0,5	2,72±0,6	-	-	-	-
NDF_SS	%	17,51±1,2	15,44±1,2	18,41±1,0	16,61±1,8	43,27±2,1	43,87±1,2	44,04±1,0	43,78±2,1
ADF_SS	%	-	-	-	-	24,28±3,2	24,54±2,1	24,47±1,0	23,74±2,1
N_NH3_SS	%	2,45±0,2	2,59±0,3	3,06±0,5	1,94±0,6	4,70±0,2	3,80±0,2	4,67±0,3	5,63±0,3
Gluocose	%	0,97±1,8	0,90±2,0	0,81±1,0	0,47±2,0	0,44±1,7	0,40±1,2	0,52±1,4	0,49±1,6
Fructose	%	0,46±0,3	0,46±0,5	0,46±0,4	0,37±0,6	0,40±0,4	0,44±0,6	0,46±0,3	0,37±0,7
Mannitol	%	0,37±0,2	0,46±0,4	0,50±0,5	0,35±0,5	0,28±0,3	0,74±0,7	0,36±0,8	0,34±0,7
Ethanol	%	0,13±1,2	0,40±0,4	0,27±0,2	0,47±0,6	0,49±0,4	0,73±0,3	0,35±0,3	0,700,4±
Lactic acid	%	4,2±1,2	3,84±1,8	3,71±1,8	3,96±1,7	4,35±1,9	5,59±0,9	4,39±0,8	4,37±1,2
Acetica acid	%	0,09±0,05	0,36±0,1	0,32±0,02	0,29±0,02	1,2±0,8	0,23±0,9	2,1±0,7	0,79±0,4
Propionic acid	%	0,38±0,02	0,33±0,02	0,41±0,1	0,36±0,05	0,16±0,01	0,06±0,001	0,21±0,02	0,41±0,02
Butirryc acid	%	0,02±0,001	0,03±0,002	0,02±0,004	0,02±0,005	0,03±0,03	0,03±0,02	0,04±0,02	0,03±0,02
Starch	%	63,32±2,3	65,54±3,2	62,62±3,1	63,89±3,1	31,80±2,7	31,43±2,7	30,64±1,2	30,15±1,9

Table 2 - Analysis results of ear maize silages and whole plant maize silage

3.3.2 Biomass Degradation

Table 3 shows the degradation values of triticale silage within the duration of the test. DM degradation after 75 incubation days of triticale silage samples ranges between 82.69% and 86.42%, on average 84.63%. Already after 3 days from the start of the incubation period, the mean degradation percentage is equal to 40.36%. The highest degradation rate of biomass is shown at the beginning of the incubation period.

Table 4 shows the degradation rate of wheat silage. The total DM degradation rate of wheat silage after 75 days from the incubation start ranges between 80.23% and 86.64%, on average 84.23%. The highest degradation rate is observed within 3 days of incubation. For the four samples of wheat silage, the average is 47.45% ranging between 43.29% and 51.64%.

sample	Time						
	0	3	7	25	35	50	75
		degradation % of dry matter					
At	0	40,46±0,12	56,07±0,86	69,15±4,95	76,09±1,35	79,37±0,85	85,26±0,59
Bt	0	43,11±0,98	59,90±1,50	65,67±1,48	72,44±2,41	78,86±2,96	84,13±0,70
Ct	0	37,95±1,06	56,27±1,90	62,56±3,79	69,94±1,71	76,94±3,22	82,69±1,07
Dt	0	39,92±0,07	56,94±5,11	62,69±3,15	69,91±3,48	78,31±5,71	86,42±1,26
average	0	40,36±2,13	57,29±1,78	65,02±3,11	72,10±2,92	78,37±1,05	84,63±1,59

Table 3 - Degradation percentages of dry matter on triticale silage samples varying during the incubation period.

		Time					
sample	0	**3**	**7**	**25**	**35**	**50**	**75**
	degradation % of dry matter						
Aw	0	51,64±1,38	52,89±0,92	66,92±2,31	74,36±1,45	77,87±0,91	84,19±0,63
Bw	0	49,98±0,88	64,59±3,0	69,67±3,08	75,68±2,98	81,33±2,5	85,99±1,2
Cw	0	43,29±0,19	64,83±0,54	65,86±2,76	78,63±0,52	81,28±0,52	86,64±2,16
Dw	0	44,87±1,23	60,48±2,32	65,76±2,19	72,38±2,19	87,54±1,92	80,09±2,24
Average	**0**	**47,45±4,00**	**60,70±5,57**	**67,05±1,82**	**75,26±2,62**	**82,01±4,03**	**84,23±2,95**

Table 4 - Degradation rate on dry basis of wheat silage within the incubation time.

Table 5 shows degradation data of ear maize silage. The loss of DM after 75 days is, on average, 97.87%, ranging from 97.69% and 97.99%. The highest degradation rate is still observed within the first 3 days of incubation with an average value equal to 70.90% and ranging between 65.77% and 75.85%.

Table 6 shows degradation values during the incubation time of whole plant maize silage. The average degradation percentage at the end of incubation time is 89.62%, ranging between a minimum of 89.02% and a maximum of 90.65%. The highest degradation rate is observed again within the first 3 days of incubation. The average rate during this time is 52.44%, ranging between 47.81% and 56.82%.

		Time					
sample	0	3	7	25	35	50	75
	degradation % of dry matter						
Ae	0	75,58±2,85	79,05±1,95	89,96±1,13	94,59±0,65	96,73±0,23	97,94±0,29
Be	0	73,80±2,26	79,56±1,91	90,19±1,12	94,72±0,63	96,81±0,22	97,99±0,28
Ce	0	65,77±1,67	76,53±2,20	88,73±1,28	93,94±0,73	96,33±0,26	97,69±0,32
De	0	68,46±3,47	78,29±2,03	89,58±1,19	94,39±0,67	96,61±0,24	97,87±0,30
Average	0	70,90±4,57	78,36±1,33	89,62±0,64	94,41±0,34	96,62±0,21	97,87±0,13

Table 5- Degradation rate on dry basis of ear maize silage within the incubation time.

	Time						
Sample	0	3	7	25	35	50	75
	degradation % of dry matter						
Am	0	47,81±0,77	60,01±2,98	80,58±1,30	84,80±0,39	87,07±0,08	89,26±1,94
Bm	0	52,29±2,89	65,19±2,59	83,09±2,87	86,76±0,34	88,74±0,07	90,65±1,69
Cm	0	52,82±2,23	59,32±3,03	80,24±3,36	84,53±0,40	86,84±0,9	89,08±1,97
Dm	0	56,82±1,16	60,80±2,92	80,96±3,23	85,09±0,39	87,32±0,8	89,47±1,90
Average	0	52,44±3,19	61,33±2,29	81,22±1,11	85,30±0,87	87,49±0,74	89,62±0,61

Table 6 - Degradation percentage of dry matter of whole plant maize silage within the incubation time.

3.3.3 Calculation of digestate mass

Table 7 reports the results about the digestate production. Digestate mass is calculated according to the water content and to the dry matter residue in the biomass after 75 days of incubation in anaerobic conditions.

After 74 fermentation days, triticale silage produces a digestate mass on average equal to 80.49% of fresh matter.

On average, wheat silage produces a digestate mass equal to 83.66% of the initial fresh matter.

Ear maize silage produces a digestate mass equal to 38.00% of the initial biomass fresh matter, on average.

Whole plant maize silage produces a digestate mass on average equal to 75.19% of fresh matter.

Biomass	% average biomass water content	% average mass of digestate /mass biomass	SD of digestate
Triticale silage	65,11	80,49	1,93
Wheat silage	67,89	83,66	2,45
Ear maize silage	35,87	38,00	1,47
maize silage	64,81	75,19	1,22

Table 7. Percentage values of digestate production/ mass of biomass after 75 incubation days.

3.4 Discussion

Nylon bags technique was created and used to evaluate the digestibility of feed for ruminants. The bacteria inoculum is made of liquid rumen and can be used in vitro or in vivo by introducing the bags directly in the rumen of the living animal through fistulas.

The rumen, as the fermenter, is an anaerobic ecosystem. They both have biologic similar conditions. From this hypothesis came the idea of using the nylon bags technique also for estimating biomass degradation for the fermentation with an energetic goal.

However, the use of nylon bags technique to evaluate the anaerobic degradation of biomasses by simulating the fermenter conditions for biogas production does not have any bibliographic confirmation.

The maximum incubation time (75 days) is in accordance with the average retention time of real scale fermenters.

All biomasses showed degradation percentages higher than 80%.

The highest degradation rates were observed in ear maize silage samples (on average, 97.7%) and in maize silage (on average, 89.62%). On the opposite, winter cereals silages (triticale and wheat) show lower percentages, on average 84%.

The lower degradability of triticale and wheat silages is probably due to the higher content of NDF, ADF and ashes if compared with maize and ear maize silages. In addition, maize and ear maize silages have a higher starch content.

NDF represents the cellulose, hemicellulose and lignin content of plant biomasses. ADF represents the cellulose and lignin of vegetable biomasses. Therefore, the difference is due to hemicellulose [21].

The cellulose, hemicellulose and lignin is mainly refractory under anaerobic conditions although there is evidence that shows its (partial) degradation in anaerobic environments [22, 23].

The starch consists of straight or branched chains of glucose and is digested relatively easily in the biogas process [24].

The mean degradation curves are shown in Figure 1. Here, the degradation speed of biomasses is shown.

The curves are all made of an initial closely similar trait, characterized by strong slope. The slope states for an high degradation speed. Afterwards, the degradation speed sharply diminishes and gradually decreases.

From the tendency of the curves it can be assumed that biomasses show a pool of transient compounds (organic acids, simple carbohydrates, starch, fats and proteins) that are quickly degraded at the beginning of the incubation time. Then, more and more recalcitrant compounds are degraded within a longer time (cellulose, hemicellulose, structured proteins incorporated in complex carbohydrates).

Triticale and wheat silages' curves show the same tendency of the other biomasses since their composition is much similar to each other.

Ear maize silage's curve shows an initial trait characterized by a higher degradation speed. It is certainly due to the high starch content (> 60%) and to the fast bacteria degradation [24].

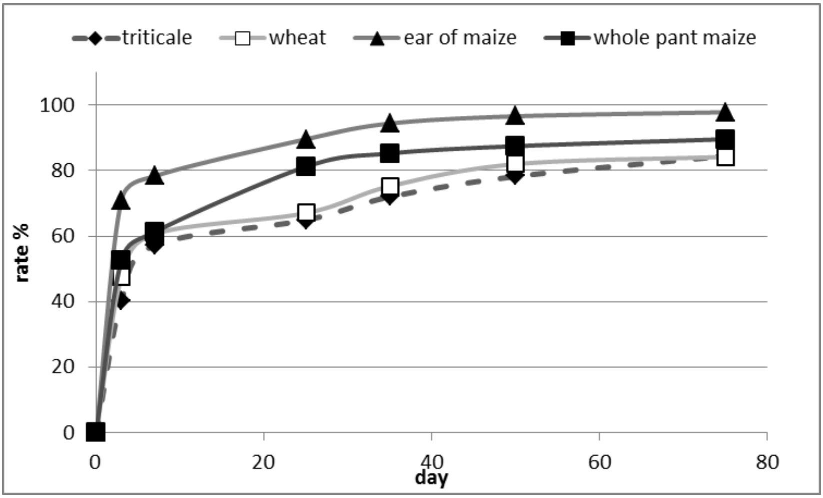


Figure 1 - Degradation kinetics for the different silages.

The kinetics of the degradation curve of maize silage shows the initial trait being similar to the curves of winter cereals silages. After 3 days though, the degradation speed decreases remaining, however, faster than that of triticale and wheat silages.

The estimate of digestate mass considers the biomass' content in the not fermentable compounds: water and still not degraded dry matter in the conditions and time established for the lab test. These lab assumptions simulate those of real scale fermenters.

The digestate mass of each biomass depends on the DM content and on the degradability itself.

3.5 Conclusions

In Italy, biogas production from anaerobic digestion had a very strong and widespread growth in the agricultural sector. It first grew thanks to silage crops traditionally used for feeding. In particular, in the Po Valley the most interesting crops are maize silage as summer crop and triticale and wheat as winter crop.

In this study the biological degradability in anaerobic conditions was evaluated. The anaerobic conditions were similar to those of a real scale biogas plant. In addition, the digestate mass attributable to the single biomass was calculated as well. The biomass composition conditions the degradability of the biomass itself and of the digestate production. Biomasses with a low or null fiber content have hight degradation rates and lower digestate production. DM is easily degradable within 3 days from the start of the incubation. In all the tested biomasses this amount is higher than 40%. Ear maize silage is the most degradable biomass (>97%). As a consequence, it generates the lowest digestate mass per mass unit (38%). The higher degradability of ear maize silage is due to the high starch content in the biomass (>60%) and to the low fiber content. Whole plant maize silage is less degradable (about 90%) than ear maize silage. Triticale and wheat silages, because of their strongly similar composition, show degradation rates and kinetics very similar to each other. Moreover, because of the higher fiber content than maize and ear maize silages, they are less degradable.

Further studies will aim to better evaluate the kinetics of biomasses degradation deepening the NDF and ADF degradation.

3.6 Acknowledgements

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Chapter 4

A detailed monitoring of an anaerobic digestion plant in northern Italy

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A detailed monitoring of an anaerobic digestion plant in northern Italy.

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Abstract

For the achievement of European Union objectives, the Anaerobic Digestion (AD) of energy crops and agro-industrial by-products and/or wastes appears as one of the most promising agro-energy processes.

In Italy there are about 1000 AD plants in the agricultural sector. The economic performance is guaranteed by the

high levels of contribution subsidies, but the energetic and environmental aspects must be carefully evaluated.

This paper reports the results of the detailed monitoring of an AD plant located in Piedmont. The AD plant is based on a single stage process; it has two CSTR digesters (total volume of 5340 m^3) operating in mesophilic conditions. The electric and thermal power are 998 kW_{EE} (η_{EE} = 40.9%) and 577 kW_{TE} (η_{TE} = 23.6%), respectively. Heat is recovered only from engine water and oil cooling jacket.

Over the year, it co-digests energy crops (maize silage, triticale silage, and ryegrass silage), pig and cattle slurry, poultry manure, by-products of maize industry and food wastes.

The AD plant has been monitored for one year. Daily data of: biomass consumptions; temperature; organic loading rate; biogas production and its composition; gross electricity production, electricity consumption and net electricity production have been collected. Laboratory tests have been carried out to measure the specific biogas production.

The potential biogas production, calculated considering the laboratory test results and the biomasses introduced into the digesters, has been compared with the biogas volume measured at the plant in order to estimate the efficiency of the AD process.

The biogas produced by the AD plant during the monitoring represents 96% of the potential biogas production; the CHP engine has produced 8378 MWh_{EE} with an average electrical power of 968 kW_{EE}. The overall electric self-consumption has been equal to 653 MWh_{EE} (7.79% of the gross electricity production). Each day, 10782 m^3_N/biogas are produced, on average.

Keywords: anaerobic digestion, biogas, efficiency, energy, monitoring

4 .1 Introduction

Throughout the years, the attention on the quantification of the environmental impacts derived from agricultural production systems has increased considerably. The agricultural contribution to greenhouse gases (GHG) emissions is incontestable [1]. Agricultural activities are responsible for about 10 % of the total Europe GHG emissions [2]. Furthermore, considering the European objectives regarding the reduction of fossil fuel consumption and GHG emissions, the production of energy from renewable sources is a priority [3].

In Italy, in 2011, the energy production from RES reached 11.6 % of the global energy consumption and the 23.5 % of the total electric consumption. In this framework, during the past 10 years, the agricultural biogas production was considerably increased. Nowadays, about 1000 agricultural biogas plants are running mainly in northern regions with a total electrical power of 756 MW. This Fig. corresponds to 1.65 % of the global electric consumption. Strong public incentives are granted for electricity produced from biogas. From 2013 with the [4] t public incentives framework has been changed giving more importance to heat and by-products valorization. Nevertheless, for the biogas plants put into operation before 31 December 2012 and with electrical power lower than 1 MW, 280 €/MWh are granted for the electricity fed into the grid without any consideration regarding heat and byproduct valorization. The granting of incentives only to the electricity has favored the idling of several big AD plants with poor consideration for overall efficiency of the system. Regarding the feeding of digesters, although the anaerobic digestion (AD) of animal manure is one of the best techniques for an energetic valorization of these by-products the cereal silages are the main feedstock for biogas production, both in Italy and in other European countries [5].

Although the AD of agricultural feedstock can be performed with different types of biogas plants [6], the most widespread technology is characterized by mesophilic conditions and single-stage digestion in continuous stirred-tank reactors [CSTR] [7].

Considering that the biogas production involves important environmental issues, especially global warming, acidification, and eutrophication [8,9]it must take place in an efficient way. Nevertheless, the increasing number of biogas plants, especially those larger than 500 kW electrical power, involves high consumptions of energy crops, large transportation distances (both for the biomass feedstock and the digestate), and difficulties with thermal energy valorization. The widespread of AD plants, beside environmental issues, involves also economic and social challenges. Over the years, the spread of biogas plants, often concentrated in specific areas (such as the provinces of Cremona, Lodi and Mantua), resulted in the considerable rising of biomass prices and concerns about the fact that more and more agricultural land is used to feed the digesters.

The achievement of high global efficiency of the biogas system is become a very important issue without which satisfactory economic and environmental results are hardly reached. In this contest, the monitoring of AD plant is the first step and it represents a useful tool capable to give information needed to well manage the plant itself.

In this study an agricultural AD plant with an electrical power of 998 kW was monitored for 12 months.

The aim of the monitoring was the evaluation of the global efficiency of the biogas plant and, in particular, to consider the exploitation of the biomass introduced into the digesters.

4.2 Methods

4.2.1 Description of the biogas plant

The AD plant is based on a single stage process, it has two CSTR (Completely Stirred Tank Reactor)

digesters operating together with a total volume of 5300 m3 (2750 m3 per digester) The AD plant has an electric output of 998 kW (ηEE = 40.9 %). Since the heat is recovered only from engine water and oil cooling jacket, thethermal power of the plant is equal to 577 kW (ηTE = 45.0 %).

It works in mesophilic conditions (T = 40 °C). Over the year, it co-digests energy crops (maize silage, triticale silage, and ryegrass silage), pig and cattle slurry, poultry manure, by-products of maize industry and food wastes.

Feeding systems and schedules are different for solid and liquid biomass: silages are put into the digesters by a screw placed on the bottom of the feeding hopper; the loading system is located between the two digesters. Slurry coming from the animal husbandry is stored in a tank and, from this, it is pumped into the digesters; the whole substrate is mixed with liquid fraction (LF) of digested matter. In this way, proper inlet Total Solid (TS) content is achieved. The AD microbial process operates at 40°C and it occurs in 2 cylindrical above-ground CSTR (Completely Stirred Tank Reactor) digestion reactors (diameter Ø = 20 m, height H = 8 m). They are made of iron-reinforced concrete and have an expanded polyurethane external insulation. Both the two digesters are covered by a gasometric dome with a spherical shaped cap.

In each reactor the mixing is obtained by 4 submerged long-axis mixers operating 5 minutes per hour. Mixers can be adjusted in height and internal angle. Regarding the heating system, the hot water (80 °C) coming from the CHP unit is used to heat the biomass inside the digestion reactors; 4 pumps circulate this hot water into in-vessel heat exchangers. Within a year, the 4 pumps have an average operating time of 5 h/day. Digestate is dumped by a lobe pump from the bottom part of the digesters. AD effluents are: (i) partly, accumulated in a storage tank and (ii) partly, separated into a liquid (LF) and solid (SF) fraction by using a screw separator. Biogas treatments (filtration, dehumidification and desulphurization) are always required before to feed the CHP i.c. engine. Filtration is carried out with a simple sand-filter. Produced biogas is filtered in a sand filter, dehumidified and desulphurizated.

Dehumidification is carried out by a refrigeration unit (15 kWe) that cools down the biogas temperature removing the water vapor while desulphurization by a wet scrubber (10 kWe). Biogas treatment devices work in series with operating on the same biogas flow rate consumed by the CHP i. c. engine. After the treatments, biogas feeds a CHP unit. Thermal energy not used for heating the biomass inside the digesters is dissipated by fan-coolers. The cogeneration unit runs constantly at 1500 rpm.

4.2.2 . Monitoring

The AD plant has been monitored for 12 months. During this period, each day, these data have been gathered: 1) feedstocks consumptions; 2) temperature inside of the two digesters; 3) organic loading rate; 4) biogas production and its composition; 5) working time of CHP, gross electricity production, electricity self-consumption, net electricity production. Each month the total solid and volatile solid content inside the two digesters has been determined by means of laboratory analysis.

The laboratory tests have been carried out also to measure the specific biogas production of the different feedstocks utilized to feed the digesters.

4.2.3 Laboratory tests

The total solid and volatile solid content (for the substrate inside the digesters as well as for the different feedstocks) has been measured according to Martillotti et al.. [10]

A laboratory device has been developed to measure the specific biogas and methane production of the different biomasses used to feed the digesters. Lab-scale unstirred fermenters were developed and placed in thermostatic baths at 40°C [11]. The fermenters were made of a hermetically sealed glass jar with one metallic cover holding the valve through which the biogas produced by the tested samples reached the corresponding gasometer by flowing into one flexible nylon hose. Gasometers are made by methacrylate Torricelli pipes with 3.5 l volume. Each gasometer has, on top, two hoses: one carrying the biogas from the fermenter and one, made of PVC, equipped with a valve for gasometer recharge. When the biogas flows from the fermenter into the gasometer, the aqueous solution is moved in a vessel equipped with one overflow device which allows to the aqueous solution to be collected in a tank. Samples of fermenting biomass from different full scale anaerobic digesters were used as inoculum. Before digestion all substrates were ground using a professional grinder (Blisxer 5 Robot coupe France)..

During the experiment the temperature in each fermenter was kept at 40°C. Fermenters were kept in these conditions as daily recorded: the centimeters ran by the aqueous solution in the gasometers were read and the equivalent volume in virtue of gasometer diameter was calculated.

Biogas composition was monitored by means of one "Binder Combigas GA-m3" (from Binder, D) portable

gas analyzer measuring the content into methane and carbon dioxide equipped with one electrochemical cell for oxygen measurement and one infrared dispersion cell for methane and carbon dioxide percentage determination.

4.2.4 Efficiency

The global potential biogas production PBG_GLOBAL_POT; m3N/year) has been compared with the global biogas volume measured at the plant in order to estimate the efficiency of the AD process. The biogas produced over the year should be the most possible similar to the PBG_GLOBAL_POT. When big differences are detected the AD process is ineffective and more biogas could be produced with the same amount of feedstocks. PBG_GLOBAL has been calculated as the summation of the potential production of each feedstock (PBG_FD*i*; m3 N/year). PBG_FD*i* is computed considering the laboratory test results and the mass of the feedstock *i* introduced into the digesters. In more details (Eq 1-2):

PBG_GLOBAL_POT = Σ PBG_FDi (1)

$PBG\_FDi = \Sigma\, mFDi \cdot PSFDi$ (2)

where: mFD*i* is mass of the feedstock *i* introduced in the digesters (twb/year); PSFD*i* is specific biogas production of the feedstock *i* (m^3N/twb); this value is the result of the laboratory tests.

4.3 Results and discussion

Table 1 shows the feedstock consumption over the year, the results about the laboratory tests and the potential biogas production for the different matrixes. Regarding the laboratory tests, as predictable, energy crops have higher specific biogas production compared to animal by-products. Food wastes show great variability although they represent suitable substrates for AD.

Energy crops are the main feedstock. In more detail, the maize silage is by the far the most important feedstock and it is the staple for digester feeding, it silage represents more than 80% of the biomass introduced into the digesters and from it stems about 85% of the potential biogas production. Slurry mass is about 6% of the global feedstock but it contribute to the biogas production is really small (0.60 %). Food wastes represent a little share of the feedstock but their contribution to the biogas production is more than proportional.

About the feeding, the monitoring has highlighted deep differences not only on the feeding amounts but also on timing and way. In fact, over the years, maize is the only feedstock continuously feed in the digesters (only in 6 days it has been not utilized). The food wastes (bread) and industry by-products (corn gluten) have not been continuously used and moreover are not put into both the digesters; their use strongly depends by their prices and availability on the market

The liquid fraction (LF) – coming from the digestate separation (6272 t/year) – and water (1266 t/year) have been added in the digesters to maintain the organic load and the percentage of dry matter (DM) at optimal level (DM: 8-9%).

Each day about 166 t/day of the substrate – contained in the digesters but not completely digested – has been circulated between the two digesters to balance the different biomass input described above. This also allowed the mixing. The average organic loading rate is 3.32 kgSV/m3 ·day.

Over the year the temperature remains in a mesophilic regime. From October and April temperature shows little variations and it ranges from 39 °C and 40 °C. It is interesting underline that, from May and September, although the heating system was off, the temperature increased up to 43.7 °C. Regarding the content of total and volatile solids inside the digesters, the results of the laboratory tests conducted monthly are reported in Fig. 1. It can be noted that, over the year, the level of total solids shows big variations (it ranges between 6 to 9% of the

Feedstock	Mass	Share	TS	SV	PS_{FD_i}	P_{BG}	Share
	t_{wb}/ha	%	$\%_{wb}$	$\%_{ST}$	$m^3{}_N/t_{SV}$	$m^3{}_N$/year	%
Maize	16575	80.67%	33.8	93.5	671,3	3440944	80.02%
Ryegrass	584	2.84%	28.7	90.5	553.3	323001	7.51%
Triticale	695	3.38%	30.1	90.5	589.2	113845	2.65%
Corn Gluten	806	3.92%	49.9	80.8	549.3	255885	5.95%
Poultry manure	296	1.44%	8.1	84.4	332.4	65578	1.53%
Bread	47	0.23%	93.7	83.6	455.3	28999	0.67%
Distiller	288	1.40%	42.5	80.2	931.2	46882	1.09%
Caw slurry	870	4.23%	90.0	96.8	712.7	19519	0.45%
Pig slurry	387	1.88%	27.5	91.3	625.5	5446	0.13%

Table 1 - Feedstocks consumption and potential biogas production

.fresh biomass) while the volatile solids have smaller variations: from June to March they ranges between 65 to 80% of the food and industry wastes, are used depending on their availability and market prices.

Considering the values reported in Table 1 the potential biogas production is equal to 4300100 m^3 N/year. The

measured biogas production is 3946311 m^3 N/year (daily biogas flow is equal to 10782 m^3N/day) and it represents about the 92% of the potential biogas production.

The biogas has an average methane content of 52.51% in volume and, consequently, its Lower Heating Value is 5.13 kWh/m^3 N. During the monitoring period, the CHP unit hasproduced 8379 MWh of Electric Energy (EE) (on average 22.89 MWh per day).

The EE daily self-consumption of the plant (for pumps, screws, mixers, biogas treatments etc.) was 653 MWh with an average value of 7.79% (1784 kWh per day). Consequently the net energy produced was 7726 MWh.

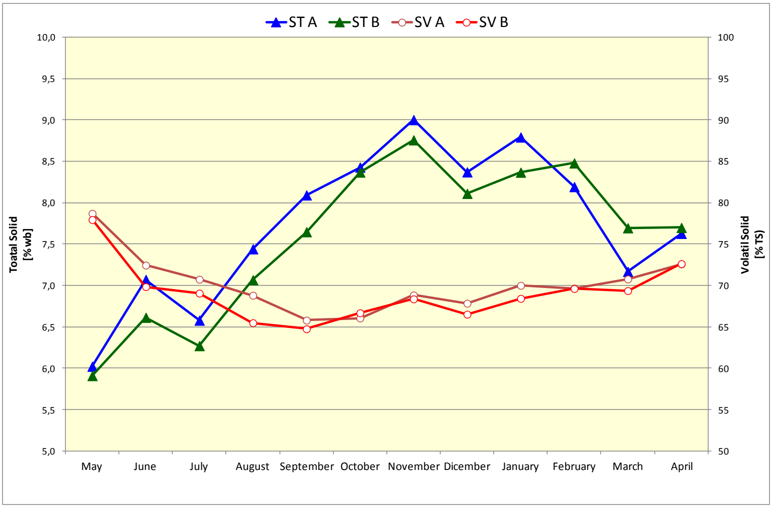

Figure - 1. Total (ST) and volatile (SV) solid variation over the year in the two digesters (A and B)

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Chapter 5

General conclusion

General conclusion

Thanks to the public incentives, in the last two decades, the electricity generation by agricultural AD plants has remarkably grown, in particular several big AD plants, characterized by an electrical power close to 1 MW have been built and, actually, are fed mainly with energy crops. Currently, in Italy, more than 1150 agricultural AD plants are running. The spreading of this renewable energy source has been supported also by a decrease of the profitability of traditional agro-livestock activities. Nowadays, due to the reduction of CAP subsidies and the considerably drop of meat and milk prices, the electricity generation by AD of fermentable biomasses is become the main revenues source for many farms. Beside this, the good economic performances achievable by the AD process are become an interesting investment opportunity also for non-agricultural companies.

However, it must be underlined that, unfortunately, in several cases, the spreading of AD plants took place without any consideration regarding the landscape management in particular about biomass supply and the digestate management.

The energy production system for the AD can be subdivided in 3 main subsystems: biomass production or recovery, biomass storage, biomass transformation in biogas and then in energy and, finally, digestate management.

Among the different biomasses the maize silage is the most suitable to feed the AD plants. In the Po valley area, the maize is traditionally grown to produce forage for animal feeding thanks to the production high amount of biomass easily conservable. Maize cultivation is carried out mainly with two cropping systems: single and double crop. In the second, the maize follows a winter crop (mainly triticale and wheat). Cereal silages are feedstock easily fermentable thanks to: (i) high carbohydrates and organic acids content; (ii) presence of fibre that, although not easily degradable, enhances the bacteria development and is carbonate sources (useful to create the buffer system). Considering the average biomass yields for Po valley Area, to supply a AD plant with 1 MW of electric power 350-400 ha are needed.

The digestate represents the main by-product of the AD process and it is a material rich of nutrient elements (in particular in N, P and K), it can be properly used as organic fertilizers. The digestate spreading during pre-seeding fertilization of energy crops closes the nutrient cycle between the AD plant and its supply shed.

Nowadays, for the electricity generation from agricultural biogas plants some issues must be faced: (1) the legislative decree that will define definitively the classification and the use of digestate is ongoing to publish; (2) the subsidy framework is changing, the incentives will be reduced and/or new taxes will be introduced. This will lead to a reduction revenues coming from energy process and, probably, will force the biogas operators to improve the AD plants efficiency, for example, valorising the thermal energy cogenerated by the CHP engine (e.g. to heat greenhouse of pig stable, to dry agricultural products, etc.)

Finally, the revision of the CAP, with the new regulation about "greening" will lead a changes about crop production system; in particular, crop diversification and crop rotation over the farm area will be favoured. With the "greening" also the feeding of the AD plants will change because, compared to nowadays, there will be available different feedstock and less cereal silages. "New" energy crops such as rye, barley, sorghum, sunflower and Italian ryegrass will be necessarily used to feed the digesters.