

Article

Energy and Nutrients' Recovery in Anaerobic Digestion of Agricultural Biomass: An Italian Perspective for Future Applications

Federico Battista *, Nicola Frison and David Bolzonella 

Department of Biotechnology, University of Verona, Strada Le Grazie 15, I-37134 Verona, Italy

* Correspondence: federico.battista@univr.it

Received: 3 June 2019; Accepted: 22 August 2019; Published: 26 August 2019



Abstract: Anaerobic digestion (AD) is the most adopted biotechnology for the valorization of agricultural biomass into valuable products like biogas and digestate, a renewable fertilizer. This paper illustrates in the first part the actual situation of the anaerobic digestion sector in Italy, including the number of plants, their geographical distribution, the installed power and the typical feedstock used. In the second part, a future perspective, independent of the actual incentive scheme, is presented. It emerged that Italy is the second European country for the number of anaerobic digestion plants with more than 1500 units for a total electricity production of about 1400 MW_{el}. More than 60% of them are in the range of 200 kW–1 MW installed power. Almost 70% of the plants are located in the northern part of the Country where intensive agriculture and husbandry are applied. Most of the plants are now using energy crops in the feedstock. The future perspectives of the biogas sector in Italy will necessarily consider a shift from power generation to biomethane production, and an enlargement of the portfolio of possible feedstocks, the recovery of nutrients from digestate in a concentrated form, and the expansion of the AD sector to southern regions. Power to gas and biobased products will complete the future scenario.

Keywords: anaerobic digestion; biomethane potential tests; Italy; biogas; manure; energy crops; agriculture residues; digestate

1. Introduction

Anaerobic digestion (AD) technology is widely present in the European rural context as it enables the bioconversion of organic matter present in manure and other agro-waste (residual crops or residual streams of food processing) while recovering biogas for electricity or biomethane production [1,2] and a renewable fertilizer, digestate [3]. Recent studies showed how biogas from agro-waste allows for the production of biofuels with a relatively low environmental impact because of their reduced emission in terms of greenhouse gases (GHG) [4].

Because of its intrinsic benefits and a generous program of incentives in several countries, AD is largely diffused in Europe [5,6]. The European Biogas Association reports that the anaerobic digestors in operation in Europe numbered more than 17,200 units, with installed electrical capacity of 8000 MW_{el}, while biomethane upgrade units number more than 400 (data from the Annual Report of the European Biogas Association [7]).

These anaerobic plants are mainly farm-based (around 80%) and are fed with agricultural biomasses like energy crops, livestock effluents, and other agro-waste [8]. Sometimes, the necessity to maximize the energy production (i.e., incomes), and an erroneous designing and business planning approach, determined a distorted situation where energy crops, and maize silage in particular, are massively used as feedstock, determining a strong local impact [9]. Corn (*Zea mays* L.) is a typical

example of concern because of its use in the food and feed sectors as well bioenergy with a consequent increase in prices of this crop.

To solve these controversial situations Germany, for example, revised the Renewable Energies Act in 2012, 2014 and 2016/2017 and introduced the so-called maize cap, that is a limit of 60% from 2014 on and 50% since 2016 for energy crops in the feedstock [10].

Moreover, some studies demonstrated how subsidies for bioenergy generation determined the displacement of grasslands and other crops. On the other hand, some energy crops, such as switchgrass (*Panicum virgatum*) can impact favorably on soil properties (erosion prevention) and carbon sequestration [11].

Considering the depicted scenario, it is believed that agro-wastes are the best substrates for anaerobic digestion, as they are not in competition with food/feed production [12].

Beside biogas, an energy vector, digestate, a so called renewable fertilizer, is produced [13]. Moreover, digestate allows for the supplementation of stable carbon on fields thus increasing the carbon sink capability of soils [14].

Digestate is particularly rich in nitrogen (N), phosphorus (P), and potassium (K), vital elements for intensive agriculture. Moreover, it is important to emphasize that P and K are typically mined and are present in defined geographical regions at a global level [15]. Interestingly, these nutrients can be recovered from in concentrated forms: livestock manure in particular, can be considered a mine for these elements. In fact, during anaerobic digestion, the organic backbone of molecules is (at least partially) destroyed while N, P, and K are made available: N and K will be found in soluble forms while is mainly bound to particulate matter. Therefore, agricultural digestate can be used as it is on fields [16,17] or further treated to recover concentrated nutrients to be then transferred in other agricultural areas. The excessive presence of nutrients is a typical problem of some European regions [18]. Today, commercial technologies like stripping, drying, evaporation and membranes technology are available to recover nutrients from digestate [19–21].

Therefore, it is obvious to imagine anaerobic digestion at the center of a future biorefinery approach where agro-waste are converted into high added-value biobased products other than biofuels. This new bioeconomy approach is crucial for the rural renaissance of Europe [22].

Italy is an important actor in this scenario: with its 1500 AD plants, mainly in rural areas, it represents the second European market after Germany and the third in the world after China [7].

In this paper we will report in the first part of the manuscript a picture of the actual Italian scenario for the agricultural biogas sector and will critically analyse the actual situation, then we will expose our vision of the future development of the sector, considering in particular modification of the feedstock recipes based on territorially available biomass, especially in the southern part of the country, and report some full scale experience about nutrients recovery.

2. Materials and Methods

The most abundant substrates from Italian agricultural and farming activities have been tested to determine their biomethane potential (BMP). In particular, the substrates tested along this work have been selected considering their abundance in rural area of some administrative regions in northern, central and southern Italy. Moreover, the portrait of the distribution of the anaerobic digestion plants and their energetic capabilities along the Italian territory have been discussed. Lastly, to close the circular economy approach, the conventional and the more innovative tendencies for the digestate valorization in valuable fertilizers have been analyzed.

2.1. Data Analysis

Data analysis considered the number of AD plants and their installed capacity as well as the main Italian crop production.

The number of the biogas plants located in the different Italian administrative regions, their power capabilities and the relative electrical power production have been obtained combining official data

from the official annual reports of the Consorzio Italiano Biogas (CIB), the Gestore Servizi Energetici (GSE) and the data available through the European Project ISAAC (Increasing Social Awareness and ACceptance of biogas and biomethane) [23–25].

The amounts of the most diffused cultivations in Italy have been taken from official web site of the Italian National Institute of Statistics for agricultures and food activities, Agristat [26]. In particular, data of the most cultivated crops, vegetables and fruits have been reported for the two Italian regions with the highest number of biogas plants in North Italy (Lombardia and Veneto), Central Italy (Toscana and Lazio) and South Italy (Campania and Puglia).

2.2. Analytical Methods

To avoid the degradation, the substrates were kept at $-18\text{ }^{\circ}\text{C}$ until the experimental campaign started. The substrates considered by this work, were physically and chemically characterized. In particular, the concentrations of dry matter (TS), volatile solids (TVS), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN) and total phosphorus (TP) were determined according to the standard methods [27]. For the measurement of TKN and TP contents, a high-performance Ethos-One microwave digestion system by Milestone (Italy) and the UDK 129 distillation unit by Velp Scientifica (Italy) were used.

2.3. Biomethane Potential of Substrates

The BMP tests of the most abundant substrates in Italy were conducted according the methods by Angelidaki et al. [28]. They were fed in triplicate in 1 L sealed bottles, with 0.5 L working volume. The duration of the tests was established by a more recent protocol (Holliger et al. [29]) which decided to stop the BMP tests when the daily biogas production is lower than 1% of the cumulative amount, at least for three consecutive days. Inoculum, was taken from a full scale reactor operating in mesophilic condition and treating a mixture of cow and chicken manures and energy corps residues (maize silage, sorghum silage, triticale silage). Before its utilization, the inoculum was filtered at 2 mm to remove coarse material, diluted two-fold with the digestate and, then, kept at the operative mesophilic temperature ($37\text{ }^{\circ}\text{C}$) for one week to assure the endogenous methane production. Microcrystalline cellulose BMP tests were used as positive control [28,29]. All the reactors were manually stirred once a day. The inoculum was also characterized in terms of TS and TVS contents. The average solids content of inoculum was $26.5 \pm 12.8\text{ g}\cdot\text{kg}^{-1}$, while its volatile content was $63 \pm 4\%$ on TS. The volume of biogas generated during the batch trials was determined by water displacement method, while the methane content was determined using a portable biogas analyser (Geotech Biogas 5000 by GeoTech, London, UK).

2.4. Definition of the Hydrolysis Rate

To gain an indication of the degradability index of each substrates, the hydrolysis rate constant, K_h , was determined following the first order model described in Angelidaki et al. [28]. In particular, the biogas production derived from the first 5 days after beginning the experiment was considered. The first order equation, reported below, was recognized a kinetic model describing adequately the methane yield by a recent work [13]:

$$-k_h t = \ln \frac{B_{\infty} - B}{B_{\infty}} \quad (1)$$

where “ B ” is the cumulative methane yield ($\text{L CH}_4\cdot\text{kg VS}_{\text{fed}}^{-1}$) at digestion time “ t ” days and “ B_{∞} ” is the ultimate methane potential of the substrate $\text{L CH}_4\cdot\text{kg VS}_{\text{fed}}^{-1}$ which is obtained at the end of the tests.

Another indication of the degradation kinetic of the substrates is provided by T-50, which is the required time, in days, to produce half of the total cumulative methane production. It was calculated considering the daily cumulated methane production from each BMP test.

3. Results and Discussion

3.1. The Actual Italian Scenario for Biogas Production

During the period 2008–2012 Italy benefited of one of the most generous incentive schemes for power generation from biogas thanks to the so-called “all inclusive” tariff of 280 €/MWh for plants able to generate up to 999 kW_{el}. Once granted, the incentive is valid for a period of 15 years. As a consequence, the AD sector grew up considerably, invested more than €4 billion euros and installed a total energy capacity of some 1000 MW_{el} in the period 2008–2012 [30]. In the following years, up today, the tariff system was modified and substantially decreased determining a reduced rate of new plants and installation. In particular, three different ranges for installed power were identified, and different corresponding tariffs were introduced which depend on the feedstock fed in the bioreactor. For agro by products and energy crops the tariffs are: 180 €/MWh up to 300 kW_{el}, 160 €/MWh from 300 to 600 kW_{el}, and 140 € per MWh produced for AD plants with an installed capacity larger than 600 kW_{el}. However, the tariffs are higher if the substrates are represented by livestock effluents: 236 €/MWh up to 300 kW_{el}, 206 €/MWh from 300 to 600 kW_{el}, and 178 € per MWh produced for AD plants with an installed capacity larger than 600 kW_{el}. The intention to incentivise the adoption of anaerobic digestion for agro wastes and by-products’ valorisation in Italian rural area is clear [31].

Today, after 10 years from the first incentive scheme, the total number of AD plants operating in the agricultural sector in Italy is around 1500 units for an installed capacity of some 1400 MW_{el} (average electrical capacity of 700 kW_{el} per AD plant): these represent the 90% of the total AD plants in operation [24]. More than 62% of the Italian biogas plants are represented by a power class in the range 200 kW–1 MW. Only 5% and 15% of AD plants are classified as lower than 50 kW and within 50–200 kW, respectively. The remaining biogas plants have power capacity higher than 1 MW but lower than 10 MW [24]. These numbers make Italy the second biogas producer in Europe and third at global scale after China and Germany [7]. However, the number of installed plants is very different in the 20 different administrative regions: biogas generation is concentrated in the northern part of the country (Po valley) where intensive agriculture and husbandry are present while in the South other alternative energetic sources, such as wind and solar power, are present. Figure 1 reports both plants and their installed capacity in the 20 administrative regions (data elaborated from ISAAC Project [25]).

It should be also considered that the northern part of the country is in proximity of Austria and Germany where the biogas experience in Europe originated: it was therefore easy to transfer technologies and knowledge to the southern side of the Alps.

As a consequence, about 500 of the AD plants operating in the agricultural sector are placed in Lombardy, 220 in Veneto, while 180 are in Emilia Romagna and Piemonte, respectively. All the other regions reported less than 100 AD units on their administrative territories. In total, 67% of the plants and 75% of the installed power are based in the northern part of the country.

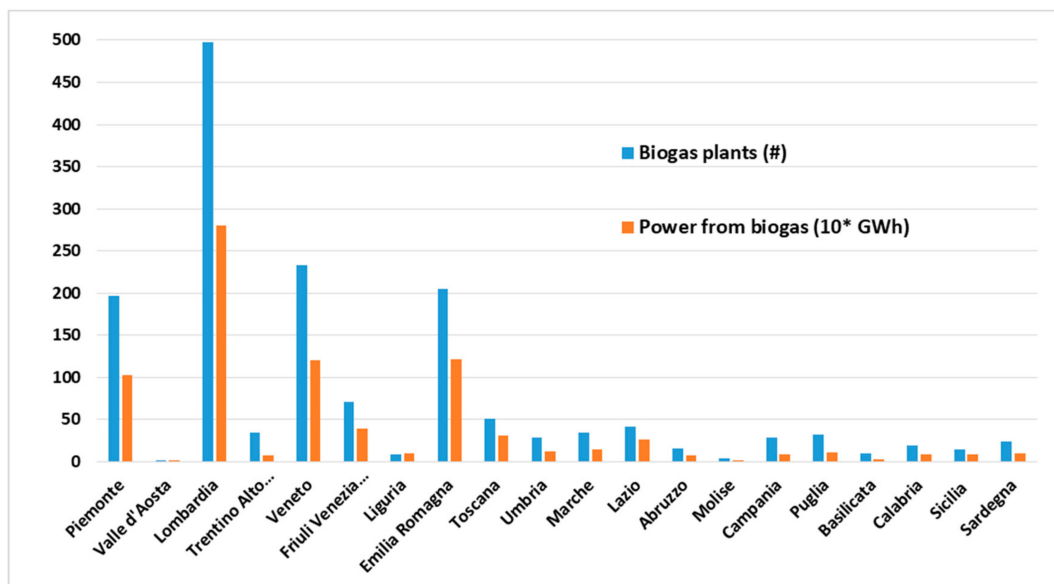


Figure 1. The number and the power capabilities of biogas plants in the 20 Italian administrative regions (data source ISAAC Project [25], modified).

3.2. Typical Feedstocks for the Actual Italian Scenario

According to a specific survey carried out by the Italian Biogas Association [23] and reported in the deliverables of the ISAAC project [25], the typical feedstock composition is due to livestock effluents, energy crops, and agricultural by-products. In particular, it was found that half of the biogas plants in Italy are fed by a mixture of manure and by-products and/or energy crops while the other half are fed with a mixture where energy crops are predominant.

As a consequence, energy crops, especially maize and triticale silage, are the main and sometimes only substrate used for the feeding of AD reactors. Maize is by far the most used crop in anaerobic digestion feedstock: in fact, more than 40 tons of maize per hectare can be produced in southern Europe and its biogas yield is up to $0.35 \text{ m}^3\text{CH}_4$ per kg VS (after silaging). The typical cost for growth, transport and silaging in northern Italy is around 30 € per ton. In these conditions, the typical feedstock costs for producing 1 MWh is around 2000 € per day, while incentives can arrive at 5800 € per day. This difference allows for a rapid payback of plants which cost is around 4–5 million € per MW. Since energy crops growth requires for land, water and fertilizers, these substrates are not sustainable on a long term perspective and should be replaced by agro-waste.

The anaerobic codigestion of manure and agro-waste is the normal practice in Italy and Europe in general [32]. Livestock production, in fact, is one of the main activities in rural areas within the European Union. Italy, especially in its northern part (Po valley), is one of these areas: as a consequence, livestock effluents are the typical substrates treated in anaerobic digestion plants. For example, the amount of liquid and solid manure produced in the Veneto Region in 2010 accounted for 6 and 5 million cubic meters, respectively, cattle manure being the dominant (67%) part [26]. A similar scenario is observed also for Lombardia, Piemonte and Emilia Romagna Regions [26].

On the other hand, the very high tariff for the production of renewable energy, leads to the use of substrates characterized by high organic content, energy density, and biogas yields like energy crops (especially maize silage) and agro-waste [32]. These co-substrates present similar characteristics in terms of total and volatile solids, thus COD, lower nutrients content and higher biogas yields.

3.3. Actual Use of Digestate

Nitrogen and phosphorus concentrations in livestock effluents are in the range 5–15 kgN/ton and 0.1–1 kgP/ton, respectively, while concentrations in energy crops and other biodegradable by-products

are typically lower [26]. The European production of digestate is estimated in 56 Mtons per year [33]: this can be a real renewable mine for nutrients recovery for the European agricultural sector: the new directive on fertilizers will probably act as a driver in this sense [34].

Digestate is usually valorised because of its nutrients content into fertilizers or soil improvers production, considering its high nitrogen and phosphorus contents not mentioning potassium. Interestingly, N and K will be mainly present in the liquid form after organic substrates undergo the anaerobic digestion process while P is mainly present in the solid form. As a consequence, digestate can be used as it is nearby the farm [16,17].

The efficacy of digestate as a fertilizer [35] was proved for example by Grigatti et al. [36], which conducted pot tests using phosphorous salts from different digestates. ^{31}P nuclear magnetic resonance (NMR) showed how orthophosphate was the main form determining different fertilization potentials. In particular, anaerobic digestates from livestock effluents and energy crops demonstrated to be good alternatives to fertilization with chemical P.

4. Future Perspective for the Biogas Sector in Italy

When considering the future perspective for the biogas sector in Italy one should consider that in 2018 a new decree came into force with the aim to incentive the biogas valorisation into biomethane after biogas up-grading. Biomethane can be injected in the national grid or adopted as automotive fuel [37]. The decree introduced particular tariffs for the biomethane originated from biogas produced from agricultural feedstocks like manure rather than dedicated energy crops.

The fact that the biogas sector is already developed in the North while the South is still waiting for the implementation of infrastructures and that new incentives for biomethane are coming into force together with the necessity to decarbonize the industrial sector together determine the necessity to develop anaerobic digestion sector in the southern part of the country: it should be emphasized here that there are important potentials for the development of the biogas sector in rural areas in Campania, Apulia and Sicily in particular, as will be analyzed in more detail in the following paragraph.

The estimated biogas production is around 5 billion cubic meter per year, making Italy the fourth country in the world for biogas production [23]. Because of the most recent regulatory framework part of this biogas will be converted into biomethane in the next future. However, the estimation by SNAM, the Italian company responsible for methane net and distribution, puts future biogas production at 10 billion cubic meters [38].

4.1. Future Feedstocks

The necessity to make the biogas sector sustainable and to respond to specific requests for biomethane production, open the doors to the use of several by-products which can be used in the feedstock instead of energy crops [39]. Because of their abundance in the Italian territory, agro-wastes from agriculture and animal farm activities can be considered ideal substrates for the co-digestion process instead of energy crops.

Tables 1 and 2 show the most abundant cultivations and farmed animals, respectively in the selected regions of North, Central and South Italy (Agristat [26]). Table 3 shows the main characteristics of the considered substrates.

Table 1. The most diffused cultivations, vegetables and fruits in some administrative regions of North, Central and South Italy with the highest number of biogas plants.

Crops, Fruits (Tons)	NORTH ITALY		CENTRAL ITALY		SOUTH ITALY		
	Veneto	Lombardia	Toscana	Lazio	Puglia	Campania	Italy
Wheat (common + durum)	709,795	410,952	318,658	194,560	1,026,600	246,863	7,054,799
Chickpea	843	3828	7580	1190	3032	534	47,438
Beans and string beans	6018	6830	1698	3220	7670	46,893	151,452
Onions	30,592	10,227	5757	2190	39,650	34,155	382,634
Carrots	30,021	Low	1143	88,180	33,370	4620	480,824
Fennel	557	88	2430	17,260	146,400	63,819	537,444
Lettuce	9390	18,493	1547	16,750	100,480	33,139	349,017
Fresh fruits (apples, pears, apricots, cherries)	405,819	66,154	35,744	13,528	72,274	172,199	3,516,837
Olive oil	24,371	4987	120,364	88,434	565,100	112,926	1,867,662
Wine (DOP *, IGP **, table wine)	1,015,801	148,833	270,830	131,961	955,257	132,749	5,043,610
Citrus fruits (oranges, tangerines, lemons)	Low	Low	122	3411	115,023	49,700	2,080,377

* DOP stays for the Italian “Denominazione Origine Protetta”, that means “Protected Designation of Origin”;

** IGP stays for the Italian “Indicazione Geografica Protetta, that means “Protected Geographical Indication”.

Table 2. The number of animals farmed in the selected Italian regions grouped in different categories.

Substrates (Tons)	NORTH ITALY		CENTRAL ITALY		SOUTH ITALY		
	Veneto	Lombardia	Toscana	Lazio	Puglia	Campania	ITALY
Farm Animals' Categories (#)							
Ovines	11,178	81,356	199,300	511,088	170,950	151,369	2,984,336
Bovines	546,171	542,209	36,484	26,203	60,867	195,862	2,651,010
Swines	437,428	4,265,523	272,445	93,999	70,698	195,383	11,380,546
Poultry and Rabbits	108,841,000	66,043,108	6,145,918	414,186	18,770,251	114,747	606,062,235
Equines	12,382	3497	225	2589	31,144	679	67,005

Table 3. Summary of chemical-physical characteristics of the organic biomass more abundant in the Italian context. Energy crops.

	Total Solids (%)	Total Volatile Solids (%)	TVS/TS (%)	COD (g·kg ⁻¹)	TKN (g·kg ⁻¹)	TP (g·kg ⁻¹)
Energy Crops						
Millet— <i>Panicum Miliaceum</i> L.	21.8	20.1	92.0	-	-	-
Barley— <i>Hordeum distichon</i> L.	25.8–66.3	25.1–59.1	89.3–97.2	517	7.0–19.9	0.8–3.9
Maize— <i>Zea mays</i> L.	40–66.50	38.3–64.0	90.7–96.5	293–304	4.0–4.8	0.3–0.6
Sorghum— <i>Sorghum</i> spp.	28.6–39.6	25.5–35.4	89.3–94.0	302–353	3.2–13.0	0.5
Triticale— <i>Triticum aestivum</i> L.	30–30.8	27.9	90.4–93.1	296	13.5	0.7
Vegetables and fruits by products						
Carrot Leaves— <i>Daucus carota</i> L.	14.8	12.3	83.6	258	3.1	-
Radicchio Leaves— <i>Red Cichorium</i> L.	10.4	9.3	89.0	38.1	0.9	0.3
Potato Peels— <i>Solanum tuberosum</i> L.	11.8	10.7	90.6	186	4.8	0.5
Apple Pomace— <i>Malus domestica</i> L.	50.2	47.9	95.6	580	4.2	-
Tomato Pomace— <i>Solanum lycopersicum</i> L.	30.1	29.0	96.1	380	7.7	-
Grape Marcs— <i>Vitis vinifera</i> L.	29.6–36.7	27.8–34.3	93.1–93.7	312–347	5.7–9.2	2.8–3.3
Grape Vinasse— <i>Vitis vinifera</i> L.	35.6–64.2	28.5–53.1	80.0–82.7	178–324	17.6–37.4	-
Lemon Pomace— <i>Citrus lemon</i> L.	12.6–85.5	12.0–64.3	75.1–95.3	127–692	1.7–6.1	0.3–0.4
Livestock effluents						
Bovine Slurry	4.9–14.5	3.6–12.2	72.5–100	48.0–128	2.1–6.2	0.3–1.2
Bovine Manure	15.6–47.7	13.5–32.1	48.7–99.8	135–291	3.2–7.1	0.2–1.5
Pig Manure	36.1	35.9	99.3	381	-	-
Pig Slurry	0.7–6.4	0.5–5.3	75.0–82.7	5.2–46.6	0.2–5.0	0.1–1.5
Poultry Manure	31.5–78.3	21.3–51.7	44.7–84.1	235–586	2.3–38.9	5.2–15.3

Several authors reported in recent years the possibility to use different by-products, typically originated from the food-processing industry instead of dedicated energy crops [34]. Table 4 shows the great methane potentials from agro-waste byproducts which is comparable, and in some cases higher (radicchio and carrots leaves and potatoes and onions peels) than energy crops.

Table 4. K_h , T-50 and methane yields of biomasses considered in this study.

	K_h (d ⁻¹)	T-50 (d)	CH ₄ Yield (LCH ₄ ·kg TVS ⁻¹)
Energy Crops			
Millet— <i>Panicum miliaceum</i> L.	0.080	13.1	253
Barley— <i>Hordeum distichon</i> L.	0.097	8.1	290 ± 83
Maize— <i>Zea mays</i> L.	0.135 ± 0.06	6.2	289 ± 86
Sorghum— <i>Sorghum</i> spp.	0.091 ± 0.06	10.6	313 ± 73
Triticale— <i>Triticum aestivum</i> L.	0.154 ± 0.07	10.3	351 ± 5
Vegetables and Fruits by-Products			
Carrot Leaves— <i>Daucus carota</i> L.	0.096	7.0	312
Radicchio Leaves— <i>Red Cichorium</i> L.	0.185	3.0	431
Potato Peels— <i>Solanum tuberosum</i> . L.	0.063	3.9	446
Onion Peels— <i>Allium cepa</i> L.	0.213	3.0	455
Apple Pomace— <i>Malus domestica</i> L.	0.148	0.0	204
Tomato Pomace— <i>Solanum lycopersicum</i> L.	0.068	10.9	239
Grape Marcs— <i>Vitis vinifera</i> . L.	0.103 ± 0.04	11.4	248 ± 48
Grape Vinasse— <i>Vitis vinifera</i> . L.	0.162	5.3	274 ± 123
Lemon Pomace— <i>Citrus lemon</i> L.	0.226 ± 0.06	4.3	355 ± 10
Livestock Effluents			
Bovine Slurries	0.039 ± 0.02	14.1	35.2 ± 4.3
Bovine Manure	0.038 ± 0.02	12.3	97.5 ± 9.3
Pig Manure	0.090	8.0	128
Pig Slurries	0.120	8.0	187 ± 89
Poultry Manure	0.098 ± 0.03	6.8	208 ± 103

Schievano et al. [39] reported operating with different mixtures, where municipal organic waste, waste molasses, fruits waste, can substitute energy crops but guarantee the same biogas production while lowering the feedstock costs.

Giuliano et al. [40] demonstrated how, in thermophilic conditions, rotten onions and potatoes can substitute maize silage maintaining the same operational conditions (Organic Load Rate and Hydraulic Retention Time) of the anaerobic digester.

De Menna et al. [41] investigated the BMP potential of five different varieties of artichokes, whose cultivation is particular important in Sardinia. They found a methane yield of 292 LCH₄/kg_{VS}. Considering the regional availability of artichokes by-products, this means that about 20 × 10⁶ Nm³ CH₄ could be produced.

In the last few years, several studies dealt with the definition of the potential for biogas production in the southern regions of Italy. In fact, even if it was already remarked that the national biogas production is concentrated in North Italy, and in particular in Lombardia, Veneto, and Emilia Romagna (Figure 1), Tables 1 and 2 show that agricultural and animal farm activities are very strong in the Central and South regions of Italy, with a consequent by-products production which can be exploited by biorefinery for biogas production. Southern Italian regions are leaders in unique agriculture products, which are exported around the world, such as extra virgin olive oil [42] and citrus productions [43].

With almost 1.9 Mtons of olives per year (Table 1), Italy is a large producer of olive oil. The cultivation of olive trees and olive oil extraction are mainly concentrated in southern Italy, especially in Puglia where it was estimated to be located about the 40% of the national olive oil production. Battista et al. [42] realized a study for biogas production on a pilot reactor working in

continuous mode with a feed represented by 75% *v/v* of olive oil byproducts and 25% *v/v* by cheese whey. The daily biogas was of 1.4 L/L day for a potential annual production of 55 GJ. Taking into account the annual amounts of olive oil and dairy productions' residues, this biogas production rate would assure the generation of about 375,000 GJ, able to cover approximately the 0.015% of Puglia's energy demand.

Valenti et al. [43] focused their attention on the most abundant agro-wastes in Sicily: the by-products of lemon (citrus pulp), olive oil (olive pomace), poultry manure, Italian sainfoin and nopals of prickly pears (*opuntia indica*). The BMP tests investigated different mix of these substrates and showed that all these substrates can be used as feedstock in biogas plants, with methane production between 240 and 260 LCH₄/kgVS. It was estimated that agro-waste and by-products from the agro-food sector could produce 562 million Nm³/year of biomethane in Sicily in 2030. This is equivalent to 8% of the total Italian generation [44]. Although these encouraging estimations, the effective biogas production in Central and South Italy is far from the North Italy situation, where there is already an adequate level of valorisation of the agro-wastes byproducts. Instead, in the southern and central Italian regions the major part of the substrates remain unused in the better cases, and often are simply disposed of on the soil or burned in the open air with negative consequences on human health and increasing contamination of the air, soil and aquifers [42].

In these years our lab characterized several substrates in terms of chemico-physical characteristics, BMP and tendency to biodegradability, showed in Table 4. By this way, it is possible to estimate the great potential of the most abundant Italian agro-waste byproducts.

To have a complete scenario of the Italian situation one should consider that because of the specific climatic conditions two harvesting shift are normally possible during the summer season: this concept is at the base of the "biogas done right" model, where on the same land both crops for food/feed and dedicated energy crops for biogas production are cultivated.

4.2. Recovery of Nutrients from Digestate

In perspective, digestate can be separated in two distinct streams, one liquid and the other solid, with different fertilizing characteristics. These two streams can be further processed to obtain concentrated nutrient forms so as to minimize the transport costs to different agricultural areas [19,20].

However, there are now several technological options for digestate treatment available on the market. Drying of the whole digestate or of its solid fraction, evaporation of the whole digestate or its fractions, membrane filtration of the liquid fraction or stripping of ammonia from the liquid fraction are examples of different options [18–20].

Drying consists in removing water from digestate using hot air generated from the engines burning biogas. Vapors produced within the process are treated to recovery volatilize ammonia. The two main outputs are, therefore, a solid dried fraction and a liquid phase rich in nitrogen [19,20].

Ammonia nitrogen in digestate can be displaced using vapor or can be blocked in an acidic environment after adding mineral acids. Once evaporated, gaseous ammonia can be recovered by means of scrubbing or osmosis. Since the digester sludge is diluted (<10% total solids), the amount of heat recovered from the CHP unit is insufficient to treat all the digestate produced [45].

In the stripping systems, digestate is previously sent to a solid/liquid separation. Then, the liquid phase is fed to a packed bed tower where gaseous ammonia (NH₃) is stripped, passing from the aqueous to the gas phase. The gas stream, rich in ammonia, is then sent to a second tower where NH₃ is absorbed in an acidic media, typically sulfuric acid, producing ammonium sulfate at 25–35% [18–20].

In membrane filtration systems digestate is separated from coarse solids and then the liquid phase of digestate is treated in ultrafiltration (UF) and reverse osmosis (RO) systems: here most of the nutrients are concentrated and separated from water: the obtained concentrated stream is normally from 20% to 30% of the initial treated volume [19,20,46].

Recently, Battista and Bolzonella [13] reported the use solar energy for simultaneous digestate drying and ammonium sulfate recovery. In particular, they tested four digestates, different for

origin and characteristics in a transparent greenhouse exposed to solar irradiation. The liquid phase evaporation was favored by three solar air fans, which also addressed the ammonia rich vapors to a Drechsle trap filled with 38% w/w sulfuric acid solution. In this way, ammonia reacted with sulfuric acid, forming a solution of ammonium sulfate to be used as fertilizer. It was found that substrates rich in proteins (thus nitrogen and ammonia), like animal manure and food wastes were indicated for ammonium sulfate recovery. The solution in the Drechsle trap reached concentrations up to 2 M.

4.3. Biogas, Power to Gas and Added-Value Biobased Compounds

Another interesting perspective for the biogas sector is the transformation of AD farm-based plants into biorefineries. In fact, there is a growing interest in the production of biobased chemicals like volatile fatty acids, lactic acid, succinic acid, poly-hydroxy-alkanoates, and single cell proteins [22,47].

In this approach mixed cultures fermentative processes are applied to produce high added products like carboxylic acids [48] or bioplastics [22] while anaerobic digestion for biogas production is the last process of the biorefinery train and is dedicated to eventual energy recovery (thermal or power).

The strength of this vision is mainly related to the fact that farm-based AD plants are already in existence and have been paid for, and therefore infrastructure is already available without excessive capital costs expenditures.

Another important perspective for the biogas sector is the integration of biogas plants with other renewable energy technologies like solar and wind power to generate hydrogen from water lysis and combine then hydrogen and carbon dioxide present in biogas to further produce methane [49]. This process, known as power to gas, can be one of the future developments of the rural biogas sector when associated with photo-voltaic or wind power generation: this allows for the storage of pick power generation typically associated with sun and wind cycles into a carbon-based energy vector, which is easy to store and liquify and which can be used for several purposes, including transportation.

5. Conclusions and Perspectives

Anaerobic digestion is widely applied in the European rural scenario; in fact, this technology is complementary to other renewable energy technologies like photovoltaic, wind and hydro and is, therefore, a fundamental piece of the energy puzzle.

By contrast with the other technologies, power generated from AD can be modulated (biogas can be stored) while biogas can be upgraded to biomethane and used as biofuel.

The biogas sector within the European Union is still largely dependent on energy crops like maize silage, thus opening the competition with the food and feed sector, but it is rapidly changing to the treatment of livestock effluents and other agro-waste, thus participating in the reduction of the environmental burden associated with these streams. Residual digestate can be used as it is, directly in the farm or nearby, while in some situations it can be necessary to apply a technique which allows for the recovery of nutrients in concentrated forms easy to be transported and used in other rural areas.

Author Contributions: Conceptualization, D.B. and F.B.; Methodology, all the authors; Software, all the authors; Validation, all the authors; Writing—Original Draft Preparation, F.B. and D.B.; Writing—Review & Editing, F.B. and D.B.; Supervision, D.B.

Funding: Part of the results of this research paper is financed by Eranet Med Biogasmena (project number 72-026), which contemplates the optimization of technologies for biogas production and nutrients recovery from digestate in the MENA (Middle East and North Africa) regions.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Poeschl, M.; Ward, S.; Owende, P. Evaluation of energy efficiency of various biogas production and utilization pathways. *Appl. Energy* **2010**, *87*, 3305–3321. [CrossRef]
2. Wall, D.M.; O’Kiely, P.; Murphy, J.D. The potential for biomethane from grass and slurry to satisfy renewable energy targets. *Bioresour. Tech.* **2014**, *149*, 425–431. [CrossRef] [PubMed]
3. Arthurson, V. Closing the global energy and nutrient cycles through application of biogas residue to agricultural land—Potential benefits and drawbacks. *Energies* **2009**, *2*, 226–242. [CrossRef]
4. Czyrnek-Deletre, M.M.; Smyth, B.M.; Murphy, J.D. Beyond carbon and energy: The challenge in setting guidelines for life cycle assessment of biofuel systems. *Renew. Energy* **2017**, *105*, 436–448. [CrossRef]
5. Del Pablo-Romero, M.; Sánchez-Braza, A.; Salvador-Ponce, J.; Sánchez-Labrador, N. An overview of feed-in tariffs, premiums and tenders to promote electricity from biogas in the EU-28. *Renew. Sustain. Energy Rev.* **2017**, *73*, 1366–1379. [CrossRef]
6. Scheffelowitz, M.; Becker, R.; Thran, D. Improved power provision from biomass: A retrospective on the impacts of German energy policy. *Biomass Bioenergy* **2018**, *111*, 1–12. [CrossRef]
7. European Biogas Association. Annual Report. 2015. Available online: <http://european-biogas.eu/2015/12/16/biogasreport2015/> (accessed on 28 May 2019).
8. Gruda, N.; Bisbis, M.; Tanny, J. Impacts of protected vegetable cultivation on climate change and adaptation strategies for cleaner production—A review. *J. Clean. Prod.* **2019**, *225*, 324–339. [CrossRef]
9. Hamelin, L.; Naroznova, I.; Wenzel, H. Environmental consequences of different carbon alternatives for increased manure-based biogas. *Appl. Energy* **2014**, *114*, 774–782. [CrossRef]
10. Theuerl, S.; Herrmann, C.; Heiermann, M.; Grundmann, P.; Landwehr, N.; Kreidenweis, U.; Prochnow, A. The Future Agricultural Biogas Plant in Germany: A Vision. *Energies* **2019**, *12*, 306. [CrossRef]
11. Cobuloglu, H.I.; Büyüktaktakin, I.E. Food vs. biofuel: An optimization approach to the spatio-temporal analysis of land-use competition and environmental impacts. *Appl. Energy* **2015**, *140*, 418–434. [CrossRef]
12. Garcia, N.H.; Mattioli, A.; Gil, A.; Frison, N.; Battista, F.; Bolzonella, D. Evaluation of the methane potential of different agricultural and food processing substrates for improved biogas production in rural areas. *Renew. Sustain. Energy Rev.* **2019**, *112*, 1–10. [CrossRef]
13. Battista, F.; Bolzonella, D. Exploitation of Solar Energy for Ammonium Sulfate Recovery from Anaerobic Digestate of Different Origin. *Waste Biomass Valoris.* **2019**. [CrossRef]
14. Lal, R. Digging deeper: A wholistic perspective of factors affecting Soil Organic Carbon sequestration. *Glob. Change Biol.* **2018**, *24*, 3285–3301. [CrossRef] [PubMed]
15. Mehta, C.M.; Khunjar, W.O.; Nguyen, V.; Tait, S.; Batstone, D.J. Technologies to recover nutrients from waste streams: A critical review. *Crit. Rev. Environ. Sci. Technol.* **2015**, *45*, 385–427. [CrossRef]
16. Moller, K.; Müller, T. Effects of anaerobic digestion on digestate nutrient availability and crop growth: A review. *Eng. Life Sci.* **2012**, *12*, 242–257. [CrossRef]
17. Vaneekhaute, C.; Darveau, O.; Meers, E. Fate of micronutrients and heavy metals in digestate processing using vibrating reversed osmosis as resource recovery technology. *Sep. Purif. Technol.* **2019**, *223*, 81–87. [CrossRef]
18. Bernet, N.; Beline, F. Challenges and innovations on biological treatment of livestock effluents. *Bioresour. Technol.* **2009**, *100*, 5431–5436. [CrossRef] [PubMed]
19. Fuchs, W.; Drogg, B. Assessment of the state of the art of technologies for the processing of digestate residue from anaerobic digesters. *Water Sci. Technol.* **2013**, *67*, 1984–1993. [CrossRef]
20. Drogg, B.; Fuchs, W.; Al Seadi, T.; Madsen, M.; Linke, B. *Nutrient Recovery by Biogas Digestate Processing*; IEA Bioenergy: Paris, France, 2015; ISBN 978-1-910154-15-1.
21. Bolzonella, D.; Fatone, F.; Gottardo, M.; Frison, N. Nutrients recovery from anaerobic digestate of agro-waste: Techno-economic assessment of full scale applications. *J. Environ. Manag.* **2018**, *216*, 111–119. [CrossRef]
22. Gontard, N.; Sonesson, U.; Birkved, M.; Majone, M.; Bolzonella, D.; Celli, A.; Angellier-Coussy, H.; Jang, G.W.; Verniquet, A.; Broeze, J.; et al. A research challenge vision regarding management of agricultural waste in a circular bio-based economy. *Crit. Rev. Environ. Sci. Technol.* **2018**, *48*, 614–654. [CrossRef]
23. Consorzio Italiano Biogas. 2019. Available online: <https://www.consorziobiogas.it/> (accessed on May 2019).

24. Gestore Servizi Energetici. Rapporto Statistico: Energia da Fonti Rinnovabili in Italia. Anno 2016. 2018. Available online: https://www.gse.it/documenti_site/Documenti%20GSE/Rapporti%20statistici/Rapporto%20statistico%20GSE%20-%202016.pdf (accessed on 28 May 2019).
25. ISAAC. Increasing Social Awareness and Acceptance of Biogas and Biomethane. Available online: <http://www.isaac-project.it/> (accessed on 28 May 2019).
26. Agristat, Istituto Nazionale di Statistica per l'Agricoltura e la Zootecnia. Available online: <http://agri.istat.it/> (accessed on 28 May 2019).
27. American Public Health Association, American Water Works Association and Water Pollution Control Federation. *APHA, AWWA & WPCF Standard Methods for the Examination of Water and Wastewater*, 17th ed.; American Public Health Association, American Water Works Association and Water Pollution Control Federation: Washington, DC, USA, 1989.
28. Angelidaki, I.; Alves, M.; Bolzonella, D.; Borzacconi, L.; Campos, J.L.; Guwy, A.J.; Kalyuzhnyi, S.; Jenicek, P.; van Lier, J.B. Defining the biomethane potential (BMP) of solid organic wastes and energy crops: A proposed protocol for batch assays. *Water Sci. Technol.* **2009**, *59*, 927–934. [[CrossRef](#)] [[PubMed](#)]
29. Holliger, C.; Alves, M.; Andrade, D.; Angelidaki, I.; Astals, S.; Baier, U.; Bougrier, C.; Buffière, P.; Carballa, M.; De Wilde, V.; et al. Towards a standardization of biomethane potential tests. *Water Sci. Technol.* **2016**, *74*, 2515–2522. [[CrossRef](#)] [[PubMed](#)]
30. Benato, A.; Macor, A. Italian Biogas Plants: Trend, Subsidies, Cost, Biogas Composition and Engine Emissions. *Energies* **2019**, *12*, 979. [[CrossRef](#)]
31. Ragazzoni, A. Analisi della Redditività Degli Impianti per la Produzione di Biogas alla Luce delle Nuove Tariffe Incentivanti 2013. Available online: http://www.crpa.it/media/documents/crpa_www/Convegni/20130314_BiogasBiometano_RA/Ragazzoni_RA_14-3-2013.pdf (accessed on 28 May 2019).
32. Weiland, P. Biogas production: Current state and perspectives. *Appl. Microbiol. Biotechnol.* **2010**, *2010*, 85, 849–860. [[CrossRef](#)]
33. Beggio, G.; Schievano, A.; Bonato, T.; Hennebert, P.; Pivato, A. Statistical analysis for the quality assessment of digestates from separately collected organic fraction of municipal solid waste (OFMSW) and agro-industrial feedstock. Should input feedstock to anaerobic digestion determine the legal status of digestate? *Waste Manag.* **2019**, *87*, 546–558. [[CrossRef](#)] [[PubMed](#)]
34. Council of the European Union. Proposal for a Regulation of the European Parliament and of the Council Laying Down Rules on the Making Available on the Market of CE Marked Fertilising Products and Amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009. 2018. Available online: <http://data.consilium.europa.eu/doc/document/ST-15103-2018-INIT/en/pdf> (accessed on 28 May 2019).
35. Tambone, F.; Scaglia, B.; D'Imporzano, G.; Schievano, A.; Orzi, V.; Salati, S.; Adani, F. Assessing amendment and fertilizing properties of digestates from anaerobic digestion through a comparative study with digested sludge and compost. *Chemosphere* **2010**, *81*, 577–583. [[CrossRef](#)]
36. Grigatti, M.; Boanini, E.; Bolzonella, D.; Sciubba, L.; Mancarella, S.; Ciavatta, C.; Marzadori, C. Organic wastes as alternative sources of phosphorus for plant nutrition in a calcareous soil. *Waste Manag.* **2019**, *93*, 34–46. [[CrossRef](#)] [[PubMed](#)]
37. Gazzetta Ufficiale della Repubblica Italiana. Decreto 2 marzo 2018. Promozione Dell'uso del Biometano e Degli Altri Biocarburanti Avanzati Nel Settore dei Trasporti. 2018. Available online: <https://www.gazzettaufficiale.it/eli/id/2018/03/19/18A01821/SG> (accessed on 28 May 2019).
38. SNAM. Available online: <http://www.snam.it/en/Natural-gas/green-energy/biomethane> (accessed on 28 May 2019).
39. Schievano, A.; D'Imporzano, G.; Adani, F. Substituting energy crops with organic wastes and agro-industrial residues for biogas production. *J. Environ. Manag.* **2009**, *90*, 2537–2541. [[CrossRef](#)] [[PubMed](#)]
40. Giuliano, A.; Bolzonella, D.; Pavan, P.; Cavinato, C.; Cecchi, F. Co-digestion of livestock effluents, energy crops and agro-waste: Feeding and process optimization in mesophilic and thermophilic conditions. *Bioresour. Technol.* **2013**, *128*, 612–618. [[CrossRef](#)]
41. De Menna, F.; Malagnino, R.A.; Vittuari, M.; Molari, G.; Seddaiu, G.; Deligios, P.A.; Solinas, S.; Ledda, L. Potential Biogas Production from Artichoke Byproducts in Sardinia, Italy. *Energies* **2016**, *9*, 92. [[CrossRef](#)]
42. Battista, F.; Ruggeri, B.; Fino, D.; Erriquens, F.; Rutigliano, L.; Mescia, D. Toward the scale-up of agro-food feed mixture for biogas production. *J. Environ. Chem. Eng.* **2013**, *1*, 1223–1230. [[CrossRef](#)]

43. Valenti, F.; Porto, S.M.C.; Selvaggi, R.; Pecorino, B. Evaluation of biomethane potential from by-products and agricultural residues co-digestion in southern Italy. *J. Environ. Manag.* **2018**, *223*, 834–840. [[CrossRef](#)] [[PubMed](#)]
44. Selvaggi, R.; Pappalardo, G.; Chinnici, G.; Fabbri, C.I. Assessing land efficiency of biomethane industry: A case study of Sicily. *Energy Policy* **2018**, *119*, 689–695. [[CrossRef](#)]
45. Vaneekhaute, C.; Lebuf, V.; Michels, E.; Belia, E.; Vanrollegheem, P.A.; Tack, F.M.G.; Meers, E. Nutrient recovery from digestate: Systematic technology review and product classification. *Waste Biomass Valor.* **2017**, *8*, 21–40. [[CrossRef](#)]
46. Kertesz, S.; Beszedes, S.; Laszlo, Z.; Szabo, G.; Hodur, C. Nanofiltration and reverse osmosis of pig manure: Comparison of results from vibratory and classical modules. *Desalin. Water Treat.* **2010**, *14*, 233–238. [[CrossRef](#)]
47. Battista, F.; Frison, N.; Pavan, P.; Cavinato, C.; Gottardo, M.; Fatone, F.; Eusebi, A.L.; Majone, M.; Zeppilli, M.; Valentino, F.; et al. Food wastes and sewage sludge as feedstock for an urban biorefinery producing biofuels and added-value bioproducts. *J. Chem. Technol. Biotechnol.* **2019**, in press. [[CrossRef](#)]
48. Agler, M.T.; Wrenn, B.A.; Zinder, S.H.; Angenent, L.T. Waste to bioproduct conversion with undefined mixed cultures: The carboxylate platform. *Trends Biotechnol.* **2011**, *29*, 70–78. [[CrossRef](#)] [[PubMed](#)]
49. Hahn, H.; Krautkremer, B.; Hartmann, K.; Wachendorf, M. Review of concepts for a demand-driven biogas supply for flexible power generation. *Rnew. Sustain. Energy Rev.* **2014**, *29*, 383–393. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).